Supplementary Material (ESI) for Chemical Communications

Redox rich dicobalt macrocycles as templates for multi-electron transformations

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Experimental Section

Preparation of Compounds

Manipulations of cobalt macrocycle complexes not in the +2 oxidation state were carried out using standard Schlenk or glovebox techniques under an N_2 atmosphere, while the syntheses of ligand precursors were generally performed in the air. Unless otherwise noted, solvents were deoxygenated and dried by thorough sparging with N_2 gas followed by passage through an activated alumina column. Deuterated solvents were purchased from Cambridge Isotopes Laboratories, Inc., and were degassed and stored over activated 3 Å molecular sieves prior to use. The compounds $L^{Ph}OH$,[1] 3,6-diacetylpyridazine[2] and PhIO[3] were prepared according to literature procedures. Dimethyl pyridazine-3,6-dicarboxylate was prepared after several to modifications on a patent protocol.[4] All other reagents were purchased from commercial vendors and used without further purification.

X-ray Structure Determinations

X-ray diffraction studies were carried out on a Bruker Circle 3 diffractometer equipped with a CCD detector. Measurements were carried out at -175 °C using Mo Kα (λ = 0.71073 Å). Crystals were mounted on a Kaptan loop with Paratone-N oil. Initial lattice parameters were obtained from a least-squares analysis of more than 100 centered reflections; these parameters were later refined against all data. Data were integrated and corrected for Lorentz polarization effects using SAINT [5] and were corrected for absorption effects using SADABS.[6]

Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined against all data using the

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[1] Mernari, B.; Lagrenee, M.; J. Heterocyc. Chem., **1996**, *33*, 2059-2061.

[2] Zong, R.; Wang, D.; Hammitt, R.; Thummel, R. P. *J. Org. Chem.* **2006**, *71*, 167-175.

[3] Saltzman, H.; Sharefkin, J. G.; *Org. Synth*., **1973**, *5*, 658

[4] Bessard, Y; Crettaz, R; Brieden, W. PCT Int. Appl. WO 2001007415 A1 20010201, 2001

[5] *SAINT Software UsersGuide*, Version 7.0; Bruker Analytical X-Ray Systems, Inc.: Madison,WI, 1999.

[6] Sheldrick, G. M. *SADABS*, Version 2.03; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 2000.

SHELXTL 5.1 software package.[7] Thermal parameters for all non-hydrogen atoms were refined anisotropically and hydrogen atoms, where added, were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogens).

Other Physical Measurements

Elemental analyses were performed by Desert or Midwest Microlab Laboratories. ^1H NMR spectra were recorded at ambient temperature using either a Varian 300 or 500 MHz spectrometer; chemical shifts were referenced to the residual solvent. IR measurements were obtained on samples prepared as KBr pellets using a Bio-Rad Excalibur FTS 3000 spectrometer. Mass spectra were collected using a Bruker Daltonics APEXIV 4.7 T Fourier transform ion cyclotron resonance mass spectrometer equipped with an electrospray ionization source. Electrochemical measurements were recorded in a glovebox under an N_2 atmosphere using a CH Instruments electrochemical analyzer, a glassy carbon or a platinum working electrode, a platinum wire auxiliary electrode, and an $Ag/AgNO_3$ nonaqueous reference electrode. Reported potentials are all referenced to the SCE couple and were determined using ferrocene as an internal standard. X-band EPR measurements were recorded using a Bruker EMX spectrometer. Solution spectra were acquired at 77 or 10 K in DMF. Samples were prepared in a glovebox under N_2 in quartz EPR tubes equipped with J. Young caps. Grants from the NSF provided instrument support to the DCIF at MIT (CHE-9808061, DBI-9729592).

Synthesis of Pyz^{H}OH

A flask containing dimethyl pyridazine-3,6-dicarboxylate (1.002g, 5.11 mmol) and dichloromethane (150 mL) was cooled to -72 °C. To the cooled flask was added a solution of DIBAL-H (10.73 mL, 1 M in hexane) over 20 minutes, causing a color change from light yellow to yellow-orange. The solution was allowed to react at -72 °C for 7 hours, and then a solution of NaOH (10 mL, 1 M) and MeOH (15 mL) was added and the slurry was stirred for 3 hours. The solution was concentrated *in vacuo* to ~20 mL and filtered through Celite and washed with water (3 x 15 mL). To the filtrate was added a solution of hydroxylamine hydrochloride (20 mL; (30g/(40 mL H_2O and 20mL MeOH)) that caused an immediate beige precipitate to form. Further precipitation was facilitated by cooling at 4 °C overnight. The beige precipitate was collected on a frit and washed with cold water (4 x 15 mL) then THF (3 x 10 mL) and dried *in vacuo*. Yield: 0.591 g (64 %) ^1H NMR (dmso-d_6, 500 MHz): δ 12.2 (s, 2H), 8.3 (s, 2H), 8.0 (s, 2H). IR (KBr, cm^{-1}): ν 1500 m, 1313 m, 1006 s. ESI$^+$-MS: *m/z* 167 $[LH]^+$.

Synthesis of Pyz^{Me}OH

Methanol (10 mL) was added to a flask containing 3,6-diacetylpyridazine (0.6088 g, 3.708 mmol). An excess of a hydroxylamine hydrochloride solution (8 mL, (30g/(40 mL H_2O and 20mL MeOH)) was added, and the solution was heated to 60 °C for 16 h. The solution was poured into 15 mL of water and extracted with diethyl ether (4 x 10 mL), then dried over Na_2SO_4, and the solvent was removed by rotary evaporation to afford a white solid. Yield: 0.464 g (65 %) ^1H NMR (dmso-d_6, 500 MHz): δ 12.0 (s, 2H), 8.0 (s, 2H), 2.3 (s, 6H). Anal. Calcd for $C_8H_{10}N_4O_2$: C, 49.48; H, 5.19; N, 28.85. Found: C,

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[7] Sheldrick, G. M. *SHELXTL*, Version 6.12; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1999. Analytical X-Ray Systems, Inc.: Madison, WI, 2000.

49.10; H, 5.19; N, 28.80. IR (KBr, cm^{-1}): 3196 (br), 1628 (m), 1592 (m), 1155 (s), 1118 (s), 1012 (s). ESI$^+$-MS: *m/z* 195 [LH]$^+$

General synthesis of [M$_2$L^R][BF$_4$]$_2$:
All of the **[L^{R}Co$_2$]**$^{2+}$ complexes were synthesized analogously, and a representative procedure is given for **[L^{Me}Co$_2$]**$^{2+}$: L^{Me}OH (0.2114 g, 1.09 mmol) and Co(OAc)$_2$·4 H$_2$O (0.2715 g, 1.09 mmol) was suspended in 30 mL of diethyl ether under N$_2$. BF$_3$·Et$_2$O (1.77 mL) was added slowly and the mixture was stirred at room temperature for 16 h. The resultant red-brown suspension was filtered through a frit and the precipitate was washed with diethyl ether (5 x 10 mL). Acetonitrile was added (*ca*. 25 mL) and the solution was filtered and collected in a flask, then diethyl ether (10 mL) was added and the dark red solution was cooled overnight at 4 °C. The red crystals that formed on the flask walls were collected and washed with diethyl ether, while 2-3 mL of diethyl ether was added to the mother liquor, which was cooled to obtain a second crop. Yield: 0.42 g (41 %). Anal. Calcd for $C_{22}H_{25}B_4Co_2F_{12}N_{11}O_4$(assuming loss of one CH$_3$CN): C, 29.47; H, 2.8; N, 17.18. Found: C, 29.93; H, 2.73; N, 17.46. IR (KBr, cm^{-1}): 1635 (m), 1576 (w), 1174 (sh), 1105 (s), 1058 (sh), 1033 (sh), 974 (sh). UV-vis (MeCN); λ_{max} (nm), ε (M^{-1} cm^{-1}): 409 (7740), 456 (8612), 501(5260). $E_{1/2}$ (MeCN, V): 1.21, 1.10, -0.01, -0.30.

Characterization for [**Co$_2$L^H][BF$_4$]**$_2$:
Anal. Calcd for $C_{18}H_{17}B_4Co_2F_{12}N_{11}O_4$ (assuming loss of one CH$_3$CN): C, 25.72; H, 2.08; N, 18.33. Found: C, 25.32; H, 2.48; N, 18.43. IR (KBr, cm^{-1}): 1623 (s), 1578 (m), 1187 (m), 1108 (s), 1067 (s), 1026 (s). UV-vis (MeCN); λ_{max} (nm), ε (M^{-1} cm^{-1}): 460 (6388). $E_{1/2}$ (MeCN, V): 1.32, 1.13, 0.12, -0.14.

Characterization for **[Co$_2$L^{Ph}][BF$_4$]**$_2$:
Anal. Calcd for $C_{42}H_{33}B_4Co_2F_{12}N_{11}O_4$ (assuming loss of one CH$_3$CN): C, 44.06; H, 2.91; N, 13.46. Found: C, 44.27; H, 3.23; N, 13.71. IR (KBr, cm^{-1}): 1591 (m, br) 1187 (sh), 1133 (sh), 1038 (s), 966 (sh). UV-vis (MeCN); λ_{max} (nm), ε (M^{-1} cm^{-1}): 483 (7583). $E_{1/2}$ (MeCN, V): 1.28, 1.07, 0.09, -0.17.

Characterization for **[Zn$_2$L^{Me}][BF$_4$]**$_2$:
^{1}H NMR (MeCN-*d*$_3$, 500 MHz): δ 8.60 (s, 2H), 2.54 (s, 6H)
^{19}F NMR (MeCN-*d*$_3$, 300 MHz): δ -149.6 (s), -164 (m,) IR (KBr, cm^{-1}): 1630 (s), 1578 (m), 1180 (m, sh), 1102 (s), 987 (sh).

General synthesis of [Co$_2$L^R][ClO$_4$]: All of the **[L^{R}Co$_2$]**$^+$ and **[L^{R}Co$_2$]** complexes were synthesized analogously, and a representative procedure is given for **[L^{Me}Co$_2$]**$^+$: A standard H-type bulk electrolysis cell was used for electrochemical syntheses. The cathodic chamber was charged with **[L^{Me}Co$_2$]**$^{2+}$ (30.8 mg, 0.0343 mmol) and both chambers were filled with 10 mL of a 0.1 M [^{n}BuN$_4$][ClO$_4$] MeCN solution. Controlled potential electrolysis commenced at a potential ~0.08 mV cathodic of I_{pc} until 1 or 2 electron equivalents were passed and the solution current was less than 0.5% of the initial value. Solvent was removed in vacuo and the solid was washed with DME (5 x 5mL), then taken up in MeCN (5mL), filtered and diethyl ether was added to precipitate a dark solid, which was washed further with diethyl ether (3 x 5 mL), and dried in vacuo. (Note that the high solubility of **[L^{Ph}Co$_2$]$^+$** precluded isolation of an amount greater than needed for EPR and UV-Vis studies). Crystals suitable for X-ray diffraction were grown by diffusion of diethyl ether into an acetonitrile solution. Yield: 17.8 mg (63 %). Anal. Calcd for $C_{22}H_{25}B_2ClCo_2F_4N_{11}O_8$: C, 32.13; H, 3.06; N, 18.73. Found: C, 32.46; H, 3.47; N, 18.41. UV-Vis (MeCN): 10560 cm^{-1} (ε = 4723 L mol^{-1}cm^{-1}). IR (KBr, cm^{-1}): 1651 (m) 1615 (m, sh), 1573 (m, sh), 1389 (m, br), 1300 (s), 1156 (s, sh), 1100 (s, br), 1023, (s, sh), 954 (m, sh).

Characterization for **[Co^{I}Co^{II}L^{H*}][ClO$_4$]$_3$**:
Anal. Calcd for $C_{22}H_{26}Cl_3Co_2N_{10}O_{12}$ (assuming loss of one MeCN) C, 31.21; H, 3.10; N, 16.54. Found: C, 32.01; H, 3.19; N, 16.87. IR (KBr, cm^{-1}): 1652 (m, br) 1495, 1369 (m), 1303 (m), 1243 (m), 1089 (s, br). λ_{max} (nm), ε (M^{-1} cm^{-1}): 421 (5289), 658 (1787), 975 (2704).

Characterization for **[Co^{I}Co^{I}L^{H*}][ClO$_4$]$_2$**:
λ_{max} (nm), ε (M^{-1} cm^{-1}): 410 (10655), 602 (9280). ^{1}H NMR (dmso-d_6, 500 MHz): δ 9.32 (s (br), 4H), 8.25 (s (br), 4H), 3.37 (s (br)), 2.46 (s, br), 2.07 (s, 6H). Anal. Calcd for $C_{20}H_{23}Cl_2Co_2N_9O_8$ (-1 MeCN) C, 34.01; H, 3.28; N, 17.85. Found: C, 33.70; H, 3.30; N, 17.68. IR (KBr, cm^{-1}): 1651 (m, br) 1586 (m, br), 1468 (s), 1404 (m), 1369 (m), 1342 (m), 1299 (m), 1245 (m), 1089 (s, br).

Synthesis of [Co$_2$L^{Me}][ClO$_4$]$_3$: A green solution of **[L^{Me}Co$_2$]$^{2+}$** (0.0128 g, 0.0156 mmol) and 5 mL MeCN was cooled until frozen. A suspension of PhIO (0.0068 g, 0.0309 mmol) in MeCN (4 mL) was added slowly, and the solution was allowed to warm slowly to room temperature over the course of 3 hours, then stirred at room temperature for 16 hours, which resulted in a brown solution. Diethyl ether was added to the solution (5 mL), and the solution was allowed to stand overnight. The brown solid that precipitated was isolated and washed with diethyl ether (3 x 5 mL) and THF (4 x 5 mL). Crystals suitable for X-ray diffraction were grown from diffusion of diethyl ether into an acetonitrile solution. Yield: 0.0091 g (45%), UV-Vis (MeCN): 10930 cm^{-1} (ε = 880 L mol^{-1}cm^{-1}). Anal. Calcd for $C_{24}H_{28}B_2Cl_3Co_2F_4N_{12}O_{16}$(assuming loss of two CH_3CN): C, 24.50; H, 2.26; N, 14.29. Found: C 24.86; H 2.30; N 12.71. IR (KBr, cm^{-1}): 1652 (m, br) 1574 (w, sh), 1440 (m), 1384 (m), 1300 (w), 1176 (m, sh), 1102 (s), 1028 (m, sh).

Synthesis of [Co$_2$L^{Me}Br$_4$]O$_2$H

L^{Me}OH (0.0773 g, 0.2964 mmol) and $CoBr_2$ (0.0575 g, 0.2964 mmol) was suspended in 7 mL of ethanol and heated to 70 °C. After 48 h, the suspension was cooled to room temperature, and diethyl ether was added (10 mL), then the solid was collected following filtration through a frit. The brown solid was washed with diethyl ether (5 x 10 mL) and dried in vacuo to afford a brown powder. Yield: 0.1141 g (93 %). Anal. Calcd for $C_{16}H_{18}Br_4Co_2N_8O_4$: C, 23.33; H, 2.20; N, 13.60. Found: C, 23.57; H, 2.42; N, 13.31. ^{1}H NMR (dmso-d_6, 500 MHz): δ 19.7 (s, 2H), 8.9 (s, 4H), 2.9 (s, 12H). IR (KBr, cm^{-1}): 1578 (m), 1528 (w), 1238 (m), 1119 (m), 1000 (m). UV-vis (DMA); λ_{max} (nm), ε (M^{-1} cm^{-1}): 291 (43820), 432 (sh) (9050). $E_{1/2}$ (DMF, V): 0.01, -0.35.

Synthesis of [Co$_2$L^{Me}Br$_4$]

[Co$_2$L^{Me}Br$_4$]O$_2$H (0.0560 g, 0.0680 mmol) and [^{n}Bu$_4$N][OAc] (0.3201 g, 1.062 mmol) were suspended in 8 mL of DME under N$_2$. BF$_3$·Et$_2$O (1.8 mL) was added slowly and the mixture was stirred at 70 °C for 6 days. The resultant brown suspension was filtered in a glove box and the precipitate was washed with diethyl ether (4 x 10 mL). The solid was washed with tetrahydrofuran (3 x 5 mL), acetonitrile (3 x 5 mL) then passed through the frit with DMF (8mL). Diethyl ether (20 mL) was added causing the precipitation of a brown solid, which was collected and dried by suction. Crystals suitable for X-ray diffraction were grown from diffusion of diethyl ether into a DMF solution. Yield: 0.0550 g (71 %). Anal. Calcd for $C_{22}H_{30}B_2Br_4Co_2F_4N_{10}O_6$ (assuming two addional DMF molecules, consistent with XRD analysis): C, 24.80; H, 2.84; N, 13.14. Found: C, 24.70; H, 2.76; N, 13.09. ^{1}H NMR (dmso-*d*$_6$, 500 MHz): δ 9.27 (s, 4H), 3.07 (s, 12H). IR (KBr, cm^{-1}): 1665 (s), 1614 (m), 1575 (w), 1173 (m), 1119 (s), 1063 (m), 1032 (s). UV-vis (DMF); λ_{max} (nm), ε (M^{-1} cm^{-1}): 293 (2825), 603(45), 674 (10). $E_{1/2}$ (MeCN, V): 0.37, -0.02, -0.30.

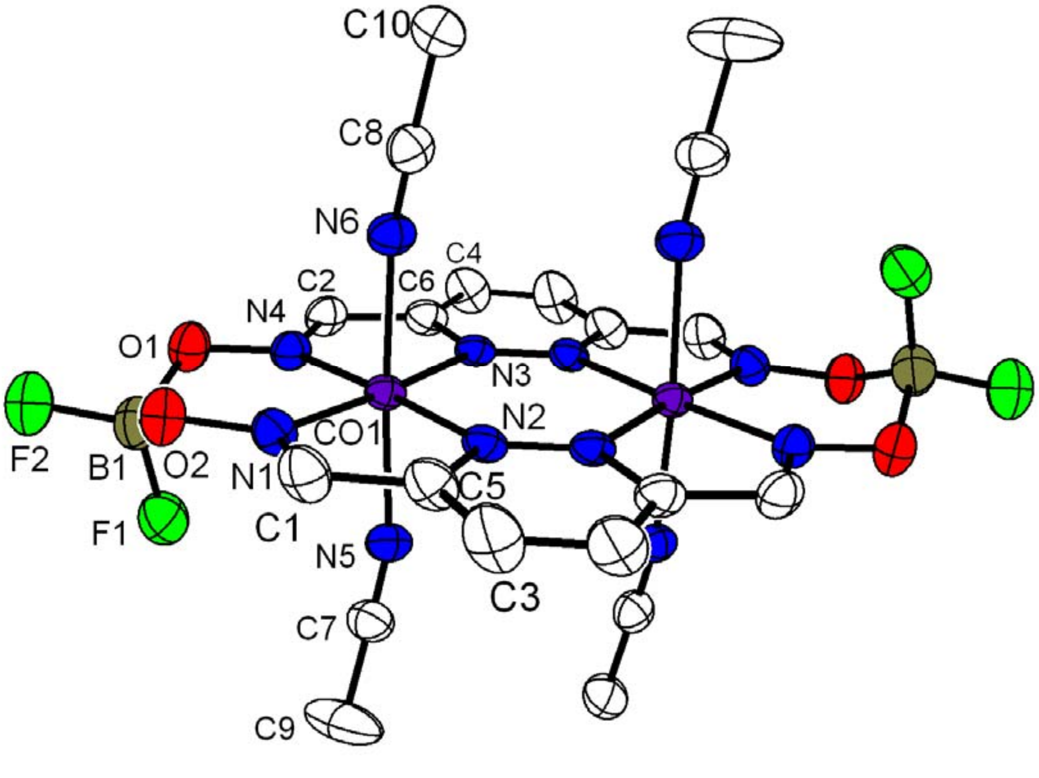

Figure S1. ORTEP of **[L^{H}Co$_2$]$^{2+}$** (50 % probability) Two BF$_4^-$ anions, solvent and hydrogen atoms omitted for clarity.

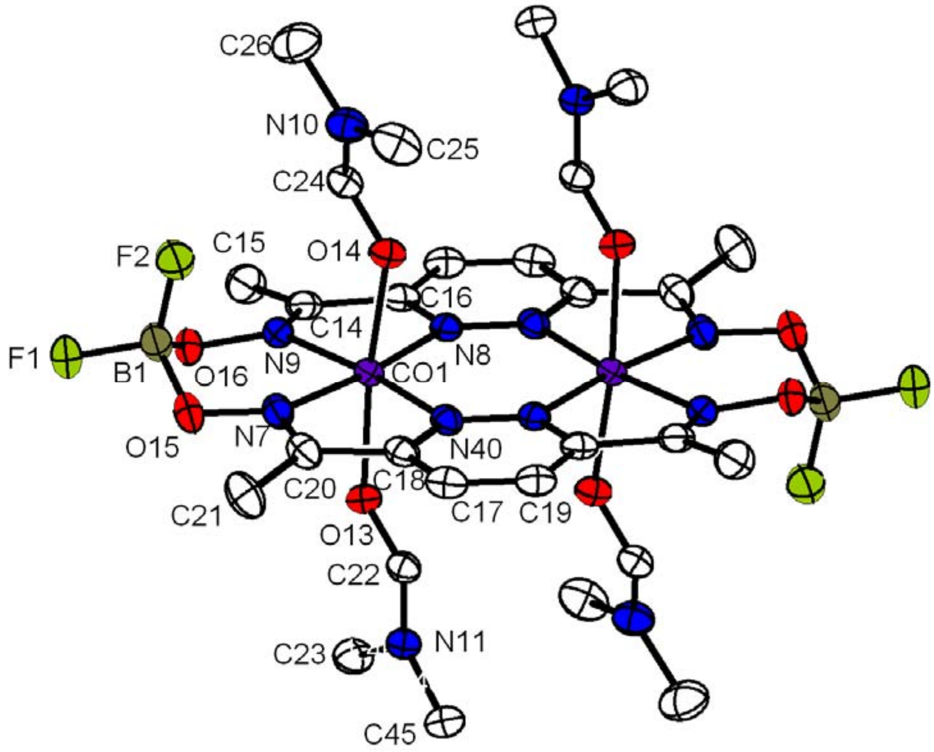

Figure S2. ORTEP of **$[L^{Me}Co_2]^{2+}$** (50 % probability) Two BF_4^- anions, solvent and hydrogen atoms omitted for clarity.

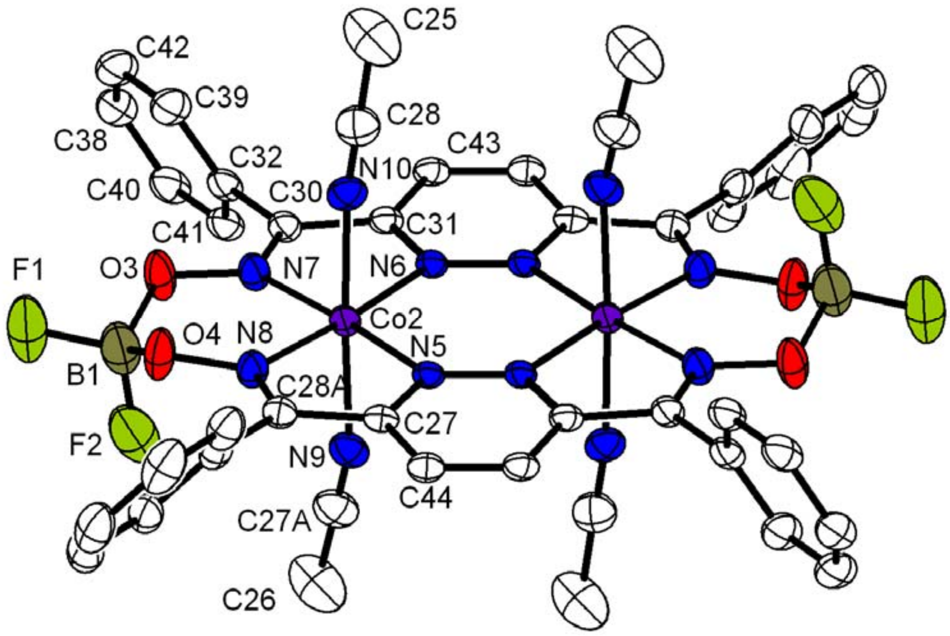

Figure S3. ORTEP of **$[L^{Ph}Co_2]^{2+}$** (50 % probability) Two BF_4^- anions, solvent and hydrogen atoms omitted for clarity.

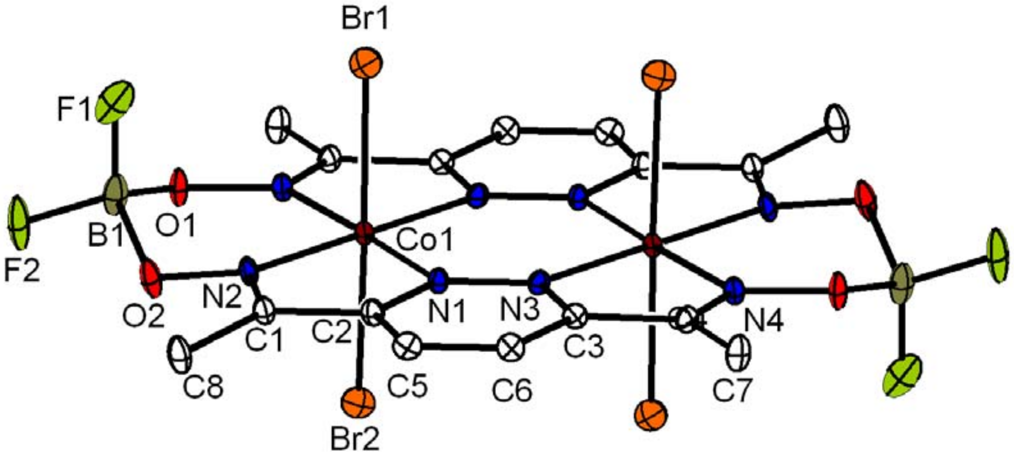

Figure S4. ORTEP of **$[L^{Me}Co^{III}Co^{III}Br_4]$** (50 % probability).

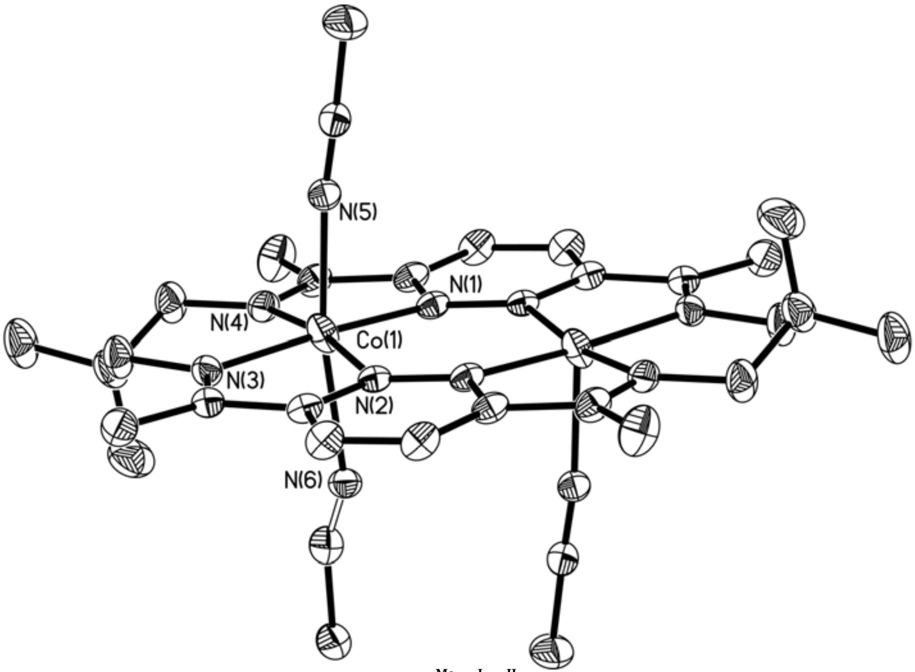

Figure S5. ORTEP of **$[L^{Me}Co^{I}Co^{II}]$** (50 % probability).

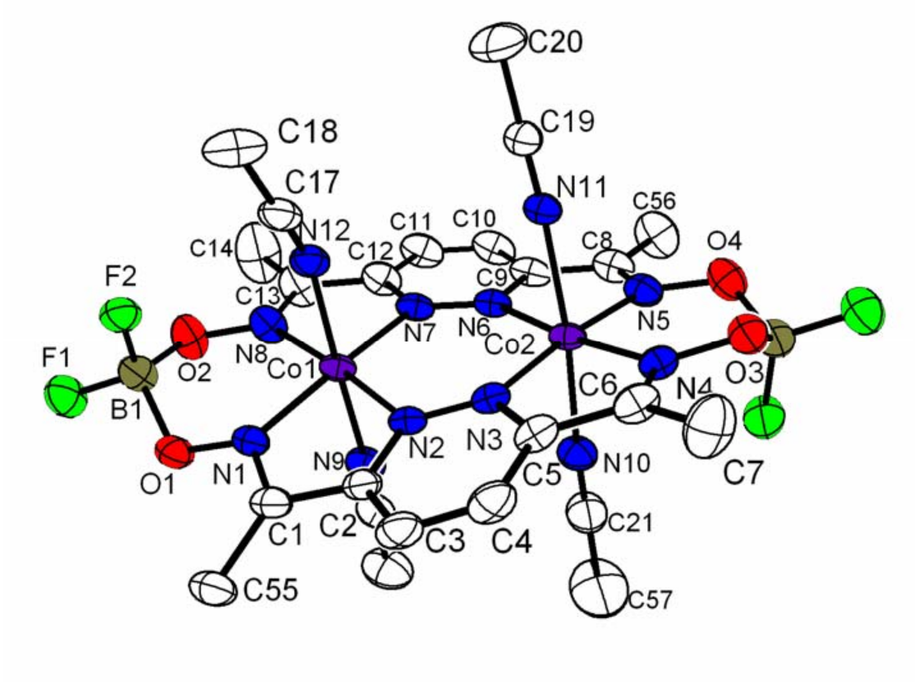

Figure S6. ORTEP of **$[L^{Me}Co^{II}Co^{III}]$** (50 % probability).

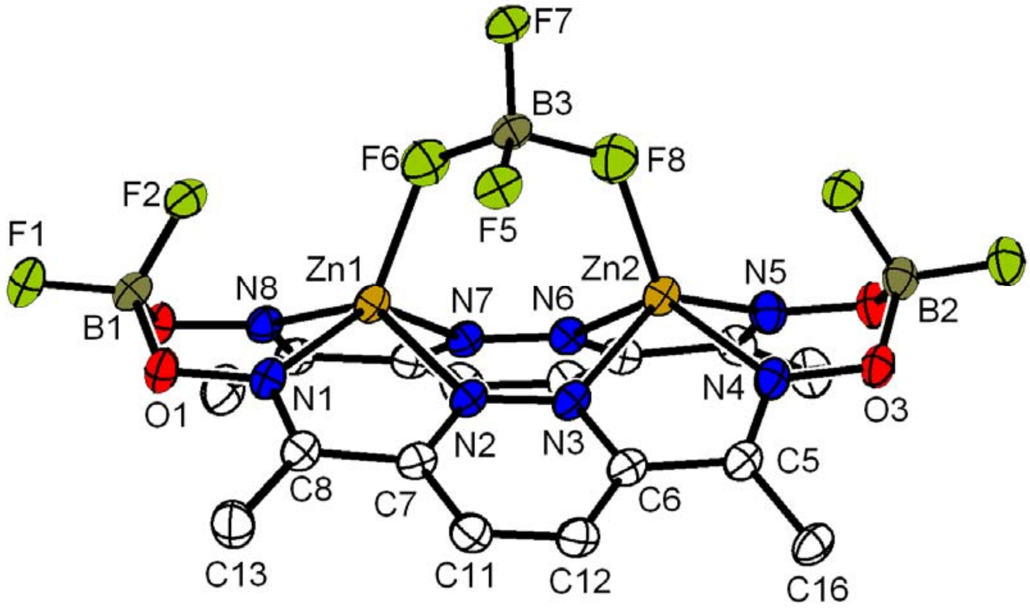

Figure S7. ORTEP of **$[L^{Me}Zn_2]^{2+}$** (50 % probability) One BF_4^- anion, solvent and hydrogen atoms omitted for clarity.

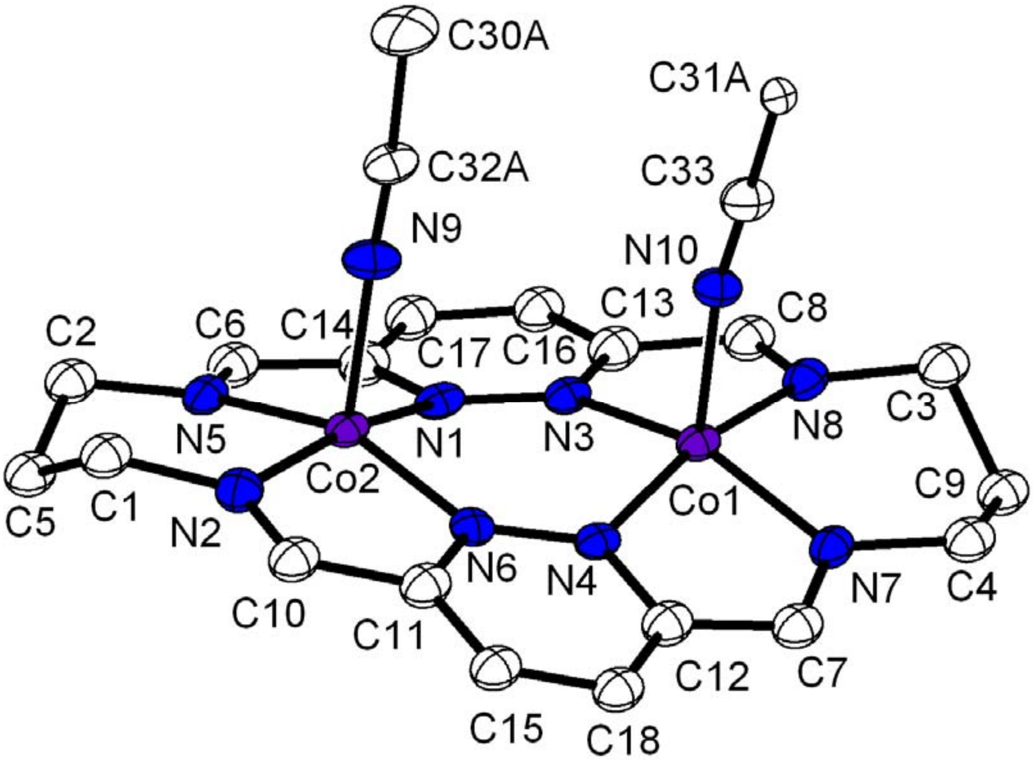

Figure S8. ORTEP of **$[L^{H*}Co(I)Co(I)]^{2+}$** (50 % probability) Hydrogen atoms and two ClO_4^- anions omitted for clarity.

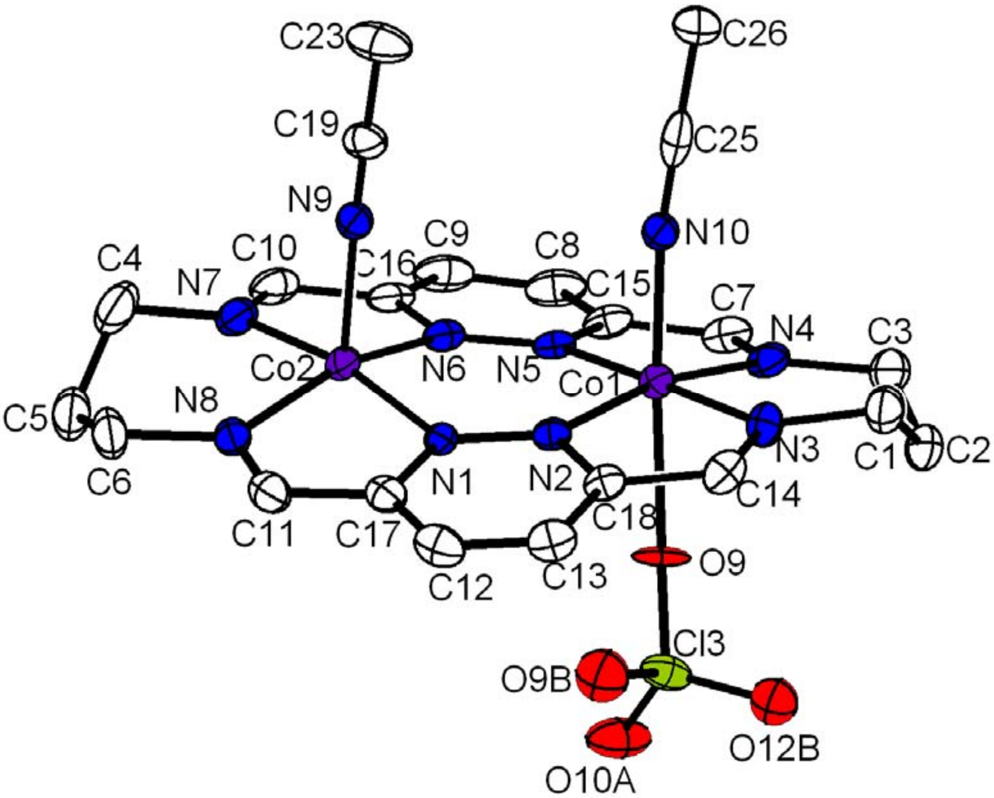

Figure S9. ORTEP of **[L^{H*}Co(II)Co(I)]$^{3+}$** (50 % probability) Hydrogen atoms omitted for clarity.

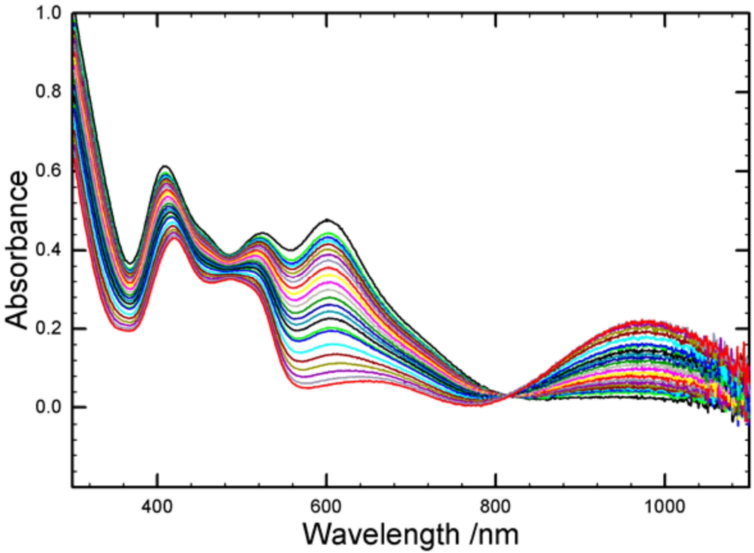

Figure S10. (a) Addition of 2 eq. HBF$_4$ to a 0.08 mM solution of **[L^{H*}Co$_2$]**$^{2+}$ in MeCN monitored over the course of 16 h.

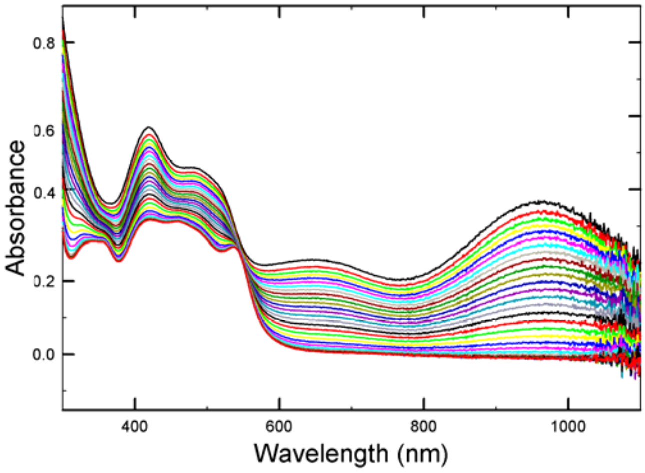

Figure S11. (a) Addition of 50 eq. HBF_4 to a 0.08 mM solution of $\mathbf{[L^{H*}Co_2]}^{2+}$ in MeCN monitored over the course of 6 hours.

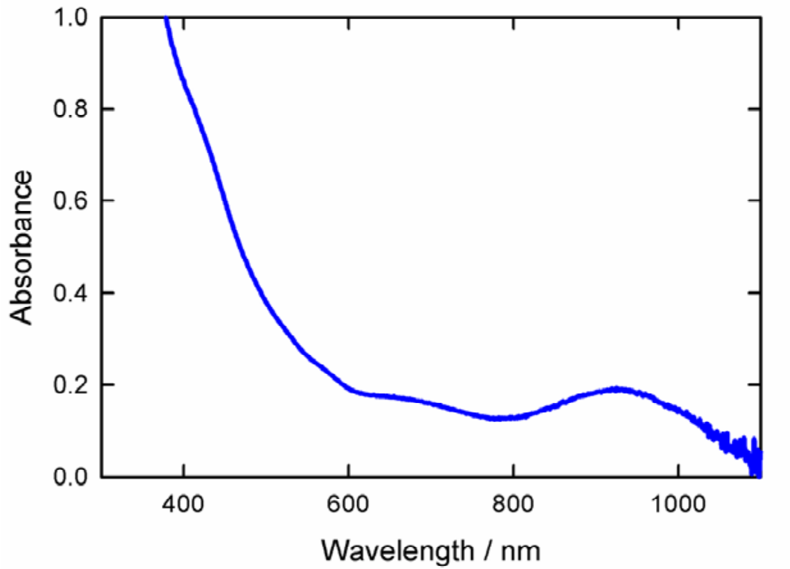

Figure S12. (a) UV-Visible spectrum of $\mathbf{[L^{H*}Co_2]}^{3+}$ in MeCN.

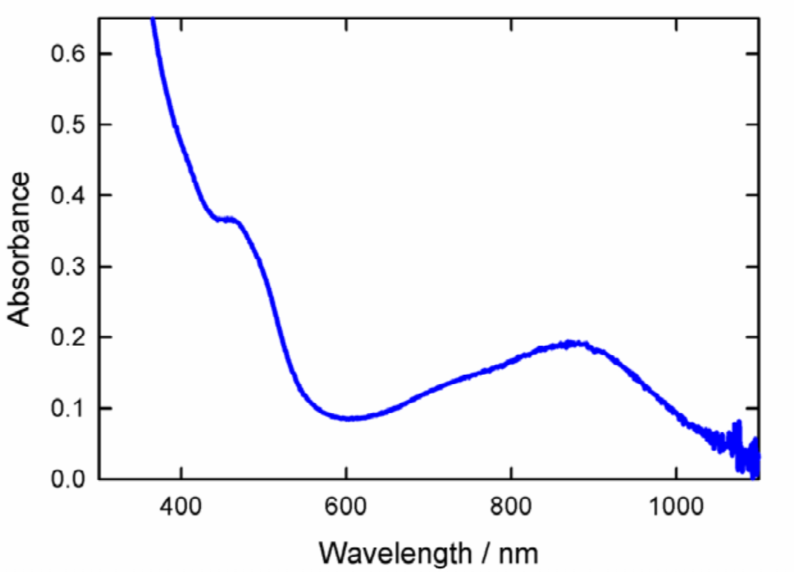

Figure S13. (a) UV-Visible spectrum of **$[L^HCo_2]^+$** in MeCN.

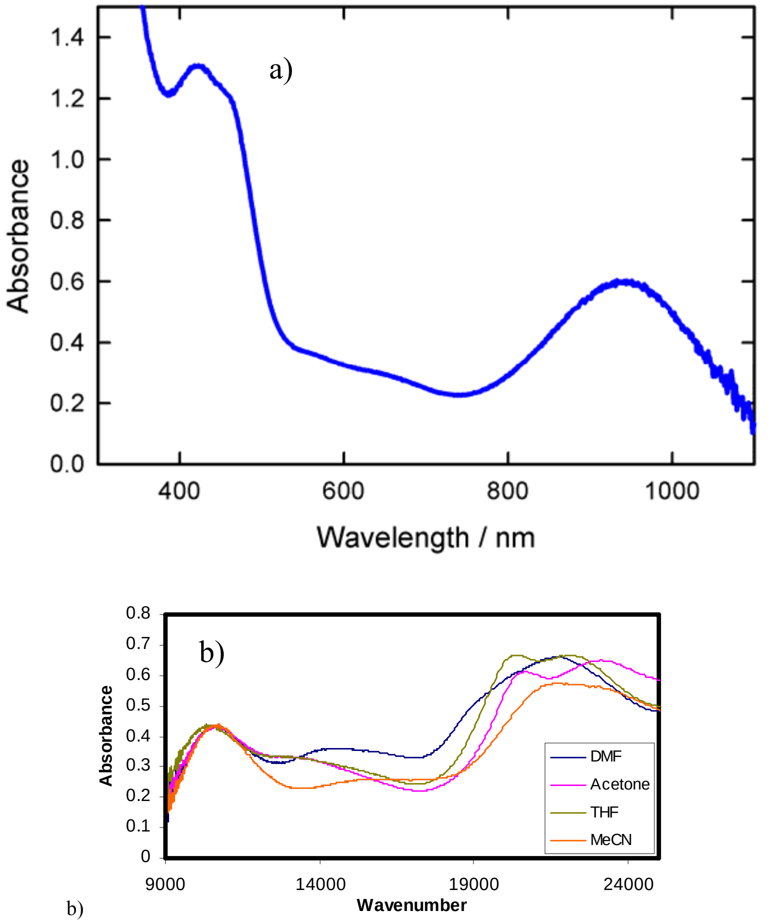

Figure S14. (a) UV-Visible spectrum of **$[L^{Me}Co_2]^+$** in MeCN. (b) UV-Visible spectrum of **$[L^{Me}Co_2]^+$** in DMF, acetone, THF, and MeCN)

The experimental bandwidth at half-height is narrower than the corresponding theoretical one, $\Delta\nu°_{½}$, determined by $\Delta\nu°_{½}=[16\ln(2)\Delta\nu_{max}RT]^{½}$ as 4930 cm^{-1}, at

300 K. The empirical parameter, Γ, provides a measure of the degree of delocalization and can be calculated given the ratio of the $\Delta\nu_{1/2}$ values (Γ=1-$\Delta\nu_{1/2}/\Delta\nu^{\circ}_{1/2}$). Using this analysis, Γ=0.53 for **[L^{Me}Co^{II}Co^{I}]$^{+}$** and is consistent with a Class II-III mixed valence species according to the Robin-Day system.

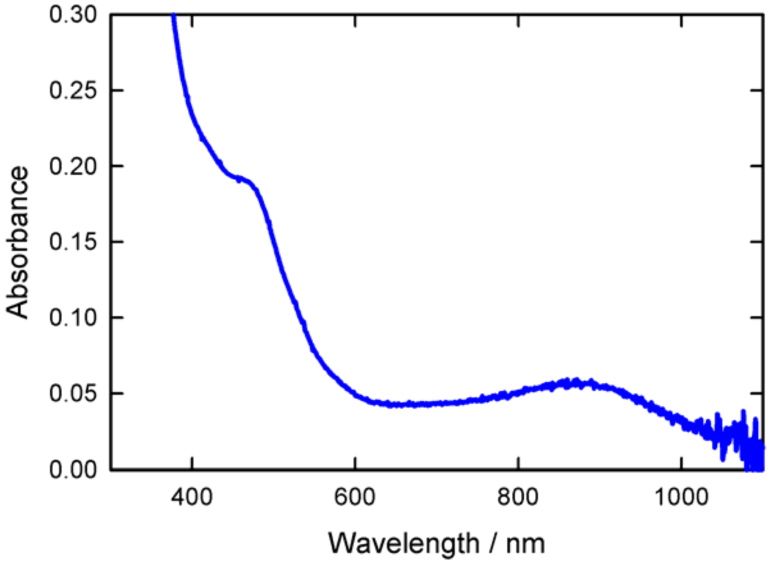

Figure S15. (a) UV-Visible spectrum of **[L^{Ph}Co$_2$]**$^{3+}$ in MeCN.

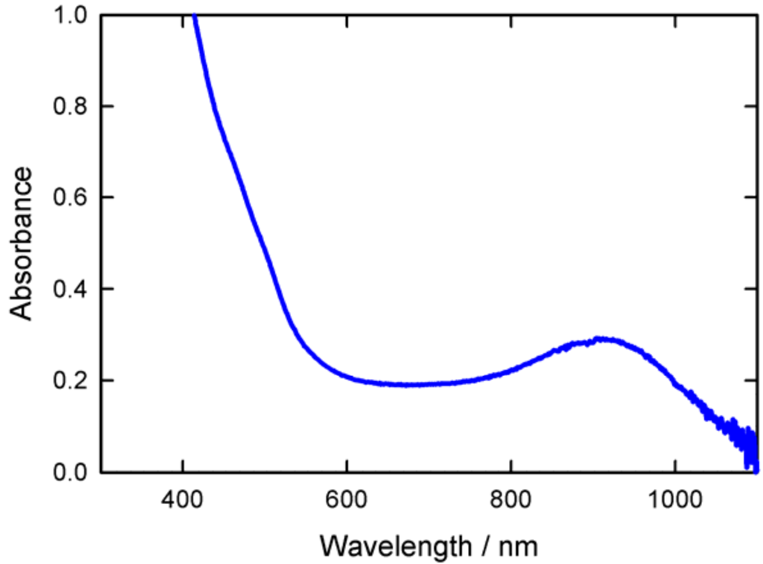

Figure S16. (a) UV-Visible spectrum of **[L^{Me}Co$_2$]**$^{3+}$ in MeCN.

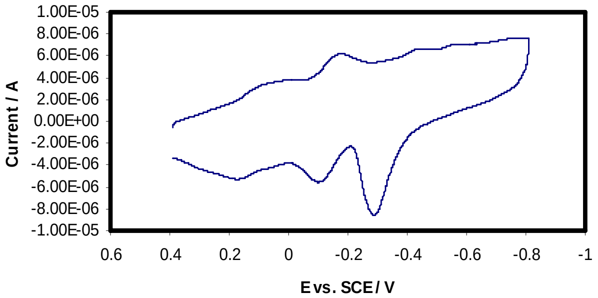

Figure S17. Cyclic voltammogram of **[L^{H}Co$_2$]**$^{2+}$ in a 0.1 M [^{n}BuN$_4$][ClO$_4$] MeCN solution showing the stripping wave on the return scan. Glassy carbon electrode, 100 mV/s scan rate.

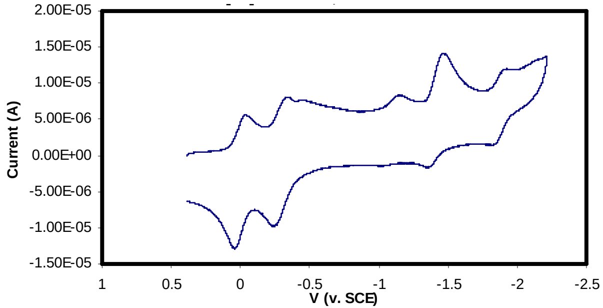

Figure S18. Cyclic voltammogram of **[L^{Me}Co$_2$]**$^{2+}$ in a 0.1 M [^{n}BuN$_4$][ClO$_4$] MeCN solution (full reductive scan). Glassy carbon electrode, 100 mV/s scan rate.

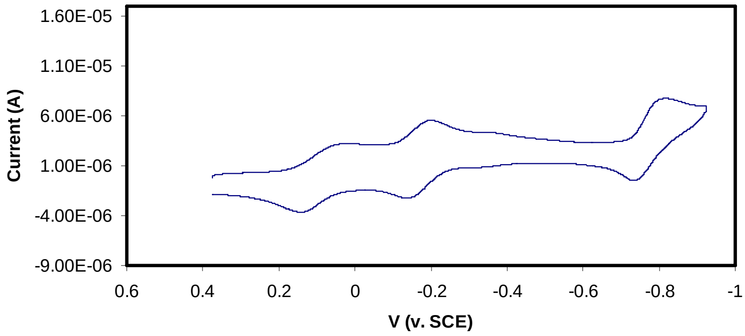

Figure S19. Cyclic voltammogram of **[L^{Ph}Co$_2$]**$^{2+}$ in a 0.1 M [^{n}BuN$_4$][ClO$_4$] MeCN solution (full reductive scan). Glassy carbon electrode, 100 mV/s scan rate.

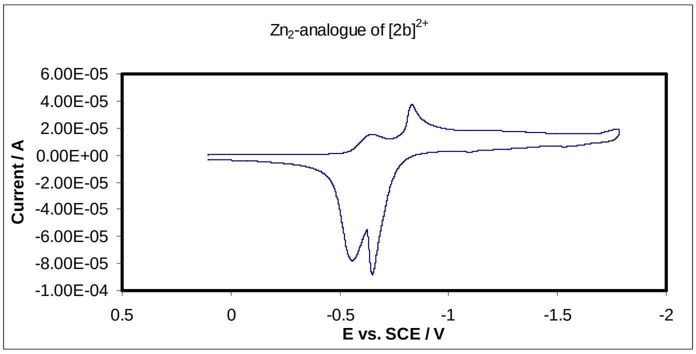

Figure S20. Cyclic voltammogram of **[L^{Me}Zn$_2$]**$^{2+}$ in a 0.1 M [^{n}BuN$_4$][ClO$_4$] MeCN solution. Glassy carbon electrode, 100 mV/s scan rate.

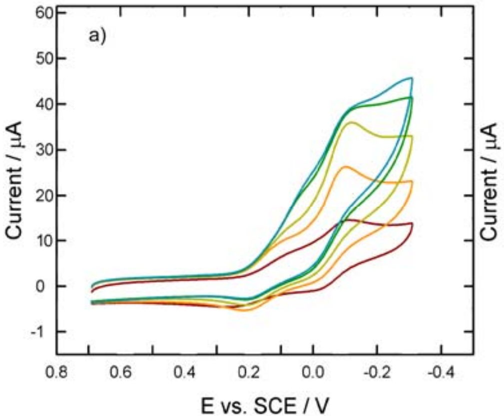

Figure S21. Cyclic voltammograms of **[L$^{\mathrm{H*}}$Co$_2$]$^{2+}$** (0.9 mM) in a 0.1 M [^{n}BuN$_4$][ClO$_4$] MeCN solution in the presence of increasing increments of HBF$_4$ (bottom to top): 0, 3.9, 8.3, 13.2, and 15.5 mM,

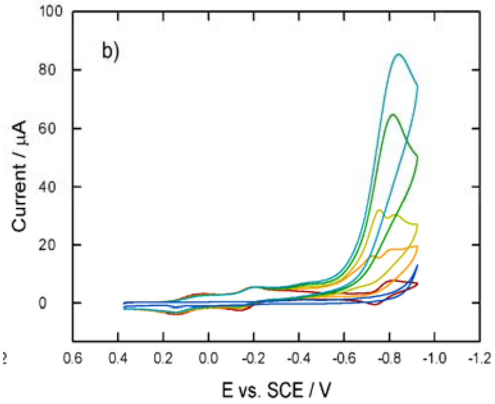

Figure S22. Cyclic voltammograms of complex **[L$^{\mathrm{Ph}}$Co$_2$]$^{2+}$** (0.2 mM) in a 0.1 M [^{n}BuN$_4$][ClO$_4$] MeCN solution in the presence of increasing increments of 2,6-dichloroanilinium tetrafluoroborate (bottom to top; the lowest blue trace is the control with acid only): 0, 1.0, 2.5, 4.5, and 9.9 mM

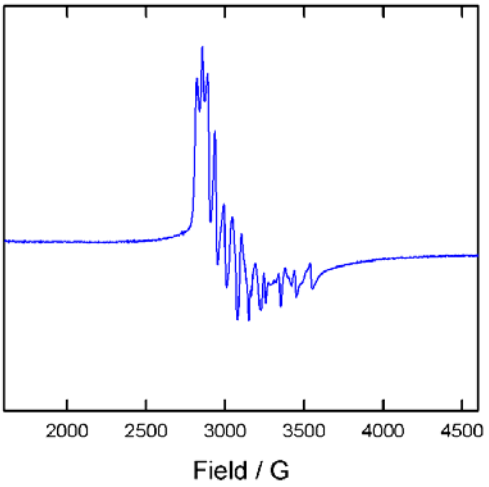

Figure S23 EPR spectrum of **[L$^{\mathrm{Me}}$Co$^{\mathrm{II}}$Co$^{\mathrm{III}}$]**$^+$ in DMF glass at 77 K, 9.376 GHz.

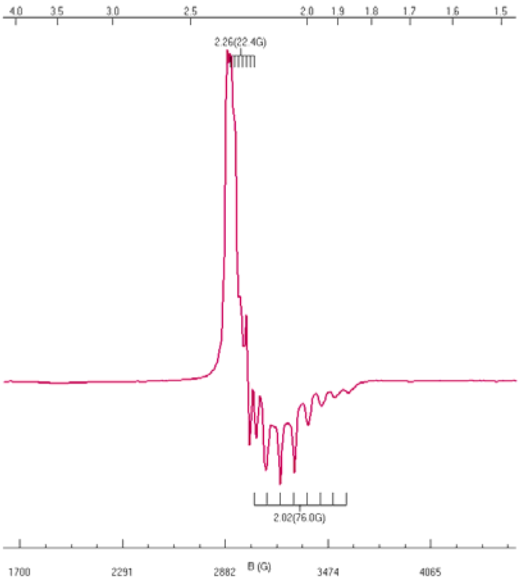

Figure S24. EPR spectrum of $[\mathbf{L^{Me}Co^{II}Co^{I}}]^+$ in DMF glass at 4 K, 9.376 GHz.

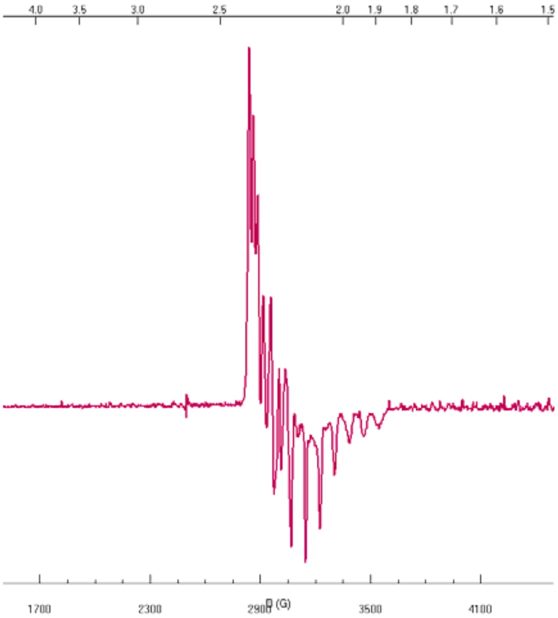

Figure S25 EPR spectrum of $[\mathbf{L^{H*}Co^{II}Co^{I}}]^+$ in DMF glass at 77 K, 9.376 GHz.

Table S1. Bulk electrolysis data

	mM [Co]	eq. acid	Faradaic Yield[a]	Coulombs Passed	Time (min)
Co_2L^{H*}	0.058	200 equiv. HBF_4	46	15.3	52
Co_2L^{H*}	0.72	50 equiv. HBF_4	36	117	90
Co_2L^{Me}	0.16	200 equiv. 2,6-dichloroanilinium tetrafluoroborate	25	66	90
	0.21	100 equiv. tosic acid	9	113	90
Co_2L^{Ph}	0.21	100 equiv. 2,6-dichloroanilinium tetrafluoroborate	37	40	30

[a] Determined by integration of the H_2 peak on a GC trace

Table S2. Crystal data and structure refinement for $[L^{H}Co_2]^{2+}[BF_4]_2$.

Empirical formula	C22 H26 B4 Co2 F12 N12 O4	
Formula weight	911.65	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 15.033(3) Å	α= 90°.
	b = 20.805(4) Å	β= 90°.
	c = 11.395(2) Å	γ = 90°.
Volume	3564.0(12) Å^3	
Z	4	
Density (calculated)	1.699 Mg/m^3	
Absorption coefficient	1.044 mm^{-1}	
F(000)	1824	
Crystal size	0.2 x 0.2 x 0.15 mm^3	
Theta range for data collection	1.96 to 29.57°.	
Index ranges	-17<=h<=20, -24<=k<=27, -15<=l<=15	
Reflections collected	32921	
Independent reflections	5000 [R(int) = 0.0550]	
Completeness to theta = 29.57°	97.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.85 and 0.8	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5000 / 0 / 304	

Goodness-of-fit on F^2	1.040
Final R indices [I>2sigma(I)]	R1 = 0.0504, wR2 = 0.1336
R indices (all data)	R1 = 0.0788, wR2 = 0.1557
Largest diff. peak and hole	0.878 and -0.497 e.Å^{-3}

Table S3. Selected bond lengths [Å] and angles [°] for $[L^{H}Co_2]^{2+}[BF_4]_2$.

Co(1)-N(4)	1.911(2)
Co(1)-N(1)	1.917(2)
Co(1)-N(2)	1.973(2)
Co(1)-N(3)	1.980(2)
Co(1)-N(6)	2.155(2)
Co(1)-N(5)	2.168(3)
N(4)-Co(1)-N(1)	93.24(11)
N(4)-Co(1)-N(2)	174.96(10)
N(1)-Co(1)-N(2)	81.74(10)
N(4)-Co(1)-N(3)	81.44(10)
N(1)-Co(1)-N(3)	174.52(10)
N(2)-Co(1)-N(3)	103.57(10)
N(4)-Co(1)-N(6)	90.74(10)
N(1)-Co(1)-N(6)	89.36(10)
N(2)-Co(1)-N(6)	88.84(9)
N(3)-Co(1)-N(6)	89.39(10)
N(4)-Co(1)-N(5)	93.37(10)
N(1)-Co(1)-N(5)	91.11(11)
N(2)-Co(1)-N(5)	87.12(10)
N(3)-Co(1)-N(5)	90.53(10)
N(6)-Co(1)-N(5)	175.83(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1 #2 x,-y+3/2,z

Table S4. Crystal data and structure refinement for $[L^{Me}Co_2][ClO_4]_2$.

Empirical formula	C24 H28 B2 Cl4 Co2 F4 N12 O20
Formula weight	1161.86
Temperature	100(2) K

Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.3016(10) Å	α= 103.927(2)°.
	b = 12.7344(11) Å	β= 94.988(2)°.
	c = 19.140(2) Å	γ = 113.2930(10)°.
Volume	2403.9(4) Å^3	
Z	2	
Density (calculated)	1.605 Mg/m^3	
Absorption coefficient	0.964 mm^{-1}	
F(000)	1168	
Crystal size	0.45 x 0.30 x 0.10 mm^3	
Theta range for data collection	1.12 to 30.52°.	
Index ranges	-15<=h<=16, -18<=k<=18, -27<=l<=27	
Reflections collected	66218	
Independent reflections	14390 [R(int) = 0.0408]	
Completeness to theta = 30.52°	98.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9058 and 0.6595	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14390 / 0 / 670	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0594, wR2 = 0.1602	
R indices (all data)	R1 = 0.0796, wR2 = 0.1772	
Largest diff. peak and hole	2.782 and -0.852 e.Å^{-3}	

Table S5. Selected bond lengths [Å] and angles [°] for $[L^{Me}Co_2][ClO_4]_2$.

Co(1)-N(9)	2.014(2)
Co(1)-N(7)	2.025(2)
Co(1)-N(40)	2.053(2)
Co(1)-N(8)	2.064(2)
Co(1)-O(14)	2.107(2)
Co(1)-O(13)	2.1325(19)
Co(2)-N(1)	2.051(3)
Co(2)-O(4)	2.052(3)

Co(2)-N(4)	2.069(3)
Co(2)-N(3)	2.076(3)
Co(2)-O(3)	2.085(4)
Co(2)-N(2)	2.085(3)

N(9)-Co(1)-N(7)	94.27(10)
N(9)-Co(1)-N(40)	172.03(9)
N(7)-Co(1)-N(40)	77.86(9)
N(9)-Co(1)-N(8)	77.53(9)
N(7)-Co(1)-N(8)	171.80(9)
N(40)-Co(1)-N(8)	110.33(9)
N(9)-Co(1)-O(14)	99.24(9)
N(7)-Co(1)-O(14)	90.78(9)
N(40)-Co(1)-O(14)	82.34(8)
N(8)-Co(1)-O(14)	90.54(8)
N(9)-Co(1)-O(13)	87.68(8)
N(7)-Co(1)-O(13)	89.78(9)
N(40)-Co(1)-O(13)	90.95(8)
N(8)-Co(1)-O(13)	89.89(8)
O(14)-Co(1)-O(13)	172.99(8)
N(1)-Co(2)-O(4)	100.24(12)
N(1)-Co(2)-N(4)	94.52(12)
O(4)-Co(2)-N(4)	94.93(12)
N(1)-Co(2)-N(3)	170.82(12)
O(4)-Co(2)-N(3)	84.87(11)
N(4)-Co(2)-N(3)	77.36(11)
N(1)-Co(2)-O(3)	87.62(14)
O(4)-Co(2)-O(3)	172.13(13)
N(4)-Co(2)-O(3)	84.06(14)
N(3)-Co(2)-O(3)	87.29(13)
N(1)-Co(2)-N(2)	77.09(11)
O(4)-Co(2)-N(2)	89.64(11)
N(4)-Co(2)-N(2)	171.07(11)
N(3)-Co(2)-N(2)	110.77(10)
O(3)-Co(2)-N(2)	92.45(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x,-y,-z

Table S6. Crystal data and structure refinement for $[L^{Ph}Co_2][BF_4]_2$.

Empirical formula	C44 H36 B4 Co2 F12 N14 O4	
Formula weight	1213.97	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 17.2357(12) Å	α= 90°.
	b = 24.1048(17) Å	β= 97.8100(10)°.
	c = 13.4470(10) Å	γ = 90°.
Volume	5534.9(7) Å^3	
Z	4	
Density (calculated)	1.457 Mg/m^3	
Absorption coefficient	0.694 mm^{-1}	
F(000)	2448	
Crystal size	0.15 x 0.15 x 0.15 mm^3	
Theta range for data collection	1.19 to 28.28°.	
Index ranges	-22<=h<=22, -32<=k<=32, -17<=l<=17	
Reflections collected	116404	
Independent reflections	13710 [R(int) = 0.0541]	
Completeness to theta = 28.28°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.95 and 0.9	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13710 / 0 / 790	
Goodness-of-fit on F^2	1.165	
Final R indices [I>2sigma(I)]	R1 = 0.0503, wR2 = 0.1292	
R indices (all data)	R1 = 0.0692, wR2 = 0.1425	
Largest diff. peak and hole	0.908 and -1.141 e.Å^{-3}	

Table S7. Selected bond lengths [Å] and angles [°] for $[L^{Ph}Co_2][BF_4]_2$.

Co(1)-N(2)	1.916(2)

Co(1)-N(3)	1.929(2)
Co(1)-N(4)	1.981(2)
Co(1)-N(1)	1.984(2)
Co(1)-N(12)	2.137(2)
Co(1)-N(11)	2.182(2)
Co(2)-N(8)	1.910(2)
Co(2)-N(7)	1.923(2)
Co(2)-N(5)	1.974(2)
Co(2)-N(6)	1.984(2)
Co(2)-N(10)	2.137(3)
Co(2)-N(9)	2.165(3)
N(2)-Co(1)-N(3)	93.51(9)
N(2)-Co(1)-N(4)	174.05(9)
N(3)-Co(1)-N(4)	81.25(9)
N(2)-Co(1)-N(1)	80.99(9)
N(3)-Co(1)-N(1)	174.41(9)
N(4)-Co(1)-N(1)	104.20(8)
N(2)-Co(1)-N(12)	91.98(9)
N(3)-Co(1)-N(12)	96.04(9)
N(4)-Co(1)-N(12)	91.36(9)
N(1)-Co(1)-N(12)	85.19(9)
N(2)-Co(1)-N(11)	87.41(9)
N(3)-Co(1)-N(11)	89.31(9)
N(4)-Co(1)-N(11)	89.72(8)
N(1)-Co(1)-N(11)	89.45(8)
N(12)-Co(1)-N(11)	174.64(9)
N(8)-Co(2)-N(7)	93.30(10)
N(8)-Co(2)-N(5)	81.46(9)
N(7)-Co(2)-N(5)	174.75(9)
N(8)-Co(2)-N(6)	174.74(9)
N(7)-Co(2)-N(6)	81.54(9)
N(5)-Co(2)-N(6)	103.71(9)
N(8)-Co(2)-N(10)	90.47(10)
N(7)-Co(2)-N(10)	91.25(10)
N(5)-Co(2)-N(10)	88.74(9)

N(6)-Co(2)-N(10)	88.64(9)
N(8)-Co(2)-N(9)	90.83(10)
N(7)-Co(2)-N(9)	90.69(10)
N(5)-Co(2)-N(9)	89.45(9)
N(6)-Co(2)-N(9)	90.25(9)
N(10)-Co(2)-N(9)	177.60(9)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z #2 -x+1,-y+1,-z+1

Table S8. Crystal data and structure refinement for [$L^{Me}Co_2Br_4$].

Empirical formula	C28 H46 B2 Br4 Co2 F4 N12 O8	
Formula weight	1213.89	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.9295(7) Å	α= 110.2380(10)°.
	b = 11.0421(7) Å	β= 99.6700(10)°.
	c = 11.0924(7) Å	γ = 102.1900(10)°.
Volume	1076.18(12) Å^3	
Z	1	
Density (calculated)	1.873 Mg/m^3	
Absorption coefficient	4.561 mm^{-1}	
F(000)	602	
Crystal size	0.2 x 0.2 x 0.1 mm^3	
Theta range for data collection	2.03 to 30.61°.	
Index ranges	-13<=h<=14, -15<=k<=15, -15<=l<=15	
Reflections collected	19848	
Independent reflections	6407 [R(int) = 0.0403]	
Completeness to theta = 30.61°	96.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.65 and 0.42	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6407 / 0 / 277	
Goodness-of-fit on F^2	1.033	

Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.0928
R indices (all data)	R1 = 0.0572, wR2 = 0.1026
Largest diff. peak and hole	0.981 and -0.736 e.Å^{-3}

Table S9. Selected bond lengths [Å] and angles [°] for [L^{Me}Co$_2$Br$_4$].

Co(1)-N(2)	1.891(2)
Co(1)-N(4)	1.903(2)
Co(1)-N(1)	1.964(2)
Co(1)-N(3)	1.972(2)
Co(1)-Br(2)	2.3677(5)
Co(1)-Br(1)	2.3706(5)
N(2)-Co(1)-N(4)	93.81(10)
N(2)-Co(1)-N(1)	81.68(10)
N(4)-Co(1)-N(1)	175.40(10)
N(2)-Co(1)-N(3)	175.31(10)
N(4)-Co(1)-N(3)	82.14(10)
N(1)-Co(1)-N(3)	102.41(10)
N(2)-Co(1)-Br(2)	85.97(8)
N(4)-Co(1)-Br(2)	89.42(8)
N(1)-Co(1)-Br(2)	91.14(7)
N(3)-Co(1)-Br(2)	91.60(7)
N(2)-Co(1)-Br(1)	92.95(8)
N(4)-Co(1)-Br(1)	89.78(8)
N(1)-Co(1)-Br(1)	89.58(7)
N(3)-Co(1)-Br(1)	89.41(7)
Br(2)-Co(1)-Br(1)	178.61(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z

Table S10. Crystal data and structure refinement for [L^{Me}Co^{I}Co^{II}][ClO$_4$].

Empirical formula	C22 H25 B2 Cl Co2 F4 N11 O8
Formula weight	822.46
Temperature	296(2) K

Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 20.2112(12) Å	α= 90°.
	b = 13.9739(8) Å	β= 120.5490(10)°.
	c = 12.7646(7) Å	γ = 90°.
Volume	3104.7(3) Å^3	
Z	4	
Density (calculated)	1.760 Mg/m^3	
Absorption coefficient	1.245 mm^{-1}	
F(000)	1660	
Crystal size	0.25 x 0.20 x 0.15 mm^3	
Theta range for data collection	1.87 to 30.51°.	
Index ranges	-28<=h<=28, -19<=k<=19, -18<=l<=18	
Reflections collected	35757	
Independent reflections	4730 [R(int) = 0.0314]	
Completeness to theta = 30.51°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8353 and 0.7461	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4730 / 0 / 258	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0349, wR2 = 0.0893	
R indices (all data)	R1 = 0.0392, wR2 = 0.0933	
Largest diff. peak and hole	0.699 and -0.783 e.Å^{-3}	

Table S11. Selected bond lengths [Å] and angles [°] for $[L^{Me}Co^{I}Co^{II}][ClO_4]$.

Co(1)-N(3)	1.8976(13)
Co(1)-N(4)	1.8988(13)
Co(1)-N(1)	1.9329(13)
Co(1)-N(2)	1.9423(12)
Co(1)-N(5)	2.1023(13)
Co(1)-N(6)	2.363(3)
N(3)-Co(1)-N(4)	92.18(6)

N(3)-Co(1)-N(1)	171.86(5)
N(4)-Co(1)-N(1)	81.95(6)
N(3)-Co(1)-N(2)	81.88(5)
N(4)-Co(1)-N(2)	171.30(5)
N(1)-Co(1)-N(2)	103.28(5)
N(3)-Co(1)-N(5)	97.18(5)
N(4)-Co(1)-N(5)	96.98(5)
N(1)-Co(1)-N(5)	89.17(5)
N(2)-Co(1)-N(5)	90.11(5)
N(3)-Co(1)-N(6)	90.89(7)
N(4)-Co(1)-N(6)	85.49(8)
N(1)-Co(1)-N(6)	83.06(7)
N(2)-Co(1)-N(6)	88.22(7)
N(5)-Co(1)-N(6)	171.44(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+3/2,-z+2   #2 -x,y,-z+3/2   #3 -x+1,y,-z+5/2

Table S12. Crystal data and structure refinement for $[L^{Me}Co^{II}Co^{III}][ClO_4]_3$.

Empirical formula	C20 H28 B2 Cl2 Co2 F4 N10 O8	
Formula weight	822.90	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 36.625(3) Å	α= 90°.
	b = 10.9319(9) Å	β= 94.1350(10)°.
	c = 20.0900(16) Å	γ = 90°.
Volume	8022.6(11) $Å^3$	
Z	10	
Density (calculated)	1.703 Mg/m^3	
Absorption coefficient	1.16 mm^{-1}	
F(000)	4160	
Crystal size	0.2 x 0.2 x 0.1 mm^3	
Theta range for data collection	1.11 to 28.36°.	
Index ranges	-48<=h<=48, -14<=k<=14, -26<=l<=26	

Reflections collected	72610
Independent reflections	9997 [R(int) = 0.0682]
Completeness to theta = 28.36°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.83 and 0.8
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9997 / 0 / 600
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0662, wR2 = 0.1835
R indices (all data)	R1 = 0.1017, wR2 = 0.2129
Largest diff. peak and hole	1.596 and -1.286 e.Å^{-3}

Table S13. Selected bond lengths [Å] and angles [°] for $[L^{Me}Co^{II}Co^{III}][ClO_4]_3$.

Co(1)-N(1)	1.908(3)
Co(1)-N(8)	1.916(4)
Co(1)-N(7)	1.970(3)
Co(1)-N(2)	1.971(3)
Co(1)-N(9)	2.181(4)
Co(1)-N(12)	2.210(4)
Co(2)-N(4)	1.915(4)
Co(2)-N(5)	1.924(4)
Co(2)-N(6)	1.972(4)
Co(2)-N(3)	1.977(3)
Co(2)-N(11)	2.170(3)
Co(2)-N(10)	2.173(4)

N(1)-Co(1)-N(8)	94.05(16)
N(1)-Co(1)-N(7)	171.29(15)
N(8)-Co(1)-N(7)	81.00(16)
N(1)-Co(1)-N(2)	80.82(14)
N(8)-Co(1)-N(2)	174.39(15)
N(7)-Co(1)-N(2)	104.37(14)
N(1)-Co(1)-N(9)	86.62(15)
N(8)-Co(1)-N(9)	90.47(16)
N(7)-Co(1)-N(9)	86.25(14)

N(2)-Co(1)-N(9)	91.49(14)
N(1)-Co(1)-N(12)	92.61(14)
N(8)-Co(1)-N(12)	93.03(15)
N(7)-Co(1)-N(12)	94.80(14)
N(2)-Co(1)-N(12)	84.97(13)
N(9)-Co(1)-N(12)	176.46(14)
N(4)-Co(2)-N(5)	93.99(16)
N(4)-Co(2)-N(6)	174.28(15)
N(5)-Co(2)-N(6)	81.12(15)
N(4)-Co(2)-N(3)	80.85(15)
N(5)-Co(2)-N(3)	173.62(15)
N(6)-Co(2)-N(3)	104.22(14)
N(4)-Co(2)-N(11)	90.68(14)
N(5)-Co(2)-N(11)	91.66(14)
N(6)-Co(2)-N(11)	86.53(13)
N(3)-Co(2)-N(11)	92.13(13)
N(4)-Co(2)-N(10)	93.52(15)
N(5)-Co(2)-N(10)	91.69(15)
N(6)-Co(2)-N(10)	89.60(15)
N(3)-Co(2)-N(10)	84.94(14)
N(11)-Co(2)-N(10)	174.43(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2 #2 -x+1/2,-y+3/2,-z

Table S14. Crystal data and structure refinement for $[L^{Me}Zn_2][BF_4]_2$.

Empirical formula	C20 H21 B6 F12 N12 O4 Zn2	
Formula weight	917.09	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.0885(9) Å	α= 90°.
	b = 12.2379(10) Å	β= 103.5470(10)°.
	c = 22.2619(18) Å	γ = 90°.
Volume	3201.7(4) $Å^3$	

Z	4
Density (calculated)	1.903 Mg/m^3
Absorption coefficient	1.622 mm^{-1}
F(000)	1820
Crystal size	0.2 x 0.2 x 0.2 mm^3
Theta range for data collection	1.73 to 29.57°.
Index ranges	-16<=h<=16, -16<=k<=16, -30<=l<=30
Reflections collected	77302
Independent reflections	8967 [R(int) = 0.0435]
Completeness to theta = 29.57°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.73 and 0.725
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8967 / 1 / 479
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0415, wR2 = 0.1099
R indices (all data)	R1 = 0.0550, wR2 = 0.1209
Largest diff. peak and hole	1.113 and -0.617 e.Å^{-3}

Table S15. Selected bond lengths [Å] and angles [°] for **[L^{Me}Zn$_2$][BF$_4$]$_2$**.

Zn(1)-F(6)	1.944(2)
Zn(1)-N(1)	2.069(2)
Zn(1)-N(8)	2.072(2)
Zn(1)-N(2)	2.131(2)
Zn(1)-N(7)	2.150(2)
Zn(2)-F(8)	1.935(2)
Zn(2)-N(5)	2.080(2)
Zn(2)-N(4)	2.103(2)
Zn(2)-N(3)	2.137(2)
Zn(2)-N(6)	2.151(2)

F(6)-Zn(1)-N(1)	126.70(9)
F(6)-Zn(1)-N(8)	115.57(8)
N(1)-Zn(1)-N(8)	87.87(9)
F(6)-Zn(1)-N(2)	105.73(8)

N(1)-Zn(1)-N(2)	75.69(9)
N(8)-Zn(1)-N(2)	137.23(9)
F(6)-Zn(1)-N(7)	95.31(8)
N(1)-Zn(1)-N(7)	137.85(9)
N(8)-Zn(1)-N(7)	75.04(8)
N(2)-Zn(1)-N(7)	91.09(8)
F(8)-Zn(2)-N(5)	120.55(9)
F(8)-Zn(2)-N(4)	121.46(8)
N(5)-Zn(2)-N(4)	84.69(9)
F(8)-Zn(2)-N(3)	104.49(8)
N(5)-Zn(2)-N(3)	134.75(9)
N(4)-Zn(2)-N(3)	74.89(8)
F(8)-Zn(2)-N(6)	105.73(8)
N(5)-Zn(2)-N(6)	75.01(8)
N(4)-Zn(2)-N(6)	132.54(9)
N(3)-Zn(2)-N(6)	89.70(8)

Table S16. Crystal data and structure refinement for $[L^{H*}Co_2][ClO_4]_2$.

Empirical formula	C24 H30 Cl3 Co2 N11 O10	
Formula weight	856.80	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.599(2) Å	α= 74.162(3)°.
	b = 11.925(2) Å	β= 82.285(3)°.
	c = 12.693(2) Å	γ = 73.895(2)°.
Volume	1619.5(5) Å^3	
Z	2	
Density (calculated)	1.757 Mg/m^3	
Absorption coefficient	1.345 mm^{-1}	
F(000)	872	
Crystal size	0.45 x 0.25 x 0.10 mm^3	
Theta range for data collection	1.67 to 29.07°.	
Index ranges	-15<=h<=15, -16<=k<=16, -17<=l<=17	

Reflections collected	32839
Independent reflections	8592 [R(int) = 0.0774]
Completeness to theta = 29.07°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8773 and 0.5829
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8592 / 0 / 373
Goodness-of-fit on F^2	1.085
Final R indices [I>2sigma(I)]	R1 = 0.0726, wR2 = 0.2102
R indices (all data)	R1 = 0.0943, wR2 = 0.2321
Largest diff. peak and hole	1.157 and -3.010 e.Å^{-3}

Table S17. Selected bond lengths [Å] and angles [°] for $[L^{H*}Co_2][ClO_4]_2$.

Co(1)-N(8)	1.899(4)
Co(1)-N(7)	1.907(4)
Co(1)-N(4)	1.914(4)
Co(1)-N(3)	1.929(3)
Co(1)-N(10)	2.007(3)
Co(2)-N(5)	1.901(4)
Co(2)-N(2)	1.906(4)
Co(2)-N(1)	1.918(4)
Co(2)-N(6)	1.927(4)
Co(2)-N(9)	1.985(4)
N(8)-Co(1)-N(7)	91.30(16)
N(8)-Co(1)-N(4)	167.91(15)
N(7)-Co(1)-N(4)	82.72(15)
N(8)-Co(1)-N(3)	82.34(16)
N(7)-Co(1)-N(3)	155.01(14)
N(4)-Co(1)-N(3)	98.68(15)
N(8)-Co(1)-N(10)	93.05(15)
N(7)-Co(1)-N(10)	101.70(15)
N(4)-Co(1)-N(10)	98.44(14)
N(3)-Co(1)-N(10)	102.75(14)
N(5)-Co(2)-N(2)	91.41(17)

N(5)-Co(2)-N(1)	82.59(16)
N(2)-Co(2)-N(1)	166.55(15)
N(5)-Co(2)-N(6)	158.71(15)
N(2)-Co(2)-N(6)	82.31(15)
N(1)-Co(2)-N(6)	98.97(15)
N(5)-Co(2)-N(9)	99.53(16)
N(2)-Co(2)-N(9)	95.22(16)
N(1)-Co(2)-N(9)	97.63(15)
N(6)-Co(2)-N(9)	101.28(15)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1

Table S18. Crystal data and structure refinement for $[L^{H*}Co_2][ClO_4]$.

Empirical formula	C24 H29 Cl3 Co2 N11 O12	
Formula weight	887.79	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.556(3) Å	α= 90°.
	b = 29.721(8) Å	β= 118.96°.
	c = 11.189(3) Å	γ = 90°.
Volume	3362.4(16) Å^3	
Z	4	
Density (calculated)	1.754 Mg/m^3	
Absorption coefficient	1.303 mm^{-1}	
F(000)	1804	
Crystal size	0.50 x 0.20 x 0.20 mm^3	
Theta range for data collection	1.37 to 24.71°.	
Index ranges	-13<=h<=13, -34<=k<=34, -13<=l<=13	
Reflections collected	53463	
Independent reflections	5741 [R(int) = 0.0744]	
Completeness to theta = 24.71°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7806 and 0.5619	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5741 / 0 / 494
Goodness-of-fit on F^2	1.007
Final R indices [I>2sigma(I)]	R1 = 0.0479, wR2 = 0.1271
R indices (all data)	R1 = 0.0647, wR2 = 0.1352
Largest diff. peak and hole	2.677 and -1.935 e.Å^{-3}

Table S19. Selected bond lengths [Å] and angles [°] for $[L^{H*}Co_2][ClO_4]$.

Co(1)-N(3)	1.924(4)
Co(1)-N(10)	1.926(4)
Co(1)-N(4)	1.941(4)
Co(1)-N(2)	1.957(4)
Co(1)-N(5)	1.958(4)
Co(1)-O(9)	2.352(17)
Co(2)-N(7)	1.905(4)
Co(2)-N(8)	1.910(4)
Co(2)-N(1)	1.927(4)
Co(2)-N(6)	1.940(4)
Co(2)-N(9)	1.968(4)
N(3)-Co(1)-N(10)	91.51(16)
N(3)-Co(1)-N(4)	92.33(16)
N(10)-Co(1)-N(4)	94.92(15)
N(3)-Co(1)-N(2)	83.33(15)
N(10)-Co(1)-N(2)	96.21(15)
N(4)-Co(1)-N(2)	168.15(15)
N(3)-Co(1)-N(5)	174.57(15)
N(10)-Co(1)-N(5)	92.37(15)
N(4)-Co(1)-N(5)	83.55(16)
N(2)-Co(1)-N(5)	100.02(15)
N(3)-Co(1)-O(9)	90.8(4)
N(10)-Co(1)-O(9)	173.7(4)
N(4)-Co(1)-O(9)	79.1(3)
N(2)-Co(1)-O(9)	89.9(3)
N(5)-Co(1)-O(9)	85.0(4)

N(7)-Co(2)-N(8)	91.57(18)
N(7)-Co(2)-N(1)	168.18(16)
N(8)-Co(2)-N(1)	82.63(16)
N(7)-Co(2)-N(6)	82.19(17)
N(8)-Co(2)-N(6)	157.96(15)
N(1)-Co(2)-N(6)	99.37(15)
N(7)-Co(2)-N(9)	96.23(16)
N(8)-Co(2)-N(9)	102.54(15)
N(1)-Co(2)-N(9)	95.09(15)
N(6)-Co(2)-N(9)	99.16(14)

Symmetry transformations used to generate equivalent atoms: