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

Nicolaas P. van Leest, Wowa Stroek, Maxime A. Siegler, Jarl Ivar van der Vlugt, Bas de Bruin

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ABSTRACT: The influence of a redox-active ligand on spin changing events induced by coordination of exogenous donors is investigated within the cobalt complex \([\text{Co}^{\text{II}}(\text{DPP}^{\text{2}-})]\), bearing a redox-active DPP\(^{2-}\) ligand (DPP = dipyrrin-bis-(o,p-di-tert-butylphenolato) with a pentafluorophenyl moiety on the meso-position. This square planar complex was subjected to coordination of THF, pyridine, tBuNH\(_2\) and AdNH\(_2\) (Ad = 1-adamantyl), and the resulting complexes were analyzed with a variety of experimental (XRD, NMR, UV-Vis, HRMS, SQUID, Evans’ method) and computational (DFT, NEVPT2-CASSCF) techniques to elucidate the respective structures, spin states and orbital compositions of the corresponding octahedral bis-donor adducts, relative to \([\text{Co}^{\text{II}}(\text{DPP}^{\text{2}-})]\). This starting species is best described as an open-shell singlet complex containing a DPP\(^{2-}\) ligand radical that is antiferromagnetically coupled to a low-spin (\(S = \frac{1}{2}\)) cobalt(II) center. The redox-active DPP\(^{n-}\) ligand plays a crucial role in stabilizing this complex, and in its facile conversion to the triplet THF-adduct \([\text{Co}^{\text{II}}(\text{DPP}^{\text{2}-})(\text{THF})_2]\) and closed-shell singlet pyridine and amine adducts \([\text{Co}^{\text{III}}(\text{DPP}^{\text{3-}})(\text{L})_2]\) (\(\text{L} = \text{py, tBuNH}_2\) or \(\text{AdNH}_2\)). Coordination of the weak donor THF to \([\text{Co}^{\text{II}}(\text{DPP}^{\text{2}-})]\) changes the orbital overlap between the DPP\(^{2-}\) ligand radical π-orbitals and the cobalt(II) metalloradical d-orbitals, which results in a spin-flip to the triplet ground state without changing the oxidation states of the metal or DPP\(^{2-}\) ligand. In contrast, coordination of the stronger donors pyridine, tBuNH\(_2\) or AdNH\(_2\) induces metal-to-ligand single-electron transfer, resulting in formation of low-spin (\(S = 0\)) cobalt(III)-complexes \([\text{Co}^{\text{III}}(\text{DPP}^{\text{3-}})(\text{L})_2]\) containing a fully reduced DPP\(^{3-}\) ligand, thus explaining their closed-shell singlet electronic ground states.

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

Nicolaas P. van Leest,† Wowa Stroek,‡ Maxime A. Siegler,‡ Jarl Ivar van der Vlugt†‡ and Bas de Bruin*†‡

† Homogeneous, Supramolecular and Bio-Inspired Catalysis Group, van ‘t Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam, Science Park 904, 1098XH Amsterdam, The Netherlands.
‡ Department of Chemistry, John Hopkins University, Baltimore, Maryland 21218, United States.

KEYWORDS: cobalt, redox-active ligand, spin flip, metal-to-ligand single-electron transfer

ABSTRACT: The influence of a redox-active ligand on spin changing events induced by coordination of exogenous donors is investigated within the cobalt complex \([\text{Co}^{\text{II}}(\text{DPP}^2\text{•}2\text{‒})]\), bearing a redox-active DPP\(^2\text{•}2\text{‒}\) ligand (DPP = dipyrrin-bis-(o,p-di-tert-butylphenolato) with a pentafluorophenyl moiety on the meso-position. This square planar complex was subjected to coordination of THF, pyridine, \(\beta\text{BuNH}_2\) and AdNH\(_2\) (Ad = 1-adamantyl), and the resulting complexes were analyzed with a variety of experimental (XRD, NMR, UV-Vis, HRMS, SQUID, Evans' method) and computational (DFT, NEVPT2-CASSCF) techniques to elucidate the respective structures, spin states and orbital compositions of the corresponding octahedral bis-donor adducts, relative to \([\text{Co}^{\text{II}}(\text{DPP}^2\text{•}2\text{‒})]\). This starting species is best described as an open-shell singlet complex containing a DPP\(^2\text{•}2\text{‒}\) ligand that is antiferromagnetically coupled to a low-spin \((S = \frac{1}{2})\) cobalt(II) center. The redox-active DPP\(^{2\text{•}2\text{‒}}\) ligand plays a crucial role in stabilizing this complex, and in its facile conversion to the triplet THF- adduct \([\text{Co}^{\text{II}}(\text{DPP}^2\text{•}2\text{‒})(\text{THF})]\) and closed-shell singlet pyridine and amine adducts \([\text{Co}^{\text{II}}(\text{DPP}^{2\text{•}2\text{‒}})(L)\_2]\) (L = py, \(\beta\text{BuNH}_2\) or AdNH\(_2\)). Coordination of the weak donor THF to \([\text{Co}^{\text{II}}(\text{DPP}^{2\text{•}2\text{‒}})]\) changes the orbital overlap between the DPP\(^2\text{•}2\text{‒}\) ligand radical \(\pi\)-orbitals and the cobalt(II) metalloradical d-orbitals, which results in a spin-flip to the triplet ground state without changing the oxidation states of the metal or DPP\(^{2\text{•}2\text{‒}}\) ligand. In contrast, coordination of the stronger donors pyridine, \(\beta\text{BuNH}_2\) or AdNH\(_2\) induces metal-to-ligand single-electron transfer, resulting in a spin crossover to the closed-shell singlet complexes \([\text{Co}^{\text{II}}(\text{DPP}^{2\text{•}2\text{‒}})(L)\_2]\) containing a fully reduced DPP\(^{2\text{•}2\text{‒}}\) ligand, thus explaining their closed-shell singlet electronic ground states.

INTRODUCTION

Spin state changes (spin crossover) can play an important role in chemistry and material research, amongst others in biochemistry (respiration, enzymatic conversions), development of molecular magnets and spintronics, and as a potential rate-accelerating process in organometallic chemistry and catalysis. Purely metal-centered spin state changes of coordination complexes can be explained in terms of the coordination and geometry dependent energy difference between partially filled and empty \(d\)-orbitals, as described by the ligand-field splitting parameter \(\Delta\).

The respective roles of the metal and traditional (redox-innocent) ligands are well-understood in these cases. However, when a redox-active ligand, capable of bearing unpaired electrons, is present in the coordination sphere of the metal, the relative contributions and the roles and influence of metal and ligand to changes in the total spin state of the overall complex are far less well understood. The main four modes of action of redox-active ligands that have been studied thoroughly can be summarized as: (i) changing the Lewis acidity/basicity of the metal, (ii) acting as an electron reservoir, (iii) generation of a reactive ligand-centered radical, and (iv) radical-type activation of a substrate. We wish to expand upon these functions by investigating the role of a redox-active ligand in spin changing events. Specifically, by keeping the redox-active ligand and metal center constant we set out to investigate how coordination of different additional redox-innocent donors to the metal center influences the total spin state of the complex, which is governed by interactions of the metal \(d\)-orbitals and the redox-active ligand orbitals of \(\pi\)-symmetry.

In this context, we became interested in the family of dipyrrin-bisphenol ligands (DPP, Figure 1), known since the 1970s. Different substitution patterns on the backbone were explored since 2009 and complexes of Al, B, Ga, In, Ti, Zr, Ge, Sn and Mn have been reported. The DPP ligand scaffold was first described as being redox-active in 2012 after the synthesis of cobalt- and nickel-DPP complexes. Hereafter, the redox-activity was further studied in Mn, Pt, Cu and Au complexes. Catalytic applications have been reported for the Ti, Zr, G and Sn complexes (copolymerization of epoxides with CO\(_2\)) and Cu (aerobic alcohol oxidation). Contrarily, cobalt(III)-DPP complexes proved catalytically inactive in epoxide ring opening reaction with alcohols, which was attributed to the low Lewis acidity of the cobalt-center. Initial studies on cobalt-DPP complexes were mainly focused on comparison of their (redox) properties and (catalytic) reactivity with cobalt-porphyrin, -salen and -corrole analogues. The ligand was predominantly found to coordinate as a di-anionic (radical) ligand to a low-spin cobalt(II) center in neutral Co-DPP complexes. Density functional theory (DFT) calculations indicated that the triplet and broken-
symmetry open-shell singlet (BSS) ground state (inerring 
(anti)ferromagnetic coupling between the metal- and ligand- 
centered unpaired electrons) are energetically close (< 1 kcal 
mo1).127 Although a BSS (S = 0) spin state was inferred 
based on experimental data for a Co-DPP complex, DFT 
calculations indicated that the triplet state was slightly 
favoured (~1.0 kcal mol1).18 Furthermore, moreover, coordination of 
benzonitrile, DMSO and pyridine was observed, and full 
conversion to the octahedral (bis-axially-coordinated) 
complexes was described for DMSO, pyridine and NH3. Bis-
coordination of two pyridine molecules to afford the 
octahedral complex was indicated by UV-Vis studies and DFT 
calculations revealed orbital compositions expected for a 
trianionic ligand coordinated to a low-spin (B3LYP 
functional) or intermediate-spin (OLYP functional) cobalt(III) 
center. The exact electronic structure of the investigated 
species therefore remains largely unknown at this point.

Figure 1. General structure of a dipyrrin-bisphenol (DPP) ligand 
on a metal (M).

The aforementioned studies on cobalt-DPP complexes 
indicate that intermediate- and low-spin configurations on 
cobalt are energetically close and that the DPP ligand is redox-
active on cobalt. Due to these properties we selected the 
Co-DPP system as a suitable candidate to evaluate the influence of 
the redox-active ligand on the total spin state of the cobalt 
complex in the presence and absence of axial redox-innocent 
donor ligands. Specifically, in this work we study the 
electronic configuration of a neutral [Co6(DPP2−)] complex 
(with Ar = C6F5, R1 = R3 = t-Bu; R2 = H, Figure 1), bearing a 
new DPP ligand derivative, upon coordination of different 
axial donor ligands with experimental (XRD, χm, NMR, 
HRMS, UV-Vis) and computational (DFT, NEVPT2-
CASSCF) techniques. We thereby describe how the molecular 
orbitals are influenced by coordination of THF, pyridine and 
primary amines and elucidate the exact electronic structures of 
these complexes and the influence of the redox-active ligand 
on the orbital changes upon coordination of axial donors.

RESULTS AND DISCUSSION

Synthesis and open-shell singlet electronic ground state 
configuration of [Co6(DPP2−)]. The dipyrrin-bisphenol 
ligand DPPH2, bearing two tert-butyl groups on the phenol 
ring and a pentafluorophenyl substituent on the meso-position, 
was obtained via a four step synthesis in 65% overall isolated 
yield according to modified literature procedures (see 
Supporting Information and Scheme 1A).812 Coordination of 
cobalt(II) and in situ oxidation to the neutral complex was 
achieved according to an adapted literature procedure12 by 
employing Co(OAc)2·4(H2O) and NEt3 under aerobic 
conditions to afford [Co6(DPP2−)] as a purple powder in 88% 
isolated yield.

Slow evaporation of a concentrated solution of DPPH3 in 
CH2Cl2 afforded single crystals suitable for X-ray structure 
determination (Scheme 1B). Single crystals suitable for XRD 
analysis of [Co6(DPP2−)] were also obtained in a similar 
manner. The molecular structure of the latter is depicted in 
Scheme 1C and shows a slightly distorted square planar 
geometry around cobalt. This distortion is most likely caused 
by steric repulsion between the ortho-tert-butyl substituents on 
the phenolate rings. Comparison of the bond lengths in 
[Co6(DPP2−)] with those found in the fully aromatic DPPH3 liga-
d shows alternating elongation and shortening of the C–C 
bond lengths (see SI), consistent with loss of aromaticity due 
to oxidation of the DPP ligand in the complex. The bond 
lengths are similar to a previously described DPP ligand in the 
dianionic (radical) state on cobalt(II),12 thus supporting the 
proposed DPP2− oxidation state of the ligand. The two 
2-pyryllylphenolato fragments in [Co6(DPP2−)] have similar 
sand bonds, indicating a fully conjugated ligand and a 
delocalized ligand-centered radical coordinated to a cobalt(II) 
center in the neutral [Co6(DPP2−)] complex.19

1H NMR analysis of [Co6(DPP2−)] in CD2Cl2 showed two 
remarkably down-field shifted resonances at δ = 12.82 (2H) 
and 4.29 (18H) ppm. Note that these signals are observed at 
(respectively) δ = 7.03 and 1.54 ppm in DPPH3. All other 
resonances are shifted <1 ppm relative to the free ligand. 
These unusual shifts are suggestive of (minor) paramagnetic 
contributions to the observed chemical shift in the 1H NMR 
spectrum, which seems to correlate with the experimentally 
determined bond lengths from XRD that suggest a ligand-
centered radical (DPP2−) and consequently a cobalt(II) 
(radical) center. However, whether these apparent 
paramagnetic contributions are best explained by an open-
shell singlet ground state (with temperature independent 
paramagnetism, TIP) or as the result of population of an 
excited higher spin-multiplicity state (either thermally or 
induced by weak and dynamic coordination of CD2Cl2) is 
unclear at this stage. Nonetheless, these shifts are noteworthy.

Measurement of the effective magnetic moment (µeff) of 
[Co6(DPP2−)] in the solid state as a function of the 
temperature with a superconducting quantum interference 
device (SQUID), to investigate the coupling of the two 
unpaired electrons, showed no significant magnetization in the 
5–290 K range (see SI). The effective magnetic moment in 
CD2Cl2 solution, as determined by Evans’ method,20 also 
afforded a µeff of 0.2 µB. The combined XRD, NMR 
spectroscopic and magnetoochemical data thus indicate a 
diamagnetic ground state, resulting from strong 
antiferromagnetic coupling of the two unpaired electrons, 
yielding an overall (open-shell) S = 0 singlet spin state.

To study the electronic structure we initially performed 
DFT calculations at the B3LYP/def2-SVP/B3LYP/def2-
TZVP level of theory, employing an m4 grid and Grimme’s 
version 3 dispersion corrections (see SI for more details). 
The calculated bond metrics for [Co6(DPP2−)] in the open-shell 
singlet state closely resemble those found in the crystal 
structure (see SI) and show similar alternating C–C bond 
lengths, consistent with oxidation of the ligand to the 
DPP2−-redox state. The relative energies of the open-shell singlet 
(ΔG298K = +1.3 kcal mol−1), triplet (ΔG298K = 0.0 kcal mol−1) 
and closed-shell singlet (ΔG298K = +14.8 kcal mol−1) are 
consistent with the proposed open-shell (bi-radical) character of 
[Co6(DPP2−)], but fail to reproduce the experimentally 
observed (open-shell) singlet spin state being the ground state 
of the molecule.
Distinguishing between a triplet and a multireference broken-symmetry singlet (BSS) electronic structure is (nearly) impossible when relying on single reference DFT calculations.\textsuperscript{21} We therefore investigated the electronic structure of \([\text{Co}^6(\text{DPP}²^-)]\) with multiconfigurational \(N\)-electron valence state perturbation theory (NEVPT2)-corrected complete active space self-consistent field (CASSCF) calculations (see SI), a method we have previously used successfully to study the orbitals compositions of cobalt complexes bearing a redox-active ligand.\textsuperscript{22} A NEVPT2-CASSCF(18,14) calculation, employing 18 electrons in 14 active orbitals on \([\text{Co}^6(\text{DPP}²^-)]\) converged on the singlet surface and showed a dominant (>96%) contribution from a multireference open-shell singlet (OSS) electronic configuration of \([\text{Co}^6(\text{DPP}²^-)]\). A pure triplet spin state solution could not be found in this, nor in a reduced, active space. State averaging of the singlet and triplet state in a 50:50 mixture in the active space did afford a solution for the triplet spin state, but this triplet state was found to be +6.5 kcal mol\(^{-1}\) less stable than the OSS state.

A selection of the active orbitals and their occupations derived from the NEVPT2-CASSCF(18,14) calculation on \([\text{Co}^6(\text{DPP}²^-)]\) is depicted in Scheme 1D. The \(d_{yz}\) and \(d_{xz}\) orbitals are doubly filled, whereas the \(d_{x^2−y^2}\) orbital is empty. The two main contributors to the multireference OSS solution are described by the \(d_{xy}\) orbital, which has a bonding and antibonding combination with the \(\pi\)-frame of the ligand (\(L^2\) or \(L^−_2\)) or is non-bonding (\(d_{xy}\)).

Specifically, 50.6% of the total wavefunction is described by a doubly filled \(L^2\) orbital (and empty \(d_{xy}\)), while 45.5% of the wavefunction is described by a doubly filled \(d_{xy}\) (and empty \(L^−_2\) orbital). The electronic structure of \([\text{Co}^6(\text{DPP}²^-)]\) is thus best described as an open-shell singlet based on the combined experimental (XRD, \(\^1\text{H NMR}, \mu_{eff}\)) and computational (NEVPT2-CASSCF) studies. Effectively, one unpaired electron resides in the \(d_{xy}\) orbital on cobalt and another unpaired electron is fully delocalized over the ligand with a small contribution from the \(d_{x^2−y^2}\) orbital on cobalt. As such, this complex is best described as a system containing antiferromagnetically coupled cobalt(II)- and \(\text{DPP}²^-\) ligand-centered unpaired electrons.

Spin-flip to a triplet state upon coordination of THF to \([\text{Co}^6(\text{DPP}²^-)]\) to generate \([\text{Co}^5(\text{DPP}²^-)(\text{THF})]\). Whereas \([\text{Co}^6(\text{DPP}²^-)]\) is purple in non-coordinating solvents (CH\textsubscript{3}Cl, toluene) we noticed a distinct color change to green upon solvation of the complex in coordinating solvents (CH\textsubscript{3}Cl, MeCN), indicative of solvent coordination. The UV-Vis spectra of \([\text{Co}^6(\text{DPP}²^-)]\) in THF (solid green line, \(\lambda_{\text{max}} = 318, 409, 423, 474, 632 \text{ and } 833 \text{ nm}\)) and CH\textsubscript{3}Cl (solid purple line, \(\lambda_{\text{max}} = 326, 374, 556 \text{ and } 755 \text{ nm}\)) are shown in Figure 2 left. Titration of THF (guest) to a CH\textsubscript{3}Cl solution of \([\text{Co}^6(\text{DPP}²^-)]\) (host) afforded spectral changes in the UV-Vis spectra characteristic for multiple binding events (see Figure 2 left and SI). Isosbestic points are found in two regimes; between 0 and 1.3\times10\(^4\) eq. THF (solid purple to solid light green line, \(\lambda = 413, 488, 600, 667, 771 \text{ nm}\)) and between 5.2\times10\(^4\) and 1.4\times10\(^5\) eq. THF (solid orange to solid brown line, \(\lambda = 393, 489, 593, 679, 776 \text{ nm}\)). Between these two regimes the spectral crossing points are found between the isosbestic points, suggestive of the simultaneous presence of three species.
The titration data could be fitted\(^\text{23}\) to weak non-cooperative host-guest-guest binding with an overall association constant \((K_{as})\) of 1.2 M\(^{-1}\) for binding of two THF molecules (see SI). The data is therefore consistent with initial (predominant) formation of a mono-THF adduct (first regime), followed by formation of a bis-THF adduct (second regime, see SI). Full conversion to this latter species is not reached at the end of the depicted titration curve (brown solid line, Figure 2 left), and is only observed in neat THF (solid green line, Figure 2 left), as indicated by the increased absorbance of various spectral bands and the shoulder at 474 nm. Similar mono- and bis-coordination of solvent has been described in literature for related Co-DPP complexes,\(^\text{18}\) and in combination with the titration data in Figure 2 we thus propose formation of a bis-THF adduct \((\text{[Co}^{III}\text{DPP}^2\text{]}\text{(THF)}_2)\) in neat THF (Scheme 2).

To further study the coordination of THF to \([\text{Co}^{III}\text{DPP}^2\text{]}\) we followed the spectral changes in the \(^1\text{H}^\text{NMR}\) spectrum upon addition of THF to a 5.89 mM CD\(_2\)Cl\(_2\) solution of \([\text{Co}^{III}\text{DPP}^2\text{]}\) (Figure 2 right). The presence of 1.1, 2.0 or 3.8 M THF (spectra B, C, D) led to signal broadening and gradual downshifting of one resonance (labelled as a red circle), while three other resonances (labelled as a blue square, orange triangle and yellow diamond) are strongly shifted upfield, approaching the shifts observed in neat THF-\(d_8\) (spectra E). The observed sharp paramagnetically shifted resonances in the \(-65\) to \(+45\) ppm region in neat THF-\(d_8\) clearly indicate conversion toward a new open-shell species. Interestingly, concentrating and thoroughly drying the sample obtained in neat THF-\(d_8\), followed by dissolution in CD\(_2\)Cl\(_2\) afforded a purple solution for which the spectral data (\(^1\text{H}^\text{NMR}, \text{UV-Vis}\)) exactly matched that of \([\text{Co}^{III}\text{DPP}^2\text{]}\) (spectrum F). These combined data thus point to weak and reversible binding of THF to the square planar complex, consistent with the low \(K_{as}\) as derived from the UV-Vis spectroscopic titration study.

No THF adducts were observed by high resolution mass spectrometry (HRMS), presumably due to the reversible weak binding and low boiling point of THF, which is likely easily lost in the ionization process. Attempts to crystallize a THF adduct of \([\text{Co}^{III}\text{DPP}^2\text{]}\) were unfortunately unsuccessful. Determination of the effective magnetic moment of \([\text{Co}^{III}\text{DPP}^2\text{]}\text{(THF)}_2\) in THF-\(d_8\) by Evans’ method\(^\text{20}\) afforded \(\mu_{eff} = 2.91\ \mu_B\), indicating the formation of a triplet \((S = 1)\) complex.

DFT calculations (B3LYP/def2-SVP/B3LYP/def2-TZVP, m4 grid, Grimme’s version 3 dispersion corrections) indicated that both the square pyramidal mono-THF adduct \((\text{[Co}^{III}\text{DPP}^2\text{]}\text{(THF)}\)) and the octahedral bis-THF complex \((\text{[Co}^{III}\text{DPP}^2\text{]}\text{(THF)}_2)\) have a triplet spin \((S = 1)\) ground state, consistent with the experimentally determined spin state. To obtain more insight in the electronic structure of \([\text{Co}^{III}\text{DPP}^2\text{]}\text{(THF)}_2\) and to investigate possible multireference contributions to the ground-state wavefunction, we performed NEVPT2-CASSCF\((18,15)\) calculations on the singlet, triplet and quintet spin surfaces. The triplet state was again found to be the lowest in energy, with the (open-shell) singlet and quintet states being disfavoured by \(+32.2\) kcal mol\(^{-1}\) and \(+33.0\) kcal mol\(^{-1}\), respectively. Dominant multireference character was observed in the triplet spin state, leading to an interesting electronic structure wherein cobalt retains the +II oxidation state and is ferromagnetically coupled to a ligand-centered radical on the DPP\(^{2-}\) ligand (Figure 3).

With the \(d_{xy}, d_{xz}\) and \(d_{yz}\) orbitals on cobalt doubly filled, the unpaired (and uncorrelated) \(\alpha\)-spin electron on cobalt resides in the \(d_{xy}\) orbital (Figure 3). The other \(\alpha\)-spin electron mainly resides in the strongly correlated antibonding combinations of the \(d_{x^2-y^2}\) orbital with the ligand pyrrole \(\pi\)-framework \((d_{x^2-y^2} \rightleftharpoons \text{Pyr}\) \(L_{\alpha}, -0.26254\ \text{Eh}, 46.1\% \) only \(\alpha\)-spin, 1.51 total electron occupation\) and the complete ligand \(\pi\)-system \((L_{\alpha\beta} \rightleftharpoons \text{Pyr}\) \(L_{\beta}, 0.20887\ \text{Eh}, 34.9\% \) only \(\alpha\)-spin, 1.59 total electron occupation\).\(^\text{24}\) The energetically slightly higher lying \(L_{\alpha\beta}\)
orbital is more diffuse over the ligand π-system, thus leading to a smaller electron-electron repulsive interaction (i.e. pairing energy of the α and β spin electrons) upon filling of this orbital in comparison to the more localized (less diffuse) \( d_{xy} \) orbital. Consequently, in the multiconfigurational description of the total triplet spin state wavefunction, the ligand-centered unpaired electron is mainly (46.1%) localized on the least diffuse orbital (\( d_{xy} \)).

The spin-flip in the transition from \([\text{Co}^{	ext{II}}\text{DPP}^2\text{−}](\text{OSS})\) to \([\text{Co}^{	ext{II}}\text{DPP}^2\text{−}](\text{THF})_2\) (triplet) can be understood by looking at the composition of the SOMOs. The α- and β-spin electrons in \([\text{Co}^{	ext{II}}\text{DPP}^2\text{−}]\) are located in \( d_{xy} \) orbitals \( (d_{xy} \text{ and } L_{xy} \pm d_{xy}) \). A triplet state would lead to severe (α) spin-spin repulsion in this cobalt-centered orbital, and consequently an OSS solution is favoured. This is not the case for \([\text{Co}^{	ext{II}}\text{DPP}^2\text{−}](\text{THF})_2\), wherein the two unpaired electrons reside in spatially different orbitals \( (d_{x^2} \text{ and } d_{y^2}-d_{z^2}) \). In this case Hund’s rule applies, which states that the maximization of the total spin is favored for a given electronic configuration, thus leading to the observed triplet spin state.

**Figure 3.** Selected active orbitals, occupancies in parenthesis and electronic structure of cobalt and the ligand from a NEVPT2-CASSCF(18,15) calculation on \([\text{Co}^{	ext{II}}\text{DPP}^2\text{−}](\text{THF})_2\). Isosurface set at 80.

Closed-shell singlet spin state via metal-to-ligand single-electron transfer induced by coordination of stronger donors. We next set out to explore the influence of replacing the weak-field ligand THF with the stronger field ligand pyridine. Addition of excess (100 eq.) pyridine to \([\text{Co}^{	ext{II}}\text{DPP}^2\text{−}]\) in CH\(_2\)Cl\(_2\) afforded quantitative formation of the bis-pyridine adduct \([\text{Co}^{	ext{II}}\text{DPP}^2\text{−}](\text{Py})_2\) as a green powder after work-up (Scheme 3A). The six-coordinate complex was characterized **inter alia** by \(^1\)H NMR spectroscopy and positive mode cold-spray ionization (CSI) HRMS. Single crystals suitable for X-ray structure determination were grown by slow evaporation of a concentrated solution of the complex in a 5:1 mixture of CH\(_2\)Cl\(_2\) and MeOH. Three octahedral \([\text{Co}^{	ext{III}}\text{DPP}^2\text{−}](\text{Py})_2\) complexes are present in the unit cell (see SI), one of which (left structure) is depicted in Scheme 3B. The bond metrics of all three \([\text{Co}^{	ext{III}}\text{DPP}^2\text{−}](\text{Py})_2\) molecules are similar, although the relative rotation of the pyridine ligands differs from nearly parallel to perpendicular (see SI).

The experimentally determined C–C bond lengths of the DPP moiety (see SI) in the crystal structure of \([\text{Co}^{	ext{III}}\text{DPP}^2\text{−}](\text{Py})_2\) resemble the aromaticity that is also observed in the free DPPH\(_1\) ligand, thus suggesting a fully reduced tri-anionic DPP\(^3\)− redox state for the ligand and consequently a cobalt(III) center in the neutral complex. The \(^1\)H NMR resonances of \([\text{Co}^{	ext{III}}\text{DPP}^2\text{−}](\text{Py})_2\) do not show any paramagnetic shifts and are found entirely in the diamagnetic region (\( δ = 8.04-1.25 \) ppm), suggesting a closed-shell singlet electronic configuration, i.e. a low-spin Co\(^{III}\) center. SQUID analysis of solid \([\text{Co}^{	ext{III}}\text{DPP}^2\text{−}](\text{Py})_2\) did not show significant magnetization in the 4–290 K range, again consistent with a singlet ground state (see SI).

DFT calculations (B3LYP/def2-SVP//B3LYP/def2-TZVP, m4 grid, Grimme’s version 3, dispersion corrections) indicated that formation of the closed-shell singlet octahedral bis-pyridine \([\text{Co}^{	ext{III}}\text{DPP}^2\text{−}](\text{Py})_2\) complex is more exergonic (\( \Delta G^\circ_{298K} = -14.2 \) kcal mol\(^{-1}\)) than formation of the square pyramidal mono-pyridine adduct \([\text{Co}^{	ext{III}}\text{DPP}^2\text{−}](\text{Py})\) (\( \Delta G^\circ_{298K} = -9.1 \) kcal mol\(^{-1}\), \( S = 1 \)). Orbital analysis clearly showed that coordination of pyridine in \([\text{Co}^{	ext{III}}\text{DPP}^2\text{−}](\text{Py})_2\) (Scheme 3C) leads to a strongly destabilized \( d_{x^2} \) orbital \( (d_{x^2}-2N_{\text{Py}}) \), resulting in a quite large HOMO (highest occupied molecular orbitals) to LUMO (lowest unoccupied molecular orbital) gap of 0.10346 Eh, and therefore a low-spin (CSS) configuration. The \( L_{x^2}-d_{xy} \) (HOMO) is doubly filled, reflecting the reduction of the ligand to the DPP\(^2\)− state. Cobalt adopts the +III oxidation state in \([\text{Co}^{	ext{III}}\text{DPP}^2\text{−}](\text{Py})_2\) with doubly filled \( d_{3z^2}, d_{xy} \) and \( d_{yz} \) orbitals, which are stabilized due to the higher oxidation state of cobalt in comparison to \([\text{Co}^{	ext{II}}\text{DPP}^2\text{−}])\). Thus, pyridine coordination effectively results in ligand reduction via metal-to-ligand single-electron transfer. Interestingly, interaction of the pyridine-π system with the \( d_{y^2} \) orbital is observed in the \( d_{y^2}-2N_{\text{Py},y^2} \) orbital, reflecting at least some π-back donation from cobalt to the pyridine ligands.

Coordination of pure σ-donors was achieved via addition of the primary amines tert-butyl amine and 1-adamantyl amine. Complex \([\text{Co}^{	ext{II}}\text{DPP}^3\text{−}](\text{NH}_2\text{Bu})_2\) was obtained in quantitative yield as a green powder through addition of 100 equivalents \( \text{BuNH}_2 \) to \([\text{Co}^{	ext{II}}\text{DPP}^2\text{−}]) \) and subsequent concentration and drying under reduced pressure (Scheme 4A). \([\text{Co}^{	ext{II}}\text{DPP}^3\text{−}](\text{NH}_2\text{Ad})_2\) (Ad = 1-adamantyl) was obtained in 43% yield as green crystals after addition of 2 equivalents \( \text{AdNH}_2 \) to \([\text{Co}^{	ext{II}}\text{DPP}^2\text{−}]) \) and subsequent crystallization.
Scheme 3. A: formation of [Co$^{II}$I(DPP$^-$)(Py)$_2$]. B: Displacement ellipsoid plot (50% probability level) of one [Co$^{II}$I(DPP$^-$)(Py)$_2$] molecule. H atoms and disorder are omitted for clarity. D: Selection of DFT calculated orbitals and electronic structure of cobalt and the ligand in [Co$^{II}$I(DPP$^-$)(Py)$_2$]. Isosurface set at 80.

Scheme 4. A: formation of [Co$^{III}$I(DPP$^-$)(NH$_2$Bu)$_2$] and [Co$^{III}$I(DPP$^-$)(NH$_2$Ad)$_2$]. Ad = 1-adamantyl. B: Displacement ellipsoid plot (50% probability level) of [Co$^{III}$I(DPP$^-$)(NH$_2$Ad)$_2$]. C: Displacement ellipsoid plot (50% probability level) of [Co$^{III}$I(DPP$^-$)(NH$_2$Bu)$_2$]. H atoms and disorder are omitted for clarity.

The $^1$H NMR resonances of [Co$^{III}$I(DPP$^-$)(NH$_2$Bu)$_2$] and [Co$^{III}$I(DPP$^-$)(NH$_2$Ad)$_2$] are similar to the bis-pyridine adduct, found within the diamagnetic region, suggesting that both complexes are most stable in the CSS spin state. Crystals suitable for X-ray structure determination of both complexes were obtained by slow evaporation of concentrated solutions in CH$_2$Cl$_2$ and MeOH (5:1) at room temperature. The C–C and Co–DPP bond lengths obtained from the crystal structure of
[Co\textsuperscript{III}(DPP\textsuperscript{3+})(NH\textsubscript{2}Ad)\textsubscript{2}] (Scheme 4B) closely resemble those found in [Co\textsuperscript{III}(DPP\textsuperscript{3+})(Py)\textsubscript{2}] and are consistent with a fully reduced (3–) redox state of the DPP ligand and consequently a cobalt(III) center. The crystallographically independent molecules of [Co\textsuperscript{III}(DPP\textsuperscript{3+})(NH\textsubscript{2}Bu)\textsubscript{2}] found in the asymmetric unit (see SI) have mutually similar bond metrics, which are also comparable to those observed in [Co\textsuperscript{III}(DPP\textsuperscript{3+})(NH\textsubscript{2}Ad)\textsubscript{2}]. One molecule found in the crystal structure of [Co\textsuperscript{III}(DPP\textsuperscript{3+})(NH\textsubscript{2}Bu)\textsubscript{2}] is depicted in Scheme 4C.

The DFT (B3LYP/def2-SVP//B3LYP/def2-TZVP, m4 grid, Grimme’s version 3, dispersion corrections) calculated bond lengths of [Co\textsuperscript{III}(DPP\textsuperscript{3+})(NH\textsubscript{2}Bu)\textsubscript{2}] in the CSS spin state are consistent with the experimentally determined bond metrics (see SI). Moreover, the corresponding triplet spin state was found to be +4.0 kcal mol\textsuperscript{-1} less stable. DFT orbital analysis of [Co\textsuperscript{III}(DPP\textsuperscript{3+})(NH\textsubscript{2}Bu)\textsubscript{2}] (Figure 4) shows a destabilized empty d\textsubscript{xy} orbital due to coordination of the rBuNH\textsubscript{2} lone σ-pair (N\textsubscript{a,\text{r}}). However, bonding interactions of these lone pairs with the d\textsubscript{yz} and d\textsubscript{zx} orbitals are observed in the doubly filled d\textsubscript{yz}+2N\textsubscript{a,\text{r}} and d\textsubscript{zx}+2N\textsubscript{a,\text{r}} orbitals. The d\textsubscript{xy}, d\textsubscript{xz}, and d\textsubscript{y} orbitals are all doubly filled, consistent with a low-spin cobalt(III) electronic configuration formed after metal-to-ligand single electron transfer.

The electronic ground state of [Co\textsuperscript{0}(DPP\textsuperscript{2−})] is characterized as a multiconfigurational open-shell singlet, which is best described as a system containing antiferromagnetically coupled cobalt(II)- and ligand-centered unpaired electrons. Solvation of this complex in THF (sp\textsuperscript{3}-hybrid donor) affords clean formation of a THF-adduct, [Co\textsuperscript{0}(DPP\textsuperscript{2−})(THF)]\textsubscript{2}, which resides in the triplet spin state. The origin of this spin-flip is the orbital overlap of the redox-active ligand π-framework with the cobalt d-orbitals, which leads to population of two ligand-d\textsubscript{d\textsuperscript{z\textsuperscript{2}}} orbital combinations in a multiconfigurational triplet solution to reduce spin-spin repulsion. Coordination of pyridine (σ-donor, weak π-acceptor), rBuNH\textsubscript{2} or AdNH\textsubscript{2} (σ-donors) afforded the closed-shell singlet octahedral complexes via metal-to-ligand single-electron transfer. The redox-active DPP ligand is reduced to the tri-anic anionic redox state and cobalt adopts a low-spin +III oxidation state.

Concluding, we have described that a redox-active DPP ligand on cobalt can accommodate three different spin states of the complex within an integer spin system. The spin-state changes are induced via coordination of axial ligands to the square planar complex, but the relative energy and overlap of the ligand- and cobalt-centered orbitals determine the most stable spin state. The capability of the redox-active ligand to stabilize unpaired electrons and accommodate intramolecular electron transfer was found to be crucial in this context.

**EXPERIMENTAL SECTION**

**General considerations.** 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\textsubscript{2} filled glovebox or by using standard Schlenk techniques (under Ar or N\textsubscript{2}), unless noted otherwise. CH\textsubscript{3}Cl\textsubscript{2} and MeOH were distilled from CaH\textsubscript{2}, toluene was distilled from sodium, THF was distilled from sodium benzophenone ketyl. Detailed information regarding NMR, HRMS, UV-Vis, SQUID and XRD measurements are included in the SI. XRD and DFT derived bond lengths are also included in the SI. The magnetic moments in solution were determined via Evans’ method\textsuperscript{20}.

**Synthesis and characterization**

**DPPH\textsubscript{3}.** Synthesized in four steps (overall isolated yield 65%) according to adapted literature procedures\textsuperscript{8,10} Characterized by \textsuperscript{1}H and \textsuperscript{19}F NMR, HRMS-FD\textsuperscript{+}, elemental analysis and XRD (see SI).

[Co\textsuperscript{0}(DPP\textsuperscript{2−})]. Prepared in 88% isolated yield according to a literature procedure for the insertion of cobalt in a DPP ligand\textsuperscript{12} Characterized by \textsuperscript{1}H and \textsuperscript{19}F NMR, HRMS-FD\textsuperscript{+}, UV-Vis, elemental analysis, \(\mu\text{eff} (\text{Evans’ method and SQUID})\) and XRD (see SI).

[Co\textsuperscript{0}(DPP\textsuperscript{2−})(THF)]\textsubscript{2}. Quantitatively prepared by solvation of [Co\textsuperscript{0}(DPP\textsuperscript{2−})] in THF. Characterized by \textsuperscript{1}H NMR, \(\mu\text{eff} (\text{Evans’ method})\) and UV-Vis (see SI).

[Co\textsuperscript{0}(DPP\textsuperscript{2−})(Py)\textsubscript{2}]. Obtained in quantitative isolated yield by addition of pyridine (100 eq.) to a solution of [Co\textsuperscript{0}(DPP\textsuperscript{2−})] in CH\textsubscript{3}Cl\textsubscript{2}. Characterized by \textsuperscript{1}H and \textsuperscript{19}F NMR, HRMS-CSI\textsuperscript{+}, UV-Vis, elemental analysis, \(\mu\text{eff} (\text{SQUID})\) and XRD (see SI).

[Co\textsuperscript{0}(DPP\textsuperscript{3+})(NH\textsubscript{2}Bu)\textsubscript{2}]. Obtained in quantitative isolated yield by addition of rBuNH\textsubscript{2} (100 eq.) to a solution of...
[Co⁹⁹(DPP)₃⁺] in CH₂Cl₂. Characterized by ¹H and ¹⁹F NMR, HRMS-CI, UV-Vis and XRD (see SI).

[Co⁹⁹(DPP)⁺(NH₃Ad)₂]. Obtained in 43% isolated yield by addition of AdNH₂ (2.0 eq.) to a solution of [Co⁹⁹(DPP)₃⁺] in CH₂Cl₂. Characterized by ¹H and ¹⁹F NMR, HRMS-CI, UV-Vis and XRD (see SI).

Computational studies

DFT. Calculations were conducted on full atomic models at the B3LYP/def2-SVP/°/B3LYP/def2-TZVPP level of theory on an m₄ grid with Grimme’s version 3³⁸ ("zero-damping") dispersion corrections with the TURBOMOLE 7.3²⁹ software package coupled to the PQQ2 Baker optimizer³⁰ via the BOpt package.³¹ Orbital interpretation was performed by Löwdin population analysis of quasi restricted orbitals (QRO) generated with the ORCA 4.1.³² software package at the B3LYP/def2-TZVP 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.³³ Energies, xyz coordinates and more details on the calculations are included in the SI.

NEVPT2-CASSCF. The NEVPT2 corrected CASSCF calculations were performed with the ORCA 4.1.³³ software package on the geometries optimized in TURBOMOLE. The def2-TZVPP basis set was used together with the RIJCOSX³⁴ approximation in conjunction with the def2-TZVPC fitting basis set to reduce computational cost. The single root spin state was calculated. NEVPT2³⁵ calculations using the RI approximation were carried out on converged CASSCF wavefunctions. Energies, contributions to the wavefunctions, full representations of the active spaces and more details on the calculations are included in the SI.

ASSOCIATED CONTENT

Supporting Information. Experimental details, synthetic procedures, NMR-, HRMS- and UV-Vis spectra, crystallographic refinement details, geometries (xyz coordinates) and energies of DFT calculated structures, description of the NEVPT2-CASSCF calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

Accession Codes

CCDC 2012086 (DPPH), 2012087 ([Co⁹⁹(DPP)₃⁺]), 2012088 ([Co⁹⁹(DPP)⁺(Py)_₂]), 2012089 ([Co⁹⁹(DPP)⁺(NH₃Bu)_₂]) and 2012090 ([Co⁹⁹(DPP)⁺(NH₃Ad)_₂]) contain the supplementary crystallographic data and can be obtained free of charge via http://
https://www.ccdc.cam.ac.uk/structures/.

AUTHOR INFORMATION

Corresponding Author

* Email: b.debruin@uva.nl

Present Addresses

¹ Current address of J.I.v.d.V.: Bioinspired Coordination Chemistry & Homogeneous Catalysis Group, Institute of Chemistry, Carl von Ossietzky University Oldenburg, Carl-von-Ossietzky-Str. 9-11, 26129 Oldenburg, Germany.

Author Contributions

All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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TOC figure

SPIN FLIP
METAL-TO-LIGAND
SINGLE-ELECTRON TRANSFER
Electronic Supplementary Information

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

Nicolaas P. van Leest,a Wowa Stroek,a Maxime A. Siegler,b Jarl Ivar van der Vlugtac and Bas de Bruina,a

a Homogeneous, Supramolecular and Bio-Inspired Catalysis Group, van ’t Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam, Science Park 904, 1098XH Amsterdam, The Netherlands.
b Department of Chemistry, John Hopkins University, Baltimore, Maryland 21218, United States.
c Bioinspired Coordination Chemistry & Homogeneous Catalysis Group, Institute of Chemistry, Carl von Ossietzky University Oldenburg, Carl-von-Ossietzky-Str. 9-11, 26129 Oldenburg, Germany.

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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 \( \text{N}_2 \) filled glovebox or by using standard Schlenk techniques (under \( \text{Ar} \) or \( \text{N}_2 \)), unless noted otherwise. \( \text{CH}_2\text{Cl}_2 \) and \( \text{MeOH} \) were distilled from \( \text{CaH}_2 \), toluene was distilled from sodium, THF was distilled from sodium benzophenone ketyl.

*NMR spectroscopy*

\( ^1\text{H}, ^{13}\text{C}, ^{19}\text{F} \) and \( ^{31}\text{P} \) 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 \( \mu \)m. Current rate 51.2 mA/min over 1.2 min. FI Emitter, Carbotec or Linden (Germany), FI 10 \( \mu \)m. 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 \([\text{Co}^{II}(\text{DPP}^2)]\) and \([\text{Co}^{III}(\text{DPP}^3)(\text{NH}_2\text{Ad})_2]\): X-ray intensities were measured on a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator (\( \lambda = 0.71073 \) 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$_2$Bu)$_2$]: all reflection intensities were measured at 110(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Cu Kα radiation ($\lambda = 1.54178$ Å) under the program CrysAlisPro (Version CrysAlisPro 1.171.39c, 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 $U_{eq}$ of the attached C or O atoms. Crystal structures were visualized with the Mercury software package.  

Accession codes: CCDC 2012086 (DPPH$_3$), 2012087 ([Co$^{III}$(DPP$^3$)]), 2012088 ([Co$^{III}$(DPP$^3$)(Py)$_2$]), 2012089 ([Co$^{III}$(DPP$^3$)(NH$_2$Bu)$_2$]) and 2012090 ([Co$^{III}$(DPP$^3$)(NH$_2$Ad)$_2$]) 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$_8$F$_3$ 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.

[Co$^{III}$(DPP$^3$)(NH$_2$Bu)$_2$]: 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. A capillary containing the deuterated solvent and internal standard was inserted in the NMR tube and a ¹H NMR spectrum was recorded. The mass susceptibility ($\chi$ in cm³g⁻¹) of the analyte was calculated with equation (1), wherein $v_0$ 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 ($\chi_M$ in cm³mol⁻¹) can be calculated by equation (2), wherein M is the molar mass of the analyte. $\chi_M^P$ is the pure paramagnetic molar susceptibility and can be calculated by equation (3) in which $\chi_M^{Dia}$ (the diamagnetic molar susceptibility) is a correction on $\chi_M$ to account for the diamagnetic contributions within the analyte. The diamagnetic molar susceptibility ($\chi_M^{Dia}$) can be calculated by using Pascal’s constants, or estimated from the molecular mass. With equation (4), $\chi_M^P$ can be used to calculate the effective magnetic moment ($\mu_{eff}$) of the analyte, in which k is the Boltzmann constant, T is the temperature in Kelvin, $N_A$ is the Avogadro constant and $\mu_B$ 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).

\[
\chi = \frac{3000 \times \Delta \nu}{4\pi \times v_0 \times c}
\]

\[
\chi_M = \chi \times M
\]

\[
\chi_M^P = \chi_M - \chi_M^{Dia}
\]

\[
\mu_{eff} = \sqrt{\frac{3 \times k \times T \times \chi_M^P}{N_A \times \mu_B^2}} \approx 2.82787 \sqrt{T \times \chi_M}
\]

\[
\mu_{eff} = g \sqrt{S(S + 1)}
\]

**DFT calculations**

DFT studies were performed on full atomic models (no simplifications) using TURBOMOLE 7.3⁸ coupled to the PQS Baker optimizer⁹ via the BOpt package. The geometry optimizations and frequency analysis was
performed at the B3LYP\textsuperscript{11}/def2-SVP\textsuperscript{12} level of theory (unless noted otherwise) on an m4 grid, using Grimme’s version 3 (disp3, “zero damping”) dispersion corrections.\textsuperscript{13} All minima (no imaginary frequencies) were characterized by numerically calculating the Hessian matrix. Final orbital and energy evaluation was performed at the B3LYP\textsuperscript{11}/def2-TZVP\textsuperscript{14} level of theory (unless noted otherwise) on an m4 grid, using Grimme’s version 3 (disp3, “zero damping”) dispersion corrections,\textsuperscript{15} on the optimized geometries. Energy output was reported in Hartree and was converted to kcal mol\textsuperscript{-1} by multiplication with 627.503.

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

$$
\varepsilon \approx \frac{S^2_{S+1} \times \varepsilon_S - S^2_S \times \varepsilon_{S+1}}{S^2_{S+1} - S^2_S}
$$

Orbital interpretation was done by Löwdin population analysis of quasi restricted orbitals (QRO) generated with the ORCA 4.1\textsuperscript{16} software package at the B3LYP\textsuperscript{11}/TZVP\textsuperscript{12} 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\textsuperscript{17} 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\textsuperscript{16} software package on the geometry optimized in TURBOMOLE at the experimentally found spin state. The def2-TZVP\textsuperscript{12} basis set was used together with the RIJCOSX\textsuperscript{18} approximation in conjunction with the def2-TZVP/C fitting basis set to reduce computational cost. The single root spin state was calculated. NEVPT2\textsuperscript{19} calculations using the RI approximation were carried out on converged CASSCF wavefunctions. Canonical orbitals were generated for visualization using IboView.\textsuperscript{17} Energy output was reported in Hartree and was converted to kcal mol\textsuperscript{-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.
   \[[!BP86 def2-TZVP def2-TZVP/C RIJCOSX UNO Normalprint KeepDens] \]
   \[%scf rotate {orbital number, active space location} end end\]

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 $\pi$ orbitals and relevant metal-ligand bonding and antibonding orbitals) and rotate these into the active space.
   \[[! ROKS BP86 def2-TZVP def2-TZVP/C RIJCOSX Normalprint noiter MOREAD %moinp "orbitals.gbw"]\]

4. The single root CASSCF calculation was performed.
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.

```plaintext
#!/ 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]
```

```plaintext
#!/ 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$^{2-}$].

Pyrrolylsodium,$^2_0$ 1,$^2_1$ and 2$^{22}$ 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.$^{22}$ 2-(3,5-di-tert-butyl-2-methoxyphenyl)-1H-pyrrole (2, 4.00 g; 14.0 mmol; 1.0 eq) was dissolved in CH$_2$Cl$_2$ (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$_2$Cl$_2$ (9:1) as the eluent. The product was obtained as an orange powder in 4.91 g; 6.6 mmol; 94% yield.
1H NMR (300 MHz, Methylene Chloride-d2) 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).

19F NMR (282 MHz, Methylene Chloride-d2) δ -137.79 – -141.33 (m), -154.07 (t, J = 21.0 Hz), -160.32 – -164.08 (m).

13C 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 13C resonances corresponding to the C_{6}F_{5} fragment are absent due to broadening of the signal as a result of coupling with 19F. Similar signal loss in DPPF-derived ligands was reported in literature. Similar loss of signal intensity was observed in 13C NMR analysis of a highly concentrated pentafluorobenzaldehyde solution. Which gave relative peak intensities of 1 (13C=O) : 0.78 (13C-F) : 0.13 (13C-F) : 0.82 (13C-F) : 0.33 (13C=C=O).

HRMS-FD*: calc. for [C_{45}H_{31}F_{5}N_{4}O_{5}]^+: 746.3871, found: 746.3899 [M]^*.

DPPH₃: Adapted from a literature procedure for the deprotection reaction. 3 (0.400 g; 0.54 mmol; 1.0 eq) was dissolved in CH₂Cl₂ (20 mL) and cooled to 0 °C in a flame dried Schlenk under a nitrogen atmosphere compound. BBr₃ (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 BBr₃. 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 NaHCO₃ solution (100 mL). The obtained pink suspension was extracted with EtOAc (100 mL), washed with brine (100 mL), dried over Na₂SO₄, 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.

1H 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).

19F NMR (282 MHz, Methylene Chloride-d2) δ -139.84 (m), -153.77 (t, J = 20.9 Hz), -162.00 (m).

13C NMR (75 MHz, Methylene Chloride-d2) 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 13C NMR signal are missing for the reasons as explained in the characterization of 3 (vide supra).

HRMS-FD*: calc. for [C_{45}H_{31}F_{5}N_{4}O_{5}]^+: 718.3558, found: 718.3559 [M]^*.

Elemental analysis: calc. for C_{45}H_{31}F_{5}N_{4}O_{5}: 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 CH₂Cl₂ 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. DPPH₃, C_{45}H_{31}F_{5}N_{4}O_{5}, FW = 718.82, pink-purple plate, 0.29 mm × 0.14 mm × 0.05 mm, monoclinic, P2₁/c, a = 21.9848(4) Å, b = 15.9671(3) Å, c = 10.8173(2) Å, β = 96.9017(18)°, V = 3769.72(12) Å³, Z = 4, μ = 0.78 mm⁻¹; 25014 reflections were measured with (sin θ/λ)max = 0.616 Å⁻¹. 7407 Reflections were unique (Rint = 0.034) of which 5443 were observed [I > 2σ(I)]. Residual electron density between −0.23 and 0.61 e/Å³. S = 1.041. Refinement: RF(F² > 2σ(F²)) = 0.043, wR(F²) = 0.124, number of reflections: 7407, number of parameters: 501, number of restraints: 10.
[Co(DPP$^{2-}$)], Adapted from a literature procedure for the insertion of cobalt into the ligand.\textsuperscript{24} DPPH\textsubscript{3} (1.00 g; 1.39 mmol; 1.0 eq) and [Co(OAc)$_2$]·4H$_2$O (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$_2$Cl$_2$ 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$_2$) $\delta$ 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$_2$) $\delta$ -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$_2$) $\delta$ 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}$CoF$_5$N$_2$O$_2$]$^+$: 774.2655, found: 774.2604 [M]$^+$. X-band EPR: silent at r.t. and 20 K.

UV-Vis (32.27 $\mu$M, CH$_2$Cl$_2$, 1.0 cm cuvet) nm {$\varepsilon$, cm$^{-1}$M$^{-1}$}: 230, 269 {26.3$x10^3$}, 326 {25.7$x10^3$}, 374 {20.6$x10^3$}, 556 {21.0$x10^3$}, 755 {5.67$x10^3$}.

Elemental analysis: calc. for C$_{43}$H$_{44}$CoF$_5$N$_2$O$_2$: 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 13.49; O 5.13.

$\mu_{eff}$(Evans' method, CD$_2$Cl$_2$ with toluene as internal standard, 297.2 K, 7.9 mM, $\Delta\nu = 0$ Hz): 0 $\mu_B$

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$_2$Cl$_2$ 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(DPP$^{2-}$)]. C$_{43}$H$_{44}$CoF$_5$N$_2$O$_2$, FW = 774.73, 0.45 mm $\times$ 0.14 mm $\times$ 0.12 mm, black block, monoclinic, C2/c, $a$ = 11.7070(6) Å, $b$ = 22.5631(15) Å, $c$ = 28.4794(15) Å, $\beta$ = 95.793(2), $V$ = 7484.3(7) Å$^3$, $Z$ = 8, $\mu$ = 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/$\AA^3$. 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 $[\text{Co}^{II}(\text{DPP}^{3-})]$ between 5 K and 290 K, corrected for presence of small oxide nanoparticles.
Table S1. Atom numbering scheme for DPPH₃ and [Co⁰(DPP²⁻)] and bond lengths derived from the single crystal XRD measurements and the DFT calculated structure (B3LYP/def2-SVP).

| Bond     | DPPH₃ (XRD, Å) | [Co⁰(DPP²⁻)] (XRD, Å) | [Co⁰(DPP²⁻)] (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^2)•(THF)]**: Obtained when dissolving [Co^II(DPP^2•)] in THF.

^1H NMR (500 MHz, THF-d8) 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 CH3 resonances (of the tBu groups) are missing. This signal is gradually disappearing upon addition of THF to a CD2Cl2 solution of [Co^II(DPP^2•)] (see NMR in main text). Coordinated THF is not visible because THF-d8 was used as the solvent.

UV-Vis (32.27 μM, THF, 1.0 cm cuvet) nm {ε, cm⁻³M⁻¹}: 318 {28.0×10³}, 409 {16.3×10³}, 423 {16.5×10³}, 474 {12.3×10³}, 632 {22.9×10³}, 833 {15.3×10³}.

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

µ_eff (Evans’ method, THF-d8 with toluene as internal standard, 297.2 K, 13.4 mM, Δν = 21.4 Hz, diamagnetic contribution = -0.00039): 2.91 μB.

HRMS measurements afforded only detection of [Co^II(DPP^2•)] due to the relatively weak coordination of THF and the evaporation of THF under the measurement conditions.

The association constant (K_assoc) for coordination of THF (guest, G) to [Co^II(DPP^2•)] (host, H, 32.27 μM in CH2Cl2) 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^2•)].
Figure S3. Residual errors of the fit of the changes in the absorption at 833 nm upon titration of THF to [Co<sup>II</sup>(DPP<sup>2</sup>•)].

Figure S4. Calculated molar ratios from the fit of the changes in the absorption at 833 nm upon titration of THF to [Co<sup>II</sup>(DPP<sup>2</sup>•)].

[Co<sup>II</sup>(DPP<sup>3</sup>•)(Py): [Co<sup>II</sup>(DPP<sup>2</sup>•)] (0.100 g; 0.13 mmol; 1.0 eq) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (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.

<sup>1</sup>H NMR (500 MHz, THF-<em>d</em><sub>8</sub>) δ 8.04 (d, <em>J</em> = 5.7 Hz, 4H), 7.60 (t, <em>J</em> = 7.6 Hz, 2H), 7.41 (d, <em>J</em> = 2.5 Hz, 2H), 7.21 (d, <em>J</em> = 4.6 Hz, 2H), 7.17 (d, <em>J</em> = 2.6 Hz, 2H), 7.08 (t, <em>J</em> = 6.7 Hz, 4H), 6.96 (d, <em>J</em> = 4.5 Hz, 2H), 1.59 (s, 18H), 1.25 (s, 18H).

<sup>19</sup>F NMR (282 MHz, Methylene Chloride-<em>d</em><sub>2</sub>) δ -140.91 (d, <em>J</em> = 23.4 Hz), -154.76 (t, <em>J</em> = 20.8 Hz), -161.59 – -163.84 (m).

<sup>13</sup>C NMR (75 MHz, Methylene Chloride-<em>d</em><sub>2</sub>) δ 158.83, 153.37, 138.13, 124.05, 36.71, 31.36. Most of the <sup>13</sup>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_{5}N_{4}O_{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 CH₂Cl₂ + 10 μL pyridine, 1.0 cm cuvet) nm \{ε, cm⁻¹M⁻¹\}: 337 {25.0×10³}, 479 {15.0×10³}, 661 (shoulder) {13.8×10³}, 723 {26.3×10³}. 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 CH₂Cl₂ 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.

Table S2. [Co^{III}(DPP^{3−})(Py)₂], C_{53}H_{54}CoF_{5}N_{4}O_{2}, FW = 932.93, black needle, 0.36 mm × 0.05 mm × 0.04 mm, triclinic, P-1, a = 15.8847(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) Å³, Z = 6, μ = 3.21 mm⁻¹; 96163 reflections were measured with (sin θ/λ)_{max} = 0.617 Å⁻¹. 29269 Reflections were unique (R_{int} = 0.089) of which 19036 were observed [I > 2σ(I)]. Residual electron density between −0.53 and 0.65 e/Å³. S = 0.96. Refinement: R[F² > 2σ(F²)] = 0.056, wR(F²) = 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 CH₂Cl₂ solution of [Co^{II}(DPP^{2−})].
Figure S6. Single crystal XRD measured molecular structure of $[\text{Co}^{III}(\text{DPP}^3)(\text{Py})_2]$, 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 \([\text{Co}^{II}(\text{DPP}^3\text{-})(\text{Py})] \) (labelled A, B and C in Figure S6), and the DFT (B3LYP/def2-TZVP geometry optimization) calculated structure. Ar = C₆F₅.

| 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(2)   | 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

| Dihedral angle of the pyridine planes | A (°) | B (°) | C (°) | DFT (°) |
|--------------------------------------|------|------|------|--------|
| C22–N3–Co–N4                         | 10.80 | 51.39 | 176.11 | 14.74  |
| C23–N4–Co–N3                         | 10.80 | 7.47  | 84.50 | 11.80  |

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Figure S7. SQUID measurement of [Co(III)(DPP-)(Py)2] between 4 K and 290 K, corrected for the presence of oxide nanoparticles.

[Co(III)(DPP-)(NH2tBu)2]: [Co(III)(DPP-)] (0.100 g; 0.13 mmol; 1.0 eq) was dissolved in CH2Cl2 (10 mL) and t-butyamine (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).

1H NMR (500 MHz, Methylene Chloride-d2) 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).

13C NMR (126 MHz, Methylene Chloride-d2) 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 13C signal is missing, presumably due to overlap. Five 13C NMR signal are missing for the reasons as explained in the characterization of 3 (vide supra).

19F NMR (282 MHz, Methylene Chloride-d2) δ -137.36 – -141.36 (m), -154.75 (t, J = 21.2 Hz), -160.77 – -164.48 (m).

UV-Vis (32.27 μM, CH2Cl2: tBuNH2 = 2.0 : 0.01, 1.0 cm cuvet) nm {ε, cm⁻¹M⁻¹}: 276, 336 (30.1×10³), 487 (16.5×10³), 650 (shoulder, 16.9×10³), 705 (30.7×10³). See Figure S8. Addition of tBuNH2 was necessary to prevent decoordination of the amine.

HRMS-CSI+ calc. for [C51H66CoF5N4O2]: 920.4438, found: 847.374 [M-tBuNH2]+, 774.283 [M-2tBuNH2]+.

XRD: XRD quality single crystals were grown by slow evaporation of a concentrated solution in CH2Cl2 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-)(NH2tBu)2]. 3(C51H66CoF5N4O2)-CH3O, 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) Å³, Z = 2, μ = 3.15 mm⁻¹; 74031 reflections were measured with (sin θ/λ)max = 0.616 Å⁻¹. 29771 Reflections were unique (Rint = 0.075) of which 19074 were observed [I > 2σ(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 $[\text{Co}^{\text{III}}(\text{DPP}_3-)(\text{tBuNH}_2)_2]$ (32.27 μM) via addition of 10 μL tBuNH$_2$ to a 2.0 mL CH$_2$Cl$_2$ solution of $[\text{Co}^{\text{II}}(\text{DPP}^+)]$. 

**Figure S9.** Left: single crystal XRD measured molecular structure of $[\text{Co}^{\text{III}}(\text{DPP}_3-)(\text{NH}_2\text{tBu})_2]$, 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 $[\text{Co}^{\text{III}}(\text{DPP}_3-)(\text{NH}_2\text{tBu})_2]$ (molecule A). H atoms (except NH) are omitted for clarity.
Table S3. Atom numbering scheme for the three crystallographically independent molecules of [Co\textsuperscript{III}(DPP\textsuperscript{3}‒)(NH\textsubscript{2}tBu)]\textsubscript{2} (labelled A, B and C) and DFT (B3LYP/def2-TZVP geometry optimization) calculated structure. Ar = C\textsubscript{6}F\textsubscript{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   |
[CoII(DPP3‒)(NH2Ad)]•: [CoIII(DPP2‒)] (10.0 mg; 13.0 µmol; 1.0 eq) and 1-adamantylamine (3.9 mg; 26.0 µmol; 2.0 eq) were dissolved in CH2Cl2 (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 CH2Cl2 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.

1H NMR (500 MHz, Methylene Chloride-d2) 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 [C36H78CoF5N4O2]+: 1076.5371, found: 1076.5386 [M]+.

XRD: XRD quality single crystals were grown by slow evaporation of a concentrated solution in CH2Cl2 and MeOH (5:1) at room temperature. The displacement ellipsoid plot (50% probability level) with relevant bond lengths is provided in Table S4.

Table S4. [CoII(DPP3‒)(NH2Ad)]•, C36H78CoF5N4O2, FW = 1077.22, 0.71 mm × 0.15 mm × 0.15 mm, green block, orthorhombic, Pbcn, a = 18.0240(10) Å, b = 24.2843(13) Å, c = 25.7668(14) Å, α = β = γ = 90°, V = 11278.1(11) Å3, Z = 8, μ = 0.368 mm−1; 299626 reflections were measured. 12941 Reflections were unique (Rint = 0.062) of which 10510 were observed [I > 2σ(I)]. Residual electron density between −0.59 and 0.76 e−/Å3. S = 1.12. Refinement: R[F2 > 2σ(F2)] = 0.053, wR(F2) = 0.118, number of reflections: 12941, number of parameters: 892, number of restraints: 869.
Table S4. Atom numbering scheme for $[\text{Co}^{III}(\text{DPP}^{3-})(\text{NH}_2\text{Ad})_2]$, single crystal XRD measured structure and relevant bond lengths. Ellipsoid level set at 50% probability. Hydrogen atoms (except NH) and disorder in $t\text{Bu}$, $C_6F_5$ and adamantyl are omitted for clarity. $\text{Ar} = C_6F_5$.

| 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.

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

The energy for the singlet state and its contributors for \([\text{Co}^{II}(\text{DPP}^2\text{-})]\) 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 >86% multireference 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 \([\text{Co}^{II}(\text{DPP}^2\text{-})]\). 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 : 222222222000000 |
|              |                                  | 0.40887 : 222222220200000 |
|              |                                  | 0.03292 : 22222221111000  |
|              |                                  | 0.01103 : 22222220202000  |
|              |                                  | 0.01002 : 22222220022000  |
|              |                                  | 0.00461 : 22202222020200  |
|              |                                  | 0.00437 : 22222121100100  |
|              |                                  | 0.00417 : 22202222002000  |
|              |                                  | 0.00413 : 22202222020200  |
|              |                                  | 0.00378 : 2222212200011   |
|              |                                  | 0.00375 : 22202222020200  |
|              |                                  | 0.00340 : 2222212120011   |
**Figure S10.** Active space and occupancies of the orbitals in parenthesis of a NEVPT2-CASSCF(18,14) calculation on \([\text{Co}^\text{II}(\text{DPP}^- \cdot 2\text{-}\text{THF})_2]\). Isosurface set to 80.

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

The total and relative energies for the singlet, triplet and quintet states and their contributors for \([\text{Co}^\text{II}(\text{DPP}^- \cdot 2\text{-}\text{THF})_2]\) 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 \([\text{Co}^{II}(\text{DPP}^2-)(\text{THF})_2]\). 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: 2222220221100020 |
|              |                                             | 0.01025: 222221211110000 |
|              |                                             | 0.00938: 222022221100002 |
|              |                                             | 0.00926: 220222221100002 |
|              |                                             | 0.00504: 222111221120000 |
|              |                                             | 0.00494: 222222212100000 |
|              |                                             | 0.00477: 222222201100200 |
|              |                                             | 0.00473: 2222222021120000 |
|              |                                             | 0.00452: 202222221100002 |
|              |                                             | 0.00446: 222222211110000 |
|              |                                             | 0.00427: 222222220110200 |
|              |                                             | 0.00406: 222221121100200 |
|              |                                             | 0.00361: 222221211110100 |
|              |                                             | 0.00356: 221122221200001 |
|              |                                             | 0.00338: 222220221100200 |
|              |                                             | 0.00312: 222221121100200 |
|              |                                             | 0.00266: 222220221120000 |
| 3 (triplet)  | -2676639.862 (= 0)                           | 0.36435: 222222221120000 |
|              |                                             | 0.27900: 222222221100000 |
|              |                                             | 0.13337: 222222221220000 |
|              |                                             | 0.01962: 222122221200000 |
|              |                                             | 0.01209: 222222221202000 |
|              |                                             | 0.01001: 222222221100000 |
|              |                                             | 0.00755: 221222212100100 |
|              |                                             | 0.00637: 222222221120000 |
|              |                                             | 0.00636: 222222221200000 |
|              |                                             | 0.00578: 212222222200000 |
|              |                                             | 0.00564: 212222222100000 |
|              |                                             | 0.00553: 220222221120200 |
|              |                                             | 0.00530: 122222222020100 |
|              |                                             | 0.00472: 221222221201000 |
|              |                                             | 0.00305: 222222222110000 |
|              |                                             | 0.00270: 220222221202000 |
|              |                                             | 0.00259: 221122221201000 |
|              |                                             | 0.00258: 222222222200000 |
|              |                                             | 0.00252: 221222221101000 |
| 5 (quintet) | -2676606.869 (+33.0)                         | 0.82815: 222222221110000 |
|              |                                             | 0.01094: 112222221221000 |
|              |                                             | 0.00906: 221222221111000 |
|              |                                             | 0.00634: 222222221111100 |
|              |                                             | 0.00602: 222222221111100 |
|              |                                             | 0.00569: 112222221210000 |
|              |                                             | 0.00366: 222222221110000 |
|              |                                             | 0.00359: 221222221111100 |
|              |                                             | 0.00321: 222211211110011 |
Figure S11. Active space and occupancies of the orbitals in parenthesis of a NEVPT2-CASSCF(18,15) calculation on [Co\textsuperscript{II}(DPP\textsuperscript{2}‒)(THF)\textsubscript{2}]. 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 $<s^2>$, $\Delta H_{298K}^\circ$, $\Delta S_{298K}^\circ$ and $\Delta G_{298K}^\circ$ (in Hartree) for all relevant compounds is depicted in Table S7. Relevant bond lengths are depicted above in Table S1, Table S2 and Table S3.

Table S7. Calculated $<s^2>$, SCF corrections, ZPE corrections, enthalpy corrections and $\Delta G_{298K}^\circ$ (in Hartree) and relative energies (in kcal mol$^{-1}$ relative to [Co$^{II}$DPP$^2\text{-}2$]) or [Co$^{II}$DPP($^1\text{-}3$)])$^\ast$ 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) | $\Delta G_{298K}^\circ$ (Hartree) | Relative energy (kcal mol$^{-1}$) |
|------------|------------|---------|---------------|--------------------------|-------------------------------|-------------------------------|-------------------------------|------------------------|
| [Co$^{II}$DPP$^2\text{-}2$] | OSS        | 1.0250  | -3806.67821   | 0.77833                  | 0.82930                      | 0.69608                      | -3805.98213                 | $= 0$ $^{a,b}$           |
|            | OSS/Triplet | 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($^1\text{-}3$)])$^\ast$ | OSS        | 1.0301  | -4039.10798   | 0.89644                  | 0.95382                      | 0.80579                      | -4038.30219                 | $-3.1$ $^{b}$           |
|            | OSS/Triplet | 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                      | 0.80308                      | -4038.30072                 | $-3.4$                 |
| (DPP$^2\text{-}2$) | OSS        | 1.0288  | -4271.53298   | 1.01440                  | 1.07829                      | 0.91420                      | -4270.61878                 | $-4.2$ $^{b}$           |
|            | OSS/Triplet | 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                 | $-5.9$                 |
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 \([\text{Co}^{II}(\text{DPP}^{2-})(\text{THF})]\) and \([\text{Co}^{III}(\text{DPP}^{2-})(\text{THF})_2]\) are overestimated by the DFT calculations due to over-estimation of the dispersion corrections. We therefore exchanged CH₂Cl₂ (in \([\text{Co}^{II}(\text{DPP}^{2-})] \cdot \text{CH}_2\text{Cl}_2\) and \([\text{Co}^{III}(\text{DPP}^{2-})] \cdot (\text{CH}_2\text{Cl}_2)_2\) 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 CH₂Cl₂ 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 S8. The (nearly) thermoneutral formation energies are consistent with the observed weak binding of THF.

| Correction (kcal mol⁻¹) | Formation of \([\text{Co}^{II}(\text{DPP}^{2-})(\text{THF})]\) | Formation of \([\text{Co}^{III}(\text{DPP}^{2-})(\text{THF})_2]\) |
|-------------------------|--------------------------------------------------|--------------------------------------------------|
| +6.0                    | −0.7 kcal mol⁻¹                                  | −1.2 kcal mol⁻¹                                  |
| +7.5                    | +0.9 kcal mol⁻¹                                  | +1.8 kcal mol⁻¹                                  |
Geometries were optimized at the B3LYP/def2-SVP/m4/disp3 level of theory.

[Co^9(DPP^2^-)] (BSS/OSS)

97 atoms

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 10.5831912 6.1115962
H 5.0817669 11.3454246 5.455928
H 3.9697154 11.1062757 6.8199593
H 4.001361 9.9241763 5.4936212
C 7.2369010 10.1855262 -6.4337124
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 3.690909 5.5501650
H 11.6830512 4.8909559 4.2614403
C 10.1361837 2.6019472 3.7384997
H 9.5741534 3.4951158 3.4422698
H 8.9825863 3.2720958 4.7883318
H 9.7893027 1.755810 3.1177687
C 11.0873265 7.074854 5.916538
H 11.1539040 6.9622546 4.8284580
H 11.8715055 6.4550045 6.3782974
H 11.294576 8.1293512 6.1699654
C 7.0355051 8.8085323 -4.5005006
F 6.4454084 8.1272301 -5.4779435
C 12.3494074 1.5024558 4.0118198
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 -0.7230640
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 8.3574258
C 5.8489020 11.3537837 8.4282227
H 7.0362352 11.5183312 7.1072909
C 4.9825163 6.7798083 7.8063133
C 4.3931926 6.0593584 7.2157492
H 4.2970616 9.3040186 8.4924958
H 5.6932793 8.2059086 8.4215932
C 9.4100741 5.169111 6.1732194
H 8.4178124 4.8912615 6.5652057
C 10.1603750 4.5355531 6.6714967
C 9.4341149 4.9536980 5.1007258
C 7.9118854 6.8602450 8.7972132
C 9.8945924 7.9102944 8.2577440

Coordinates (xyz) for the most stable spin state of the calculated structures.
[\text{Co}^\text{II}(\text{THF})_{\text{2}}] (\text{Triplet})

110 atoms

C 4.477167 10.4243987 5.9815870
H 4.8726450 11.1950659 5.3004926
C 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 -0.1978277
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
C 11.7830306 5.1091331 4.0774634
H 10.3753756 2.7001530 3.8599671
H 9.7379275 3.5242841 3.5184700
H 10.2164282 2.5640620 4.9417945
C 10.0545733 1.7771913 3.3495228
C 11.198185 7.3277628 5.7201503
H 11.1425566 7.1871371 4.6362417
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
C 12.3735667 0.8312509 3.5726359
H 12.4908594 1.6367704 5.1540696
C 13.7580499 1.9006606 3.9357849
C 13.5564280 0.1624038 -0.6700403
C 13.4864008 -0.1464793 0.3843474
C 14.2356134 -0.5421881 -1.1785014
C 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
C 6.8346909 11.5247612 6.9174836
C 4.9580834 8.6879928 7.7145114
H 4.4044963 7.9202357 7.1505875
C 4.2523788 9.1881975 3.3987158
C 7.3891560 8.3007295 3.6096289
H 5.7106160 8.1730055 8.3315029
C 9.6017387 5.3180280 6.1151884
H 8.6497241 4.9826965 6.5582622
C 10.4174716 4.7617174 6.6032058
C 9.5981304 5.0656148 5.0511710
C 8.3714919 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 2.028604
C 12.2243254 9.7932607 2.8011682
C 10.9026481 9.3956954 2.1402702
| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| H    | 9.4563200  | 4.9982362  | 5.2139278  |
| C    | 9.7761361  | 6.8576431  | 8.114392   |
| H    | 9.9674183  | 7.9016837  | 8.407947   |
| Co   | 9.4208522  | 6.6471585  | 1.8833985  |
| O    | 11.1105061 | 8.1311312  | 2.159834   |
| C    | 12.4603226 | 7.6415512  | 2.1900991  |
| C    | 13.3319584 | 8.8085351  | 2.0046493  |
| H    | 12.4671989 | 9.168720   | 1.0516297  |
| Co   | 9.4208522  | 6.6471585  | 1.8833985  |
| O    | 11.1105061 | 8.1311312  | 2.159834   |
| C    | 12.4603226 | 7.6415512  | 2.1900991  |
| C    | 13.3319584 | 8.8085351  | 2.0046493  |
| H    | 12.4671989 | 9.168720   | 1.0516297  |

**[Co^9(DPP^2)(Py)] (Triplet)**

108 atoms
119 atoms

[Co\sup\text{III}] (DPP\textsuperscript{3}) (Py\textsubscript{2})\textsubscript{(CSS)}

O 10.5726227 4.9908021 2.2913571
O 9.3645949 6.7807129 3.7191409
N 8.3452375 8.0291426 1.4743160
C 10.8369298 5.3923626 -0.5698020
N 9.9468300 6.2811261 -0.0664071
C 8.0244397 8.5598908 0.2267326
H 8.3616717 6.1273179 8.4429823
H 10.1114631 5.8757561 8.6054141
C 11.4050265 4.2502631 1.5980131
C 7.5981077 8.6717798 2.4039547
C 9.4612021 7.0475302 -1.1216406
C 11.6058060 4.4294924 0.1936130
C 10.0581321 6.5879260 -2.335708
H 9.8640083 6.9911148 -3.3271262
C 8.5230801 7.4930012 4.4217556
C 12.5639886 3.6450577 -0.496533
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
H 6.7924160 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 7.5623535 7.9896858 7.6671780
H 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 10.082383 -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
C 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 -3.6966685
F 8.7198071 11.9620972 -3.9785524
C 4.6397135 10.5767425 6.0995785
H 5.1836369 11.3631082 5.5223800
H 3.9272887 11.0755722 6.7762081
C 4.0536590 9.9939310 5.3711170
C 7.3295221 10.1497948 -4.5705033
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 4.395932
Pyridine (Py) (CSS)
11 atoms
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  1.206924  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

rBuNH₂ (CSS)
16 atoms
N  1.0039775  1.8495204  5.3308355
H  3.4919014  2.6902035  4.6739121
C  1.3361844  2.9477220  4.4076059

CH₂Cl₂ (CSS)
5 atoms
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
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