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Supporting Information

A Stable Aminyl Radical Coordinated to Cobalt

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A. General information

All reactions and manipulations were performed under a dry nitrogen or argon atmosphere, using standard Schlenk techniques. Argon was provided by PANGAS and further purified with an MBraun 100 HP gas purification system. Glassware was flame dried under high vacuum or dried at 120 °C overnight prior to use. Solvents were distilled under argon from sodium/benzophenone (THF, diethyl ether, *n*-hexane), sodium (toluene) or calcium hydride (methylene chloride). Air sensitive compounds were stored and weighed in a glovebox (M Braun: 150-GI or lab master 130). Reactions in small quantities were performed within a glovebox. The following organic compounds and metal precursors were prepared using the methods described in the literature: bis(5*H*-dibenzo[*a,d*]cyclohepten-5-yl)-amine (trop₂NH),^[S1] [Co(HMDS)₂] (HMDS = bis(trimethylsilyl)amido).^[S2] The following commercially available compounds were used as received: CoBr₂, Li[N(SiMe₃)₂], 2,2'-bipyridine (bpy), Zn, BrCH₂COOH, NaOTf, NaBAR^F₄, KPF₆, [FeCp₂]PF₆, and compound listed in Table 5. NMR spectra were recorded on a Bruker Avance 500 spectrometer. The chemical shifts (δ) were measured according to IUPAC^[S3] and expressed in parts per million (ppm) relative to TMS, CFCl₃, and H₃PO₄ for ¹H, ¹³C, ¹⁹F and ³¹P respectively. Deuterated solvents were purchased from Eurisotop, degassed and distilled from the proper drying agent, and stored over 4 Å molecular sieves. Coupling constants *J* are given in Hertz (Hz) as absolute values, unless otherwise stated. The multiplicity of the signals is indicated as *s*, *d*, *t*, *q*, or *m* for singlets, doublets, triplets, quartets, or multiplets, respectively. The abbreviation br. is given for broadened signals. Quaternary carbon atoms are indicated as C^{quat}, aromatic units as CH^{ar} and CH^{ar} when not noted otherwise. The olefinic protons and ¹³C atoms of the C=C_{trop} unit in the central seven-membered ring are indicated as CH^{olef} and CH^{olef}. The benzylic protons and ¹³C atoms in the central seven-membered ring are indicated as CH^{benzyl} and CH^{benzyl}. IR spectra were recorded on a Perkin-Elmer-Spectrum 2000 FT-IR-Raman spectrometer with KBr beam splitter (range 500-4000 cm⁻¹). The ATR technique was applied. The absorption bands are described as follows: strong (*s*), very strong (*vs*), middle (*m*), weak (*w*), or broad (*br*). GC-MS analysis was done with a Trace GC Ultra and Polaris Q device from Thermo Finnigan, equipped with a Zebtron ZB-5MS (30 m x 0.25 mm x 25 μm) column, Electronic Impact (ion source) and ion trap (mass analyzer). Elemental analyses were performed by the microanalytical laboratory of the ETH Zürich. High resolution ESI-MS and MALDI-MS were performed using a Bruker Daltonics maxis ESI-QTOF and a Varian HiResMALDI by ETH Zürich DCHAB/LOC MS-Service. Values are given as *m/z*.

B. Syntheses of Cobalt Complexes

Preparation of bis[bis(trimethylsilyl)amido]cobalt(II), [Co(HMDS)₂]. CoBr₂(THF)₂ (8.0 g, 22.04 mmol) and Li[N(SiMe₃)₂] (7.5 g, 44.96 mmol) were placed in a two-neck round-bottom flask which was connected to a cold finger with an argon inlet. The flask was cooled to -20 °C in ice/NaCl bath and dry THF (20 mL) was added to the reagents. The mixture was stirred for 6 h at -20 °C and then slowly warmed up to room temperature overnight. The solvent was evaporated to dryness and the dark residue was sublimed *in situ* under reduced pressure (100 °C at 0.6 mmHg, cold finger at -80 °C). Bright green crystals were obtained. X-ray diffraction analysis confirmed the identity of the desired product. Yield: 4.0 g, 48%.

Preparation of [Co(trop₂N)(bpy)]·THF (1). [Co(HMDS)₂] (190.0 mg, 0.50 mmol), trop₂NH (216.8 mg, 0.55 mmol), 2,2'-bipyridine (82.1 mg, 0.53 mmol) and Zn powder (982.0 mg, 15.00 mmol) were combined in a Schlenk. Dry and degassed THF (3 mL) was added and the mixture was stirred at room temperature overnight. The dark suspension was filtered and layered with *n*-hexane (10 mL). Dark crystals were obtained, which were washed with *n*-hexane (3 x 3 mL) and dried under Ar stream. Yield: 240.0 mg, 70%. ¹H NMR (500.2 MHz, THF-*d*₈): δ [ppm] = 8.34 (d, ³J_{HH} = 5.2 Hz, 1H, CH^{ar}), 8.25 (d, ³J_{HH} = 4.7 Hz, 1H, CH^{ar}), 8.20 (d, ³J_{HH} = 8.0 Hz, 1H, CH^{ar}), 8.15 (d, ³J_{HH} = 7.9 Hz, 1H, CH^{ar}), 7.87 (td, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.5 Hz, 1H, CH^{ar}), 7.63 (td, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.5 Hz, 1H, CH^{ar}), 7.39 (t, ³J_{HH} = 6.4 Hz, 1H, CH^{ar}), 7.08-7.07 (m, 2H, CH^{ar}), 6.92 (d, ³J_{HH} = 7.4 Hz, 2H, CH^{ar}), 6.82 (t, ³J_{HH} = 6.4 Hz, 1H, CH^{ar}), 6.78-6.75 (m, 2H, CH^{ar}), 6.60-6.58 (m, 8H, CH^{ar}), 6.52-6.51 (m, 2H, CH^{ar}), 5.38 (d, ³J_{HH} = 9.4 Hz, 2H, CH^{olef}), 3.96 (d, ³J_{HH} = 9.4 Hz, 2H, CH^{olef}), 3.61 (m, 4H, CH₂ from THF solvate), 3.04 (s, 2H, CH^{benzyl}), 1.77 (m, 4H, CH₂ from THF solvate); ¹³C {¹H} NMR (125.8 MHz, THF-*d*₈): δ [ppm] = 155.9 (s, C^{quat}), 153.5 (s, C^{quat}), 151.6 (s, CH^{ar}), 149.3 (s, CH^{ar}), 143.3 (s, C^{quat}), 142.5 (s, C^{quat}), 140.6 (s, C^{quat}), 138.5 (s, C^{quat}), 136.5 (s, CH^{ar}), 134.9 (s, CH^{ar}), 127.3 (s, CH^{ar}), 126.7 (s, CH^{ar}), 126.2 (s, CH^{ar}), 126.1 (s, CH^{ar}), 126.0 (s, CH^{ar}), 125.9 (s, CH^{ar}), 125.6 (s, CH^{ar}), 124.3 (s, CH^{ar}), 123.9 (s, CH^{ar}), 123.3 (s, CH^{ar}), 121.5 (s, CH^{ar}), 120.5 (s, CH^{ar}), 79.4 (s, CH^{benzyl}), 73.5 (s, CH^{olef}), 71.2 (s, CH^{olef}), 68.0 (s, CH₂, THF solvate), 26.2 (s, CH₂, THF solvate). ATR IR (ν in cm⁻¹): 3058 w, 3036 w, 3002 m, 2972 m, 2847 m, 1900 w, 1594 m, 1576 m, 1484 s, 1465 s, 1441 s, 1417 m, 1398 m, 1300 m, 1264 s, 1246 s, 1211 s, 1155 s, 1124 s, 1068 s, 1046 s, 1028 s, 989 s, 908 m, 882 m, 837 m, 823 m, 761 s, 739 vs, 733 vs, 704 s, 661 m, 645 m, 620 w. EA Calcd. for C₄₀H₃₀CoN₃·C₄H₈O, C 77.29, H 5.60, N 6.15; found: C 77.60, H 5.78, N 6.18. HRMS (ESI): m/z calcd. for C₄₀H₃₁CoN₃ 612.1844 [M+H]⁺; found: 612.1860. Air sensitive.

Preparation of [Co(trop₂NH)(bpy)][OTf] (2a), [Co(trop₂NH)(bpy)][BAR^F₄] (2b) and [Co(trop₂NH)(bpy)][PF₆] (2c). Bromoacetic acid (14.0 mg, 0.10 mmol) dissolved in THF (1 mL) was added dropwise to a solution of [Co(trop₂N)(bpy)]·THF (68.4 mg, 0.10 mmol) in THF (2 mL) while stirring. An orange suspension was obtained rapidly, which was stirred at room temperature for 4 h. The solvent was decanted and the solid was washed with diethyl ether (3 x 3 mL). Yield 69.1 mg, 92% as orange solid. The obtained [Co(trop₂NH)(bpy)][O₂CH₂Br] (52.5 mg, 70 μmol) was suspended in THF (3 mL) and NaOTf (13.1 mg, 76 μmol), NaBAR^F₄ (64.7 mg, 73 μmol) or KPF₆ (13.4 mg, 73 μmol) was added accordingly. The mixture was stirred overnight at room temperature. After filtration the orange-reddish clear filtrate was layered with n-hexane (10 mL). Yield: 35.0 mg, 60% (**2a**); 86.0 mg, 79% (**2b**); 31.8 mg, 60% (**2c**). [Co(trop₂NH)(bpy)]PF₆ (**2c**) was also prepared by addition of 2,2,6,6-tetramethylpiperidine-1-ol (4.1 mg, 26 μmol) or Ph₂PH (4.9 mg, 26 μmol) to a solution of [Co(trop₂N)(bpy)]PF₆ (18.0 mg, 24 μmol) in THF (1 mL). The orange-reddish solution was layered with diethyl ether (4 mL). The complex **2c** was isolated as an orange solid. Yield: 16.0 mg, 89%.

[Co(trop₂NH)(bpy)][OTf] (2a)

¹H NMR (500.2 MHz, THF-*d*₈): δ [ppm] = 8.63 (d, ³J_{HH} = 7.9 Hz, 1H, CH^{ar}), 8.45 (d, ³J_{HH} = 5.5 Hz, 1H, CH^{ar}), 8.42 (d, ³J_{HH} = 7.9 Hz, 1H, CH^{ar}), 7.98 (td, ³J_{HH} = 7.2 Hz, ⁴J_{HH} = 3.2 Hz, 2H, CH^{ar}), 7.55 (t, ³J_{HH} = 6.1 Hz, 1H, CH^{ar}), 7.49-7.48 (m, 3H, CH^{ar}), 7.35 (d, ³J_{HH} = 7.4 Hz, 2H, CH^{ar}), 7.20 (t, ³J_{HH} = 6.1 Hz, 1H, CH^{ar}), 7.00 (td, ³J_{HH} = 7.4 Hz, ⁴J_{HH} = 1.0 Hz, 2H, CH^{ar}), 6.93-6.85 (m, 10H, CH^{ar}), 6.21 (d, ³J_{HH} = 9.5 Hz, 2H, CH^{olef}), 4.79 (d, ³J_{HH} = 9.5 Hz, 2H, CH^{olef}), 4.34 (s, 2H, CH^{benzyl}), 0.86 (br, 1H, NH); ¹³C {¹H} NMR (125.8 MHz, THF-*d*₈): δ [ppm] = 156.0 (s, C^{quat}), 155.0 (s, C^{quat}), 151.7 (s, CH^{ar}), 149.2 (s, CH^{ar}), 138.8 (s, CH^{ar}), 138.0 (s, CH^{ar}), 136.7 (q, ¹J_{FC} = 244.7 Hz, CF₃), 129.7 (s, CH^{ar}), 129.3 (s, CH^{ar}), 129.2 (s, CH^{ar}), 128.7 (s, CH^{ar}), 127.9 (s, CH^{ar}), 127.6 (s, C^{quat}), 127.5 (s, CH^{ar}), 127.4 (s, C^{quat}), 126.3 (s, CH^{ar}), 125.5 (s, CH^{ar}), 123.9 (s, CH^{ar}), 123.2 (s, CH^{ar}), 75.7 (s, CH^{olef}), 75.6 (s, CH^{olef}), 70.6 (s, CH^{benzyl}); ¹⁹F {¹H} NMR (188.3 MHz, THF-*d*₈): δ [ppm] = -78.79 (s). EA Calcd. for C₄₁H₃₁CoF₃N₃O₃S·0.5C₄H₈O, C 64.74, H 4.42, N 5.27; found for: C 64.45, H 4.57, N 5.27. MS (MALDI-TOF): m/z calcd. for C₄₀H₃₁CoN₃ 612.1844 [M]⁺; found: 612.1836. Air sensitive.

[Co(trop₂NH)(bpy)][BAR^F₄] (2b)

¹H NMR (500.2 MHz, THF-*d*₈): δ [ppm] = 8.59 (d, ³J_{HH} = 7.8 Hz, 1H, CH^{ar}), 8.41 (d, ³J_{HH} = 4.9 Hz, 1H, CH^{ar}), 8.32 (d, ³J_{HH} = 7.7 Hz, 1H, CH^{ar}), 8.14 (m, 1H, CH^{ar}), 8.02 (t, ³J_{HH} = 7.4 Hz, 1H, CH^{ar}), 7.80 (m, 8H, CH^{ar}), 7.58 (m, 3H, CH^{ar}), 7.51 (t, ³J_{HH} = 6.2 Hz, 1H, CH^{ar}), 7.46 (d, ³J_{HH} = 6.0 Hz, 2H, CH^{ar}), 7.28 (m, 3H, CH^{ar}), 7.11 (m, 4H, CH^{ar}), 7.06-7.02 (m, 4H, CH^{ar}), 6.95 (m, 4H, CH^{ar}), 6.75 (d, ³J_{HH} = 5.6 Hz, 2H, CH^{ar}), 6.25 (d, ³J_{HH} = 9.4 Hz, 2H, CH^{olef}), 4.91 (d, ³J_{HH} = 9.5 Hz, 2H, CH^{olef}), 4.02 (s, 2H, CH^{benzyl}), 0.43 (br, 1H, NH); ¹⁹F {¹H} NMR (188.3 MHz, THF-*d*₈): δ [ppm] = -62.27 (s). ATR IR (ν in cm⁻¹): 3074 *w*, 3022 *w*, 2976 *br*, 2870 *br*, 1607 *m*, 1478 *m*, 1444 *w*, 1353 *s*, 1272 *vs*, 1156 *s*, 1114 *br* and *vs*, 886 *s*, 838 *s*, 752 *br* and *s*, 710 *s*, 681 *s*, 668 *s*, 617 *w*. Air sensitive.

[Co(trop₂NH)(bpy)][PF₆] (2c)

¹H NMR (500.2 MHz, THF-*d*₈): δ [ppm] = 8.69 (d, ³J_{HH} = 8.1 Hz, 1H, CH^{ar}), 8.56 (d, ³J_{HH} = 5.9 Hz, 1H, CH^{ar}), 8.45 (d, ³J_{HH} = 8.2 Hz, 1H, CH^{ar}), 8.17-8.03 (m, 1H, CH^{ar}), 7.82-6.75 (m, 20H, CH^{ar}), 6.37 (d, ³J_{HH} = 9.5 Hz, 2H, CH^{olef}), 4.95 (d, ³J_{HH} = 9.3 Hz, 2H, CH^{olef}), 4.51 (s, 2H, CH^{benzyl}), 0.58 (br, 1H, NH); ¹³C {¹H} NMR (125.8 MHz, THF-*d*₈): δ [ppm] = 154.9 (s, C^{quat}), 151.2 (s, C^{quat}), 147.4 (s, CH^{ar}), 138.9 (s, CH^{ar}), 138.2 (s, CH^{ar}), 137.6 (s, CH^{ar}), 136.8 (s, CH^{ar}), 130.5 (s, CH^{ar}), 130.4 (s, CH^{ar}), 129.9 (s, CH^{ar}), 129.4 (s, CH^{ar}), 128.6 (s, CH^{ar}), 127.9 (s, C^{quat}), 127.3 (s, CH^{ar}), 127.2 (s, C^{quat}), 126.9 (s, CH^{ar}), 125.5 (s, CH^{ar}), 124.8 (s, CH^{ar}), 123.3 (s, CH^{ar}), 75.1 (s, CH^{olef}), 74.9 (s, CH^{olef}), 69.8 (s, CH^{benzyl}); ¹⁹F {¹H} NMR (188.3 MHz, THF-*d*₈): δ [ppm] = -72.7 (d, ¹J_{PF} = 708.0 Hz); ³¹P {¹H} NMR (202.5 MHz, THF-*d*₈): δ [ppm] = -142.8 (m, ¹J_{PF} = 708.0 Hz). Air sensitive.

Preparation of [Co(trop₂N)(bpy)]PF₆ (3). [Co(trop₂N)(bpy)].THF (1) (160.0 mg, 0.23 mmol) and [FeCp₂]⁺PF₆⁻ (80.6 mg, 0.24 mmol) were combined in a Schlenk. Dry and degassed toluene (3 mL) was added and the mixture was stirred at room temperature overnight. A pale green precipitate was formed. The solvent was decanted and the product was washed with toluene (2 x 2 mL) and *n*-hexane (3 x 3 mL). The obtained green powder was dried under vacuum. Single crystals suitable for X-ray analysis were obtained from CH₂Cl₂/*n*-hexane mixtures. Yield: 80.0 mg, > 99%. MS (MALDI-TOF): *m/z* calcd. for C₄₀H₃₀CoN₃ 611.177 [M]⁺; found: 612.013. μ_{eff,1} = 1.9 μ_B (2 K to 105 K) and μ_{eff,2} = 2.4 μ_B. (29 to 100). EPR (X-band, 9.49 GHz, toluene/THF, 120 K): *g*-tensor/MHz (2.089, 2.057, 2.050), ⁵⁹Co (I = 7/2) A-tensor/MHz (303, 50, 50), ¹⁴N_{aminy1} (I = 1) A-tensor/MHz (not resolved, 76, not resolved). Air sensitive.

C. Selected NMR spectra

C.1. ^1H NMR of **1** and **2a**

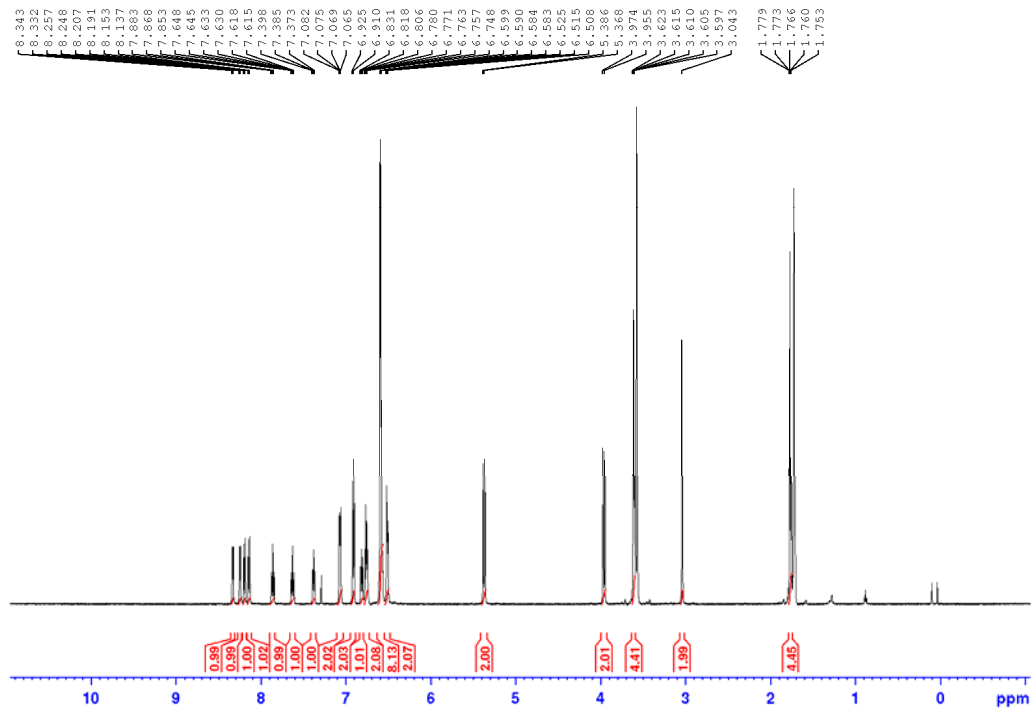


Figure S1. ^1H NMR spectra (500.2 MHz) at 298 K of **1** in $\text{THF-}d_8$.

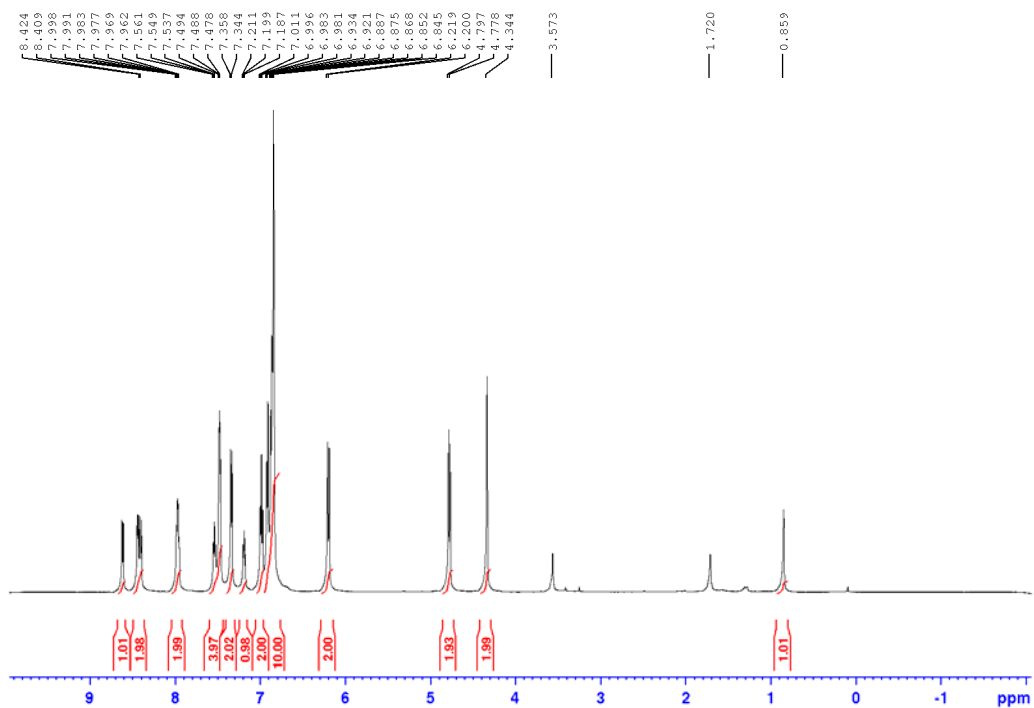


Figure S2. ^1H NMR spectra (500.2 MHz) at 298 K of **2a** in $\text{THF-}d_8$.

C.2. $^{13}\text{C}\{^1\text{H}\}$ NMR of **1** and **2a**

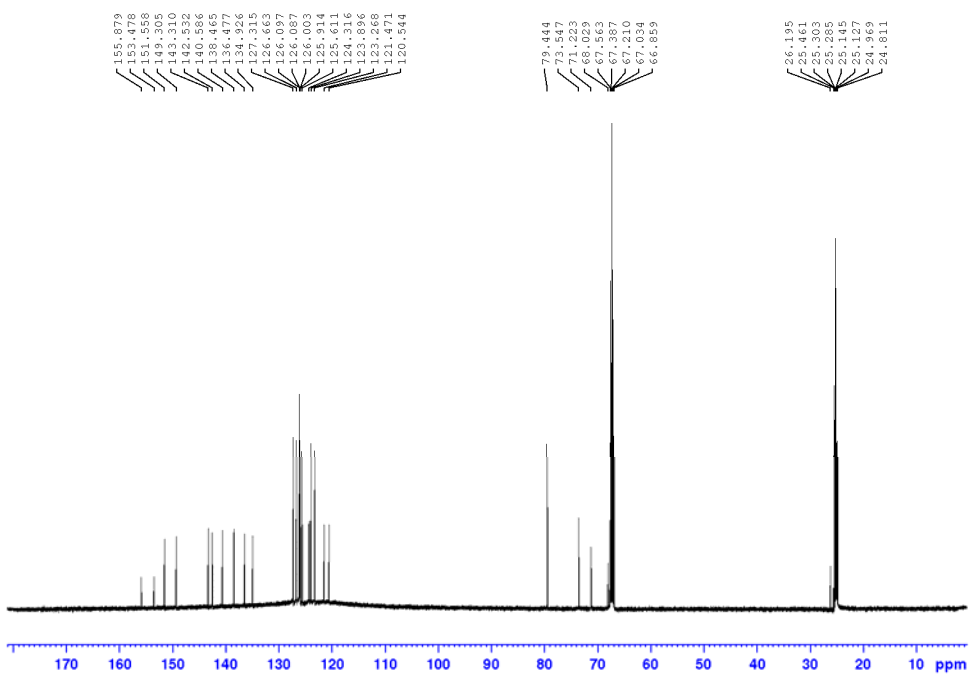
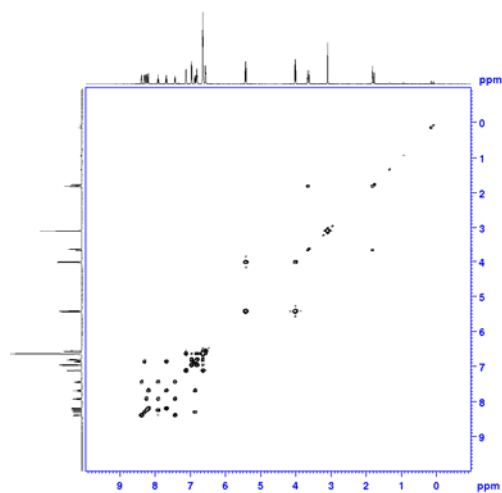


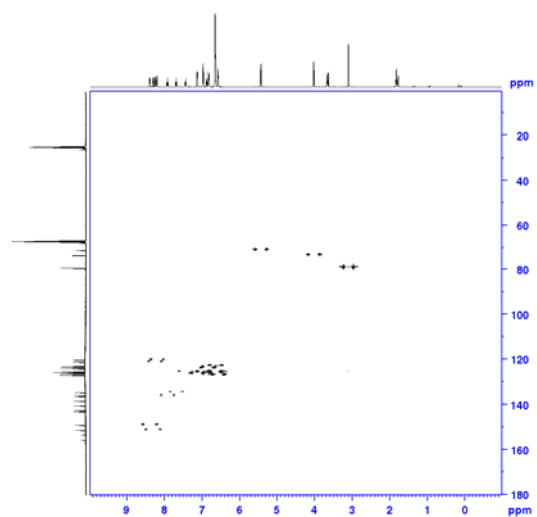
Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (125.8 MHz) at 298 K of **1** in $\text{THF-}d_8$.

C.3. 2D NMR of **1** and **2a**

a)



b)



c)

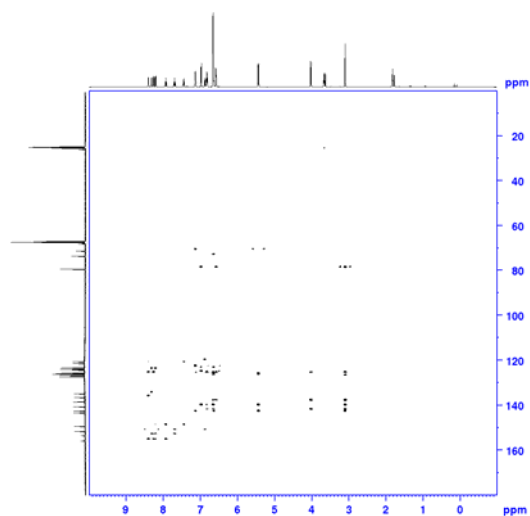


Figure S5. 2D NMR spectra at 298 K of **1** in THF-*d*₈: a) 500.2 MHz ¹H-¹H COSY-DQF, b) ¹³C-¹H HMQC, c) ¹³C-¹H HMBC.

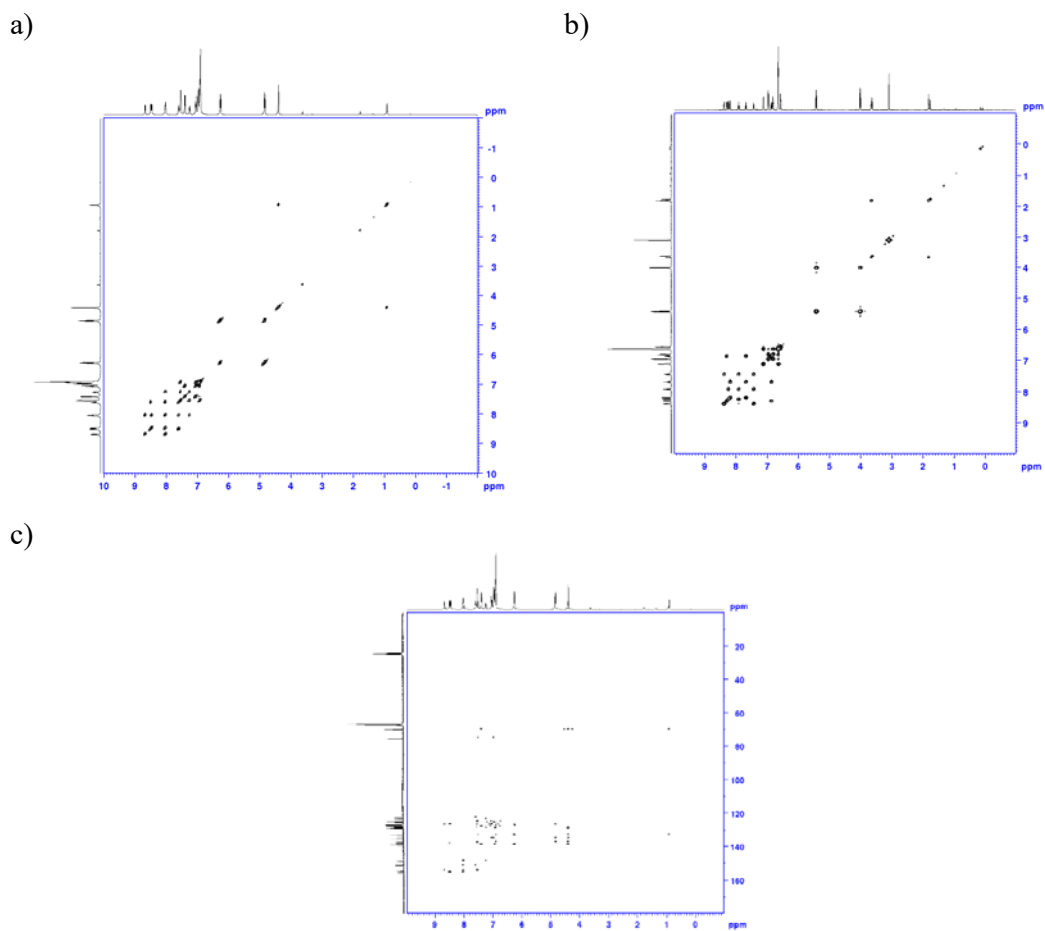


Figure S6. 2D NMR spectra at 298 K of **2a** in THF-*d*₈: a) 500.2 MHz ¹H-¹H COSY-DQF, b) ¹³C-¹H HMQC, c) ¹³C-¹H HMBC.

D. Cyclic Voltammetry

Cyclic voltammetry investigations were performed using a *Princeton Applied Research* potentiostat/galvanostat model 263A or model 283. The measurements were performed on a septum-capped glass vial using 0.1 mol/L $[N^iBu_4]PF_6$ as electrolyte in THF. Conditions: room temperature, purge time: 0 s, equilibration time: 10 s, scan rate: 100 mV/s unless otherwise noted. Electrode system: glassy carbon indicator electrode, Pt (1 mm thick wire) counter electrode and Ag wire for electrical conductivity. At the end of each measurement, ferrocene was added as internal standard for calibration (+0.352 V vs. Ag/AgCl).

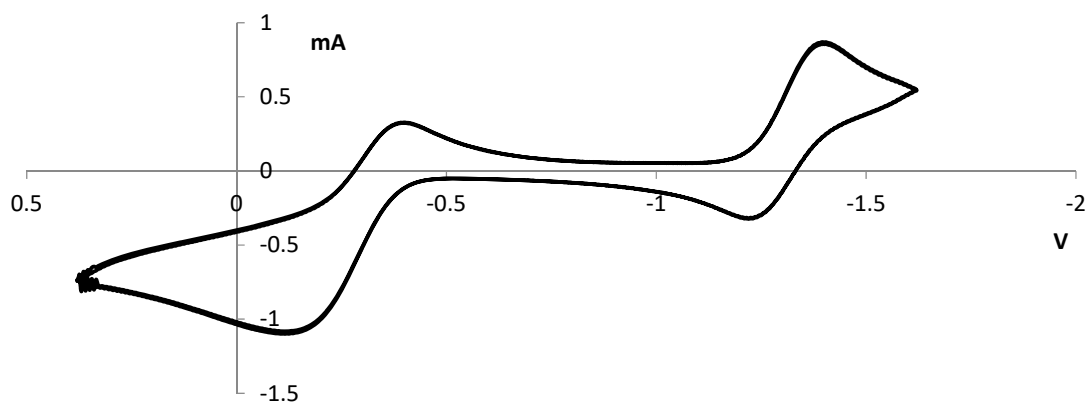


Figure S7. Cyclic voltammetry of **1** in THF containing 0.1 M $[NBu_4]^+PF_6^-$. Scan rate 100 mV/s, scan range between +1 to -1 V (0.38 to -1.62 V vs. Fc/Fc⁺ couple).

E. X-ray diffractions

X-ray diffraction measurements were performed using a *Bruker SMART Apex II* diffractometer with CCD area detector; MoK α radiation (0.71073 Å) at T = 100 K. The refinement against full matrix (versus *F*²) was done with SHELXTL (ver. 6.12) and SHELXL-97. Empirical absorption correction was done with SADABS (ver. 2.03). All non-hydrogen atoms were refined anisotropically where not noted otherwise. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC- 1520295 (**1**), 1520288 (**2c**) and 1520289 (**3**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

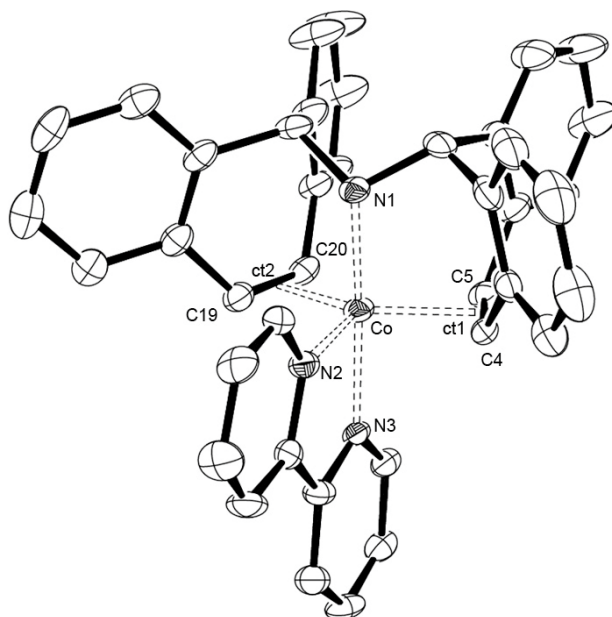


Figure S8. ORTEP drawing of the molecular structure of **1**. Thermal ellipsoids are drawn at 50% probability level. Non relevant hydrogen atoms and a hexane solvate molecule have been removed for clarity. ct is the centroid of the coordinated C4=C5 and C19=C20 bonds, respectively. Two independent molecules per unit cell were found. The values reported for selected bond distances and angles correspond to the average. Selected bond distances [\AA] and angles [$^\circ$]: Co-N1 1.954(2), Co-N2 2.004(3), Co-N3 1.991(2), C4-C5 1.429(4), C19-C20 1.416(4), Co-ct1 1.921(3), Co-ct2 1.923(3); N1-Co-N3 171.7(1), ct1-Co-ct2 135.6(1), N1-Co-N2 91.6(1); $\Sigma^\circ\text{N1}$ 343.6(2).

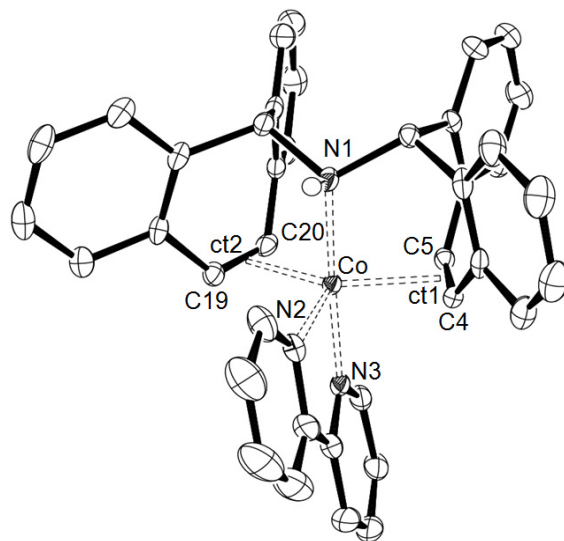


Figure S9. ORTEP drawing of the molecular structure of **2c**. Thermal ellipsoids are drawn at 50% probability level. The counter anion PF_6^- , a solvate molecule of DME and all hydrogen atoms except at N1 are omitted for clarity. ct is the centroid of the coordinated C4=C5 and C19=C20 bonds, respectively. Three independent molecules per unit cell were found. The values reported for selected bond distances and angles correspond to the average. Selected bond distances [\AA] and angles [$^\circ$]: Co-N1 2.004(3), Co-N2 2.030(3), Co-N3 1.944(3), C4-C5 1.411(5), C19-C20 1.420(5), Co-ct1 1.946(3), Co-ct2 1.953(3); N1-Co-N3 175.2(1), ct1-Co-ct2 135.4(2), N1-Co-N2 94.5(1); $\Sigma^\circ\text{N1}$ 347.0(2).

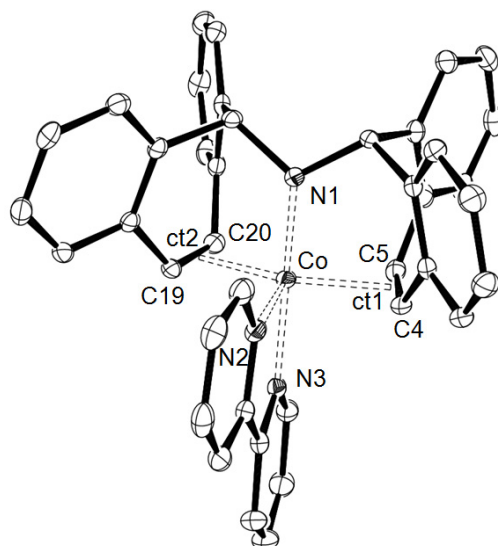


Figure S10. ORTEP drawing of the molecular structure of **3**. Thermal ellipsoids are drawn at 50% probability level. The counter anion PF_6^- and all hydrogen atoms are omitted for clarity. ct is the centroid of the coordinated C4=C5 and C19=C20 bonds, respectively. Selected bond distances [\AA] and angles [$^\circ$]: Co-N1 1.842(2), Co-N2 2.025(2), Co-N3 1.991(2), C4-C5 1.401(3), C19-C20 1.404(3), Co-ct1 2.004(2), Co-ct2 1.983(2); N1-Co-N3 178.7(1), ct1-Co-ct2 143.0(2), N1-Co-N2 98.8(2); $\Sigma^\circ\text{N1}$ 358.4(3).

Table S1. Selected bond length (\AA) and angles ($^\circ$) for **1**, **2c**, **3**.

	1 ^[a]	2c ^[b]	3
M-N1	1.954(2)	2.004(3)	1.842(2)
M-N2	2.004(3)	2.030(3)	2.025(2)
M-N3	1.991(2)	1.944(3)	1.991(2)
M-ct1	1.921(3)	1.946(3)	2.004(2)
M-ct2	1.923(3)	1.953(3)	1.983(2)
C4-C5	1.429(4)	1.411(5)	1.401(3)
C19-C20	1.416(4)	1.420(5)	1.404(3)
N1-M-N3	171.7(1)	175.2(1)	178.7(1)
ct1-M-ct2	135.6(1)	135.4(2)	143.0(2)
N1-M-N2	91.6(1)	94.5(1)	98.8(2)
$\Sigma^\circ\text{N1}$	343.6(2)	347.0(2)	358.4(3)

[a] Two independent molecules per unit cell were found. The values reported correspond to the average. [b] Three independent molecules per unit cell were found. The values reported correspond to the average.

Table S2. Crystal data and structure refinement for **1**, **2c**, **3**.

	1	2c	3
Empirical formula	C ₈₆ H ₇₄ Co ₂ N ₆	C ₄₄ H ₄₁ CoF ₆ N ₃ O ₂ P	C ₄₀ H ₃₀ CoF ₆ N ₃ P
Formula weight	1309.37	847.70	756.57
Temperature	95(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P2(1)/C	P2(1)/n
Unit cell dimensions	a, b, c / Å = 11.9983(15), 12.4860(15), 24.705(3) α, β, γ / ° = 99.662(2), 98.028(2), 109.760(2)	a, b, c / Å = 35.2780(5), 17.6354(2), 18.7703(2) α, β, γ / ° = 90, 97.1890(10), 90	a, b, c / Å = 10.6753(7), 17.1784(11), 17.6350(12) α, β, γ / ° = 90, 94.2410(10), 90
Volume	3355.9(7) Å ³	11586.0(2) Å ³	3225.1(4) Å ³
Z	2	12	4
Density (calculated)	1.296 g/cm ³	1.458 g/cm ³	1.558 g/cm ³
Absorption coefficient	0.547 mm ⁻¹	0.558 mm ⁻¹	0.653 mm ⁻¹
F(000)	1372	5256	1548
Crystal size	0.35 x 0.32 x 0.10 mm ³	0.27 x 0.20 x 0.10 mm ³	0.22 x 0.18 x 0.11 mm ³
Theta range for data collection	0.86 to 26.37°	1.16 to 24.71°	1.66 to 28.28°
Index ranges	-14 ≤ h ≤ 14, 15 ≤ k ≤ 15, 0 ≤ l ≤ 30	-41 ≤ h ≤ 41, 20 ≤ k ≤ 20, -22 ≤ l ≤ 22	-14 ≤ h ≤ 14, 22 ≤ k ≤ 22, -23 ≤ l ≤ 23
Reflections collected	13638	64734	32863
Independent reflections	13638 [R(int) = 0.0000]	19759 [R(int) = 0.0687]	8002 [R(int) = 0.0724]
Completeness to theta = 26.37	99.4 %	100.0 %	100.0 %
Absorption correction	Empirical	None	None
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	13638 / 9 / 1048	19759 / 0 / 1788	8002 / 0 / 576
Goodness-of-fit on F ²	0.932	0.981	0.936
Final R indices [I > 2σ(I)]	R1 = 0.0523, wR2 = 0.1068	R1 = 0.0487, wR2 = 0.1044	R1 = 0.0403, wR2 = 0.0792
R indices (all data)	R1 = 0.0974, wR2 = 0.1183	R1 = 0.0818, wR2 = 0.1162	R1 = 0.0607, wR2 = 0.0844
Largest diff. peak and hole	0.635 and -0.459 e.Å ⁻³	1.187 and -1.133 e.Å ⁻³	0.614 and -0.360 e.Å ⁻³

F. EPR, DFT calculations and spin density

The EPR spectrum was recorded with a *Bruker EMX* X-band spectrometer, 9.51 GHz, 50-400 mT (500-4000 Gauss). Parameters and conditions: Field: 333.5-343.5 mT, modulation amplitude: 0.4 mT, modulation frequency: 100 Hz, microwave power: 2 mW, frozen solvent: toluene/THF, temperature: 120 K. The spectrum was analysed and simulated using the W95EPR program of Prof. Dr. Frank Neese.^[S4]

DFT calculations: Geometry optimizations were carried out with the Turbomole program package^[S5] coupled to the PQS Baker optimizer^[S6] at the ri-DFT^[S7] level using the BP86^[S8] functional and SV(P) basis set.^[S9] Calculated EPR spectra were obtained with both the ADF^[S10] program at the DFT BP86,^[S11] TZP^[S12] level, and with the Orca^[S13] program at the DFT b3-lyp, TZVP level, using the Turbomole optimized geometries.

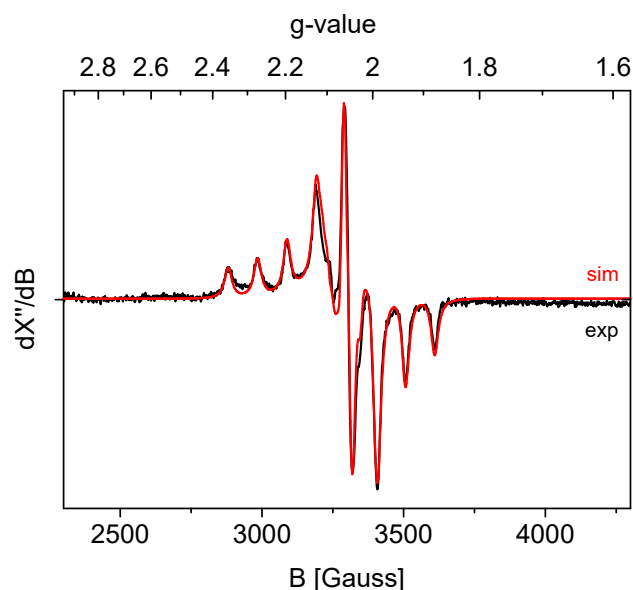


Figure S11. Experimental and simulated X-band EPR spectrum of **3**, in a frozen toluene/THF mixture measured at 120K. Frequency 9.4920 GHz; microwave power 2 mW; modulation amplitude 1 G. Simulation: red, experimental: black.

Table S3. Experimental^[a] and DFT calculated^[b,c] EPR parameters of **3**.

g-tensor		g_z	g_x	g_y	
	Exp.	2.089	2.057	2.050	
	DFT ^[b]	2.095	2.068	2.023	
	DFT ^[c]	2.085	2.048	2.022	
A-tensor ^[d]		A_x	A_y	A_z	spin density ^[e]
Cobalt	Exp	303	50 (PR)	50 (PR)	
⁵⁹ Co (I = 7/2)	DFT ^[b]	265	52	-49	51%
	DFT ^[c]	-223	-45	49	47%
N _{aminy} radical	Exp.	NR	76 (PR)	NR	
¹⁴ N (I = 1)	DFT ^[b]	-1	75	-1	55%
	DFT ^[c]	-1	70	-1	51%

[a] Spectral simulation; see Figure S12. [b] Orca, B3LYP, TZVP. [c] ADF, BP86, TZP. [d] Hyperfine couplings in MHz. [e] Mulliken atomic spin density. NR = not resolved; PR = poorly resolved.

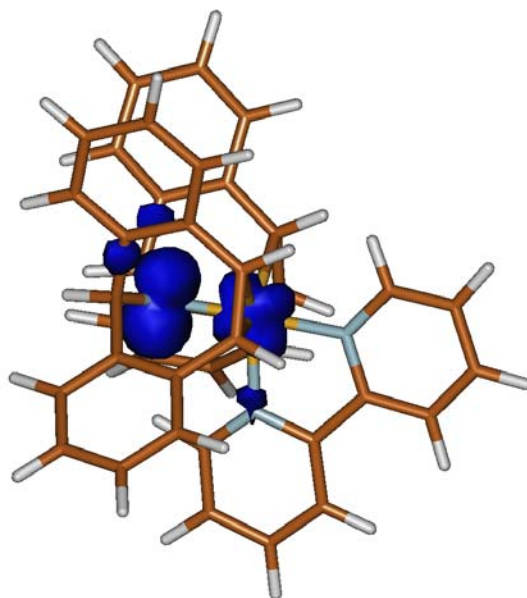
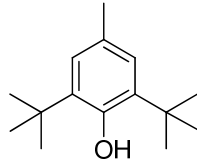
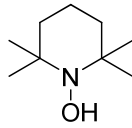
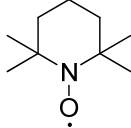


Figure S12. Spin density plot of $[\text{Co}(\text{trop}_2\text{N})(\text{bpy})]^+$.

G. Reactivity tests

$[\text{Co}(\text{trop}_2\text{N})(\text{bpy})]\text{PF}_6$ (18.0 mg, 24 μmol) and XH (26 μmol) were combined in a Schlenk flask (for the list of substrates, see Table 5). THF (1 mL) was added and the mixture was stirred at room temperature. The initial green suspension becomes a clear orange solution when the reaction takes place. An aliquot of the reaction mixture was taken, evaporated to dryness and analyzed by ^1H NMR to confirm formation of **2c**. Additionally, for the reaction with *n*-Bu₃SnH as H-donor GC-MS analysis was performed to detect (*n*-Bu₃S)₂. For the reaction with 2,2,6,6-tetramethylpiperidine-1-ol an EPR spectrum was recorded to identify the TEMPO radical. The reaction with Ph₂PH was followed by $^{31}\text{P}\{^1\text{H}\}$ NMR.

Table S4. Substrates H–Y used in the H-atom transfer reaction. The bond dissociation energies (BDEs) are given in kJ mol⁻¹. All reactions were carried out at room temperature in THF.^[a]

Entry	H–X	BDE (H–Y) (kJ mol ⁻¹)	Reaction (time)	Product
1	ⁿ Bu ₃ SnH	310 ^[S14]	No	No
2	ⁿ BuSH	364 ^[S14]	Yes (minutes)	ⁿ BuS–S ⁿ Bu
3	Ph ₃ SiH	371 ^[S14]	No	No
4	Ph ₃ CH	339 ^[S15]	No	No
5		340 ^[S16]	No	No
6		289 ^[S17]	Yes (2.5h)	
7	Ph ₂ PH	376 ^[S14]	Yes (4h)	Ph ₂ P–PPh ₂

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