Supporting Information

Ligand-Mediated Spin-State Changes in a Cobalt-Dipyrrin-Bisphenol Complex

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General considerations

Chemicals and solvents

All reagents were of commercial grade and used without further purification, unless noted otherwise. All reactions were performed under an inert atmosphere in a N_2 filled glovebox or by using standard Schlenk techniques (under Ar or N_2), unless noted otherwise. CH_2Cl_2 and MeOH were distilled from CaH_2, toluene was distilled from sodium, THF was distilled from sodium benzophenone ketyl.

NMR spectroscopy

^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker DRX 500, Bruker AMX 400, Bruker DRX 300 or Varian Mercury 300 spectrometer at room temperature, unless noted otherwise.

Mass spectrometry

CSI mass spectra were collected on an AccuTOF LC, JMS-T100LP Mass spectrometer (JEOL, Japan). The CSI apparatus features a liquid nitrogen cooling device to maintain the temperature of the capillary and spray itself between 0 °C and –50 °C. Typical measurement conditions are as follows: Positive-ion mode; Needle voltage 2000V, Orifice 1 voltage 90V, Orifice 2 voltage 9V, Ring Lens voltage 22V. Orifice 300C, Desolvating Chamber 30 °C, spray temperature –40 °C. FD Mass spectra were collected on an AccuTOF GC v 4g, JMS-T100GCV Mass spectrometer (JEOL, Japan). FD/FI probe (FD/FI) equipped with FD Emitter, Carbotec or Linden (Germany), FD 13 μm. Current rate 51.2 mA/min over 1.2 min. FI Emitter, Carbotec or Linden (Germany), FI 10 μm. Flashing current 40 mA on every spectra of 30 ms. Typical measurement conditions are: Counter electrode –10kV, Ion source 37V.

UV-Vis spectroscopy

UV-Vis spectra were recorded on a Hewlett Packard 8453 or a double beam Shimadzu UV-2600 spectrometer in a 1.0 cm quartz cuvette.

Elemental Analysis

Was performed by Mikroanalytisches Laboratorium Kolbe (Oberhausen, Germany).

SQUID

Measured with a SQUID susceptometer (Quantum Design) 7T, 4K - 290K range and acquisition software MultiVu.

Single Crystal X-ray Crystallography

For **$[Co^{II}(DPP^{\bullet 2-})]$** and **$[Co^{III}(DPP^{3-})(NH_2Ad)_2]$**: X-ray intensities were measured on a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator (λ = 0.71073 Å) and a CMOS Photon 100 detector at a temperature of 150(2) K. Intensity data were integrated with the Bruker APEX2 software.[1] Absorption correction and scaling was performed with SADABS.[2] The structures were solved using intrinsic phasing with the program SHELXT.[3] Least-squares refinement was performed with SHELXL-2013[4] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were

placed at calculated positions using the instructions AFIX 13, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times U_{eq} of the attached C atoms.

For **$DPPH_3$**, **[$Co^{III}(DPP^{3-})(Py)_2$]** and **[$Co^{III}(DPP^{3-})(NH_2tBu)_2$]**: all reflection intensities were measured at 110(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Cu *K*α radiation (λ = 1.54178 Å) under the program CrysAlisPro (Version CrysAlisPro 1.171.39.29c, Rigaku OD, 2017). The same program was used to refine the cell dimensions and for data reduction. The structures were solved with the program SHELXS-2018/3 (Sheldrick, 2018) and were refined on F^2 with SHELXL-2018/3 (Sheldrick, 2018). Analytical numeric absorption correction using a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions (unless otherwise specified) using the instructions AFIX 43, AFIX 137 or AFIX 147 with isotropic displacement parameters having values 1.2 or 1.5 Ueq of the attached C or O atoms. Crystal structures were visualized with the Mercury software package.[5]

Accession codes:
CCDC 2012086 (**$DPPH_3$**), 2012087 (**[$Co^{II}(DPP^{\bullet 2-})$]**), 2012088 (**[$Co^{III}(DPP^{3-})(Py)_2$]**), 2012089 (**[$Co^{III}(DPP^{3-})(NH_2tBu)_2$]**) and 2012090 (**[$Co^{III}(DPP^{3-})(NH_2Ad)_2$]**) contain the supplementary crystallographic data and can be obtained free of charge via http:// https://www.ccdc.cam.ac.uk/structures/.

Additional refinement details:

$DPPH_3$: The structure is mostly ordered. The H atoms attached to N1, N2, O1 and O2 were found from difference Fourier maps, and the coordinates were refined pseudofreely using the DFIX instruction in order to keep the N–H and O–H distances within some acceptable ranges. The disordered sets of H atoms (H1N1, H1O1, H1O2) and (H2N2, H2O1, H2O2) occur with equal probability. If N1 is protonated, then the H atom attached to O1 points away from N1, and the H atom attached to O2 points toward N2. If N2 is protonated, then the H atom attached to O2 points away from N2, and the H atom attached to O1 points toward N1.

[$Co^{III}(DPP^{3-})(Py)_2$]: The asymmetric unit contains three crystallographically independent molecules of the target compound (labelled A, B and C). The structure is partly disordered. One $-C_6F_5$ group and one *t*-butyl group are found to be disordered over two orientations, and the occupancy factors of the major components of the disorder refine to 0.781(8) and 0.553(7), respectively. The asymmetric unit also contains some amount of lattice solvent molecules that are very disordered and most likely partially occupied. Their contribution has been removed using the SQUEEZE procedure in Platon.[6]

[$Co^{III}(DPP^{3-})(NH_2tBu)_2$]: The asymmetric unit contains three crystallographically independent molecules of the target compound (labelled A, B and C). The H atoms attached to N3X and N4X (X = A, B and C) were found from difference Fourier maps, and their coordinates were refined pseudofreely using the DFIX instruction in order to keep the N–H distances within an acceptable range. The structure is mostly ordered. The structure contains some small amount of very disordered and/or partially occupied MeOH solvent

molecules. In the final refinement, their contribution has been removed using the SQUEEZE procedure in Platon (Spek, 2009).

EPR spectroscopy

EPR spectra were recorded on a Bruker EMX X-band spectrometer equipped with a He cryostat. The spectra were analyzed and simulated using the W95EPR program of Prof. F. Neese (MPI Mülheim a/d Ruhr).

Magnetic moment measurements using Evans' method

Magnetic moments were determined according to reported procedures by solvation of a known amount of the analyte in a known amount of deuterated solvent with an internal standard in an NMR tube.[7] A capillary containing the deuterated solvent and internal standard was inserted in the NMR tube and a ^{1}H NMR spectrum was recorded. The mass susceptibility (χ in cm^3g^{-1}) of the analyte was calculated with equation (1), wherein ν_0 is the operating frequency of the NMR spectrometer (Hz) and c is the concentration of the analyte in the solution ($g\ L^{-1}$). The molar susceptibility (χ_M in cm^3mol^{-1}) can be calculated by equation (2), wherein and M is the molar mass of the analyte. χ_M^P is the pure paramagnetic molar susceptibility and can be calculated by equation (3) in which χ_M^{Dia} (the diamagnetic molar susceptibility) is a correction on χ_M to account for the diamagnetic contributions within the analyte. The diamagnetic molar susceptibility (χ_M^{Dia}) can be calculated by using Pascal's constants, or estimated from the molecular mass.[7] With equation (4), χ_M^P can be used to calculate the effective magnetic moment (μ_{eff}) of the analyte, in which k is the Boltzmann constant, T is the temperature in Kelvin, N_A is the Avogadro constant and μ_B is the Bohr magneton. The electron spin quantum number (S) can now be calculated with equation (5) from the effective magnetic moment by solving for S. Here, g is obtained from an EPR measurement or taken as the g_e-value for the free electron (2.0023).

(1) $\chi = \frac{3000 \times \Delta\nu}{4\pi \times \nu_0 \times c}$

(2) $\chi_M = \chi \times M$

(3) $\chi_M^P = \chi_M - \chi_M^{Dia}$

(4) $\mu_{eff} = \sqrt{\frac{3 \times k \times T \times \chi_M^P}{N_A \times \mu_B^2}} \approx 2.82787 \sqrt{T \times \chi_M}$

(5) $\mu_{eff} = g\sqrt{S(S+1)}$

DFT calculations

DFT studies were performed on full atomic models (no simplifications) using TURBOMOLE 7.3[8] coupled to the PQS Baker optimizer[9] via the BOpt package.[10] We chose this software package for the DFT calculations because it is fast and we have good experience (i.e. relatively fast convergence) with this combination of software for comparable cobalt complexes.[11] The geometry optimizations and frequency analysis was performed at the B3LYP[12]/def2-SVP[13] level of theory (unless noted otherwise) on an m4 grid, using Grimme's version 3 (disp3, "zero damping") dispersion corrections.[14] All minima (no imaginary frequencies) were characterized by numerically calculating the Hessian matrix. Final orbital and energy evaluation was performed at the B3LYP[12]/def2-TZVP[15] level of theory (unless noted otherwise) on an m4 grid, using Grimme's version 3 (disp3, "zero damping") dispersion corrections,[16] on the optimized geometries. Energy output was reported in Hartree and was converted to kcal mol^{-1} by multiplication with 627.503.

When applicable, corrected broken symmetry energies ε_{BS} of the open-shell singlets (S = 0) were estimated from the energy (ε_S) of the optimized single-determinant broken symmetry solution and the energy (ε_{S+1}) from a separate unrestricted triplet single-point calculation at the same level, using the approximate correction formula (6).[10]

(6) $$\varepsilon \approx \frac{S_{S+1}^2 \times \varepsilon_S - S_S^2 \times \varepsilon_{S+1}}{S_{S+1}^2 - S_S^2}$$

Orbital interpretation was done by Löwdin population analysis of quasi restricted orbitals (QRO) generated with the ORCA 4.1[17] software package at the B3LYP[12]/TZVP[13] level, using the coordinates from the structures optimized in TURBOMOLE as the input and using the UNO keyword.

Graphical representations of orbitals were generated using IboView[18] and structures were visualized with Chimera (available at http://www.cgl.ucsf.edu/chimera).

NEVPT2-CASSCF calculation

The NEVPT2 corrected CASSCF calculations were performed with the ORCA 4.1[17] software package on the geometry optimized in TURBOMOLE at the experimentally found spin state. This approach has been used in our group before[11] and the implementation of NEVPT2-CASSCF in ORCA is relatively straightforward (see https://orcaforum.kofo.mpg.de/ for manuals), therefore justifying our choice for the ORCA software package. The def2-TZVP[13] basis set was used together with the RIJCOSX[19] approximation in conjunction with the def2-TZVP/C fitting basis set to reduce computational cost. The single root spin state was calculated. NEVPT2[20] calculations using the RI approximation were carried out on converged CASSCF wavefunctions. Canonical orbitals were generated for visualization using IboView.[18] Energy output was reported in Hartree and was converted to kcal mol^{-1} by multiplication with 627.503.

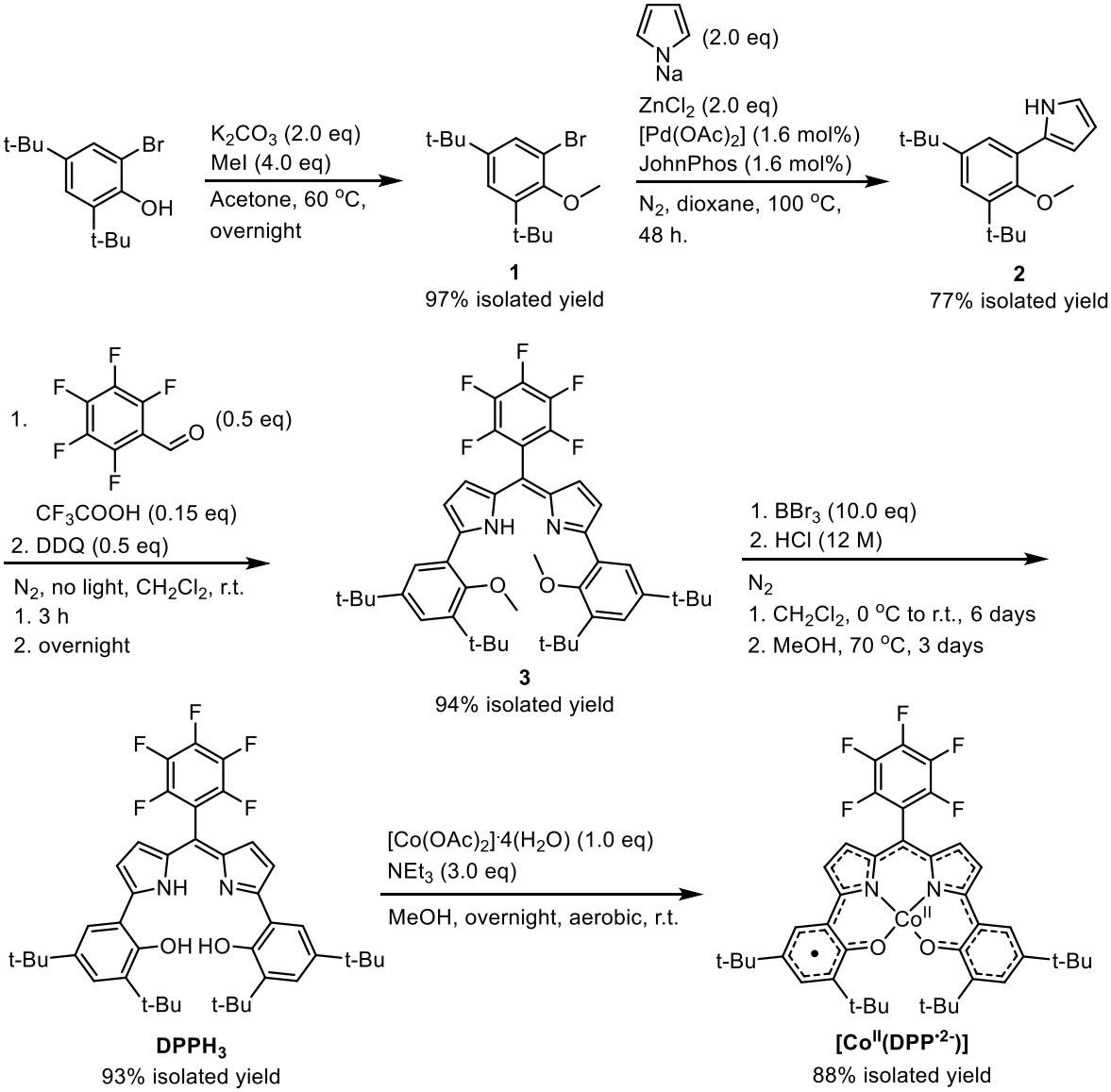
A general flow-scheme for the calculation is described below, including the input for the calculation in brackets:

1. The molecule was aligned properly along the x, y and z axis and QRO-type orbitals were generated in a single-point calculation by usage of the UNO keyword.
   [!BP86 def2-TZVP def2-TZVP/C RIJCOSX UNO Normalprint KeepDens]
2. The QRO orbitals were used for a restricted open-shell Kohn-Sham (ROKS) calculation.
   [! ROKS BP86 def2-TZVP def2-TZVP/C RIJCOSX Normalprint noiter MOREAD

%moinp "orbitals.qro"]

3. Löwdin population analysis and visualization using IboView were used to identify the orbitals of interest (all metal d orbitals, relevant ligand π orbitals and relevant metal-ligand bonding and antibonding orbitals) and rotate these into the active space.
   [! ROKS BP86 def2-TZVP def2-TZVP/C RIJCOSX Normalprint noiter MOREAD
   %moinp "orbitals.gbw"]
   %scf rotate {orbital number, active space location} end end]
4. The single root CASSCF calculation was performed.
   [! def2-TZVP def2-TZVP/C RIJCOSX Normalprint MOREAD
   %moinp "orbitals.gbw"
   %casscf
   trafostep ri
   nel (number of active electrons)
   norb (number of active orbitals)
   mult (multiplicity)
   end]
5. The converged CASSCF calculation was analyzed for convergence and preservation of the active space. The NEVPT2 correction was then applied and the orbitals were transformed to canonical orbitals for final visualization and (total) energy evaluation.
   [! def2-TZVP def2-TZVP/C RIJCOSX Normalprint MOREAD RI-NEVPT2
   %moinp "orbitals.gbw"
   %casscf
   trafostep ri
   nel (number of active electrons)
   norb (number of active orbitals)
   mult (multiplicity)
   actorbs canonorbs
   intorbs canonorbs
   extorbs canonorbs
   nevpt
   d4step fly
   end
   end]

Synthesis and characterization



Scheme S1. Synthesis of **DPPH$_3$** and **[Co^{II}(DPP$^{\cdot 2-}$)]**.

Pyrrolylsodium,[21] **1**,[22] and **2**[23] were prepared according to literature procedures, and the spectral data were found to match the reported spectra (see Scheme S1).

3: Adapted from a literature procedure for the condensation reaction.[23] 2-(3,5-di-*tert*-butyl-2-methoxyphenyl)-1*H*-pyrrole (**2**, 4.00 g; 14.0 mmol; 1.0 eq) was dissolved in CH_2Cl_2 (50 mL) under the exclusion of light in a flame dried Schlenk under a nitrogen atmosphere. Pentafluorobenzaldehyde (0.87 mL; 7.0 mmol; 0.5 eq) and trifluoroacetic acid (0.16 mL; 2.1 mmol; 0.15 eq) were added sequential and the mixture was stirred for 3 hours at r.t. to yield a blue solution. DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone, 1.59 g; 7.0 mmol; 0.5 eq) was added, yielding a purple solution and stirred at r.t. overnight. The purple solution was washed three times with saturated aqueous $NaHCO_3$ (30 mL). The organic layer was further purified by filtration over silica using hexane/CH_2Cl_2 (9:1) as the eluent. The product was obtained as an orange powder in 4.91 g; 6.6 mmol; 94% yield.

^{1}H NMR (300 MHz, Methylene Chloride-d_2) δ 7.55 (d, J = 2.5 Hz, 2H), 7.41 (d, J = 2.5 Hz, 2H), 6.84 (d, J = 4.3 Hz, 2H), 6.53 (d, J = 4.3 Hz, 2H), 3.64 (s, 6H), 1.43 (s, 18H), 1.33 (s, 18H).

^{19}F NMR (282 MHz, Methylene Chloride-d_2) δ -137.79 – -141.33 (m), -154.07 (t, J = 21.0 Hz), -160.32 – -164.08 (m).

^{13}C NMR (75 MHz, Chloroform-d) δ 156.30, 155.78, 145.59, 142.27, 140.77, 126.73, 126.43, 125.47, 125.06, 120.27, 120.17, 61.93, 35.39, 34.58, 31.56, 31.04. All four ^{13}C resonances corresponding to the C_6F_5 fragment are absent due to broadening of the signal as a result of coupling with ^{19}F. Similar signal loss in DPP-derived ligands was reported in literature.[24] Similar loss of signal intensity was observed in ^{13}C NMR analysis of a highly concentrated pentafluorobenzaldehyde solution. Which gave relative peak intensities of 1 (^{13}C=O) : 0.78 (^{13}C–F) : 0.13 (^{13}C–F) : 0.82 (^{13}C–F) : 0.33 (^{13}C–C=O).

HRMS-FD$^+$: calc. for [$C_{45}H_{51}F_5N_2O_2^+$]: 746.3871, found: 746.3899 [M]$^+$.

DPPH$_3$: Adapted from a literature procedure for the deprotection reaction.[23] **3** (0.400 g; 0.54 mmol; 1.0 eq) was dissolved in CH_2Cl_2 (20 mL) and cooled to 0 °C in a flame dried Schlenk under a nitrogen atmosphere compound. BBr_3 (0.52 mL; 5.4 mmol; 10 eq) was added dropwise to give a blue solution that was stirred while warming to r.t. and stirred for 6 more days. MeOH (30 ml) was added slowly to quench the unreacted BBr_3. The blue mixture was concentrated and dissolved in MeOH (50 mL), 30 mL concentrated $HCl_{(aq)}$ solution was added and the mixture was refluxed at 70 °C for 3 days. The reaction mixture was neutralized with a saturated aqueous $NaHCO_3$ solution (100 mL). The obtained pink suspension was extracted with EtOAc (100 mL), washed with brine (100 mL), dried over Na_2SO_4, filtered and the filtrate was concentrated. The crude product was purified by filtration over silica using hexane as eluent. The product was obtained as pink crystalline powder in 0.356 g; 0.50 mmol; 93% yield. In order to speed up the reaction, it is advised to perform the work up each day and start the reaction again until full conversion is reached.

^{1}H NMR (300 MHz, Methylene Chloride-d2) δ 7.61 (d, J = 2.4 Hz, 2H), 7.41 (d, J = 2.4 Hz, 2H), 7.03 (d, J = 4.5 Hz, 2H), 6.56 (d, J = 4.5 Hz, 2H), 1.54 (s, 18H), 1.35 (s, 18H).

^{19}F NMR (282 MHz, Methylene Chloride-d_2) δ -139.84 (m), -153.77 (t, J = 20.9 Hz), -162.00 (m).

^{13}C NMR (75 MHz, Methylene Chloride-d_2) δ 153.69, 142.90, 139.54, 136.51, 128.61, 126.78, 123.87, 120.17, 118.39, 118.08, 35.36, 34.87, 31.79, 30.66. Five ^{13}C NMR signal are missing for the reasons as explained in the characterization of **3** (*vide supra*).

HRMS-FD$^+$: calc. for [$C_{43}H_{47}F_5N_2O_2^+$]: 718.3558, found: 718.3559 [M]$^+$.

Elemental analysis: calc. for $C_{43}H_{47}F_5N_2O_2$: C 71.85; H 6.59; F 13.21; N 3.90; O 4.45; found: C 71.95; H 6.63; F 13.14; N 3.87; O 4.29.

XRD: XRD quality single crystals were grown by slow evaporation of a concentrated solution in CH_2Cl_2 at room temperature. The 50% thermal ellipsoid probability plot is included in the main text, and the relevant bond lengths and atom numbering are depicted in Table S1. **DPPH$_3$**, $C_{43}H_{47}F_5N_2O_2$, FW = 718.82, pink-purple plate, 0.29 mm × 0.14 mm × 0.05 mm, monoclinic, $P2_1/c$, a = 21.9848(4) Å, b = 15.9671(3) Å, c = 10.8173(2) Å, β = 96.9017(18)°, V = 3769.72(12) Å^3, Z = 4, μ = 0.78 mm^{-1}; 25014 reflections were measured with $(\sin\theta/\lambda)_{max}$ = 0.616 Å^{-1}. 7407 Reflections were unique (R_{int} = 0.034) of which 5443 were observed [$I > 2\sigma(I)$]. Residual electron density between –0.23 and 0.61 e$^-$/Å^3. S = 1.041. Refinement: $R[F^2 > 2\sigma(F^2)]$ = 0.043, $wR(F^2)$ = 0.124, number of reflections: 7407, number of parameters: 501, number of restraints: 10.

[$Co^{II}(DPP^{\bullet 2-}$)]: Adapted from a literature procedure for the insertion of cobalt into the ligand.[25] **$DPPH_3$** (1.00 g; 1.39 mmol; 1.0 eq) and $[Co(OAc)_2]\cdot 4H_2O$ (0.347 g; 1.39 mmol; 1.0 eq) were dissolved in MeOH (50 mL) to afford a purple solution. Triethylamine (0.582 mL; 4.18 mmol; 3.0 eq) was added and the mixture was stirred at r.t. overnight under aerobic conditions. The obtained green suspension was concentrated, extracted with CH_2Cl_2 and concentrated yielding a purple powder, which was washed with MeOH (50 mL) and dried. The product was obtained as a purple powder in 0.954 g; 1.23 mmol; 88% yield.

^{1}H NMR (300 MHz, Methylene Chloride-d_2) δ 12.82 (d, J = 5.1 Hz, 2H), 8.58 (d, J = 2.3 Hz, 2H), 7.78 (d, J = 5.1 Hz, 2H), 6.96 (d, J = 2.3 Hz, 2H), 4.29 (s, 18H), 1.27 (s, 18H).

^{19}F NMR (282 MHz, Methylene Chloride-d_2) δ -137.16 (dd, J = 23.4, 7.8 Hz), -152.98 (t, J = 20.8 Hz), -160.58 (td, J = 23.6, 22.5, 8.0 Hz).

^{13}C NMR (75 MHz, Methylene Chloride-d_2) δ 169.35, 158.47, 158.16, 156.03, 153.02, 152.19, 149.86 (w), 141.68 (w), 140.83 (w), 138.44 (w), 125.04, 124.82, 118.15, 117.60, 115.13 (w, t, J = 21.3 Hz), 37.81, 35.28, 34.68, 31.30. Low-intensity signals are denoted by w, which is caused by the reasons as explained in the characterization of **3** (*vide supra*).

HRMS-FD$^+$: calc. for $[C_{43}H_{44}CoF_5N_2O_2^+]$: 774.2655, found: 774.2604 $[M]^+$.

X-band EPR: silent at r.t. and 20 K.

UV-Vis (32.27 μM, CH_2Cl_2, 1.0 cm cuvet) nm {ε, $cm^{-1}M^{-1}$}: 230, 269 {26.3×10^3}, 326 {25.7×10^3}, 374 {20.6×10^3}, 556 {21.0×10^3}, 755 {5.67×10^3}.

Elemental analysis: calc. for $C_{43}H_{44}CoF_5N_2O_2$: C 66.66; H 5.72; Co 7.61; F 12.26; N 3.62; O 4.13; found: C 65,72; H 5.87; Co 7.43; F 11.97; N 3.49; O 5.13.

μ_{eff} (Evans' method, CD_2Cl_2 with toluene as internal standard, 297.2 K, 7.9 mM, Δν = 0 Hz): 0 μ_B

SQUID: constant susceptibility observed in the 5 K – 290 K range (Figure S1).

XRD: XRD quality single crystals were grown by slow evaporation of a concentrated solution in CH_2Cl_2 at room temperature. The displacement ellipsoid plot (50% probability level) is depicted in the main text, and the atom numbering and relevant bond lengths are provided in Table S1. **[$Co^{II}(DPP^{\bullet 2-}$)]**, $C_{43}H_{44}CoF_5N_2O_2$, FW = 774.73, 0.45 mm × 0.14 mm × 0.12 mm, black block, monoclinic, *C2/c*, a = 11.7070(6) Å, b = 22.5631(15) Å, c = 28.4794(15) Å, β = 95.793(2), V = 7484.3(7) Å^3, Z = 8, μ = 0.523 mm^{-1}; 84122 reflections were measured. 7650 Reflections were unique (R_{int} = 0.039) of which 6588 were observed [$I > 2\sigma(I)$]. Residual electron density between –0.43 and 0.50 e$^-$/Å^3. S = 1.07. Refinement: $R[F^2 > 2\sigma(F^2)]$ = 0.039, $wR(F^2)$ = 0.092, number of reflections: 7650, number of parameters: 562, number of restraints: 235.

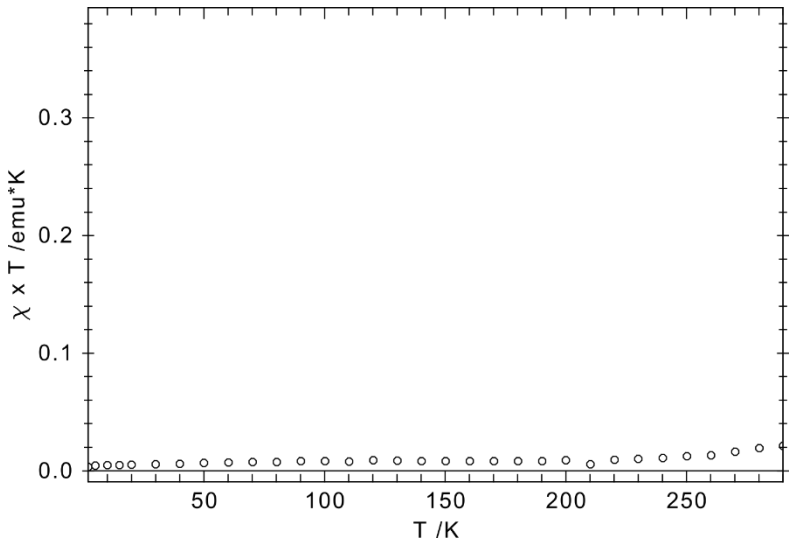
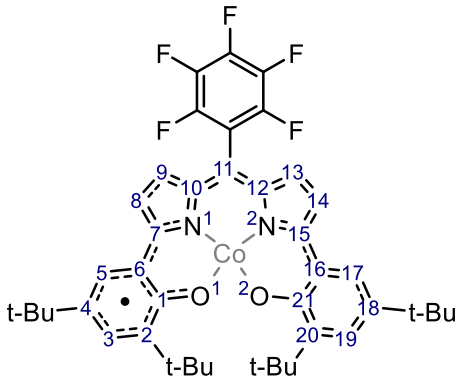
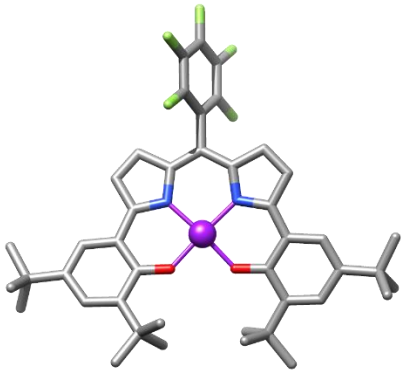


Figure S1. SQUID measurement of **[$Co^{II}(DPP^{\bullet 2-})$]** between 5 K and 290 K, corrected for presence of small oxide nanoparticles.

Table S1. Atom numbering scheme for **DPPH$_3$** and **[Co^{II}(DPP$^{\bullet 2-}$)]** and bond lengths derived from the single crystal XRD measurements and the DFT calculated structure (B3LYP/def2-SVP).





Bond	DPPH$_3$ (XRD, Å)	[Co^{II}(DPP$^{\bullet 2-}$)] (XRD, Å)	[Co^{II}(DPP$^{\bullet 2-}$)] (DFT, Å)
C1–C2	1.411(2)	1.443(3)	1.454
C2–C3	1.395(2)	1.371(3)	1.380
C3–C4	1.395(2)	1.420(3)	1.427
C4–C5	1.385(2)	1.364(3)	1.376
C5–C6	1.403(2)	1.416(3)	1.425
C6–C1	1.408(2)	1.426(3)	1.446
C6–C7	1.463(2)	1.413(3)	1.427
C7–C8	1.426(2)	1.441(3)	1.450
C8–C9	1.368(2)	1.342(3)	1.364
C9–C10	1.422(2)	1.438(3)	1.441
C10–C11	1.400(2)	1.390(3)	1.402
C11–C12	1.395(2)	1.393(3)	1.402
C12–C13	1.426(2)	1.434(3)	1.441
C13–C14	1.364(2)	1.344(3)	1.364
C14–C15	1.425(2)	1.445(3)	1.450
C15–C16	1.462(2)	1.404(3)	1.427
C16–C17	1.406(2)	1.418(3)	1.425
C17–C18	1.382(2)	1.359(3)	1.376
C18–C19	1.393(2)	1.422(3)	1.427
C19–C20	1.395(2)	1.371(3)	1.380
C20–C21	1.406(2)	1.444(3)	1.454
C21–C16	1.403(2)	1.431(3)	1.446
C1–O1	1.3644(18)	1.300(2)	1.287
C21–O2	1.3678(18)	1.288(2)	1.287
C7–N1	1.3519(19)	1.368(2)	1.368
C10–N1	1.383(2)	1.382(2)	1.381
C12–N2	1.388(2)	1.377(2)	1.381
C15–N2	1.3493(19)	1.375(2)	1.368
Co–O1	-	1.8432(13)	1.893
Co–O2	-	1.8457(13)	1.894
Co–N1	-	1.8610(16)	1.913
Co–N2	-	1.8696(15)	1.913

[Co^{II}(DPP$^{\bullet 2-}$)(THF)$_2$]: Obtained when dissolving **[Co^{II}(DPP$^{\bullet 2-}$)]** in THF.

^{1}H NMR (500 MHz, THF-d_8) δ 37.51 (s, 2H), 9.34 (s, 18H), 2.51 (6H) -24.49 (s, 2H), -34.04 (s, 2H), -60.49 (s, 2H). Part of the CH_3 resonances (of the *t*Bu groups) are missing. This signal is gradually disappearing upon addition of THF to a CD_2Cl_2 solution of **[Co^{II}(DPP$^{\bullet 2-}$)]** (see NMR in main text). Coordinated THF is not visible because THF-d_8 was used as the solvent.

UV-Vis (32.27 μM, THF, 1.0 cm cuvet) nm {ε, cm^{-1}M^{-1}}: 318 {28.0×10^3}, 409 {16.3×10^3}, 423 {16.5×10^3}, 474 {12.3×10^3}, 632 {22.9×10^3}, 833 {15.3×10^3}.

X-band EPR: silent at r.t. and 20 K.

μ_{eff} (Evans' method, THF-d_8 with toluene as internal standard, 297.2 K, 13.4 mM, Δν = 21.4 Hz, diamagnetic contribution = –0.00039): 2.91 μ_B.

HRMS measurements afforded only detection of **[Co^{II}(DPP$^{\bullet 2-}$)]** due to the relatively weak coordination of THF and the evaporation of THF under the measurement conditions.

The association constant (K_{ass}) for coordination of THF (guest, G) to **[Co^{II}(DPP$^{\bullet 2-}$)]** (host, H, 32.27 μM in CH_2Cl_2) was obtained after a titration of guest to host and fitting of the absorption band at 833 nm according to a HGG model with non-cooperative binding. The fitting was performed with the software available at http://limhes.net/optim and the results are summarized in Figure S2, Figure S3 and Figure S4.

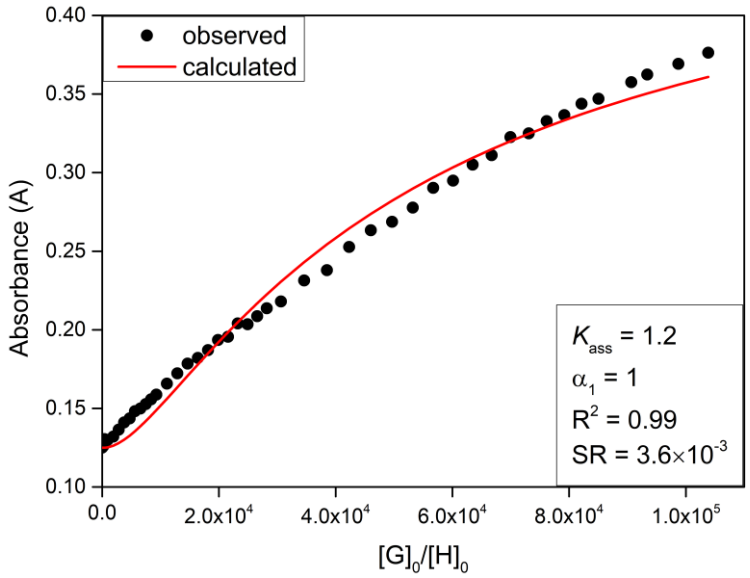


Figure S2. Fit of the changes in the absorption at 833 nm upon titration of THF to **[Co^{II}(DPP$^{\bullet 2-}$)]**.

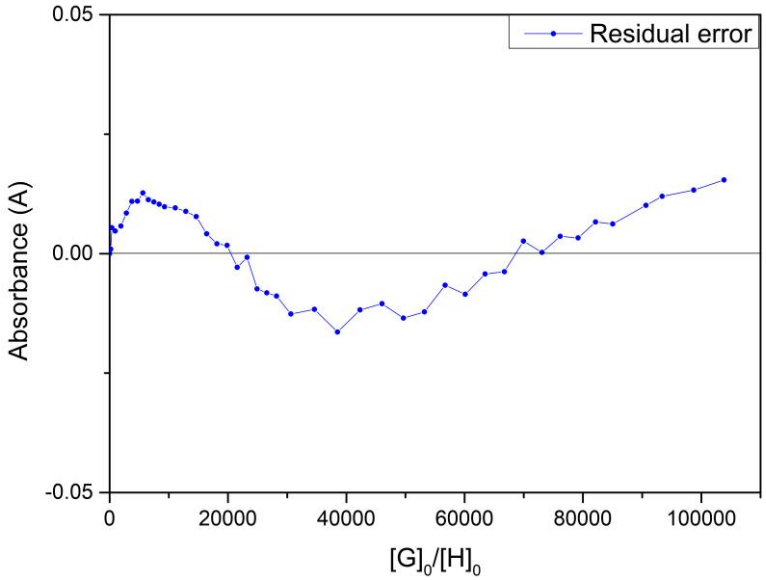


Figure S3. Residual errors of the fit of the changes in the absorption at 833 nm upon titration of THF to **[Co^{II}(DPP$^{\bullet 2-}$)]**.

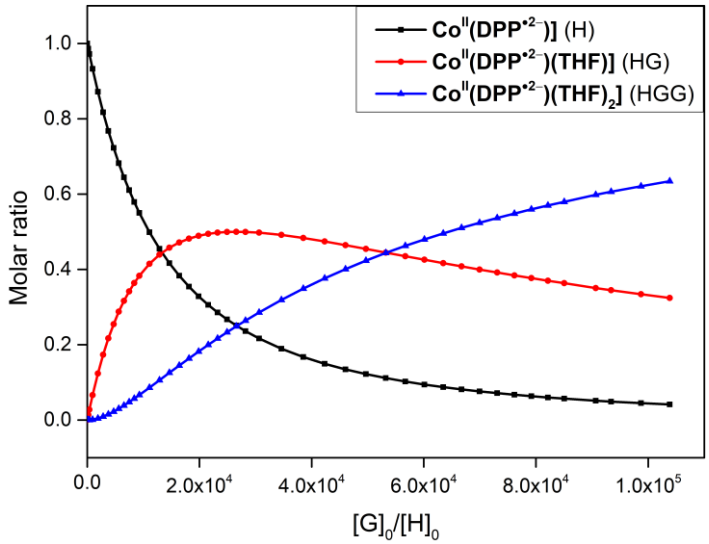


Figure S4. Calculated molar ratios from the fit of the changes in the absorption at 833 nm upon titration of THF to **[Co^{II}(DPP$^{\bullet 2-}$)]**.

[Co^{III}(DPP^{3-})(Py)$_2$]: **[Co^{II}(DPP$^{\bullet 2-}$)]** (0.100 g; 0.13 mmol; 1.0 eq) was dissolved in CH_2Cl_2 (10 mL) and pyridine (1.05 mL; 13.0 mmol; 100 eq) was added to yield a dark green solution, which was stirred for 3 hours, concentrated and dried under reduced pressure. The product was obtained as a green powder in 120 mg; 0.13 mmol; quantitative yield.

^{1}H NMR (500 MHz, THF-d_8) δ 8.04 (d, J = 5.7 Hz, 4H), 7.60 (t, J = 7.6 Hz, 2H), 7.41 (d, J = 2.5 Hz, 2H), 7.21 (d, J = 4.6 Hz, 2H), 7.17 (d, J = 2.6 Hz, 2H), 7.08 (t, J = 6.7 Hz, 4H), 6.96 (d, J = 4.5 Hz, 2H), 1.59 (s, 18H), 1.25 (s, 18H).

^{19}F NMR (282 MHz, Methylene Chloride-d_2) δ -140.91 (d, J = 23.4 Hz), -154.76 (t, J = 20.8 Hz), -161.59 – -163.84 (m).

^{13}C NMR (75 MHz, Methylene Chloride-d_2) δ 158.83, 153.37, 138.13, 124.05, 36.71, 31.36. Most of the ^{13}C

NMR signals are missing for unknown reasons and partially due to the reasons as explained in the characterization of **3** (*vide supra*).

HRMS-CSI$^+$: calc. for [$C_{53}H_{54}CoF_5N_4O_2^+$]: 932.3499, found: 932.358 [M]$^+$, 853.315 [M-Py]$^+$, 774.272 [M-2Py]$^+$.

SQUID: constant susceptibility observed in the 5 K – 290 K range (Figure S7).

UV-Vis (32.27 μM, 2.00 mL CH_2Cl_2 + 10 μL pyridine, 1.0 cm cuvet) nm {ε, $cm^{-1}M^{-1}$}: 337 {25.0×10^3}, 479 {15.0×10^3}, 661 (shoulder) {13.8×10^3}, 723 {26.3×10^3}. See Figure S5. Addition of pyridine was necessary to prevent partial decoordination of pyridine.

XRD: XRD quality single crystals were grown by slow evaporation of a concentrated solution in CH_2Cl_2 and MeOH (5:1) at room temperature. The displacement ellipsoid plot (50% probability level) depicted in the main text and the three crystallographically independent molecules in the asymmetric unit are depicted in Figure S6. The atom numbering scheme and bond distances are provided in

Table **S2**. **[Co^{III}(DPP^{3-})(Py)$_2$]**, $C_{53}H_{54}CoF_5N_4O_2$, FW = 932.93, black needle, 0.36 mm × 0.05 mm × 0.04 mm, triclinic, *P*-1, a = 15.5847(7) Å, b = 20.0568(8) Å, c = 26.1206(9) Å, α = 69.329(3)°, β = 78.077(3)°, γ = 85.913(3)°, V = 7474.3(5) Å^3, Z = 6, μ = 3.21 mm^{-1}; 96163 reflections were measured with $(\sin\theta/\lambda)_{max}$ = 0.617 Å^{-1}. 29269 Reflections were unique (R_{int} = 0.089) of which 19036 were observed [$I > 2\sigma(I)$]. Residual electron density between –0.53 and 0.65 e$^-$/Å^3. S = 0.96. Refinement: $R[F^2 > 2\sigma(F^2)]$ = 0.056, $wR(F^2)$ = 0.153, number of reflections: 29269, number of parameters: 1908, number of restraints: 529.

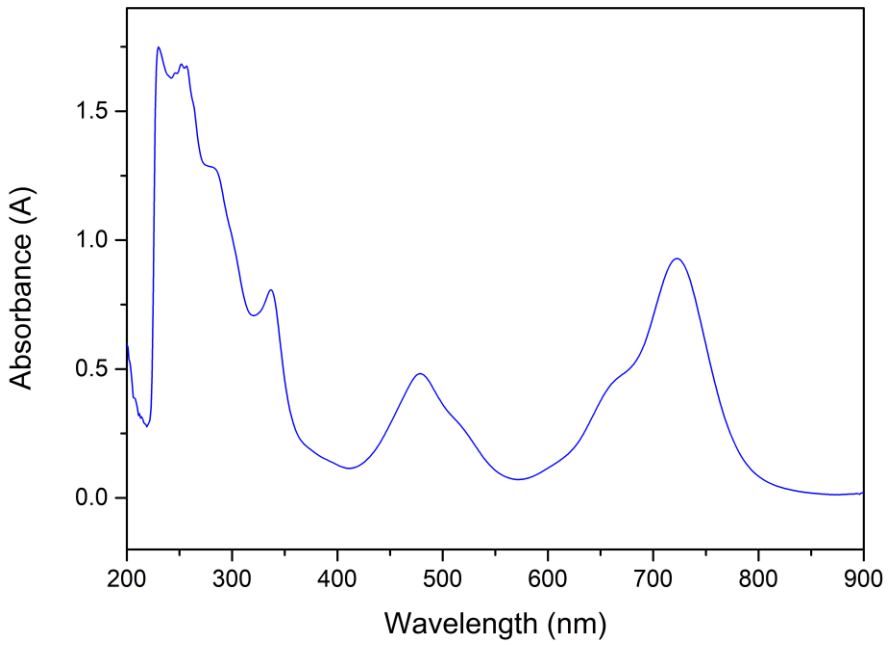


Figure S5. UV-Vis spectrum of **[Co^{III}(DPP^{3-})(Py)$_2$]** (32.27 μM) via addition of 10 μL pyridine to a 2.0 mL CH_2Cl_2 solution of **[Co^{II}(DPP$^{\bullet2-}$)]**.

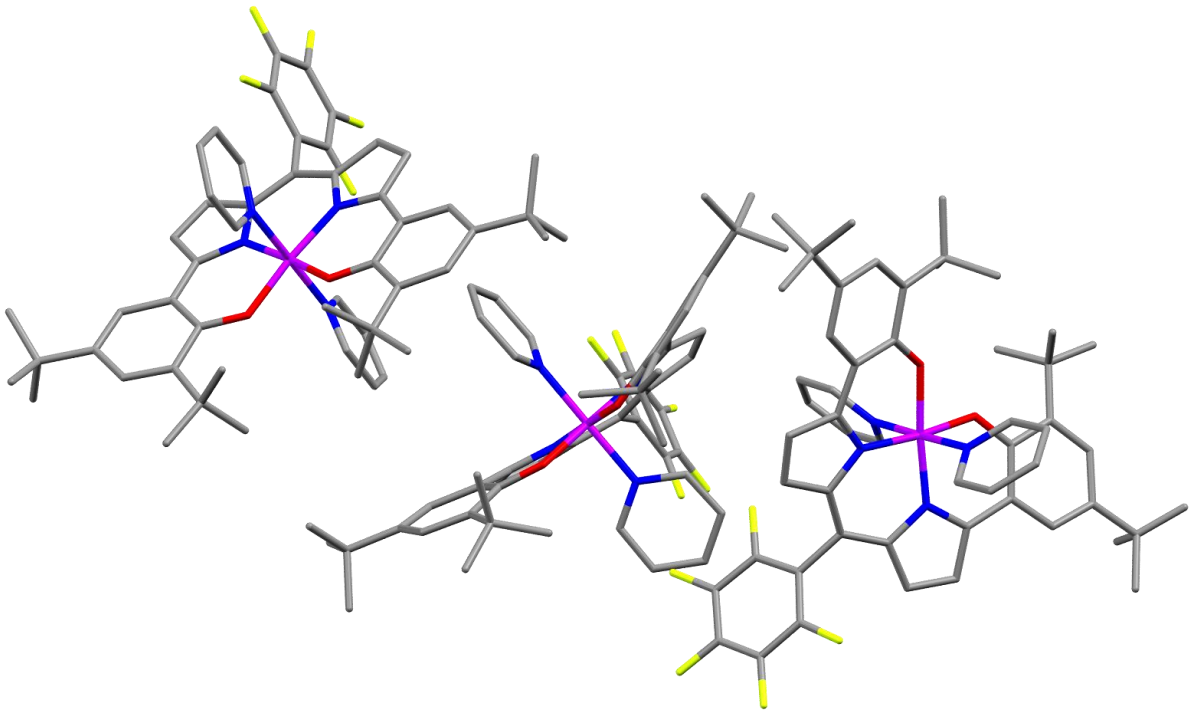
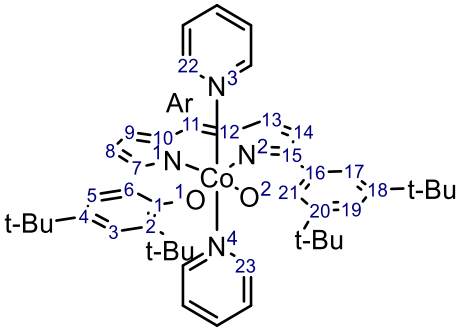
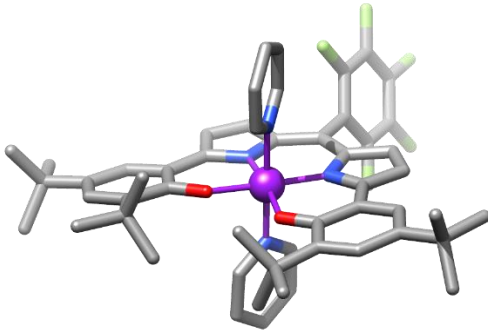


Figure S6. Single crystal XRD measured molecular structure of **[Co^{III}(DPP^{3-})$(Py)_2$]**, showing the three crystallographically independent molecules in the asymmetric unit (A, B and C from left to right), depicted as wireframes. H atoms and disorder are omitted for clarity.

Table S2. Atom numbering scheme, bond lengths and dihedral pyridine angles for the three crystallographically independent molecules of **[Co^{III}(DPP^{3-})(Py)$_2$]** (labelled A, B and C in Figure S6), and the DFT (B3LYP/def2-TZVP geometry optimization) calculated structure. Ar = C_6F_5.





Bond	A (XRD, Å)	B (XRD, Å)	C (XRD, Å)	DFT (Å)
C1–C2	1.435(5)	1.443(5)	1.433(5)	1.447
C2–C3	1.395(5)	1.393(5)	1.397(5)	1.391
C3–C4	1.394(5)	1.403(6)	1.400(5)	1.412
C4–C5	1.369(5)	1.365(5)	1.369(5)	1.382
C5–C6	1.400(4)	1.420(5)	1.408(5)	1.418
C6–C1	1.429(4)	1.413(5)	1.408(5)	1.429
C6–C7	1.453(5)	1.446(5)	1.455(5)	1.449
C7–C8	1.438(4)	1.429(5)	1.420(5)	1.440
C8–C9	1.357(5)	1.354(5)	1.364(5)	1.374
C9–C10	1.420(4)	1.418(5)	1.413(5)	1.429
C10–C11	1.382(5)	1.384(5)	1.388(5)	1.399
C11–C12	1.394(4)	1.390(4)	1.380(5)	1.399
C12–C13	1.415(5)	1.413(5)	1.414(5)	1.429
C13–C14	1.358(5)	1.363(5)	1.367(5)	1.374
C14–C15	1.435(5)	1.435(4)	1.432(5)	1.440
C15–C16	1.441(5)	1.442(4)	1.440(5)	1.449
C16–C17	1.411(5)	1.416(4)	1.414(4)	1.418
C17–C18	1.368(5)	1.380(5)	1.370(5)	1.382
C18–C19	1.395(5)	1.405(5)	1.393(5)	1.412
C19–C20	1.380(5)	1.386(5)	1.388(5)	1.390
C20–C21	1.437(4)	1.437(4)	1.448(5)	1.447
C21–C16	1.419(5)	1.423(5)	1.422(5)	1.430
C1–O1	1.323(4)	1.321(4)	1.323(4)	1.311
C21–O2	1.326(4)	1.318(4)	1.314(4)	1.311
C7–N1	1.356(4)	1.355(4)	1.347(4)	1.355
C10–N1	1.399(4)	1.398(4)	1.408(4)	1.391
C12–N2	1.401(4)	1.391(4)	1.408(4)	1.392
C15–N2	1.358(4)	1.353(4)	1.350(4)	1.355
Co–O1	1.923(2)	1.904(2)	1.910(2)	1.929
Co–O2	1.913(2)	1.913(2)	1.909(2)	1.929
Co–N1	1.912(2)	1.906(3)	1.913(3)	1.933
Co–N2	1.912(3)	1.903(3)	1.908(3)	1.933
Co–N3	1.975(2)	1.973(3)	1.946(3)	1.988
Co–N4	1.963(2)	1.941(3)	1.959(3)	1.986
Dihedral angle of the pyridine planes				
C22–N3–Co–N4	10.80°	51.39°	176.11°	14.74°
C23–N4–Co–N3	10.80°	7.47°	84.50°	11.80°

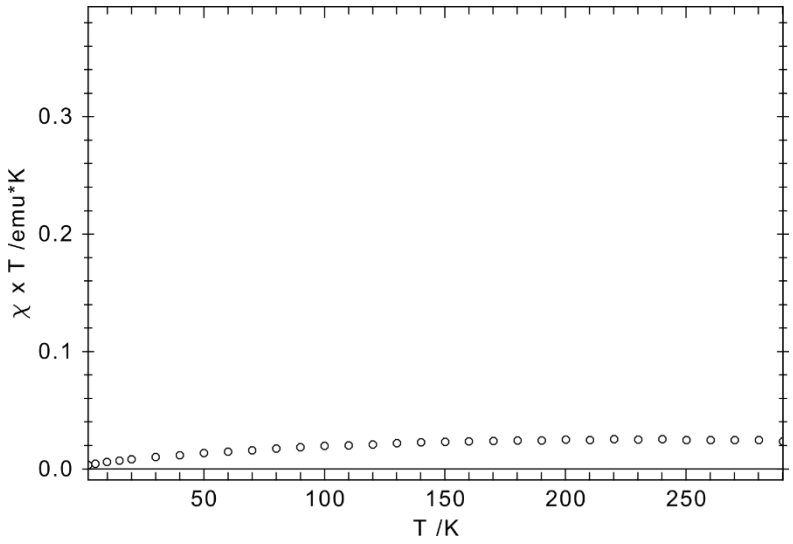


Figure S7. SQUID measurement of **[Co^{III}(DPP^{3-})(Py)$_2$]** between 4 K and 290 K, corrected for the presence of oxide nanoparticles.

[Co^{III}(DPP^{3-})(NH$_2$*t*Bu)$_2$]: **[Co^{II}(DPP$^{\bullet 2-}$)]** (0.100 g; 0.13 mmol; 1.0 eq) was dissolved in CH_2Cl_2 (10 mL) and *t*-butylamine (1.36 mL; 1.29 mmol; 100 eq) was added to yield a green solution, which was stirred for 3 hours, concentrated and dried under reduced pressure. The product was obtained as a green powder in quantitative yield (0.119 g; 0.13 mmol).

^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.67 (s, 2H), 7.31 (d, J = 2.6 Hz, 2H), 7.28 (d, J = 4.8 Hz, 2H), 6.85 (s, 2H), 2.11 (s, 4H), 1.74 (s, 18H), 1.39 (s, 18H), 0.52 (s, 18H).

^{13}C NMR (126 MHz, Methylene Chloride-d_2) δ 158.96, 156.97, 142.10, 137.80, 136.64, 130.77, 125.64, 121.84, 119.02, 115.94, 49.97, 36.15, 33.59, 31.74, 30.83. One ^{13}*C*H$_3$ signal is missing, presumably due to overlap. Five ^{13}C NMR signal are missing for the reasons as explained in the characterization of **3** (*vide supra*).

^{19}F NMR (282 MHz, Methylene Chloride-d_2) δ -137.36 – -141.36 (m), -154.75 (t, J = 21.2 Hz), -160.77 – -164.48 (m).

UV-Vis (32.27 μM, CH_2Cl_2 : *t*BuNH$_2$ = 2.0 : 0.01, 1.0 cm cuvet) nm {ε, cm^{-1}M^{-1}}: 276, 336 (30.1×10^3), 487 (16.5×10^3), 650 (shoulder, 16.9×10^3), 705 (30.7×10^3). See Figure S8. Addition of *t*BuNH$_2$ was necessary to prevent decoordination of the amine.

HRMS-CSI$^+$ calc. for $[C_{51}H_{66}CoF_5N_4O_2]^+$: 920.4438, found: 847.374 [M-*t*BuNH$_2$]$^+$, 774.283 [M-2*t*BuNH$_2$]$^+$.

XRD: XRD quality single crystals were grown by slow evaporation of a concentrated solution in CH_2Cl_2 and MeOH (5:1) at room temperature. The three crystallographically independent molecules in the asymmetric unit and the displacement ellipsoid plot (50% probability level) of one molecule is depicted in Figure S9. The atom numbering scheme and relevant bond lengths are provided in Table S3. **[Co^{III}(DPP^{3-})(NH$_2$*t*Bu)$_2$]**, $3(C_{51}H_{66}CoF_5N_4O_2)\cdot CH_4O$, FW = 2795.05, dark green needle, 0.35 mm × 0.04 mm × 0.03 mm, triclinic, *P*-1, a = 12.9446(5) Å, b = 21.7384(9) Å, c = 27.2202(9) Å, α = 84.432(3)°, β = 89.826(3)°, γ = 86.438(3)°, V = 7608.7(5) Å^3, Z = 2, μ = 3.15 mm^{-1}; 74031 reflections were measured with $(\sin\theta/\lambda)_{max}$ = 0.616 Å^{-1}. 29771 Reflections were unique (R_{int} = 0.075) of which 19074 were observed [$I > 2\sigma(I)$]. Residual electron density

between −0.44 and 0.51 $e^-/Å^3$. S = 0.98. Refinement: $R[F^2 > 2\sigma(F^2)]$ = 0.056, $wR(F^2)$ = 0.139, number of reflections: 29771, number of parameters: 1812, number of restraints: 39.

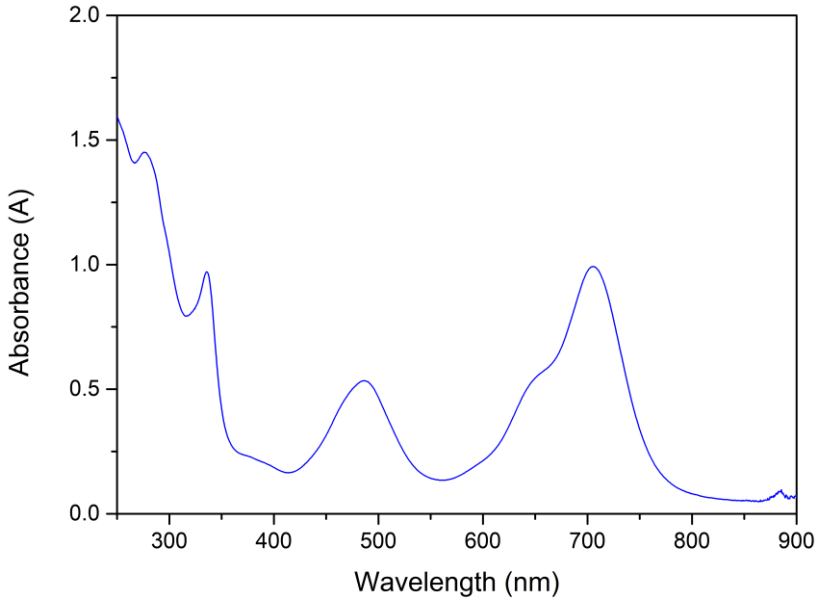


Figure S8. UV-Vis spectrum of **[Co^{III}(DPP^{3-})(*t*BuNH$_2$)$_2$]** (32.27 µM) via addition of 10 µL *t*BuNH$_2$ to a 2.0 mL CH_2Cl_2 solution of **[Co^{II}(DPP$^{\bullet 2-}$)]**.

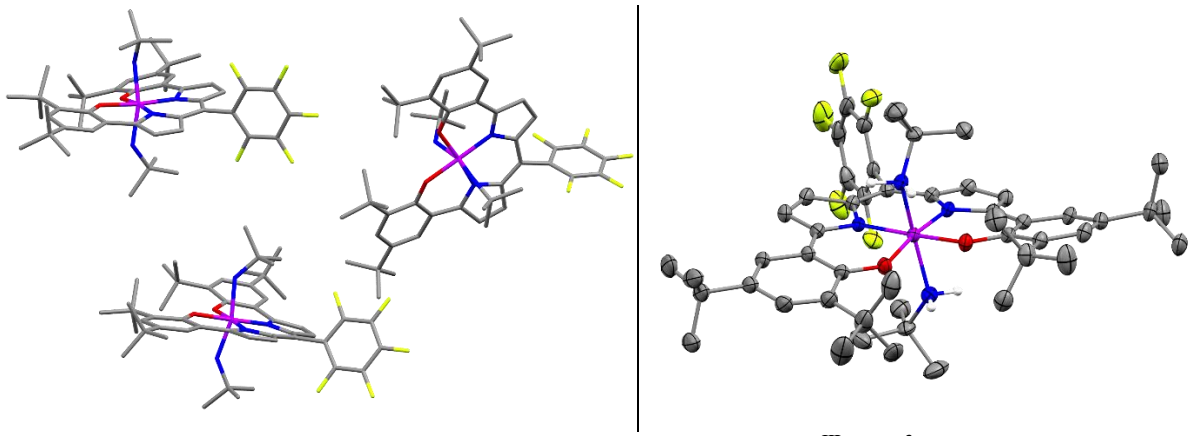
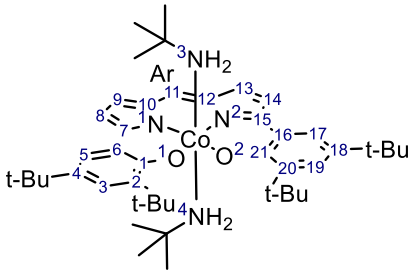
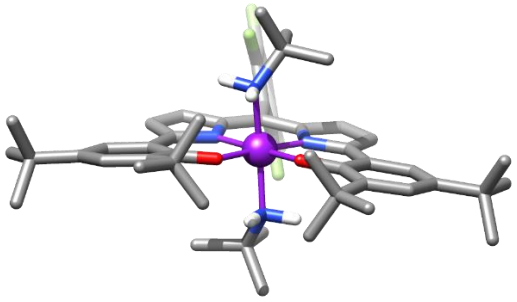


Figure S9. Left: single crystal XRD measured molecular structure of **[Co^{III}(DPP^{3-})(NH$_2$*t*Bu)$_2$]**, showing the three crystallographically independent molecules in the asymmetric unit (A, B and C from left to right), depicted as wireframes. H atoms and lattice solvent molecules are omitted for clarity. Right: Displacement ellipsoid plot (50% probability level) of**[Co^{III}(DPP^{3-})(NH$_2$*t*Bu)$_2$]** (molecule A). H atoms (except NH) are omitted for clarity.

Table S3. Atom numbering scheme for the three crystallographically independent molecules of **[Co^{III}(DPP^{3-})(NH_2tBu)$_2$]** (labelled A, B and C) and DFT (B3LYP/def2-TZVP geometry optimization) calculated structure. Ar = C_6F_5. Bond lengths derived from the single crystal XRD measurements and the DFT calculated structure are included below.





Bond	A (XRD, Å)	B (XRD, Å)	C (XRD, Å)	DFT (Å)
C1–C2	1.441(5)	1.436(4)	1.437(4)	1.445
C2–C3	1.386(5)	1.386(4)	1.390(4)	1.390
C3–C4	1.398(6)	1.406(4)	1.399(5)	1.413
C4–C5	1.375(5)	1.364(5)	1.378(5)	1.382
C5–C6	1.423(4)	1.423(4)	1.417(4)	1.418
C6–C1	1.408(5)	1.416(4)	1.416(4)	1.429
C6–C7	1.444(5)	1.437(4)	1.450(4)	1.452
C7–C8	1.425(5)	1.442(4)	1.429(4)	1.439
C8–C9	1.357(5)	1.357(5)	1.365(5)	1.375
C9–C10	1.418(4)	1.422(4)	1.422(4)	1.427
C10–C11	1.388(4)	1.390(5)	1.384(4)	1.396
C11–C12	1.382(4)	1.398(5)	1.394(4)	1.398
C12–C13	1.420(4)	1.407(5)	1.424(4)	1.428
C13–C14	1.358(5)	1.365(5)	1.354(4)	1.375
C14–C15	1.428(4)	1.423(5)	1.425(4)	1.438
C15–C16	1.452(4)	1.444(5)	1.451(4)	1.451
C16–C17	1.417(4)	1.412(4)	1.424(4)	1.418
C17–C18	1.381(5)	1.376(5)	1.373(4)	1.383
C18–C19	1.402(5)	1.393(5)	1.399(5)	1.413
C19–C20	1.381(5)	1.396(5)	1.389(4)	1.391
C20–C21	1.431(5)	1.437(4)	1.443(4)	1.444
C21–C16	1.408(4)	1.409(5)	1.403(4)	1.427
C1–O1	1.333(4)	1.331(4)	1.330(4)	1.313
C21–O2	1.326(4)	1.339(4)	1.330(4)	1.315
C7–N1	1.359(4)	1.363(4)	1.356(4)	1.357
C10–N1	1.390(4)	1.394(4)	1.398(4)	1.390
C12–N2	1.403(4)	1.398(4)	1.391(4)	1.391
C15–N2	1.370(4)	1.361(4)	1.351(4)	1.358
Co–O1	1.917(2)	1.928(2)	1.911(2)	1.924
Co–O2	1.920(2)	1.921(2)	1.925(2)	1.935
Co–N1	1.912(3)	1.914(2)	1.912(2)	1.932
Co–N2	1.922(3)	1.913(3)	1.914(3)	1.938
Co–N3	2.003(3)	2.001(3)	1.993(3)	2.019
Co–N4	1.997(3)	2.003(3)	2.008(3)	2.024

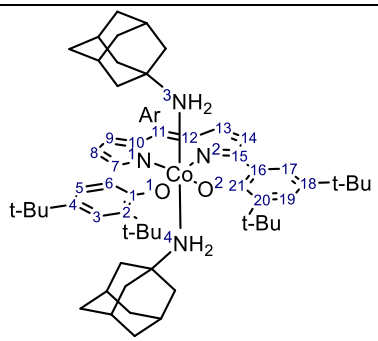
[$Co^{III}(DPP^{3-})(NH_2Ad)_2$]: **[$Co^{II}(DPP^{\bullet 2-})$]** (10.0 mg; 13.0 μmol; 1.0 eq) and 1-adamantylamine (3.9 mg; 26.0 μmol; 2.0 eq) were dissolved in CH_2Cl_2 (10 mL) and stirred for 3 hours at r.t. yielding a green solution. Single crystals suitable for XRD analysis were obtained by slow evaporation of a concentrated solution in CH_2Cl_2 and MeOH (5:1). The green crystals were filtered and washed with MeOH (2 mL). The product was obtained as green crystals in 6.0 mg; 5.6 μmol; 43% yield.

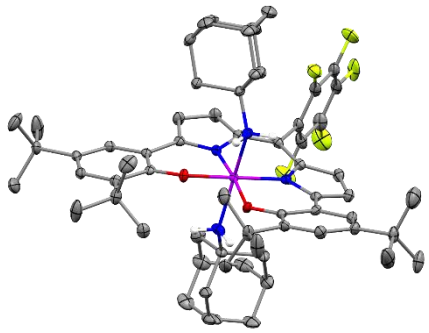
^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.54 (s, 2H), 7.38 – 7.14 (m, 4H), 6.94 (s, 2H), 2.09 (s, 4H), 1.79 – 0.59 (m, 48H).

HRMS-CSI$^+$ calc. for $[C_{63}H_{78}CoF_5N_4O_2]^+$: 1076.5371, found: 1076.5386 $[M]^+$.

XRD: XRD quality single crystals were grown by slow evaporation of a concentrated solution in CH_2Cl_2 and MeOH (5:1) at room temperature. The displacement ellipsoid plot (50% probability level) with relevant bond lengths is provided in Table **S4**. **[$Co^{III}(DPP^{3-})(NH_2Ad)_2$]**, $C_{63}H_{78}CoF_5N_4O_2$, FW = 1077.22, 0.71 mm × 0.15 mm × 0.15 mm, green block, orthorhombic, *Pbca*, a = 18.0240(10) Å, b = 24.2843(13) Å, c = 25.7668(14) Å, $\alpha = \beta = \gamma = 90^o$, V = 11278.1(11) Å^3, Z = 8, μ = 0.368 mm^{-1}; 299626 reflections were measured. 12941 Reflections were unique (R_{int} = 0.062) of which 10510 were observed [$I > 2\sigma(I)$]. Residual electron density between –0.59 and 0.76 e$^-$/Å^3. S = 1.12. Refinement: $R[F^2 > 2\sigma(F^2)]$ = 0.053, $wR(F^2)$ = 0.118, number of reflections: 12941, number of parameters: 892, number of restraints: 869.

Table S4. Atom numbering scheme for **[Co^{III}(DPP^{3-})(NH$_2$Ad)$_2$]**, single crystal XRD measured structure and relevant bond lengths. Ellipsoid level set at 50% probability. Hydrogen atoms (except NH) and disorder in *t*Bu, C_6F_5 and adamantyl are omitted for clarity. Ar = C_6F_5.





Bond	XRD (Å)	Bond	XRD (Å)
C1–C2	1.437(3)	C17–C18	1.374(3)
C2–C3	1.386(3)	C18–C19	1.406(3)
C3–C4	1.402(3)	C19–C20	1.383(3)
C4–C5	1.372(3)	C20–C21	1.432(3)
C5–C6	1.412(3)	C21–C16	1.414(3)
C6–C1	1.417(3)	C1–O1	1.326(2)
C6–C7	1.447(3)	C21–O2	1.330(2)
C7–C8	1.430(3)	C7–N1	1.352(3)
C8–C9	1.361(3)	C10–N1	1.388(3)
C9–C10	1.421(3)	C12–N2	1.393(3)
C10–C11	1.388(3)	C15–N2	1.353(3)
C11–C12	1.384(3)	Co–O1	1.9193(15)
C12–C13	1.418(3)	Co–O2	1.9332(14)
C13–C14	1.357(3)	Co–N1	1.9145(17)
C14–C15	1.431(3)	Co–N2	1.9173(17)
C15–C16	1.447(3)	Co–N3	2.0034(18)
C16–C17	1.415(3)	Co–N4	2.0103(19)

Complete Active Space Self Consistent Field Calculations

The NEVPT2 corrected CASSCF calculations were performed according to the method described in the general considerations.

[Co^{II}(DPP$^{\bullet 2-}$)] *NEVPT2-CASSCF(18,14)*

The energy for the singlet state and its contributors for **[Co^{II}(DPP$^{\bullet 2-}$)]** was obtained from NEVPT2 corrected CASSCF(18,14) calculations and are reported in Table S5. All initial active orbitals were preserved in the active space. It is observed that the singlet state has >96% multi-reference character and is best described as a broken-symmetry singlet (BSS) solution. CASSCF(18,14) or CASSCF(8,7) calculations on the triplet state did not converge after multiple attempts and the active space was not preserved in these calculations. State averaging of the singlet and triplet state in a NEVPT2-CASSCF(18,14) calculation afforded a solution which is +6.48 kcal mol^{-1} (total energy = –2385460,093 kcal mol^{-1}) less stable than the found singlet state as depicted in Table S5. These findings are consistent with the experimentally found BSS/OSS spin state. A quantitative orbital analysis of the complete active space of the broken symmetry singlet state is shown in Figure S10. The most relevant active orbitals and an assignment of the electronic structure (from Löwdin population analysis) of the broken symmetry singlet state are shown in the main text.

Table S5. Total energy (NEVPT2 corrected) for the singlet states and their contributions for the single-root NEVPT2-CASSCF(18,14) calculation on **[Co^{II}(DPP$^{\bullet 2-}$)]**. The most important contributions of the state are highlighted in grey.

Multiplicity	Total energy (kcal mol^{-1})	Contribution : state
1 (singlet)	–2385466.571	0.45476 : 22222222200000
		0.40887 : 22222222020000
		0.03292 : 22222221111000
		0.01103 : 22222220202000
		0.01002 : 22222220022000
		0.00461 : 22220222200200
		0.00437 : 22222212110010
		0.00417 : 22202222200200
		0.00413 : 22220222020200
		0.00378 : 22222112200011
		0.00375 : 22202222020200
		0.00340 : 22222112020011

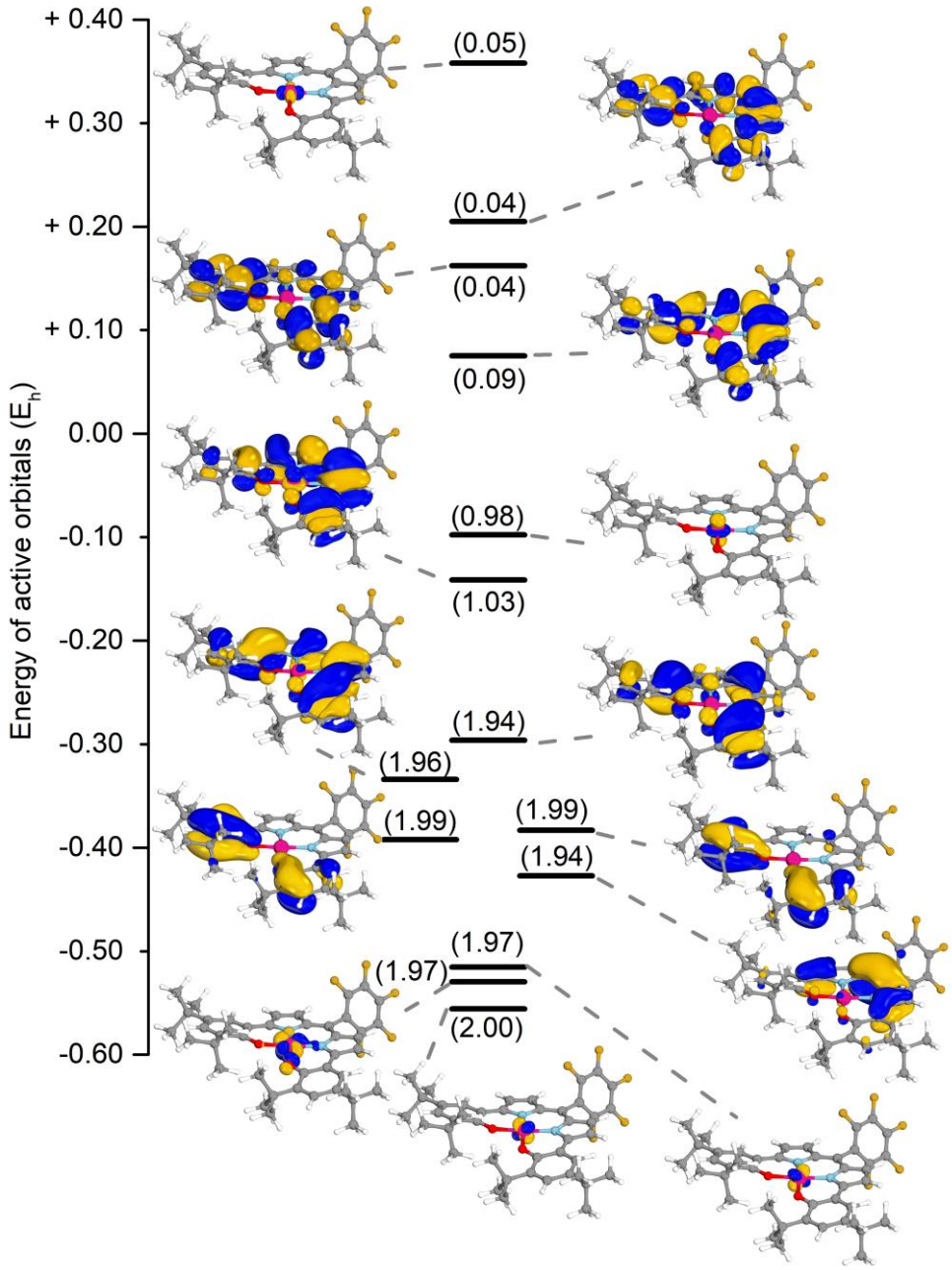


Figure S10. Active space and occupancies of the orbitals in parenthesis of a NEVPT2-CASSCF(18,14) calculation on **[Co^{II}(DPP$^{\bullet 2-}$)]**. Isosurface set to 80.

[Co^{II}(DPP$^{\bullet 2-}$)(THF)$_2$] *NEVPT2-CASSCF(18,15)*

The total and relative energies for the singlet, triplet and quintet states and their contributors for **[Co^{II}(DPP$^{\bullet 2-}$)(THF)$_2$]** were obtained from NEVPT2 corrected CASSCF(18,15) calculations and are reported in Table S6. All initial active orbitals, except the d_{xy} orbital, were preserved in the active space. The d_{xy} orbital is found to be non-correlated and doubly filled in the inactive space. A quantitative orbital analysis of the complete active space of the triplet state is shown in Figure S11. The most relevant active orbitals and an assignment of the electronic structure (from Löwdin population analysis) of the triplet state are shown in the main text.

Table S6. Total energy (NEVPT2 corrected) for the singlet, triplet and quintet states and their contributors for the single-root NEVPT2-CASSCF(18,15) calculation on **[Co^{II}($DPP^{\bullet 2-}$)$(THF)_2$]**. The most important contributions of the states are highlighted in grey.

Multiplicity	Total and relative energy (kcal mol^{-1})	Contribution : state
1 (singlet)	–2676607.654 (+32.2)	0.81815 : 222222221100000
		0.01380 : 222212221110000
		0.01197 : 222222021100020
		0.01025 : 222221221110000
		0.00938 : 222022221100002
		0.00926 : 220222221100002
		0.00504 : 222211221120000
		0.00494 : 222222212100000
		0.00477 : 222222201100200
		0.00473 : 222202221120000
		0.00452 : 202222221100002
		0.00446 : 222222211110000
		0.00427 : 222222201102000
		0.00406 : 222221211100200
		0.00361 : 222221211101100
		0.00356 : 221122221200001
		0.00338 : 222220221100200
		0.00312 : 222221121100020
		0.00266 : 222220221120000
3 (triplet)	–2676639.862 (= 0)	0.36435 : 222222211200000
		0.27900 : 222222221100000
		0.13337 : 222221221200000
		0.01962 : 222122221200000
		0.01209 : 222222211020000
		0.01001 : 222222212100000
		0.00755 : 221222211201000
		0.00637 : 222222201120000
		0.00636 : 222222121200000
		0.00578 : 212222212200000
		0.00564 : 212222222100000
		0.00553 : 220222211202000
		0.00530 : 122222220201000
		0.00472 : 221221221201000
		0.00305 : 222221222100000
		0.00270 : 220221221202000
		0.00259 : 221122221201000
		0.00258 : 222212221200000
		0.00252 : 221222221101000
5 (quintet)	–2676606.869 (+33.0)	0.82815 : 222222211110000
		0.01094 : 112222212210000
		0.00906 : 221222211111000
		0.00634 : 222212211111000
		0.00602 : 222222111111000
		0.00569 : 112222212120000
		0.00366 : 222221221110000
		0.00359 : 222122211111000
		0.00321 : 222211211110011

	0.00313 : 222222011110020
	0.00313 : 222222011110200
	0.00286 : 220222211112000
	0.00281 : 222220211110002
	0.00277 : 221212211112000
	0.00266 : 222212111110020

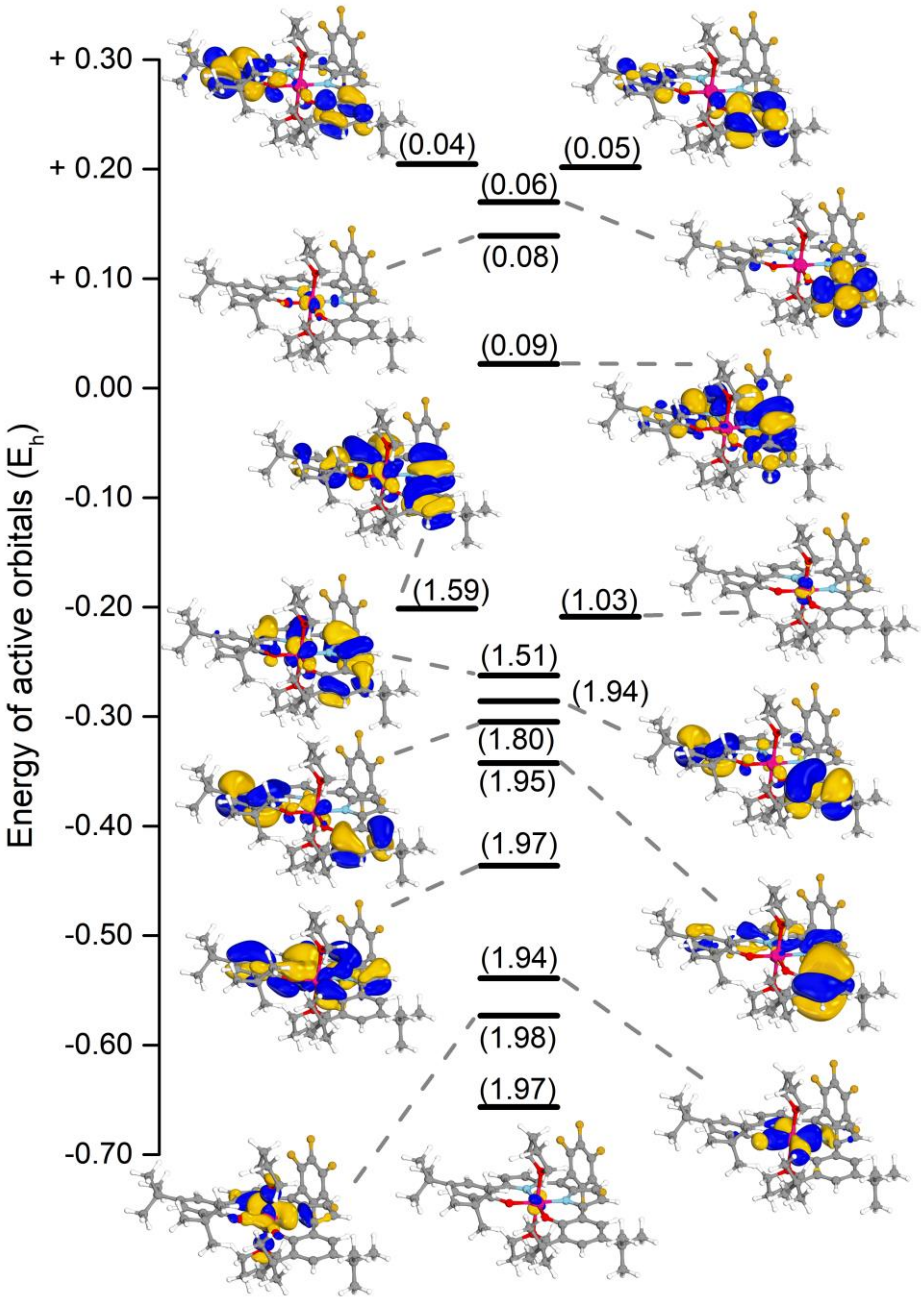


Figure S11. Active space and occupancies of the orbitals in parenthesis of a NEVPT2-CASSCF(18,15) calculation on **[$Co^{II}(DPP^{\bullet 2-})(THF)_2$]**. Isosurface set to 80.

[Co^{II}(DPP$^{\bullet 2-}$)(THF)] *NEVPT2-CASSCF(14,10)*

The total and relative energies for the singlet, triplet and quintet states and their contributors for **[Co^{II}(DPP$^{\bullet 2-}$)(THF)]** were obtained from NEVPT2 corrected CASSCF(14,10) calculations and are reported in Table S7. All initial active orbitals were preserved in the active space. A quantitative orbital analysis of the complete active space of the triplet state is shown in Figure S12. A total of 4 unpaired electrons (3 of α-spin and 1 of β-spin) in the most dominant contribution to the wavefunction on cobalt and the ligand gives rise to the most stable net triplet spin state of the complex, although the open-shell singlet (+1.1 kcal mol^{-1}, one α- and one β-spin electron in the most dominant contributor) and quintet (+1.0 kcal mol^{-1}, 4 α-spin electrons in the most dominant contributor) are very close in energy. These small energy differences between the spin states are to be expected for the conversion of an open-shell singlet (**[Co^{II}(DPP$^{\bullet 2-}$)]**) to a triplet (**[Co^{II}(DPP$^{\bullet 2-}$)(THF)$_2$]**) spin state.

Table S7. Total energy (NEVPT2 corrected) for the singlet, triplet and quintet states and their contributors for the single-root NEVPT2-CASSCF(14,10) calculation on **[Co^{II}(DPP$^{\bullet 2-}$)(THF)]**. The most important contributions of the states are highlighted in grey.

Multiplicity	Total and relative energy (kcal mol^{-1})	Contribution : state
1 (singlet)	-2531034.609 (+1.1)	0.89986 : 2222221100
		0.03375 : 2222211110
		0.02128 : 2222201120
		0.01053 : 2220221102
		0.00874 : 2202221102
		0.00532 : 2222122100
		0.00368 : 2211221201
		0.00347 : 2222112110
3 (triplet)	-2531035.758 (= 0)	0.63824 : 2222211110
		0.13044 : 2222220110
		0.10802 : 2222202110
		0.02690 : 2222111111
		0.01495 : 2222221010
		0.01335 : 2112212210
		0.01089 : 2222201210
		0.01065 : 2222011112
5 (quintet)	-2531034.798 (+1.0)	0.92161 : 2222211110
		0.02881 : 2222111111
		0.01782 : 2222011112
		0.00479 : 1222111112
		0.00427 : 1222211111
		0.00316 : 2221221110
		0.00278 : 2221121111
		0.00277 : 2212211120

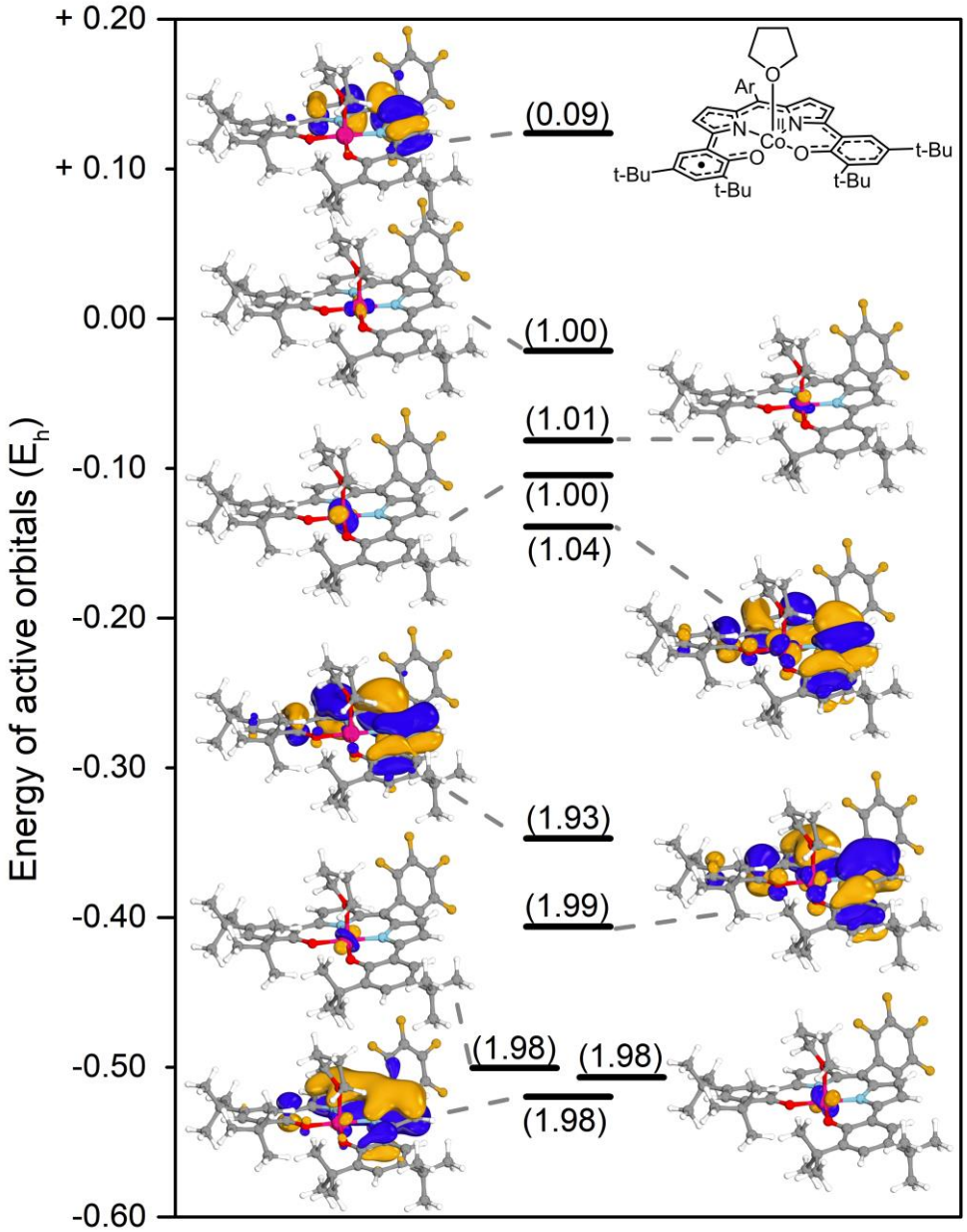


Figure S12. Active space and occupancies of the orbitals in parenthesis of a NEVPT2-CASSCF(14,10) calculation on **[Co^{II}(DPP$^{\bullet 2-}$)(THF)]** in the triplet spin state. Isosurface set to 80.

Density Functional Theory calculations

All calculations were performed according to the methods described in the general considerations. Calculations with the GGA BP86 functional were not able to reproduce the experimentally found spin states. The correlation between theory and experiment was found upon usage of the hybrid functional B3LYP. However, in combination with the def2-TZVP basis set on an m4 grid, geometry optimization and frequency analysis was too expensive (>30 days wall time). Usage of the def2-SVP basis set afforded geometries with similar bond-lengths as found in the crystal structures, we therefore optimized geometries and performed frequency analysis at the B3LYP/def2-SVP/disp3/m4-grid level of theory. A single point energy SCF calculation at the B3LYP/def2-TZVP/disp3/m4-grid level of theory was then performed for final energy evaluation, wherein the previously calculated vibrations were used.

Absolute energies for all DFT optimized structures

The relevant $<s^2>$, ΔH^o_{298K}, ΔS^o_{298K} and ΔG^o_{298K} (in Hartree) for all relevant compounds is depicted in Table S8. Relevant bond lengths are depicted above in Table S1,

Table **S2** and Table S3.

Table S8. Calculated $<s^2>$, SCF corrections, ZPE corrections, enthalpy corrections and ΔG^o_{298K} (in Hartree) and relative energies (in kcal mol^{-1} relative to **$[Co^{II}(DPP^{\bullet 2-})]$** for the different complexes and spin states at the B3LYP/def2-SVP//B3LYP/def2-TZVP level of theory on an m4 grid with Grimme's version 3 zero-damping dispersion corrections.

Compound	Spin state	$<s^2>$	**SCF** (Hartree)	**ZPE correction** (Hartree)	**Enthalpy correction** (Hartree)	**Entropy correction** (Hartree)	ΔG^o_{298K} (Hartree)	**Relative energy** (kcal mol^{1})
$[Co^{II}(DPP^{\bullet 2-})]$	OSS	1.0250	–3806.67821	0.77833	0.82930	0.69608	–3805.98213	**= 0** [a,b]
	OSS/Triplet[c]	2.0310	–3806.67909	0.77833	0.82930	0.69595	–3805.98314	-
	CSS	-	–3806.65526	0.77896	0.82972	0.69780	–3805.95746	+14.8
	Triplet	2.0312	–3806.67920	0.77843	0.82939	0.69600	–3805.98319	–1.3
$[Co^{II}(DPP^{\bullet 2-})$ (THF)]	OSS	1.0301	–4039.10798	0.89644	0.95382	0.80579	–4038.30219	-3.1 [b]
	OSS/Triplet[c]	2.0302	–4039.10975	0.89644	0.95382	0.80567	–4038.30408	-
	CSS	-	–4039.07864	0.89821	0.95486	0.80934	–4038.26930	+16.3
	Triplet	2.0298	–4039.10979	0.89658	0.95391	0.80583	–4038.30396	–5.5
	Quintet	6.0314	–4039.10110	0.89378	0.95210	0.80038	-4038.30072	–3.4
$[Co^{II}(DPP^{\bullet 2-})(THF)_2]$	OSS	1.0288	–4271.53298	1.01440	1.07829	0.91420	–4270.61878	-4.2 [b]
	OSS/Triplet[c]	2.0299	–4271.53551	1.01440	1.07829	0.91408	–4270.62144	-
	CSS	-	–4271.52490	1.01773	1.08029	0.92114	–4270.60376	+3.5
	Triplet	2.0271	–4271.53555	0.90977	1.07666	1.01200	–4270.62578	–10.3
	Quintet	6.0350	–4271.52843	1.01200	1.07666	0.90969	–4270.61874	–5.9

[Co^{II} ($DPP^{\bullet 2-}$)(Py)]	OSS	1.0301	–4054.93817	0.86876	0.92557	0.77851	–4054.15966	–6.3 [b]
	OSS/Triplet[c]	2.0318	–4054.94036	0.86876	0.92557	0.77839	–4054.16197	-
	CSS	-	–4054.92546	0.87083	0.92684	0.78231	–4054.14314	+2.6
	Triplet	2.0314	–4054.94043	0.86900	0.92570	0.77872	–4054.16171	–9.1
[Co^{III} (DPP^{3-}) ($Py)_2$]	OSS	-	-	-	-	-	-	- [d]
	CSS	-	–4303.20524	0.96311	1.02427	0.86920	–4302.33604	–14.2
	Triplet	2.0296	–4303.19337	0.95934	1.02195	0.86108	–4302.33229	–11.8
[Co^{III} (DPP^{3-}) ($tBuNH_2)_2$]	OSS	-	-	-	-	-	-	- [d]
	CSS	-	–4234.25710	1.08343	1.14921	0.98489	–4233.27221	–17.0
	Triplet	2.0269	–4234.24621	1.07951	1.14560	0.98040	–4233.26581	–13.0
[Co^{II}($DPP^{\bullet 2-}$)] •CH_2Cl_2	OSS	1.0327	–4766.31252	0.80814	0.86476	0.71639	–4765.594695[b]	
	OSS/Triplet[c]	2.0331	–4766.31379	0.80814	0.86476	0.71627	–4765.59752	
[Co^{II}($DPP^{\bullet 2-}$)] •$(CH_2Cl_2)_2$	OSS	1.0334	–5725.94574	0.83812	0.90032	0.73666	–5725.207468[b]	
	OSS/Triplet[c]	2.0336	–5725.94717	0.83812	0.90032	0.73653	–5725.21064	
THF	CSS	-	–232.40289	0.11614	0.12195	0.08876	–232.31413	-
Pyridine (Py)	CSS	-	–248.22806	0.08861	0.09382	0.06188	–248.16617	-
***t*BuNH$_2$**	CSS	-	–213.75116	0.14795	0.15551	0.11917	–213.63199	-
CH_2Cl_2	CSS	-	–959.61828	0.02899	0.03352	0.00281	–959.61547	-

Geometry optimizations and frequency analysis were performed at the B3LYP/def2-SVP/disp3/m4-grid level of theory. A single point energy SCF calculation at the B3LYP/def2-TZVP/disp3/m4-grid level of theory was then performed for final energy evaluation, wherein the previously calculated vibrations were used. Conversion from Hartree to kcal mol^{-1} can be achieved by multiplication with 627.503. [a] Although the energy for this OSS species is slightly (1.3 kcal mol^{-1}) higher in energy than the triplet, CASSCF calculations demonstrated that the BSS-state is the most stable (which is approximated by the DFT OSS solution). [b] Calculated from the approximate correction formula for the OSS as described in the general considerations. [c] SCF at the triplet spin state on the converged geometry for the OSS spin state. [d] The OSS spin state could not be found and consequently converged to the CSS solution, even when starting from orbitals and a geometry first optimized at the triplet spin state.

The formation energies of **[Co^{II}(DPP$^{\bullet 2-}$)(THF)]** and **[Co^{II}(DPP$^{\bullet 2-}$)(THF)$_2$]** are overestimated by the DFT calculations due to over-estimation of the dispersion corrections. We therefore exchanged CH_2Cl_2 (in **[Co^{II}(DPP$^{\bullet 2-}$)]•CH$_2$Cl$_2$** and **[Co^{II}(DPP$^{\bullet 2-}$)]•(CH$_2$Cl$_2$)$_2$**) for THF. However, this results in an erroneous cancelation of all translational entropy contributions to the calculated free energies because the translational entropy contributions to substrate/product association/dissociation are fully counterbalanced by the translational entropy contributions resulting from dissociation/association of the CH_2Cl_2 solvent molecule. This is not accurate for solution phase reactions, wherein the translational entropy contributions associated with substrate/product association/dissociation steps cannot be neglected. As the complexes in solution are completely surrounded by solvent molecules, these solvent association/dissociation steps lead to only small contributions to the translational entropy. These steps are of little influence on the THF association/dissociation steps and therefore the latter are not cancelled by the former in solution. Therefore, we applied a +6.0 or +7.5 kcal mol^{-1} correction term (corresponding to the translational entropy contribution) to the calculated free energies of all substrate/product association/dissociation steps. The results are summarized in Table S9. The (nearly) thermoneutral formation energies are consistent with the observed weak binding of THF.

Table S9. Corrected formation energies for **[Co^{II}(DPP$^{\bullet 2-}$)(THF)]** and **[Co^{II}(DPP$^{\bullet 2-}$)(THF)$_2$]**.

Correction (kcal mol^{-1})	Formation of **[Co^{II}(DPP$^{\bullet 2-}$)(THF)]**	Formation of **[Co^{II}(DPP$^{\bullet 2-}$)(THF)$_2$]**
+6.0	–0.7 kcal mol^{-1}	–1.2 kcal mol^{-1}
+7.5	+0.9 kcal mol^{-1}	+1.8 kcal mol^{-1}

The experimental determination of the super exchange coupling constants, to determine the coupling magnitude between the unpaired electrons in the mono- and bis-THF adducts is unfortunately not possible because these species only exist in solution (where even the mono-THF adduct is not obtained as a pure intermediate, but as a mixture with **[Co^{II}(DPP$^{\bullet 2-}$)]** and **[Co^{II}(DPP$^{\bullet 2-}$)(THF)$_2$]** according to the UV-Vis titration study). Moreover, the large NEVPT2-CASSCF calculated energy differences (*vide supra*) between the singlet, triplet and quintet spin states for **[Co^{II}(DPP$^{\bullet 2-}$)(THF)$_2$]** imply that experimental measurement of the coupling constant would require SQUID measurements at elevated temperatures, which is unfeasible due to the use of THF as solvent. However, the super exchange coupling constants[26] ($J = -\frac{E_{Triplet}-E_{OSS}}{<S^2{}_{triplet}>-<S^2{}_{OSS}>}$) of **[Co^{II}(DPP$^{\bullet 2-}$)(THF)]** and **[Co^{II}(DPP$^{\bullet 2-}$)(THF)$_2$]** were calculated with DFT (see Table S8 for energies and $<S^2>$ values). We chose DFT for these calculations because single root NEVPT2-CASSCF state averaged (50:50 singlet:triplet ratio) calculations with the employed active spaces proved to be too computationally demanding in terms of memory usage. The DFT calculated *J* values were found to be 816 cm^{-1} (**[Co^{II}(DPP$^{\bullet 2-}$)(THF)]**) and 2140 cm^{-1} (**[Co^{II}(DPP$^{\bullet 2-}$)(THF)$_2$]**) and clearly reflect the stronger ferromagnetic coupling within the bis-THF adduct, as was also inferred based on the relative stabilities of the singlet, triplet and quintet spin states obtained from NEVPT2-CASSCF calculations (*vide supra*). In addition, the positive sign of the calculated *J* values is (as expected) consistent with ferromagnetic coupling.

Coordinates (xyz) for the most stable spin state of the calculated structures.

Geometries were optimized at the B3LYP/def2-SVP/m4/disp3 level of theory.

[$Co^{II}(DPP^{\bullet 2-}$)] (BSS/OSS)

97 atoms

Co	9.5047922	6.5850587	1.7298959
O	10.5904076	5.0975803	2.1708129
O	9.2417878	6.7725029	3.5953948
N	8.2105994	7.9522464	1.3908842
C	10.9986942	5.6288501	-0.6107119
N	10.0236637	6.4447108	-0.1059657
C	7.8638592	8.4608321	0.1551276
H	8.7732089	6.5323346	8.4520250
H	10.5246836	6.2562709	8.4106556
C	11.3790172	4.3383504	1.4937876
C	7.3850560	8.5316705	2.3149464
C	9.5590106	7.2219432	-1.1481614
C	11.6852753	4.6029241	0.1052151
C	10.2917239	6.9031224	-2.3478492
H	10.1451943	7.3677535	-3.3200794
C	8.4698543	7.5068565	4.3174720
C	12.6411207	3.7944657	-0.5756668
H	12.8751445	4.0374801	-1.6083252
C	11.9872668	3.1752384	2.1196526
C	11.1802349	5.9219511	-2.0194902
H	11.8878820	5.4376601	-2.6863461
C	12.8838438	2.4344185	1.3771562
H	13.3501116	1.5706998	1.8471122
C	8.0745357	8.8544213	-2.2868035
C	6.5595654	9.0742738	4.5707382
H	5.7886772	9.6784223	4.1005743
C	6.7569946	9.3720111	0.3049617
H	6.2690762	9.9121253	-0.5030188
C	8.6027823	7.5014068	5.7654338
C	6.4592504	9.4170418	1.6350781
H	5.6818421	10.0117391	2.1062384
C	8.5155457	8.1525515	-1.0471186
C	11.6611067	2.8087206	3.5768421
C	7.7032765	8.2452249	6.5013385
H	7.7918973	8.2324637	7.5859142
C	6.6514651	9.0324137	5.9430079
C	5.7012641	9.7903816	6.8828159
C	13.2546752	2.7214315	0.0288871
C	7.4581463	8.3565537	3.7292600
C	8.2640224	10.2339734	-2.4486729
F	8.8509509	10.9426798	-1.4863097
C	14.5730625	2.2861213	-2.1126658
H	13.6677636	2.2516461	-2.7396381
H	15.3213728	1.6239158	-2.5762349
H	14.9746127	3.3116804	-2.1415401
C	7.4534783	8.1610440	-3.3349547
F	7.2457793	6.8496619	-3.2346294
C	9.6946996	6.6621611	6.4490478
C	14.2879990	1.8260576	-0.6721206
C	7.8533346	10.9031663	-3.6044570
F	8.0481751	12.2120662	-3.7333308
C	4.6315735	10.5833192	6.1115962
H	5.0817669	11.3454246	5.4555928
H	3.9697154	11.1062757	6.8199593
H	4.0011361	9.9241763	5.4936212
C	7.2369010	10.1855262	-4.6337124
F	6.8433485	10.8108140	-5.7361061
C	15.6165844	1.8616907	0.1190854
H	16.0161403	2.8873973	0.1679980
H	16.3713029	1.2212954	-0.3671591
H	15.4912534	1.5008359	1.1517404
C	12.1741138	3.9411143	4.4937059
H	13.2621352	4.0686084	4.3698140
H	11.9796252	3.6990909	5.5501650
H	11.6830512	4.8909559	4.2614403
C	10.1361837	2.6019472	3.7384997
H	9.5741534	3.4951158	3.4422698
H	9.8925863	2.3720958	4.7883318
H	9.7983027	1.7555810	3.1177687
C	11.0873265	7.0764854	5.9165388
H	11.1539040	6.9622546	4.8284580
H	11.8715055	6.4550045	6.3782974
H	11.2945476	8.1293512	6.1699654
C	7.0355051	8.8085323	-4.5005006
F	6.4454084	8.1272301	-5.4779435
C	12.3494074	1.5024558	4.0181198
H	12.0460082	0.6432033	3.3982711
H	12.0637912	1.2772697	5.0577829
H	13.4482650	1.5790221	3.9911961
C	13.7577395	0.3739846	-0.7230364
H	13.5736091	-0.0331239	0.2832319
H	14.4890715	-0.2855076	-1.2193760
H	12.8112435	0.3220425	-1.2847875
C	6.5150297	10.7850113	7.7433453
H	7.2729382	10.2745978	8.3574528
H	5.8489020	11.3357837	8.4282227
H	7.0362352	11.5183312	7.1072090
C	4.9825163	8.7790803	7.8063133
H	4.3931926	8.0593584	7.2157492
H	4.2970616	9.3040186	8.4924958
H	5.6932793	8.2059086	8.4215932
C	9.4100741	5.1691111	6.1732194
H	8.4178124	4.8912615	6.5652057
H	10.1603750	4.5355531	6.6714967
H	9.4341149	4.9536980	5.1007258
C	9.7118854	6.8602450	7.9772132
H	9.8945924	7.9102944	8.2577440

[Co^{II}($DPP^{\bullet 2-}$)(THF)] (Triplet)

110 atoms

O	10.6232323	5.1133047	2.0707022
O	9.2334949	6.7870106	3.4862402
N	8.1236381	7.8727642	1.2683360
C	10.8281984	5.4567951	-0.7648817
N	9.8810688	6.2949289	-0.2531797
C	7.7742594	8.3716485	0.0315724
H	8.9420443	6.7262197	8.3607398
H	10.7068177	6.5766181	8.2661803
C	11.3624093	4.3053741	1.3903748
C	7.2903927	8.4458490	2.1887752
C	9.4233563	7.0812459	-1.2895333
C	11.5462623	4.4572071	-0.0327406
C	10.1189993	6.7281782	-2.5007866
H	9.9676520	7.1870406	-3.4751602
C	8.4442288	7.5117445	4.2000016
C	12.4323648	3.5876752	-0.7282584
H	12.5555326	3.7317378	-1.7979917
C	12.0539082	3.2155713	2.0579560
C	10.9830855	5.7204016	-2.1809776
H	11.6631305	5.2094638	-2.8567170
C	12.8886851	2.4139684	1.3041136
H	13.4156221	1.6042720	1.8051555
C	8.0290349	8.8174310	-2.3886043
C	6.4700201	8.9923451	4.4473552
H	5.6604554	9.5413680	3.9742587
C	6.6609802	9.2727535	0.1761819
H	6.1678210	9.8032944	-0.6354208
C	8.6115813	7.5684508	5.6435125
C	6.3530548	9.3120872	1.5068594
H	5.5644312	9.8950902	1.9740713
C	8.4213057	8.0525545	-1.1706704
C	11.8682250	2.9796746	3.5657956
C	7.6879830	8.2838882	6.3793010
H	7.8036697	8.3146621	7.4610871
C	6.5832230	8.9904326	5.8203950
C	5.6031032	9.7157155	6.7555731
C	13.1135427	2.5716360	-0.0939425
C	7.3891560	8.3007295	3.6090689
C	8.3131674	10.1864612	-2.4913843
F	8.9465269	10.8123550	-1.4988985
C	14.1976870	1.9321035	-2.3149713
H	13.2300601	1.8401740	-2.8335098
H	14.8969657	1.2271504	-2.7918820
H	14.5846907	2.9495321	-2.4851080
C	7.3686851	8.2119699	-3.4655469
F	7.0716378	6.9149984	-3.4212456
C	9.7809236	6.8370274	6.3223965
C	14.0741124	1.6125536	-0.8147026
C	7.9557619	10.9304078	-3.6182462
F	8.2409414	12.2276020	-3.6921654
C	4.4777167	10.4243987	5.9815870
H	4.8726450	11.1950659	5.3004926
H	3.7952763	10.9245070	6.6869169
H	3.8800622	9.7138422	5.3887494
C	7.2964826	10.3000457	-4.6778972
F	6.9515862	10.9969193	-5.7540364
C	15.4801900	1.7221752	-0.1798727
H	15.8737027	2.7471513	-0.2743010
H	16.1839697	1.0363992	-0.6805748
H	15.4697262	1.4638665	0.8902709
C	12.3694844	4.2225540	4.3357462
H	13.4288602	4.4161928	4.0982045
H	12.2913776	4.0604902	5.4221989
H	11.7830306	5.1091331	4.0774634
C	10.3753756	2.7001530	3.8599671
H	9.7379275	3.5242841	3.5184700
H	10.2164282	2.5640620	4.9417945
H	10.0545733	1.7771913	3.3495228
C	11.1198185	7.3277628	5.7201503
H	11.1425566	7.1871371	4.6336241
H	11.9646775	6.7744341	6.1608887
H	11.2643818	8.3992492	5.9385233
C	7.0014651	8.9356891	-4.6035196
F	6.3711400	8.3382369	-5.6107529
C	12.6727201	1.7668120	4.0718780
H	12.3735667	0.8312509	3.5726359
H	12.4908594	1.6367704	5.1504696
H	13.7580499	1.9006606	3.9357849
C	13.5564280	0.1624038	-0.6700403
H	13.4864008	-0.1464793	0.3844374
H	14.2356134	-0.5421881	-1.1785014
H	12.5549901	0.0582613	-1.1174677
C	6.3668501	10.7785296	7.5794140
H	7.1617697	10.3299876	8.1950990
H	5.6783736	11.3066776	8.2601067
H	6.8349609	11.5247612	6.9174836
C	4.9580834	8.6879928	7.7145114
H	4.4044963	7.9202357	7.1505875
H	4.2523788	9.1881975	8.3987158
H	5.7106160	8.1730055	8.3315029
C	9.6017387	5.3180280	6.1151884
H	8.6497241	4.9826965	6.5582622
H	10.4174716	4.7617174	6.6032058
H	9.5981304	5.0656148	5.0511710
C	9.8371491	7.1010890	7.8392647
H	9.9497372	8.1727130	8.0707837
Co	9.5095281	6.5839345	1.6135154
O	11.1080355	8.0557775	1.6599602
C	12.4733144	7.6431931	1.8255680
C	13.2456412	8.9439343	2.0288604
C	12.2243254	9.7932607	2.8011682
C	10.9026481	9.3956954	2.1402702

H	12.7675714	7.0721998	0.9323175
H	12.5471681	6.9757610	2.7009788
H	14.1912506	8.7954440	2.5713927
H	13.4767698	9.4084363	1.0556361
H	12.4177308	10.8747175	2.7438342
H	12.2173405	9.5020418	3.8637105
H	10.6503202	10.0373026	1.2775939
H	10.0486630	9.3951552	2.8336067

[$Co^{II}(DPP^{\bullet 2-})(THF)_2$] (Triplet)

123 atoms

O	10.5738492	5.1838926	2.2771109
O	9.1370624	6.7734110	3.7588619
N	8.1190251	8.0410450	1.5862515
C	10.8612993	5.7125391	-0.5250646
N	9.8946293	6.5124756	0.0135529
C	7.7200597	8.5210077	0.3565982
H	8.8498063	6.5221576	8.6050318
H	10.6005634	6.2453348	8.5104072
C	11.3245606	4.4151817	1.5629257
C	7.3120288	8.6077741	2.5280273
C	9.4016846	7.3059100	-1.0013371
C	11.5608218	4.6655132	0.1647095
C	10.1103477	7.0162579	-2.2182605
H	9.9423880	7.4982515	-3.1790664
C	8.4292705	7.5535053	4.5001549
C	12.4694656	3.8429539	-0.5560395
H	12.6409753	4.0687890	-1.6049729
C	11.9649363	3.2617300	2.1688627
C	11.0160888	6.0322396	-1.9256675
H	11.7148061	5.5674666	-2.6156716
C	12.8242051	2.5060743	1.3931387
H	13.3135443	1.6485165	1.8512750
C	7.8749396	8.9290577	-2.0803276
C	6.6019386	9.1957275	4.8142469
H	5.8510925	9.8415341	4.3670506
C	6.6016044	9.4097769	0.5323733
H	6.0733704	9.9276134	-0.2654866
C	8.6071138	7.5421589	5.9421981
C	6.3448771	9.4628452	1.8740531
H	5.5658837	10.0401937	2.3641524
C	8.3465972	8.2183143	-0.8582300
C	11.6947673	2.9083655	3.6402780
C	7.7588787	8.3145834	6.7120238
H	7.8828095	8.2956474	7.7932574
C	6.7273957	9.1439197	6.1865999
C	5.8349448	9.9400507	7.1522952
C	13.1167673	2.7730240	0.0262831
C	7.4397682	8.4427295	3.9462716
C	8.1013427	10.3009861	-2.2498547
F	8.7550236	10.9887855	-1.3128705
C	14.2925395	2.2989941	-2.1900925
H	13.3466676	2.2489469	-2.7527730
H	15.0113329	1.6302004	-2.6899034
H	14.6853338	3.3253965	-2.2675506
C	7.1957961	8.2529342	-3.1017964
F	6.9531909	6.9475795	-2.9900765
C	9.7142533	6.6887221	6.5812191
C	14.1073962	1.8682949	-0.7242763
C	7.6686681	10.9829743	-3.3897633
F	7.9006681	12.2853387	-3.5300202
C	4.7807169	10.7807616	6.4107887
H	5.2463274	11.5253156	5.7455675
H	4.1590351	11.3284942	7.1369299
H	4.1084934	10.1512133	5.8062054
C	6.9902834	10.2838349	-4.3926875
F	6.5735866	10.9210792	-5.4805918
C	15.4855660	1.9284833	-0.0250085
H	15.8799747	2.9574125	-0.0264175
H	16.2118154	1.2808931	-0.5445027
H	15.4295607	1.5925396	1.0220246
C	12.2105844	4.0582206	4.5335466
H	13.2903885	4.2109149	4.3708513
H	12.0591333	3.8194569	5.5979165
H	11.6870668	4.9927454	4.3117423
C	10.1772281	2.6835987	3.8423353
H	9.6045070	3.5668199	3.5382417
H	9.9555189	2.4711674	4.9004790
H	9.8383255	1.8219754	3.2432435
C	11.0852130	7.1265655	6.0108485
H	11.0984035	7.0717109	4.9159648
H	11.8885788	6.4838377	6.4055615
H	11.3033062	8.1660738	6.3066083
C	6.7521612	8.9134030	-4.2506182
F	6.1038564	8.2512193	-5.2048403
C	12.4144848	1.6181991	4.0766326
H	12.1040419	0.7463399	3.4784374
H	12.1669293	1.4030094	5.1283048
H	13.5104417	1.7102974	4.0105027
C	13.5885620	0.4114899	-0.7114433
H	13.4768469	0.0235376	0.3128517
H	14.2896367	-0.2530990	-1.2438050
H	12.6063339	0.3416717	-1.2059910
C	6.7101361	10.8969597	7.9949681
H	7.4604330	10.3524707	8.5887237
H	6.0853641	11.4741885	8.6971090
H	7.2467943	11.6087428	7.3472664
C	5.0964544	8.9585302	8.0920093
H	4.4606062	8.2680437	7.5148080
H	4.4530374	9.5096255	8.7984122
H	5.7978840	8.3515111	8.6851394
C	9.4363372	5.1976605	6.2888280
H	8.4480947	4.9092475	6.6841376
H	10.1930317	4.5608924	6.7736529

H	9.4563200	4.9982362	5.2139278
C	9.7761361	6.8576431	8.1114392
H	9.9674183	7.9016837	8.4072947
Co	9.4208522	6.6471585	1.8833985
O	11.1105061	8.1311312	2.1598334
C	12.4603226	7.6415512	2.1900991
C	13.3319584	8.8805351	2.0046493
C	12.4671989	9.7168720	1.0516297
C	11.0572794	9.4474063	1.5816284
H	12.6052848	6.9223138	1.3658009
H	12.6137033	7.1110100	3.1403726
H	13.4642992	9.4052269	2.9657486
H	14.3285414	8.6421981	1.6032394
H	12.5623211	9.3360879	0.0209419
H	12.7207048	10.7875079	1.0444537
H	10.2873899	9.4658598	0.7977766
H	10.7654541	10.1637938	2.3701464
O	7.7480074	5.1589322	1.6501505
C	6.9373546	4.7395468	2.7613924
C	6.5800481	3.2778916	2.4774694
C	6.6312121	3.2207870	0.9435031
C	7.8129852	4.1402042	0.6434435
H	6.0442815	5.3881297	2.8034750
H	7.5118145	4.8812452	3.6873702
H	7.3455762	2.6112326	2.9058958
H	5.6042608	2.9908849	2.8972049
H	5.7053013	3.6347259	0.5097979
H	6.7714245	2.2042858	0.5455406
H	7.7702626	4.6280992	-0.3417083
H	8.7763193	3.6050421	0.7252424

[$Co^{II}(DPP^{\bullet 2-})(Py)$] (Triplet)

108 atoms

O	10.5079136	5.0069327	2.1849959
O	9.1429371	6.6833793	3.6234494
N	8.1663419	7.9237916	1.4062490
C	10.8516712	5.4925667	-0.6208921
N	9.8719688	6.2980543	-0.1176339
C	7.7716020	8.3815600	0.1642856
H	8.1167278	6.0378401	8.3135627
H	9.8149546	5.5373934	8.4592809
C	11.3395960	4.2857863	1.5126276
C	7.4248068	8.5909669	2.3398234
C	9.3410368	7.0098707	-1.1729119
C	11.6376196	4.5588085	0.1279059
C	10.0057050	6.6250483	-2.3912698
H	9.7870215	7.0156356	-3.3825953
C	8.4019653	7.4511385	4.3453055
C	12.6811914	3.8460822	-0.5253287
H	12.9208259	4.1182517	-1.5498292
C	12.0083984	3.1595546	2.1423363
C	10.9418334	5.6893219	-2.0522368
H	11.6129650	5.1662368	-2.7277793
C	12.9977001	2.5089628	1.4297418
H	13.5233928	1.6869863	1.9119811
C	7.8920932	8.6788078	-2.2926976
C	6.7497752	9.2855244	4.6000245
H	6.1222463	10.0367098	4.1287871
C	6.7267306	9.3573627	0.3248950
H	6.2123254	9.8715252	-0.4840393
C	8.4206580	7.3327348	5.7963527
C	6.5108027	9.4891730	1.6676390
H	5.7792684	10.1339292	2.1462382
C	8.3399753	7.9820782	-1.0529279
C	11.6398807	2.7267880	3.5712226
C	7.6231350	8.1859001	6.5327880
H	7.6423810	8.1002091	7.6174369
C	6.7771410	9.1859142	5.9735610
C	5.9589387	10.0893543	6.9093106
C	13.3885749	2.8427995	0.1011896
C	7.5299844	8.4425815	3.7600093
C	8.2171415	10.0236615	-2.5134656
F	8.9314067	10.6939529	-1.6064382
C	14.8206617	2.5642169	-1.9931348
H	13.9469672	2.4165169	-2.6477415
H	15.6597937	1.9977037	-2.4273282
H	15.0928621	3.6314851	-2.0175352
C	7.1536406	8.0203397	-3.2839955
F	6.8214321	6.7411260	-3.1273624
C	9.3290561	6.3046817	6.4905534
C	14.5469041	2.0782829	-0.5589283
C	7.8234214	10.6965477	-3.6722863
F	8.1505739	11.9722749	-3.8602661
C	5.1162771	11.1175872	6.1344794
H	5.7465464	11.7883566	5.5290216
H	4.5473391	11.7439985	6.8398046
H	4.3901564	10.6293217	5.4651758
C	7.0854939	10.0149475	-4.6450696
F	6.7071082	10.6425060	-5.7521860
C	15.8327066	2.2852779	0.2755610
H	16.0979804	3.3536399	0.3263143
H	16.6791318	1.7416897	-0.1768013
H	15.7153543	1.9196530	1.3075185
C	11.9923497	3.8670659	4.5491298
H	13.0663561	4.1101204	4.4869983
H	11.7716584	3.5708458	5.5866208
H	11.4116083	4.7643522	4.3212162
C	10.1306293	2.3924042	3.6365931
H	9.5159102	3.2442053	3.3225847
H	9.8437014	2.1209812	4.6654482
H	9.9007104	1.5364462	2.9811091
C	10.8016710	6.6786373	6.2025935
H	10.9912992	6.7309191	5.1252102
H	11.4859466	5.9355711	6.6424280

H	11.0356367	7.6627716	6.6408260
C	6.7480621	8.6721315	-4.4521443
F	6.0452905	8.0261996	-5.3780129
C	12.4105734	1.4703271	4.0195945
H	12.2195671	0.6088705	3.3596954
H	12.0849530	1.1890572	5.0336150
H	13.4985636	1.6403374	4.0612248
C	14.2083291	0.5705201	-0.6154547
H	14.0466238	0.1464792	0.3875619
H	15.0327293	0.0078446	-1.0846559
H	13.2940101	0.3963615	-1.2051175
C	6.9186582	10.8596390	7.8462597
H	7.5224950	10.1794983	8.4666772
H	6.3496834	11.5141833	8.5275984
H	7.6121084	11.4883542	7.2649159
C	5.0023488	9.2187490	7.7568190
H	4.3033512	8.6632720	7.1112383
H	4.4113718	9.8496888	8.4416242
H	5.5485141	8.4847814	8.3691998
C	8.9912752	4.8852292	5.9817382
H	7.9397095	4.6426245	6.2070700
H	9.6249271	4.1367238	6.4830859
H	9.1429921	4.7994542	4.9018797
C	9.1472555	6.2961733	8.0210573
H	9.4059461	7.2634441	8.4807502
Co	9.5060293	6.5788097	1.7549219
N	11.2036030	7.9143892	1.9211683
C	13.4138701	9.5931197	2.1312294
C	12.2525885	7.5616762	2.6746317
C	11.2334368	9.0798912	1.2623355
C	12.3197385	9.9528091	1.3393475
C	13.3805038	8.3725112	2.8103814
H	12.1748407	6.5930166	3.1719389
H	10.3566861	9.3153868	0.6529151
H	12.3016454	10.8942260	0.7860379
H	14.2131082	8.0460343	3.4371999
H	14.2810928	10.2535370	2.2151675

[$Co^{III}(DPP^{3-})(Py)_2$] (CSS)

119 atoms

O	10.5726227	4.9908021	2.2913571
O	9.3645949	6.7807129	3.7119409
N	8.3452375	8.0291426	1.4743160
C	10.8369298	5.3922362	-0.5698020
N	9.9468300	6.2811261	-0.0664071
C	8.0244397	8.5549806	0.2267321
H	8.3611671	6.1273179	8.4429823
H	10.1114631	5.8757561	8.6054141
C	11.4050265	4.2520631	1.5980013
C	7.5981077	8.6717798	2.4039825
C	9.4612021	7.0475302	-1.1216406
C	11.6058060	4.4294924	0.1936130
C	10.0581321	6.5879260	-2.3353708
H	9.8640083	6.9911148	-3.3271262
C	8.5230801	7.4930012	4.4217556
C	12.5639886	3.6450577	-0.4965333
H	12.7066598	3.8324139	-1.5571924
C	12.1570560	3.2051736	2.2552297
C	10.9080447	5.5625321	-1.9983415
H	11.5188722	4.9795347	-2.6814813
C	13.0725943	2.4749138	1.5055773
H	13.6438669	1.6981789	2.0097387
C	8.1292198	8.8100279	-2.2281547
C	6.6589884	9.0985658	4.6350803
H	5.9491076	9.7557540	4.1400426
C	7.0578938	9.5923565	0.4006536
H	6.6245594	10.1920898	-0.3971122
C	8.5169022	7.3746821	5.8635980
C	6.7921460	9.6679273	1.7466008
H	6.1079562	10.3576087	2.2324187
C	8.5553154	8.1047878	-0.9866568
C	11.9536104	2.8800947	3.7488917
C	7.5709185	8.0953253	6.5842632
H	7.5622355	7.9896858	7.6671780
C	6.6114291	8.9576564	6.0094547
C	5.5950777	9.6817380	6.9086630
C	13.3186428	2.6701691	0.1286152
C	7.5970494	8.4063289	3.8287270
C	8.6216632	10.0822383	-2.5385427
F	9.4912936	10.6776301	-1.7191375
C	14.4969008	2.1763207	-2.0817764
H	13.5491564	2.0146959	-2.6198726
H	15.2623505	1.5450803	-2.5611387
H	14.7967282	3.2270820	-2.2228095
C	7.2264746	8.2239229	-3.1217539
F	6.7246666	7.0144400	-2.8638071
C	9.5322612	6.4817215	6.6047836
C	14.3747191	1.8139876	-0.5909411
C	8.2343579	10.7555580	-3.6996685
F	8.7198071	11.9620972	-3.9785524
C	4.6397135	10.5767425	6.0995785
H	5.1836369	11.3631082	5.5522380
H	3.9272887	11.0755722	6.7762081
H	4.0536590	9.9939310	5.3711170
C	7.3295221	10.1479438	-4.5760533
F	6.9529025	10.7781970	-5.6824832
C	15.7542837	2.0317904	0.0722819
H	16.0560858	3.0897146	0.0072728
H	16.5272383	1.4220755	-0.4257976
H	15.7441965	1.7518502	1.1371369
C	12.2837150	4.1187308	4.6079809
H	13.3126258	4.4612746	4.4085352
H	12.2068042	3.8814567	5.6808021
H	11.5904163	4.9356031	4.3959532

C	10.4931540	2.4261201	3.9724039
H	9.7893437	3.1732054	3.5934416
H	10.2914458	2.2674809	5.0445371
H	10.3039091	1.4784193	3.4424220
C	10.9632350	6.9856401	6.3094980
H	11.7145196	6.3142909	6.7568436
H	11.1069900	7.9935892	6.7317422
H	11.1441106	7.0400329	5.2319014
C	6.8211381	8.8773103	-4.2884033
F	5.9572305	8.3046141	-5.1219833
C	12.8652906	1.7367322	4.2381269
H	12.6866732	0.7967855	3.6926662
H	12.6597198	1.5420455	5.3029673
H	13.9339236	1.9902555	4.1498155
C	13.9877537	0.3205727	-0.4883709
H	13.9234026	-0.0145252	0.5585868
H	14.7365432	-0.3117286	-0.9950808
H	13.0081411	0.1380519	-0.9587673
C	6.3452873	10.5732567	7.9249318
H	7.0179867	9.9841287	8.5672923
H	5.6324421	11.0991360	8.5826755
H	6.9557739	11.3292162	7.4052518
C	4.7473573	8.6382357	7.6721980
H	4.1963871	7.9929031	6.9690201
H	4.0141156	9.1364095	8.3291386
H	5.3724917	7.9877729	8.3034493
C	9.3626351	5.0144117	6.1588897
H	8.3281738	4.6761855	6.3355332
H	10.0375407	4.3532254	6.7251209
H	9.5965723	4.9011172	5.0979877
C	9.3459955	6.5137576	8.1351317
H	9.4643441	7.5275575	8.5489188
Co	9.5405029	6.5466425	1.8050935
N	7.9532577	5.3547598	1.7350851
C	5.7622190	3.6362479	1.7373640
C	7.1724274	5.2505167	0.6471025
C	7.6631878	4.6273587	2.8240515
C	6.5760799	3.7563466	2.8647018
C	6.0687074	4.4008279	0.6094565
H	7.4370553	5.8613080	-0.2136918
H	8.3261909	4.7691292	3.6722031
H	6.3839773	3.1861160	3.7753864
H	5.4656407	4.3496004	-0.2990303
H	4.9027494	2.9609325	1.7370856
N	11.1397848	7.7230730	1.9065636
C	13.4157430	9.3106646	2.1454593
C	12.1233338	7.3763023	2.7501122
C	11.2666586	8.8416415	1.1737324
C	12.3892003	9.6619881	1.2661928
C	13.2770172	8.1438116	2.8984026
H	11.9639877	6.4548093	3.3016680
H	10.4509478	9.0872928	0.4971379
H	12.4441222	10.5614384	0.6500485
H	14.0472014	7.8178718	3.5998177
H	14.3081303	9.9347640	2.2396085

[Co^{III}(DPP^{3-})(*t*$BuNH_2$)$_2$] (CSS)

129 atoms

Co	9.3462153	6.6697331	1.9470832
O	10.6988684	5.3849663	2.4163197
O	9.0250524	6.7444917	3.8538672
N	8.0013485	8.0303933	1.6397175
C	10.6075868	5.5590218	-0.4732432
N	9.7503022	6.4598662	0.0696845
C	7.7077519	8.6132834	0.4114099
H	4.7664889	5.2441405	2.1478770
N	8.1780003	5.0234802	1.9173273
C	11.3762209	4.5292107	1.6871347
C	7.2430238	8.6485735	2.5821002
C	9.2151199	7.2147632	-0.9679920
C	11.3772604	4.5690903	0.2586912
C	9.7830760	6.7737067	-2.2010649
H	9.5635219	7.1884172	-3.1824574
C	8.2236078	7.4889173	4.5831443
C	12.1686171	3.6528928	-0.4801772
H	12.1386551	3.7123149	-1.5646967
C	12.1634096	3.5041810	2.3323519
C	10.6430370	5.7444749	-1.8993334
H	11.2486146	5.1803486	-2.6027364
C	12.9291932	2.6576808	1.5392593
H	13.5302036	1.8968566	2.0334538
C	7.8325912	8.9668579	-2.0305742
C	6.3415555	9.0616470	4.8363653
H	5.5997973	9.6951285	4.3573246
C	6.7147100	9.6208391	0.6031959
H	6.2828366	10.2396387	-0.1804876
C	8.3025562	7.4270738	6.0240182
C	6.4235242	9.6447653	1.9465146
H	5.7185056	10.3042598	2.4441374
C	8.2768085	8.2363040	-0.8081633
C	12.0949150	3.2884407	3.8559098
C	7.3623865	8.1305103	6.7691084
H	7.4118590	8.0615489	7.8540142
C	6.3455496	8.9390814	6.2137647
C	5.3377996	9.6455377	7.1363093
C	12.9661652	2.7010429	0.1272921
C	7.2688752	8.3806195	4.0079245
C	8.2793980	10.2660246	-2.2976121
F	9.1194241	10.8696609	-1.4552776
C	13.7581493	1.9148274	-2.1689078
H	12.7320359	1.7612486	-2.5395149
H	14.4089346	1.1920763	-2.6867121
H	14.0827586	2.9253247	-2.4645502
C	6.9565782	8.3780140	-2.9497951

F	6.4980697	7.1439316	-2.7375552
C	9.4223851	6.6385399	6.7303921
C	13.8515753	1.7093792	-0.6465150
C	7.8710549	10.9629960	-3.4377098
F	8.3115891	12.1959819	-3.6720709
C	4.3046174	10.4670187	6.3449574
H	4.7830209	11.2638892	5.7534071
H	3.5968130	10.9493367	7.0380445
H	3.7195084	9.8338230	5.6589574
C	6.9947265	10.3520174	-4.3399199
F	6.5998635	11.0043834	-5.4268880
C	15.3262954	1.9006377	-0.2235365
H	15.6662757	2.9252854	-0.4443987
H	15.9807420	1.1962980	-0.7644750
H	15.4685721	1.7263497	0.8543291
C	12.4446399	4.5856027	4.6155869
H	13.4671558	4.9117627	4.3610626
H	12.4030618	4.4187109	5.7039169
H	11.7483613	5.3880580	4.3605276
C	10.6627953	2.8098599	4.1913945
H	9.9187534	3.5425511	3.8565853
H	10.5359416	2.6651743	5.2757984
H	10.4570807	1.8506160	3.6891180
C	10.7882870	7.2398317	6.3235998
H	10.9298048	7.1915262	5.2377844
H	11.6162288	6.6846720	6.7929143
H	10.8548086	8.2933533	6.6403722
C	6.5323770	9.0550037	-4.0962910
F	5.6951774	8.4775389	-4.9534672
C	13.0691171	2.1989670	4.3464463
H	12.8537857	1.2117795	3.9082117
H	12.9770477	2.0970162	5.4396091
H	14.1175936	2.4547899	4.1240899
C	13.4109247	0.2622872	-0.3270991
H	13.4945929	0.0369843	0.7473820
H	14.0388850	-0.4644404	-0.8697613
H	12.3620777	0.0985550	-0.6230965
C	6.0906058	10.6046175	8.0870918
H	6.8205251	10.0694762	8.7141469
H	5.3845235	11.1176858	8.7618919
H	6.6382134	11.3713046	7.5155496
C	4.5769175	8.5901407	7.9713564
H	4.0275250	7.8952465	7.3159126
H	3.8501041	9.0762321	8.6440826
H	5.2597064	7.9924440	8.5950360
C	9.3464137	5.1486896	6.3444398
H	8.3760810	4.7218890	6.6484894
H	10.1424231	4.5762081	6.8471058
H	9.4628689	5.0256369	5.2653620
C	9.3300825	6.7238561	8.2667260
H	9.4088828	7.7592488	8.6345763
H	10.1606886	6.1525392	8.7112968
H	8.3918419	6.2912939	8.6490616
H	5.9823512	5.2969952	3.4506318
C	6.7702364	4.7523460	1.4833195
C	6.6053620	5.1618991	0.0175091
H	5.6110961	4.8620605	-0.3469643
H	6.6992633	6.2462320	-0.1052999
H	7.3632990	4.6815582	-0.6217978
C	6.5350852	3.2372930	1.6406211
H	7.2250214	2.6593533	1.0027142
H	5.5065004	2.9743874	1.3487844
H	6.6840931	2.9186192	2.6858187
C	5.8036172	5.5242030	2.3867031
H	5.9068737	6.6064193	2.2503485
N	10.6584767	8.1403879	2.4088276
H	13.7973966	8.0304720	1.0464844
H	13.1153948	7.0473781	2.3716054
C	11.8616394	8.7200421	1.7314494
C	11.4349799	9.4205260	0.4385827
H	12.2910614	9.9603994	0.0062054
H	11.0739226	8.7013183	-0.3055412
H	10.6307124	10.1513165	0.6198120
C	12.4743826	9.7443354	2.7069024
H	11.7638739	10.5585123	2.9283756
H	13.3792635	10.1962709	2.2720054
H	12.7580204	9.2650533	3.6587764
C	12.8687044	7.6012695	1.4522835
H	12.4756116	6.8832931	0.7244953
H	10.9570454	7.7193370	3.2927942
H	10.0386357	8.9098195	2.6765321
H	8.7878500	4.3612525	1.4304870
H	8.2699143	4.7949864	2.9120928

$[Co^{II}(DPP^{\bullet 2-})]\bullet CH_2Cl_2$ (BSS/OSS)

102 atoms

Co	9.5219335	6.5032256	1.7428936
O	10.6415705	5.0420587	2.1963262
O	9.2300515	6.6781871	3.6120738
N	8.1867148	7.8363146	1.4008343
C	10.9616057	5.5033709	-0.6134639
N	9.9999211	6.3290570	-0.1067245
C	7.8790569	8.3853074	0.1733221
H	9.0661344	6.7789265	8.4941353
H	10.8314041	6.6900757	8.3549090
C	11.4018753	4.2622670	1.5131464
C	7.3091684	8.3583100	2.3122385
C	9.5965525	7.1672233	-1.1267249
C	11.6305754	4.4610566	0.0988729
C	10.3502477	6.8677007	-2.3188793
H	10.2506798	7.3756786	-3.2753008
C	8.4461911	7.4077905	4.3184512
C	12.5210522	3.5978937	-0.6014980
H	12.6745808	3.7727800	-1.6627687

C	12.0706066	3.1485167	2.1666632
C	11.1864564	5.8355587	-2.0074055
H	11.8971709	5.3527779	-2.6722234
C	12.9071770	2.3566099	1.4071509
H	13.4121439	1.5253901	1.8954469
C	8.2592341	8.9640688	-2.2027765
C	6.4256847	8.8293680	4.5624468
H	5.5964565	9.3491394	4.0899111
C	6.7506858	9.2690474	0.3123085
H	6.2862832	9.8318671	-0.4944388
C	8.6335597	7.4973079	5.7579479
C	6.3883455	9.2425875	1.6291085
H	5.5775620	9.7988733	2.0911312
C	8.5852825	8.1296559	-1.0121382
C	11.8649551	2.8894777	3.6681076
C	7.6890758	8.1843730	6.4910512
H	7.8153395	8.2387415	7.5706762
C	6.5469183	8.8369206	5.9338633
C	5.5476800	9.5301810	6.8722423
C	13.1651135	2.5500175	0.0169480
C	7.3705786	8.1725003	3.7246981
C	8.5548018	10.3340162	-2.2077335
F	9.1422021	10.8916607	-1.1447400
C	14.2852088	1.9506441	-2.1972856
H	13.3270732	1.8905809	-2.7378767
H	14.9815115	1.2456156	-2.6786307
H	14.6946833	2.9646573	-2.3317028
C	7.6564088	8.4292286	-3.3483786
F	7.3535872	7.1341833	-3.3983772
C	9.8463023	6.8328467	6.4284867
C	14.1241985	1.5936515	-0.7090474
C	8.2637267	11.1491198	-3.3033042
F	8.5600882	12.4450721	-3.2828970
C	4.3801084	10.1747662	6.1046996
H	4.7288532	10.9562199	5.4107684
H	3.6828984	10.6495231	6.8131685
H	3.8107665	9.4291140	5.5271462
C	7.6600509	10.5882658	-4.4333794
F	7.3784224	11.3510106	-5.4821499
C	15.5179785	1.6620674	-0.0417950
H	15.9302581	2.6822757	-0.0994526
H	16.2205958	0.9780821	-0.5467047
H	15.4805750	1.3746944	1.0203146
C	12.4014766	4.1052308	4.4585467
H	13.4706034	4.2599315	4.2382386
H	12.3011843	3.9328778	5.5414837
H	11.8566357	5.0201326	4.2045258
C	10.3641206	2.6476663	3.9560442
H	9.7511585	3.4986208	3.6372374
H	10.2035749	2.4891648	5.0346301
H	10.0150701	1.7471193	3.4241719
C	11.1525788	7.3390271	5.7695156
H	11.1764494	7.1286657	4.6948053
H	12.0246130	6.8548493	6.2384980
H	11.2520071	8.4288324	5.9014031
C	7.3555902	9.2239562	-4.4584076
F	6.7800211	8.6938755	-5.5329971
C	12.6322731	1.6448239	4.1545709
H	12.3107778	0.7283176	3.6338504
H	12.4393800	1.4982047	5.2290557
H	13.7219047	1.7510838	4.0292438
C	13.5785671	0.1495356	-0.6140846
H	13.4797860	-0.1855510	0.4300236
H	14.2573604	-0.5530810	-1.1259109
H	12.5858891	0.0742227	-1.0862570
C	6.2745426	10.6393995	7.6683694
H	7.0973618	10.2371336	8.2793652
H	5.5720357	11.1469849	8.3504496
H	6.6994317	11.3948119	6.9880202
C	4.9639221	8.4889051	7.8556060
H	4.4365729	7.6888454	7.3116300
H	4.2468465	8.9679825	8.5431193
H	5.7476155	8.0174400	8.4684161
C	9.7101520	5.3014542	6.2888003
H	8.7824822	4.9535192	6.7723844
H	10.5576933	4.7933262	6.7750176
H	9.6870925	5.0043767	5.2363642
C	9.9316926	7.1633789	7.9310099
H	10.0103325	8.2475866	8.1124031
H	10.1685306	9.6471337	0.9455478
C	10.9164241	9.8010734	1.7306757
H	11.6441546	10.5702269	1.4475386
Cl	10.0823220	10.3241301	3.2153689
Cl	11.8188481	8.2592852	1.9350347

$[Co^{II}(DPP^{\bullet 2-})]\bullet(CH_2Cl_2)_2$ (BSS/OSS)

107 atoms

Co	9.6201641	6.5379878	1.7959536
O	10.7617143	5.0953011	2.2539750
O	9.3597740	6.7438723	3.6685612
N	8.3114245	7.8990353	1.4539782
C	11.0903927	5.5692612	-0.5532055
N	10.1282741	6.3929606	-0.0488914
C	7.9923783	8.4321524	0.2234874
H	9.1063714	6.7527392	8.5446484
H	10.8701309	6.6113853	8.4313255
C	11.4923176	4.2984658	1.5624264
C	7.4240415	8.4076151	2.3651298
C	9.7285764	7.2337421	-1.0673967
C	11.7429974	4.5139355	0.1541380
C	10.4921165	6.9416066	-2.2568098
H	10.3987112	7.4555641	-3.2107530
C	8.5644221	7.4581291	4.3736871
C	12.6389468	3.6535627	-0.5422335

H	12.8212226	3.8487773	-1.5953975
C	12.1066139	3.1453518	2.2006825
C	11.3277655	5.9104576	-1.9445453
H	12.0441887	5.4315919	-2.6061092
C	12.9490008	2.3563941	1.4451945
H	13.4184104	1.4987363	1.9234555
C	8.3509161	8.9875397	-2.1611133
C	6.5480899	8.8856482	4.6161087
H	5.7266587	9.4172723	4.1429878
C	6.8404411	9.2825722	0.3550981
H	6.3600850	9.8260060	-0.4555428
C	8.7361883	7.5275025	5.8169774
C	6.4793661	9.2588579	1.6753685
H	5.6557327	9.8004160	2.1323551
C	8.7065567	8.1814510	-0.9603910
C	11.8336575	2.8434710	3.6831373
C	7.7966504	8.2217714	6.5489700
H	7.9145953	8.2644963	7.6300530
C	6.6682512	8.8944041	5.9879919
C	5.6817021	9.6103325	6.9228497
C	13.2555433	2.5853420	0.0699518
C	7.4888413	8.2232176	3.7788872
C	8.5920125	10.3681912	-2.1838711
F	9.1643772	10.9602396	-1.1321098
C	14.4423916	2.0339586	-2.1216490
H	13.5018250	1.9898902	-2.6936367
H	15.1521359	1.3385601	-2.5972700
H	14.8581669	3.0496185	-2.2185797
C	7.7610561	8.4164723	-3.2966192
F	7.5099785	7.1099775	-3.3358130
C	9.9209878	6.8194681	6.4925437
C	14.2329228	1.6419803	-0.6483569
C	8.2602916	11.1589334	-3.2857549
F	8.5057156	12.4658357	-3.2819357
C	4.5272657	10.2741357	6.1520067
H	4.8914238	11.0449725	5.4542675
H	3.8395116	10.7660614	6.8579404
H	3.9432776	9.5371046	5.5779794
C	7.6693491	10.5625669	-4.4042000
F	7.3481889	11.3019600	-5.4585810
C	15.6047024	1.6909229	0.0648078
H	16.0203527	2.7111531	0.0441503
H	16.3220769	1.0168613	-0.4325884
H	15.5320939	1.3796786	1.1183961
C	12.4072731	3.9968256	4.5380895
H	13.4909076	4.0972635	4.3618101
H	12.2564435	3.7917457	5.6094417
H	11.9248015	4.9501539	4.2985571
C	10.3118461	2.6776689	3.9118871
H	9.7623175	3.5795482	3.6199396
H	10.1058541	2.4761329	4.9754672
H	9.9266562	1.8292592	3.3226263
C	11.2536356	7.2943060	5.8637232
H	11.2902948	7.0988188	4.7865194
H	12.1013515	6.7763975	6.3413632
H	11.3843309	8.3783953	6.0145828
C	7.4196441	9.1870824	-4.4119131
F	6.8563166	8.6227508	-5.4758714
C	12.5112793	1.5389097	4.1448626
H	12.1624694	0.6649638	3.5711770
H	12.2668811	1.3587305	5.2036696
H	13.6092396	1.5889649	4.0672395
C	13.6824405	0.1973738	-0.6057603
H	13.5514134	-0.1634328	0.4260982
H	14.3756520	-0.4939192	-1.1135771
H	12.7046835	0.1359335	-1.1099341
C	6.4303868	10.7091397	7.7132242
H	7.2458346	10.2936304	8.3250866
H	5.7386434	11.2337250	8.3934173
H	6.8695857	11.4525569	7.0288578
C	5.0773808	8.5864095	7.9117885
H	4.5344860	7.7938133	7.3721931
H	4.3697400	9.0832505	8.5964641
H	5.8513176	8.1030773	8.5275667
C	9.7374647	5.2955046	6.3231269
H	8.7924634	4.9697412	6.7884431
H	10.5613705	4.7514504	6.8108392
H	9.7185848	5.0174823	5.2653024
C	9.9923979	7.1199707	8.0021438
H	10.1015406	8.1978812	8.2043261
H	10.3264218	9.6272528	0.9927226
C	11.0776202	9.8093916	1.7689803
H	11.7815255	10.5950195	1.4711866
Cl	10.2401560	10.3316590	3.2540017
Cl	12.0177853	8.2944300	1.9864568
H	5.3374865	4.7376203	1.0714992
C	6.2636692	5.3059461	0.9263033
H	6.1499642	6.3503985	1.2370635
Cl	6.6822081	5.2790454	-0.8063593
Cl	7.5188991	4.5622627	1.9722501

THF (CSS)

13 atoms

O	0.0000840	-1.2489620	0.0000402
C	-1.1615662	-0.4366997	0.1381694
C	-0.7316401	0.9881237	-0.2306953
C	0.7315552	0.9882179	0.2306570
C	1.1616419	-0.4365757	-0.1381353
H	-1.5296611	-0.4790003	1.1836927
H	-1.9613562	-0.8298851	-0.5132232
H	-0.7870229	1.1362654	-1.3227522
H	-1.3491143	1.7632406	0.2485656
H	0.7869212	1.1364205	1.3227065
H	1.3489420	1.7633802	-0.2486430

H	1.9614782	-0.8296369	0.5132752
H	1.5297383	-0.4788886	-1.1836576

Pyridine (Py) (CSS)

11 atoms

H	2.1660057	0.0000000	-1.1849204
C	1.2006924	0.0000000	-0.6723427
C	-1.1432790	0.0000000	0.7266375
C	1.1432790	0.0000000	0.7266375
C	0.0000000	0.0000000	-1.3868794
C	-1.2006924	0.0000000	-0.6723427
N	-0.0000000	0.0000000	1.4182010
H	2.0698592	0.0000000	1.3142228
H	0.0000000	0.0000000	-2.4805160
H	-2.1660057	0.0000000	-1.1849204
H	-2.0698593	0.0000000	1.3142228

***t*BuNH$_2$** (CSS)

16 atoms

N	1.0039775	1.8495204	5.3308355
H	3.4919014	2.6902035	4.6739121
C	1.3361844	2.9477220	4.4076059
C	0.3149601	2.9134825	3.2601133
H	0.5326840	3.6912676	2.5106400
H	0.3282208	1.9301442	2.7654023
H	-0.7066897	3.0897058	3.6389428
C	1.2972133	4.3275429	5.0986141
H	0.2927068	4.5287476	5.5086025
H	1.5470939	5.1451646	4.4013606
H	2.0171466	4.3644855	5.9340263
C	2.7468095	2.6819240	3.8596094
H	2.7883631	1.6958093	3.3720250
H	3.0411729	3.4523322	3.1289891
H	0.0771458	2.0040919	5.7330007
H	1.6531096	1.8528558	6.1203202

CH$_2$Cl$_2$ (CSS)

5 atoms

C	-0.0059755	0.0104918	1.0813620
H	1.0301901	0.0218903	1.4405970
H	-0.5343887	-0.8809126	1.4405193
Cl	0.0266973	-0.0459889	-0.7064267
Cl	-0.8375231	1.4515193	1.7389484

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