Trigonal Mn_3 and Co_3 Complexes Supported by Weak-Field Ligands: A Structural, Spectroscopic, Magnetic and Computational Investigation into the Correlation Between Molecular and Electronic Structure.

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General Considerations. All manipulations of metal complexes were carried out in the absence of water and dioxygen using standard Schlenk techniques, or in an MBraun inert atmosphere drybox under a dinitrogen atmosphere. All glassware was oven dried for a minimum of 8 h and cooled in an evacuated antechamber prior to use in the drybox. Diethyl ether, tetrahydrofuran, and acetonitrile were dried and deoxygenated on a Glass Contour System (SG Water USA, Nashua, NH) and stored over 4 Å molecular sieves (Strem) prior to use. Anhydrous 1,4-dioxane was purchase from Aldrich, degassed if necessary, and stored over 4 Å sieves prior to use. Acetontrile-d_3 and Benzene-d_6, were purchased from Cambridge Isotope Labs and were degassed and stored over 4 Å molecular sieves prior to use. $Mn_2(N(SiMe_3)_2)_4$,[S1] $Co_2(N(SiMe_3)_2)_4$,[S1] $^{H}LH_6$,[S2] $^{Ph}LH_6$,[S3] and 1,3,5-C_6H_9(NHPh-*o*-NH_2)$_3$ ($^{H,Cy}LH_6$)[S4] were prepared according to literature procedures. Celite® 545 (J. T. Baker) was dried in a Schlenk flask for 24 h under dynamic vacuum while heating to at least 150 °C prior to use in a drybox.

Characterization and Physical Measurements. UV/Visible spectra were recorded on a Varian Cary 50 UV/Visible spectra using quartz cuvettes and a scan rate of 300 or 600 nm/min. Extinction coefficients were determined from a minimum of four concentrations per sample, and were calculated by a linear regression fit of the absorbance vs. concentration data. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Varian Mercury 400 MHz or Varian Unity/Inova 500 MHz spectrometers. Solution magnetic susceptibilities were determined by Evans's method[S5] using trifluoromethylbenzene as an internal reference. Perpendicular mode X-band EPR spectra were recorded on Bruker ElexSys E500 EPR (fitted with a quartz dewar for measurements at 77K). The EPR spectra were calibrated with diphenylpicrylhydrazyl, DPPH (g = 2.0037) and modeled with Easyspin for Matlab. IR (KBr, 4000–500 cm^{-1}) were recorded on a Varian 1000 FT-IR. Elemental Analyses were carried out by Complete Analysis Labarotories, Inc. (Parsippany, NJ).

Synthesis of $^{Mes}LH_6$. A preformed Pd catalyst solution was made by heating a mixture of tris-(dibenzylideneacetone)dipalladium(0) (0.14 g, 0.15 mmol, 2.2 mol% Pd) and BINAP (0.28 g, 0.45 mmol) in 40 mL toluene for 30 min followed by filtration to remove the trace Pd metal impurity. The red solution was added into a sealed bomb which was charged with ^{H}L (2.75 g, 7.0 mmol), 2-bromomesitylene (4.18 g, 21.0 mmol), sodium *tert*-butoxide (3.03 g, 31.5 mmol), and toluene (200 mL). The bomb was immersed in a 100 ^{o}C oil bath with stirring for 4 days. Solvent was completely removed under vacuum after the reaction cooled to room temperature. Residue was taken up in ether (60 mL) and filtered. The filtrate was washed with H_2O (2 x 50 mL) and brine (1 x 50 mL) and then dried over $MgSO_4$. Solvent was removed, yielding the crude product as a brown oil, which was purified further by flash chromatography on silica gel eluted with ethyl acetate/hexanes (9:1). Yield: 3.77 g (72%). ^{1}H NMR ($CDCl_3$, 500 MHz, δ, ppm): 6.87-6.83 (m, 12H, aromatic C-*H*), 6.66-6.63 (m, 3H, aromatic C-*H*), 6.30 (d, 3H, aromatic C-*H*, J = 8.0 Hz), 4.71 (s, 3H, Ar-N*H*-Ar), 4.25 (t, 3H, Ar-N*H*-CH_2, J = 6.5 Hz), 3.47 (d, 6H, -NH-CH_2-C, J = 6.5 Hz), 2.31 (s, 9H, *p*-Ar-CH_3), 2.00 (s, 18H, *o*-Ar-CH_3), 1.38 (s, 3H, -C-CH_3); ^{13}C NMR ($CDCl_3$, 500 MHz, δ, ppm): 138.9, 137.2, 134.5,133.5,132.7,129.2, 121.1, 119.0, 115.7,112.1, 51.0 39.1, 21.4, 20.8, 17.9; HRMS (ESI$^+$) *m/z* calcd $C_{50}H_{61}N_6^+$[M+H]$^+$: 745.49522, found 745.49460.

Synthesis of (^{H}L)Mn$_3$(Py)$_3$ (1). Solid $Mn_2(N(SiMe_3)_2)_2$ (298 mg, 0.397 mmol) was dissolved in THF (4 mL) and cooled to −35 ^{o}C. ^{H}L ligand (100 mg, 0.256 mmol) was dissolved in THF (4 mL) and cooled to −35 ^{o}C and then added to the solution of $Mn_2(N(SiMe_3)_2)_2$. The solution was allowed to warm to room temperature and color changed from clear to dark red orange. After 7 hr the volatiles were removed *in vacuo*. The resulting light yellow solid was extensively washed with hexanes (5 x 10 mL) and then dried *in vacuo*. The solid was redissolved in THF and excess pyridine (three drops) was added. The solution color changed from red orange to dark red. The solution was concentrated in THF/hexanes, filtered through a fritted glass funnel to remove any precipitate, and crystals were grown at −35 ^{o}C. Isolated yield (crystals): 0.131 g (65%). X-ray quality crystals of **1** were grown in a concentrated solution of THF/hexanes at −35 ^{o}C. ^{1}H NMR (C_6D_6, 400 MHz, δ, ppm): 26.0 (brs), 14.99 (brs), 3.11 (brs), 0.19 (brs), −3.06 (brs), −6.22 (brs). Anal. Calcd for $C_{38}H_{39}Mn_3N_9$ (**1**): C 57.65, H 5.60, N 15.92. Found: C 57.61, H 5.65, N 15.88.

Synthesis of (^{Ph}L)Mn$_3$(Py) (2). Solid $Mn_2(N(SiMe_3)_2)_2$ (282 mg, 0.375 mmol) was dissolved in THF (5 mL) and cooled to −35 ^{o}C. ^{Ph}L ligand (150 mg, 0.242 mmol) was dissolved in THF (4 mL) and cooled to −35 ^{o}C and then added to the solution of $Mn_2(N(SiMe_3)_2)_2$. The solution was allowed to warm to room temperature and color changed from light yellow to dark red. After 7 hr the volatiles were removed *in vacuo*. The resulting yellow solid was extensively washed with hexanes (5 x 10 mL) and then dried *in vacuo*. The solid was redissolved in THF and excess pyridine (three drops) was added. The solution was concentrated in THF/hexanes, filtered through a fritted glass funnel to remove any precipitate, and crystals were grown at −35 ^{o}C. Isolated yield (crystals): 0.164 g (67%). X-ray quality crystals of **2** were grown in a concentrated solution of THF/hexanes at −35 ^{o}C. ^{1}H NMR (C_6D_6, 400 MHz, δ, ppm): 14.51 (brs), 11.99 (brs), 5.05 (brs), 3.32 (brs), −1.66 (brs), −6.81 (brs). Anal. Calcd for $C_{56}H_{51}Mn_3N_9$ (**x**): C 66.27, H 5.07, N 12.42. Found: C 66.18, H 5.13, N 12.49.

Synthesis of (^{Mes}L)Mn$_3$(Py)$_3$ (3). Solid $Mn_2(N(SiMe_3)_2)_2$ (157 mg, 0.209 mmol) was dissolved in THF (5 mL) and cooled to −35 ^{o}C. ^{Mes}L ligand (100 mg, 0.134 mmol) was dissolved in THF (4 mL) and cooled to −35 ^{o}C and then added to the solution of $Mn_2(N(SiMe_3)_2)_2$. The solution was transferred into a bomb and heated at 75 ^{o}C overnight. After 7 hr the volatiles were removed *in vacuo*. The resulting orange solid was extensively washed with hexanes (5 x 10 mL) and then dried *in vacuo*. The solid was redissolved in THF and excess pyridine (three drops) was added. The solution was concentrated in THF/hexanes, filtered through a fritted glass funnel to remove any precipitate, and crystals were grown at −35 ^{o}C. Isolated yield (crystals): 0.106 g (69%). X-ray quality crystals of **3** were grown in a concentrated solution of THF/hexanes at −35 ^{o}C. ^{1}H NMR (C_6D_6, 400 MHz, δ, ppm): 15.91 (brs), 14.69 (brs), 11.18 (brs), 5.6 (brs), –0.49 (brs), –15.3 (brs). Anal. Calcd for $C_{65}H_{51}Mn_3N_9$ (**3**): C 68.41, H 6.09, N 11.05. Found: C 68.29, H 5.99, N 10.97.

Synthesis of (^{H}L)$Co_3(PMe_3)_3$ (4a). A blue solution of $Co(N(SiMe_3)_2)_2$ (311 mg, 0.794 mmol) in 7 mL of THF was cooled to –35 °C, to which 0.5 mL of a 1.0 M trimethylphosphine solution in THF was slowly added. The mixture stirred for 5 minutes and was then re-cooled to –35 °C. The ^{H}L ligand (0.100 g, 0.256 mmol) was dissolved in THF (7 mL) and cooled to –35 °C. Upon addition of ^{H}L to the cold stirring cobalt solution the color changed from blue to brown. The mixture warmed and stirred at room temperature for 8 h. Volatiles were removed *in vacuo* to obtain a brown solid. The residue was washed with hexamethyldisiloxane (3 x 20 mL), then dissolved in benzene and filtered through a fritted glass funnel packed with Celite. The Celite was washed with more benzene (15 mL). The resulting filtrate was evaporated to dryness *in vacuo*, yielding the product as a dark brown solid. Isolated yield: 0.240 mg (80%). X-ray quality crystals of **4a** were grown by slow evaporation of benzene at room temperature. ^{1}H NMR (C_6D_6, 500 MHz, δ, ppm) 74.0, 5.94, 5.17, 4.30, 1.25, 0.04, -1.02, -17.32, -42, -51, -53, -60.06. μ_{eff} = 1.79(4) μ_B (25 °C, Evans' Method). UV–vis in THF, λ_{max} (nm) (ε, $M^{-1}cm^{-1}$): 215 (s), 295 (s), 355 (42400). Anal. Calcd for $C_{32}H_{51}Co_3N_6P_3$ (**4a**): C 48.68, H 6.51, N 10.64. Found: C 48.48, H 6.36 N 10.57.

Synthesis of (^{H}L)$Co_3(PMe_2Ph)_3$ (4b). A blue solution of $Co(N(SiMe_3)_2)_2$ (450 mg, 1.18 mmol) in 7 mL of THF was cooled to –35 °C, to which excess (0.1 mL) of dimethylphenylphosphine was slowly added. The mixture stirred for 5 minutes and was then re-cooled to –35 °C. The ^{H}L ligand (0.151 g, 0.127 mmol) was dissolved in THF (7 mL) and cooled to –35 °C. Upon addition of ^{H}L to the cold stirring cobalt solution the color changed from blue to brown. The mixture was stirred at room temperature for 8 h. Volatiles were removed *in vacuo*. The residue was washed with hexamethyldisiloxane (3 x 20 mL), then dissolved in benzene and filtered through a fritted glass funnel packed with Celite. The Celite was washed with benzene (15 mL). The resulting filtrate was evaporated to dryness *in vacuo*, yielding the product as a dark brown solid. Isolated yield: 0.274 mg (73%). X-ray quality crystals of **4b** were grown by slow evaporation of benzene at room temperature. ^{1}H NMR (C_6D_6, 400 MHz, δ, ppm) 8.26, 7.76, 6.32, -1.66, -1.93, -3.13, -9.74. μ_{eff} = 1.91(5) μ_B (25 °C, Evans' Method). Anal. Calcd for $C_{47}H_{57}Co_3N_6P_3$ (**4b**): C 57.85, H 5.89, N 8.61. Found: C 56.94, H 5.94 N 8.54.

Synthesis of (^{H,Cy}L)$Co_3(PMe_3)_3$ (5a). A blue solution of $Co(N(SiMe_3)_2)_2$ (438 mg, 1.16 mmol) in 7 mL of THF was cooled to –35 °C, to which 0.5 mL of a 1.0 M trimethylphosphine solution in THF was slowly added. The mixture stirred for 5 minutes and was then re-cooled to –35 °C. The $^{H}L_{Cy}$ ligand (0.150 g, 0.373 mmol) was dissolved in THF (7 mL) and cooled to –35 °C. Upon addition of $^{H}L_{Cy}$ to the cold stirring cobalt solution the color changed from blue to brown. The mixture was stirred at room temperature for 8 h. Volatiles were removed *in vacuo*. The residue was washed with hexamethyldisiloxane (3 x 20 mL), then dissolved in benzene and filtered through a fritted glass funnel packed with Celite. The Celite was washed with benzene (15 mL). The resulting filtrate was evaporated to dryness *in vacuo*, yielding the product as a dark brown solid. Isolated yield: 0.208 mg (70%). X-ray quality crystals of **5a** were grown by slow evaporation of benzene at room temperature. ^{1}H NMR (C_6D_6, 500 MHz, δ, ppm) 44, 34, 17.3, 11.6, 10.1, 8.0, 7.6, 6.6, 5.2, 4.6, 3.3, 2.8, 2.3, 1.7, 1.3, 0.9, 0.4, -2.2, -4.2, -4.5, -47. UV–vis in THF, λ_{max} (nm) (ε, $M^{-1}cm^{-1}$): 215 (s), 300 (s), 360 (34200), 485 (s). μ_{eff} = 1.74(6) μ_B (25 ^{O}C, Evans' Method). Anal. Calcd for $C_{33}H_{54}Co_3N_6P_3$ (**5a**): C 49.26, H 6.76, N 10.45. Found: C 48.60, H 6.32, N 10.87.

Synthesis of (^{H,Cy}L)Co$_3$(PMe$_2$Ph)$_3$ (5b). *A* blue solution of Co(N(SiMe$_3$)$_2$)$_2$ (439 mg, 1.16 mmol) in 7 mL of THF was cooled to −35 ^{o}C, to which 0.10 mL of dimethylphenylphosphine solution in THF was slowly added. The mixture stirred for 5 minutes and was then re-cooled to −35 ^{o}C. The $^{H}L_{Cy}$ ligand (0.150 g, 0.373 mmol) was dissolved in THF (7 mL) and cooled to −35 ^{o}C. Upon addition of $^{H}L_{Cy}$ to the cold stirring cobalt solution the color changed from blue to brown. The mixture was stirred at room temperature for 8 h. Volatiles were removed *in vacuo*. The residue was washed with hexamethyldisiloxane (3 x 20 mL), then dissolved in benzene and filtered through a fritted glass funnel packed with Celite. The Celite was washed with benzene (15 mL). The resulting filtrate was evaporated to dryness *in vacuo*, yielding the product as a dark brown solid. Isolated yield: 0.281 mg (71%). X-ray quality crystals of **5b** were grown by slow evaporation of benzene at room temperature. ^{1}H NMR (C_6D_6, 400 MHz, δ, ppm) 8.0, 7.65, 6.96, 6.31, 4.26, 3.25, 1.10, 0.88, 0.55, -1.43, -15.48. μ_{eff} = 1.83(4) μ_B (25 ^{O}C, Evans' Method). Anal. Calcd for $C_{48}H_{60}Co_3N_6P_3$ (**5b**): C 58.18, H 6.10, N 8.48. Found: C 58.16, H 5.98, N 8.46.

Synthesis of (^{Ph}L)Co$_3$(PMe$_2$Ph)$_3$ (6). A blue solution of Co(N(SiMe$_3$)$_2$)$_2$ (95 mg, 0.250 mmol) in 7 mL of THF was cooled to −35 ^{o}C, to which 0.10 mL of dimethylphenylphosphine solution in THF was slowly added. The mixture stirred for 5 minutes and was then re-cooled to −35 ^{o}C. The ^{Ph}L ligand (0.50 g, 0.080 mmol) was dissolved in THF (7 mL) and cooled to −35 ^{o}C. Upon addition of ^{Ph}L to the cold stirring cobalt solution the color changed from blue to brown. The mixture was stirred at room temperature for 8 h. Volatiles were removed *in vacuo*. The residue was washed with hexamethyldisiloxane (3 x 20 mL), then dissolved in benzene and filtered through a fritted glass funnel packed with Celite. The Celite was washed with benzene (15 mL). The resulting filtrate was evaporated to dryness *in vacuo*, yielding the product as a dark green solid. The solid was dissolved in diethyl ether (~10 mL). The slow evaporation of the solution yielded dark green crystals after several days (71 mg, 73%). ^{1}H NMR (C_6D_6, 400 MHz, δ, ppm) 72.56, 14.12, 7.48, 7.16, 3.63, 3.42, 2.65, 1.64, 1.11, 0.02, -4.04. μ_{eff} = 1.95(3) μ_B (25 ^{O}C, Evans' Method). Anal. Calcd. for $C_{65}H_{72}N_6Co_3P_3$ (**6**): C 64.70, H 6.01, N 6.96. Found: C 64.74, H 6.06, N 6.88.

Synthesis of (^{Ph}L)Co$_3$(PMe$_2$Ph)$_2$ (7). A blue solution of Co(N(SiMe$_3$)$_2$)$_2$ (95 mg, 0.250 mmol) in 7 mL of THF was cooled to −35 ^{o}C, to which dimethylphenylphosphine (24 mg, 0.500 mmol) was slowly added dropwise. The mixture stirred for 5 minutes and was then re-cooled to –35 °C. The ^{Ph}L ligand (0.50 g, 0.080 mmol) was dissolved in THF (7 mL) and cooled to –35 °C. Upon addition of ^{Ph}L to the cold stirring cobalt solution the color changed from blue to brown. The mixture was stirred at room temperature for 8 h. Volatiles were removed *in vacuo*. The residue was washed with hexamethyldisiloxane (3 x 20 mL), then dissolved in thf (10 mL) and filtered through a fritted glass funnel packed with Celite. The Celite was washed with thf (5 mL). The resulting filtrate was evaporated to dryness *in vacuo*, yielding the product as a dark green solid (47 mg, 54%). X-ray quality crystals were obtained from a concentrated hexane solution over several days at room temperature. ^{1}H NMR (C_6D_6, 400 MHz, δ, ppm) 7.36, 3.63, 2.32, 1.27, 1.10. μ_{eff} = 2.02(6) μ_B (25 °C, Evans' Method). Anal. Calcd. for $C_{57}H_{61}N_6Co_3P_2$ (**7**): C 64.05, H 5.75, N 7.86. Found: C 63.89, H 5.59, N 7.72.

Synthesis of [(^{H}L)Co$_3$(PMe$_3$)$_3$][PF$_6$] (8a). A red-brown solution of **4a** (90 mg, 0.114 mmol) in THF (10 mL) was cooled to –35 °C, to which ferrocenium hexafluorophosphate (38 mg, 0.114 mmol) was added as a solid. Upon warming to room temperature the color changed slightly from brown to brown/red and stirred for 2 h. Volatiles were removed *in vacuo*. The residue was washed with hexanes (3 x 20 mL) to remove ferrocene, the brown solid was dissolved in THF and filtered through a fritted glass funnel packed with Celite. The Celite was washed with THF (10 mL). The resulting filtrate was evaporated to dryness *in vacuo*, yielding the product as a dark brown/red solid. Isolated yield: 73% (77 mg). Conversion of **4a** to **8a** was quantitative as assayed by ^{1}H NMR spectroscopy. X-ray quality crystals of **8a** were grown by slow evaporation of THF at room temperature. ^{1}H NMR (C_6D_6, 400 MHz, δ, ppm) 6.13 (m, 6H, Ar), 5.86 (d, $^3J_{H\text{-}H}$ = 5.7, 3H, Ar), 5.43 (d, $^3J_{H\text{-}H}$ = 5.7, 3H, Ar), 1.14 (s, 27H, $P(CH_3)_3$), -0.22(s, 3H, $CH_3C(CH_2)_3$), -0.28 (s, 6H, $CH_3(CCH_2)_3$). ^{13}C NMR (C_6D_6, δ, ppm): 121.6 (s, 3C, Ar), 119.8 (s, 3C, Ar), 113.0 (s, 3C, Ar), 108.6 (s, 3C, Ar), 68.2 (s, 3C, $CH_3C(CH_2)_3$), 54.3 (s, 1C, $CH_3C(CH_2)_3$), 30.2, (s, 3C, $CH_3C(CH_2)_3$), 15.4 (s, 9C, $P(CH_3)_3$). ^{19}F NMR (C_6D_6, 375.8 MHz, δ, ppm) -67.4 for PF_6. No ^{31}P NMR could be observed. (UV–vis in THF, λ_{max} (nm) (ε, $M^{-1}cm^{-1}$): 215 (s), 290 (s), 355 (m), 500 (32600). Anal. Calcd for $C_{32}H_{51}Co_3F_6N_6P_4$ (**8a**): C 41.10, H 5.50, N 8.99. Found: C 40.97, H 5.64 N 8.80.

Synthesis of [(^{H}L)Co$_3$(PMe$_2$Ph)$_3$][PF$_6$] (8b). A red-brown solution of **4b** (100 mg, 0.116 mmol) in THF (10 mL) was cooled to –35 °C, to which ferrocenium hexafluorophosphate (39 mg, 0.116 mmol) was added as a solid. Upon warming to room temperature the color changed slightly from brown to brown/red and stirred for 2 h. Volatiles were removed *in vacuo*. The residue was washed with hexanes (3 x 20 mL) to remove ferrocene, then the brown solid was dissolved in THF and filtered through a fritted glass funnel packed with Celite. The Celite was washed with THF (10 mL). The resulting filtrate was evaporated to dryness *in vacuo*, yielding the product as a dark brown/red solid. Isolated yield: 82% (108 mg). Conversion of **4b** to **8b** was quantitative as assayed by ^{1}H NMR spectroscopy. X-ray quality crystals of **8b** were grown by slow evaporation of THF at room temperature.

^{1}H NMR (CD_3CN, 500 MHz, δ, ppm) 7.27 (m, 12H, P(CH_3)$_2$*Ph*), 6.12 (m, 6H, Ar), 5.79 (d, $^3J_{H-H}$ = 6.8, 3H, Ar), 5.48 (d, $^3J_{H-H}$ = 6.8, 3H, Ar), 1.54 (s, 18H, P(CH_3)$_2$Ph), -0.15(s, 6H, $CH_3C(CH_2)_3$), -0.23 (s, 3H, $CH_3(CCH_2)_3$). ^{13}C NMR (CD_3CN, δ, ppm): 163.3 (s, 3C, C_{Ar}-N), 161.4 (s, 3C, C_{Ar}-N), 139.7 (s, 3C, P*Ph*Me_2), 139.3 (s, 3C, P*Ph*Me_2), 130.9 (s, 3C, P*Ph*Me_2), 129.7 (s, 3C, P*Ph*Me_2), 128.9 (s, 3C, P*Ph*Me_2), 121.8 (s, 3C, Ar), 120.6 (s, 3C, Ar), 113.7 (s, 3C, Ar), 110.7 (s, 3C, Ar), 53.55 (s, 3C, $CH_3C(CH_2)_3$), 38.5 (s, 1C, CH-$_3C(CH_2)_3$), 23.9 (s, 1C, $CH_3C(CH_2)_3$), 13.8 (s, 6C, PPh*Me_2*). ^{19}F NMR (CD_3CN, δ, ppm): -67.2 for PF_6. No ^{31}P NMR could be observed. Anal. Calcd for $C_{32}H_{51}Co_3F_6N_6P_4$ (**8b**): C 41.10, H 5.50, N 8.99. Found: C 40.97, H 5.64 N 8.80.

Synthesis of [(^{H,Cy}L)$Co_3(PMe_3)_3$][PF_6] (9a). A brown solution of **5a** (121 mg, 0.166 mmol) in THF (10 mL) was cooled to –35 °C, to which ferrocenium hexafluorophosphate (55 mg, 0.121 mmol) was added as a solid. Upon warming to room temperature the color changed slightly from brown to brown/red and stirred for 2 h. Volatiles were removed *in vacuo*. The residue was washed with hexanes (3 x 20 mL) to remove ferrocene, then the brown solid was dissolved in THF and filtered through a fritted glass funnel packed with Celite. The Celite was washed with THF (10 mL). The resulting filtrate was evaporated to dryness *in vacuo*, yielding the product as a dark brown/red solid. Isolated yield: 77% (121 mg). Conversion of **5a** to **9a** was quantitative as assayed by ^{1}H NMR spectroscopy. X-ray quality crystals of **9a** were grown by slow evaporation of THF at room temperature. ^{1}H NMR (CD_3CN, 400 MHz, δ, ppm): 6.08 (m, 6H, Ar), 5.79 (d, $^3J_{H-H}$ = 7, 3H, Ar), 5.47 (d, $^3J_{H-H}$ = 7, 3H, Ar), 1.42 (s, 3H, C_6H_9), 1.23 (s, 27H, P(CH_3)$_3$), 0.04 (d, $^3J_{H-H}$ = 12.4, 3H, C_6H_9), -0.54 (d, $^3J_{H-H}$ = 12.4, 3H, C_6H_9). ^{13}C NMR (CD_3CN, δ, ppm): 163.1 (s, 3C, C_{Ar}-N), 160.6 (s, 3C, C_{Ar}-N), 120.6 (s, 3C, Ar), 120.1 (s, 3C, C_{Ar}-N), 112.3 (s, 3C, C_{Ar}-N), 109.4 (s, 3C, C_{Ar}-N), 38.3 (s, 3C, C_6H_9), 33.6 (s, 3C, C_6H_9), 15.3 (s, 9C, P(CH_3)$_3$ ^{31}P NMR (CD_3CN, 161.8 MHz, δ, ppm) 14.7 (brs, 3P, *P*Me_2Ph), -147.4 (septet, $^1J_{P-F}$ = 704 Hz, 1P, *P*F_6). ^{19}F NMR (CD_3CN, 375.8 MHz, δ, ppm) -68.1 (d, $^1J_{F-P}$ = 704 Hz, 6F, P*F_6*). Anal. Calcd for $C_{33}H_{54}Co_3F_6N_6P_4$ (**9a**): C 41.74, H 5.73, N 8.85. Found: C 41.95, H 5.65 N 9.06.

Synthesis of (^{H,Cy}L)$Co_3(PMe_2Ph)_3PF_6$ (9b). A brown solution of **5b** (100 mg, 0.100 mmol) in THF (10 mL) was cooled to –35 °C, to which ferrocenium hexafluorophosphate (34 mg, 0.100 mmol) was added as a solid. Upon warming to room temperature the color changed slightly from brown to red-brown and stirred for 2 h. Volatiles were removed *in vacuo*. The residue was washed with hexanes (3 x 20 mL) to remove ferrocene, the solid was dissolved in THF and filtered through a fritted glass funnel packed with Celite. The Celite was washed with THF (10 mL). The resulting filtrate was evaporated to dryness *in vacuo*, yielding the product as a dark red-brown solid. Isolated yield: 85% (98 mg). Conversion of **5b** to **9b** was quantitative as assayed by ^{1}H NMR spectroscopy. X-ray quality crystals of **9b** were grown by slow evaporation of THF at room temperature. ^{1}H NMR (CD_3CN, 400 MHz, δ, ppm) 7.23 (brs, 12H, PMe_2*Ph*), 6.13 (m, 9H, Ar), 5.43 (s, 3H, Ar), 1.77 (brs, 3H, N*H*), 1.61 (brs, 18H, P*Me_2*Ph), 0.60 (m, 3H, *C_6H_9*), -0.10 (m, 3H, *C_6H_9*), -0.48 s, 3H, *C_6H_9*). ^{31}P NMR (CD_3CN, 161.8 MHz, δ, ppm) 7.54 (brs, 3P, *P*Me_2Ph), -143.5 (septet, $^1J_{P-F}$ = 706 Hz, 1P, *P*F_6). ^{19}F NMR (CD_3CN, 375.8 MHz, δ, ppm) -73.3 (d, $^1J_{F-P}$ = 706 Hz, 6F, P*F*$_6$). Anal. Calcd for $C_{48}H_{60}Co_3F_6N_6P_4$ (**9b**): C 50.76, H 5.32, N 7.39. Found: C 50.69, H 5.26, N 7.48.

Synthesis of [(^{Ph}L)Co$_3$(PMe$_2$Ph)$_3$][PF$_6$] (10). A brown solution of **6** (50 mg, 0.042 mmol) in THF (10 mL) was cooled to –35 °C, to which ferrocenium hexafluorophosphate (14 mg, 0.042 mmol) was added as a solid. Upon warming to room temperature the color changed slightly from brown to green and stirred for 2 h. Volatiles were removed *in vacuo*. The residue was washed with hexanes (3 x 20 mL) to remove ferrocene, the solid was dissolved in THF and filtered through a fritted glass funnel packed with Celite. The Celite was washed with THF (10 mL). The resulting filtrate was evaporated to dryness *in vacuo*, yielding the product as a dark green solid (41 mg, 0.030 mmol, 73%). Conversion of **6** to **10** was quantitative as assayed by ^{1}H NMR spectroscopy. X-ray quality crystals of **10** were grown by slow evaporation of THF at room temperature. ^{1}H NMR (CD$_3$CN, 500 MHz, δ, ppm) 7.42 (m, 15H, P(CH$_3$)$_2$*Ph*), 7.37 (m, 6H, Ar), 6.42 (m, 15H, Ar), 6.16 (d, $^3J_{H\text{-}H}$ = 6.8, 3H, Ar), 6.00 (d, $^3J_{H\text{-}H}$ = 6.8, 3H, Ar), 1.79 (s, 18H, P(C*H*$_3$)$_2$Ph), -0.35(s, 3H, CH$_3$C(C*H*$_2$)$_3$), -0.67(s, 3H, CH$_3$C(C*H*$_2$)$_3$), -2.038 (s, 3H, C*H*$_3$(CCH$_2$)$_3$). ^{13}C NMR (CD$_3$CN, δ, ppm): 131.9 (s, 3C, P*Ph*Me$_2$), 130.4 (s, 3C, Ar), 129.9(s, 3C, P*Ph*Me$_2$), 129.2 (s, 3C, P*Ph*Me$_2$), 128.8 (s, 3C, Ar), 128.1 (s, 3C, P*Ph*Me$_2$), 127.0 (s, 3C, Ar), 126.2 (s, 3C, Ar), 124.4 (s, 3C, P*Ph*Me$_2$), 123.5 (s, 3C, Ar), 120.9 (s, 3C, Ar), 119.4 (s, 3C, Ar), 115.6 (s, 3C, Ar), 111.5 (s, 3C, Ar), 52.1 (s, 3C, CH$_3$C(*C*H$_2$)$_3$), 49.2 (s, 1C, CH$_3$C(CH$_2$)$_3$), 23.9 (s, 1C, CH$_3$C(CH$_2$)$_3$), 13.6 (s, 6C, PPh*Me*$_2$). C_{Ar}-N are not observed.^{19}F NMR (CD$_3$CN, 375.8 MHz, δ, ppm) -73.4 (d, $^1J_{F\text{-}P}$ = 704 Hz, 6F, P*F*$_6$). Anal. Calcd. for $C_{65}H_{72}N_6Co_3P_4F_6$ (**10**): C 57.74, H 5.37, N 6.22. Found: C 57.65, H 5.26, N 6.18.

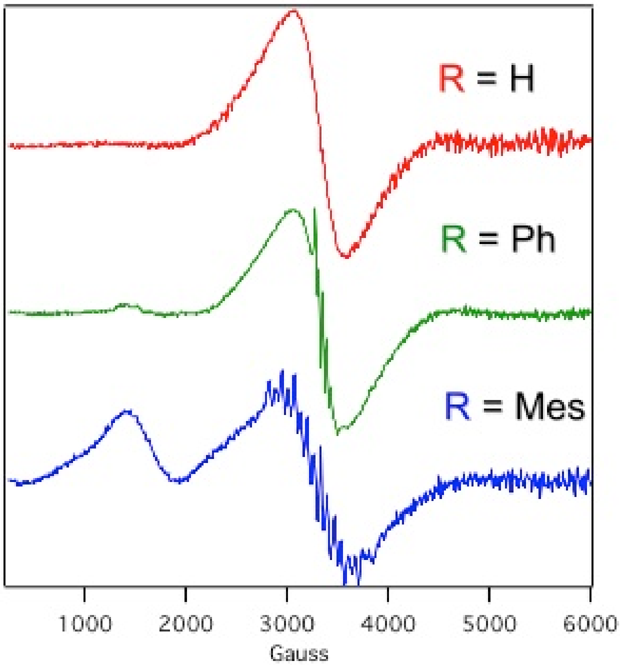


Figure S1. Perpendicular mode X-band solution EPR spectrum of **1** (red), **2** (green), and **3** (blue) at 77k in toluene solutions.

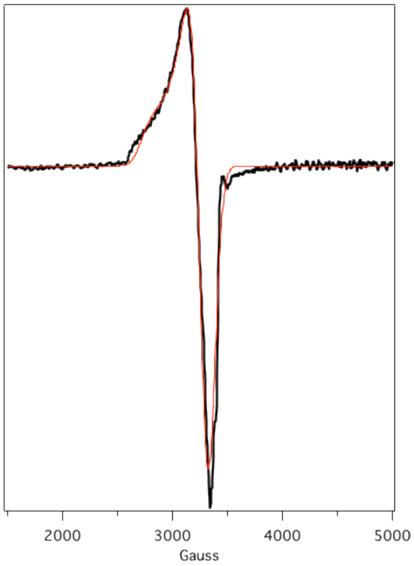


Figure S2. Perpendicular mode X-band EPR spectrum of **4b** (in black) in a toluene solution at 77K. Fit in red, with a g = 2.035126 and 2.282962 and A = 40.28234 and 164.6758.

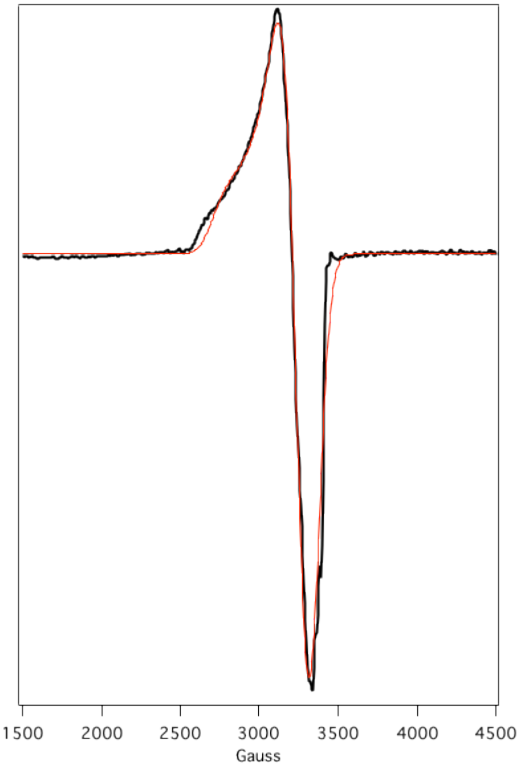


Figure S3. Perpendicular mode X-band EPR spectrum of **5b** (in black) in a toluene solution at 77K. Fit in red, with a g=2.0426 and 2.283147 and A = 45.99404, 172.0101.

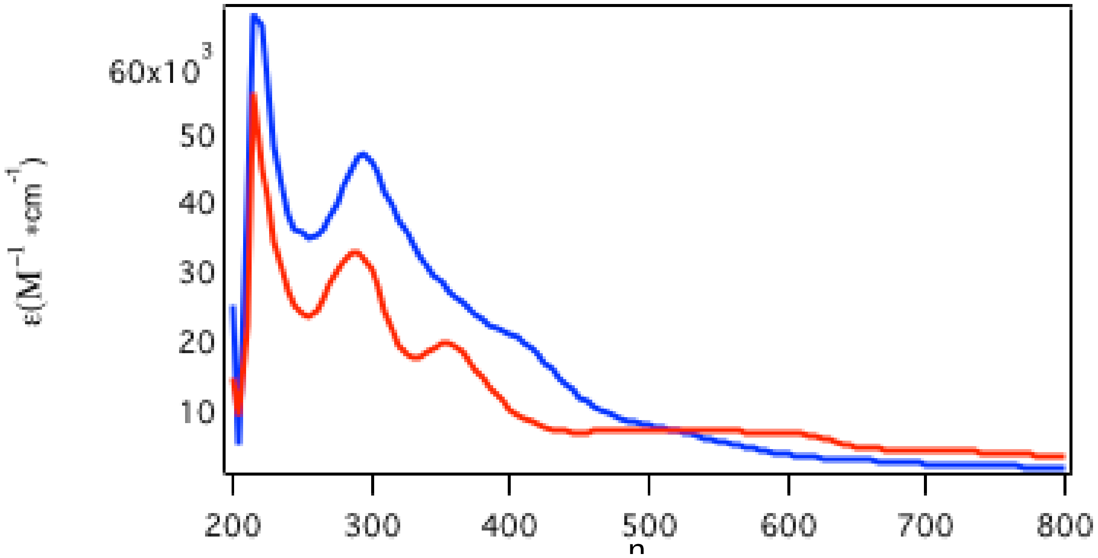


Figure S4. Uv-Vis spectrum of **4b** (blue) and **8b** (red).

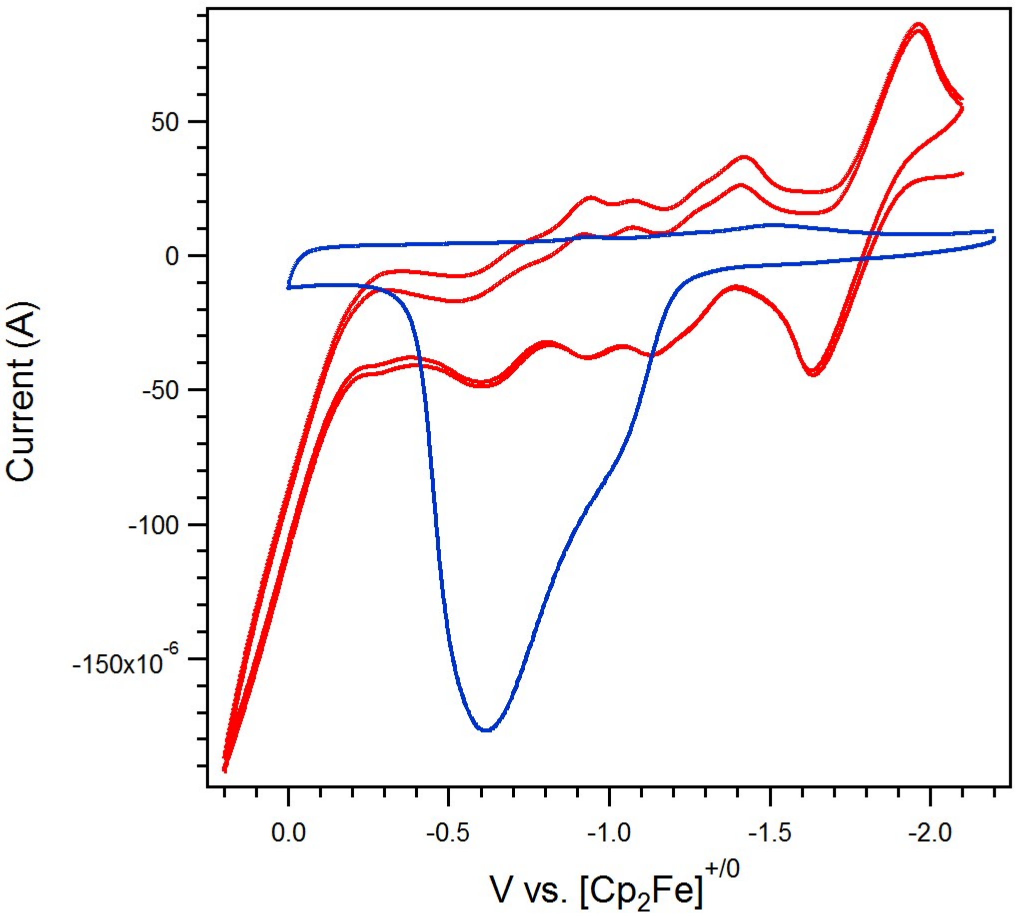


Figure S5. Cyclic voltammograms of **1** (blue) and **4a** (red).

X-Ray Diffraction Techniques. All structures were collected on a Bruker three-circle platform goniometer equipped with an Apex II CCD and an Oxford cryostream cooling device. Radiation was from a graphite fine focus sealed tube Mo Kα (0.71073 Å) source. Crystals were mounted on a cryoloop or glass fiber pin using Paratone-N oil. Structures were collected at 100 K. Data was collected as a series of φ and/or ω scans. Data was integrated using SAINT[S6] and scaled with either a numerical or multi-scan absorption correction using SADABS[S6]. The structures were solved by direct methods or Patterson maps using SHELXS-97[S7] and refined against F^2 on all data by full matrix least squares with SHELXL-97[S7]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were either located or placed at idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the atoms they are linked to (1.5 times for methyl groups). Further details on particular structures are noted below. Special refinement details are included in the combined CIF file.

$(^{H}L)Mn_3(Py)_3$ (1). The structure was solved in the orthorhombic space group P_{bca} with 16 molecules per unit cell and two in the asymmetric unit.

$(^{Ph}L)Mn_3(Py)_3$ (2). The structure was solved in the triclinic space group $P\bar{1}$ with two molecule per unit cell. The asymmetric unit contains one molecule as well as two disordered thf solvent molecules. Two of the bound pyridines are disordered as well.

$(^{Mes}L)Mn_3(Py)_3$ (3). The structure was solved in the monoclinic space group $P2(1)/n$ with four molecules in the unit cell. The asymmetric unit consists of one molecule, two thf molecules and a hexane molecule. Two of the mesityl moieties are disordered as well as all the solvent molecules.

$(^{H}L)Co_3(PMe_2Ph)_3$ (4b). The structure was solved in the triclinic space group P-1 with one molecule and one benzene molecule in the unit cell and asymmetric unit. One the bound tertiary phosphines contains a disordered phenyl ring.

$(^{H,Cy}L)Co_3(PMe_3)_3$ (5a). The structure was solved in the tetragonal space group I4cm and contains 8 molecules in the unit cell and 2/3 of a molecule in the asymmetric unit.

$(^{H,Cy}L)Co_3(PMe_2Ph)_3$ (5b). The structure was solved in the monoclinic space group $P2(1)$ and contains two molecules per unit cell. The asymmetric unit consists of two molecules, as well as a hexane molecule. This structure was twinned.

$(^{Ph}L)Co_3(PMe_2Ph)_3$ (6). The structure was solved in the trigonal space group R-3 and has 8 molecules per asymmetric unit with several thf molecules. Each of the molecules exhibits whole molecule disorder and this was taken care of using the appropriate constraints/restraints.

(^{Ph}L)Co$_3$(PMe$_2$Ph)$_2$ (7). The structure was solved in the monoclinic space group Pna21 and has 8 molecules in the unit cell and two per asymmetric unit.

[(^{H}L)Co$_3$(PMe$_3$)$_3$][PF$_6$] (8a). The structure was solved in the monoclinic space group $P2(1)/c$ with four molecules in the unit cell. The asymmetric unit consists of one molecule and three thf molecules (two of which are disordered).

[(^{H}L)Co$_3$(PMe$_2$Ph)$_3$][PF$_6$] (8b). The structure was solved in the triclinic space group P-1 with one molecule per unit cell. The asymmetric unit consists of one molecule, two disordered thf molecules, and a PF$_6$.

(^{H,Cy}L)Co$_3$(PMe$_2$Ph)$_3$PF$_6$ (9b). The structure was solved in the trigonal space group R-3 with 6 molecules per unit cell. The asymmetric unit consists of one molecule, two half-occupied and disordered PF6 anions and a benzene.

[(^{Ph}L)Co$_3$(PMe$_2$Ph)$_3$][PF$_6$] (10). The structure was solved in the trigonal space group P3 and there is one molecule per unit cell.

Table S1. Experimental Details for **1-3**.

	1	**2**	**3**
Molecular Formula	$C_{38}H_{39}Mn_3N_9$	$C_{64}H_{51}Mn_3N_9O_2$	$C_{65}H_{69}Mn_3N_9$
FW	786.60	1159.09	1141.11
Crystal System	Orthorhombic	Triclinic	Monoclinic
Space Group (Z)	Pbca (16)	P-1 (2)	P2(1)/c (4)
a (Å)	19.1130(11)	12.7326(15)	20.601(6)
b (Å)	19.1558(11)	13.2825(18)	11.979(4)
c (Å)	39.478(2)	17.604(2)	27.764(8)
α (°)	90	85.291(4)	90
β (°)	90	79.491(3)	99.332(6)
γ (°)	90	73.582(5)	90
Volume ($Å^3$)	14453.8(14)	2806.5(6)	6761(3)
Calc. ρ (g/cm^3)	1.446	1.353	1.121
μ (mm^{-1})	1.07	0.72	0.59
Crystal Size (mm)	0.33 x 0.25 x 0.08	0.16 x 0.15 x 0.14	0.17 x 0.15 x 0.11
Reflections	16604	12918	12803
Completeness (to 2θ)	100	99.7	99.3
GOF on F^2	1.02	1.04	1.07
R1, wR2[c] [I>2σ(I)]	0.036 0.102	0.033 0.089	0.051 0.114

[a] λ = 0.71073 Å; [b] T = 100(2) K; [c] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S2. Experimental Details for **4b-7**.

	4b	**5a**	**5b**	**6**	**7**
Moiety Formula	$C_{47}H_{57}Co_3N_6P_3$ 0.5 (C_6H_6)	$C_{33}H_{50}Co_3N_6P_3$	2($C_{48}H_{57}Co_3N_6P_3$), 1.5(C_6H_{14})	$C_{75}H_{176}Co_{48}N_{96}O_9P_{48}$	$C_{57}H_{58}Co_3N_6P_2$
FW	1014.74	800.49	2104.65	19912.33	1065.82
Crystal System	Triclinic	Tetragonal	Monoclinic	Trigonal	Orthorhombic
Space Group	P-1	I4cm	P 2(1)	R-3	Pna21
(Z)	(2)	(8)	(2)	(1)	(8)
a (Å)	12.5258(14)	19.9023(13)	11.0206(8)	28.5159(17)	18.2484(17)
b (Å)	12.5284(14)	19.9023(13)	36.583(3)	28.5159(17)	12.8958(12)
c (Å)	18.163(2)	19.6805(14)	12.9112(9)	28.5159(17)	41.200(4)
α (°)	70.206(2)	90	90	90	90
β (°)	85.518(2)	90	102.393(1)	90	90
γ (°)	61.611(1)	90	90	120	90
Volume ($Å^3$)	2342.0(5)	7795.5(12)	5084.1(6)	23188(2)	9695.5(15)
Calc. ρ (g/cm^3)	1.439	1.364	1.375	1.425	1.460
μ (mm^{-1})	1.195	1.415	1.103	0.981	1.127
Reflections	10252	1955	11452	27972	14419
Completeness (to 2θ)	98	99	100	100	99
GOF on F^2	1.02	1.00	1.09	1.02	1.02
R1, wR2[c] [I>2σ(I)]	0.029 0.0703	0.048 0.1295	0.031 0.090	0.070 0.1690	0.032 0.067

[a] λ = 0.71073 Å; [b] T = 100(2) K; [c] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S3. Experimental Details for **8-10.**

	8a	**8b**	**9b**	**10**
Moiety Formula	$C_{44}H_{75}Co_3F_6N_6O_3P_4$	$C_{106}H_{138}Co_6F_{12}N_{12}O_3P_8$	$C_{66}H_{75}Co_3F_6N_6P_4$	$C_{67}H_{73}Co_3F_6N_6P4O_{0.5}$
FW	1150.77	2457.62	1366.99	1384.98
Crystal System	Monoclinic	Triclinic	Trigonal	Hexagonal
Space Group	P2(1)/c	P-1	R-3	P3
(Z)	(4)	(2)	(6)	(1)
a (Å)	10.877(4)	10.877(8)	20.251(2)	12.6987(14)
b (Å)	17.822(7)	12.520(9)	20.251(2)	12.6987(14)
c (Å)	25.844(10)	20.852(15)	25.635(3)	11.4114(13)
α (°)	90	77/709(12)	90	90
β (°)	93.949(8)	77.151(13)	90	90
γ (°)	90	81.925(12)	120	120
Volume (Å^3)	4998(3)	2692(3)	9101(2)	1593.6(3)
Calc. ρ (g/cm^3)	1.529	1.516	1.497	1.417
μ (mm^{-1})	1.18	1.099	0.982	0.94
Reflections	9671	9885	4465	3777
Completeness (to 2θ)	99.3	97.6	96.2	100
GOF on F^2	1.03	0.975	1.02	1.12
R1, wR2^c	0.099	0.052	0.035	0.027
[I>2σ(I)]	0.2566	0.1433	0.088	0.073

[a] $\lambda = 0.71073$ Å; [b] T = 100(2) K; [c] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S4. Comparative bond distances and ligand bond distances (Å) for complexes **1**, **2**, **3**, **4b**, **5b**, **6**, **7**, **8a**, **8b**, **9b**, and **10.**

Compound	M–M$_{avg}$	M–N$_{top}$	M–N$_{base}$	M–L	N–C$_{Ar}$	(C–C)$_{Ar}$
1	2.8681(5)	2.193(2)	2.205(2)	2.192(2)	1.400(3)	1.399(4)
2	2.8202(4)	2.250(1)	2.191(1)	2.160(2)	1.408(2)	1.401(5)
3	3.1260(1)	2.087(2)	2.131(2)	2.225(4)	1.422(4)	1.397(5)
4b	2.3860(5)	2.016(2)	2.003(2)	2.230(1)	1.404(3)	1.397(3)
5b	2.3855(7)	2.011(4)	2.021(4)	2.230(1)	1.410(5)	1.396(4)
6	2.4270(18)	2.149(9)	1.987(8)	2.253(3)	1.409(11)	1.409(10)
7	2.4043(7)	2.033(3)	1.979(3)	2.276(1)	1.411(5)	1.393(6)
8a	2.3223(2)	1.950(10)	1.933(10)	2.201(4)	1.378(11)	1.391(10)
8b	2.3439(17)	1.968(4)	1.957(4)	2.235(2)	1.419(5)	1.385(7)
9b	2.3477(6)	1.956(2)	1.981(2)	2.231(1)	1.420(3)	1.393(13)
10b	2.3910(7)	2.096(3)	1.965(3)	2.281(1)	1.425(4)	1.391(5)

$$\text{ESD} = \sqrt{\frac{\sum_i^n (esd_i)^2}{(n-1)}}$$

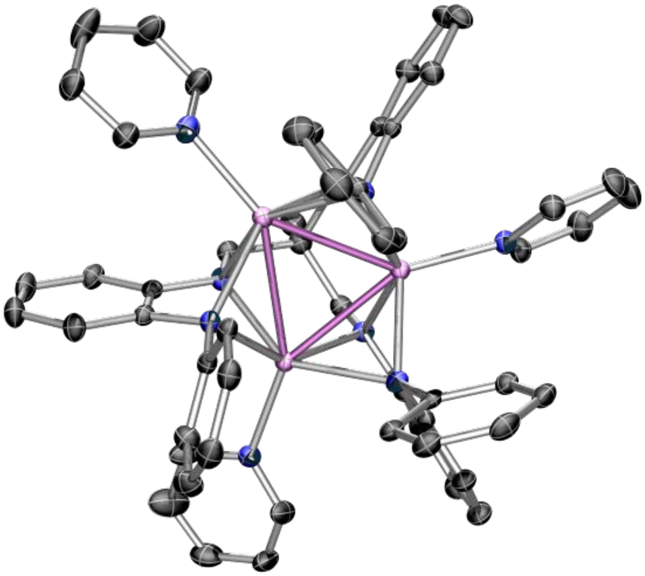


Figure S6. Solid-state molecular structure for $[(^{Ph}L)Mn_3(Py)_3$ **(2)**, with thermal ellipsoids at 50% probability level (C black, Mn magenta, N blue). Hydrogens and solvent molecules have been omitted for clarity.

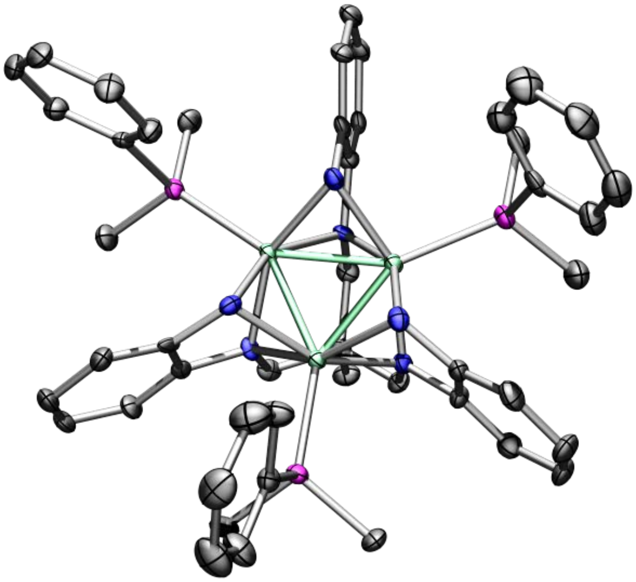


Figure S7. Solid-state molecular structure for $[(^{H}L)Co_3(PMe_2Ph)_3$ **(4b)**, with thermal ellipsoids at 50% probability level (Co aquamarine, C black, P magenta, N blue). Hydrogens and solvent molecules have been omitted for clarity.

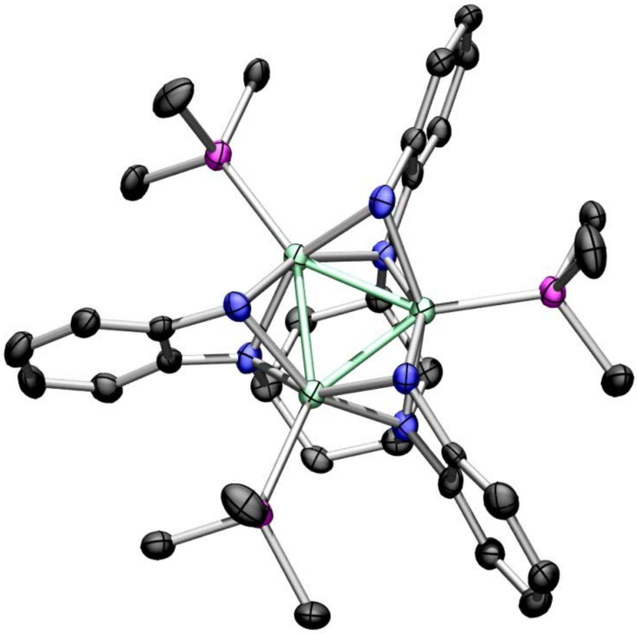


Figure S8. Solid-state molecular structure for $[(^{H}L)Co_3(PMe_3)_3]^+$ **(8a)**, with thermal ellipsoids at 50% probability level (Co aquamarine, C black, P magenta, N blue). Hydrogens, PF_6 anion and solvent molecules have been omitted for clarity.

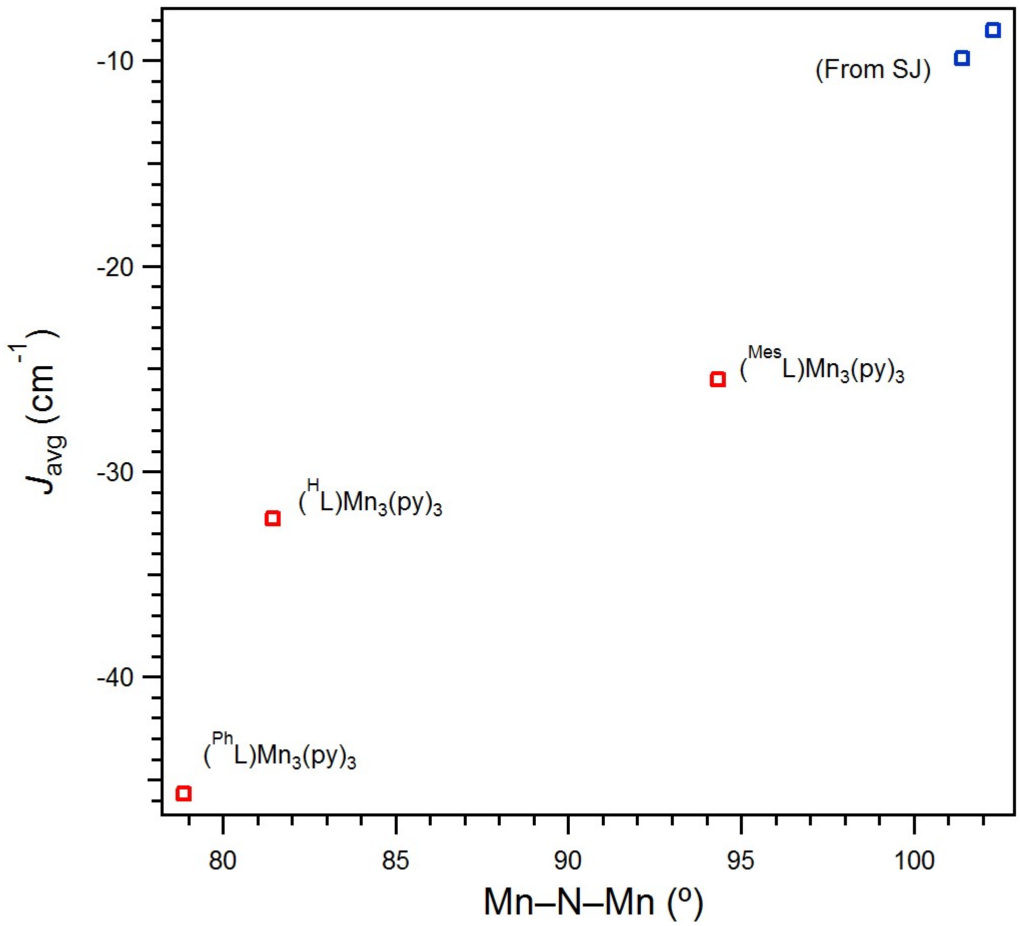
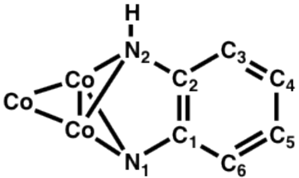


Figure S9. Correlation between average coupling to Mn–N–Mn bond angles. Blue series taken from Ref #S8.

Computational Methods. Computations were carried out utilizing *Gaussian 09*[S8] program package. The BP86[S9] functional was used with the def2-TZVP (Co, N, P) and def2-SV(P) (C, H) basis sets[S10]. The W06 auxiliary basis set[S11] was used for all atoms to utilize the density fitting method[S12] for accelerating the calculations. Geometry optimizations with no symmetry restraints were performed on $(^{H}L)Co_3(PMe_3)_3$ and $[(^{H}L)Co_3(PMe_3)_3]^+$. Starting geometries were taken from X-ray structures of $(^{H}L)Co_3(PMe_2Ph)_3$ and $[(^{H}L)Co_3(PMe_2Ph)_3][PF_6]$ and modified slightly by replacing substituting phenyl with methyl on the phosphine groups. Initial force constants were taken from a preliminary frequency calculation to make geometric convergence more facile. The energy minimum was confirmed by running a final frequency calculation, which showed zero imaginary frequencies for either species. The cation was optimized as both a restricted and unrestricted singlet, while the neutral complex was modeled as a doublet based on magnetic data. Both structures maintained near C_{3V} symmetry. The calculated energies were E(U-BP86) = -6751.31663250 hartree for $(^{H}L)Co_3(PMe_3)_3$ and E(R-BP86) = -6751.17057365 hartree for $[(^{H}L)Co_3(PMe_3)_3]^+$. The cation is 0.14607635 hartree (or 4 eV) higher in energy than the neutral complex.

Comparison of calculated bond lengths with those determined from X-ray structures showed good agreement. The average calculated Co-Co distance for the neutral complex was within 0.002 Å of the experimental value, and within 0.011 Å for the cation. For both structures all Co-N distances were within 0.005 Å of experiment and Co-P distances differed by no more than 0.010 Å. The worst disagreement for C-C and C-N bond lengths was 0.027 Å. The calculated cation LUMO, and corresponding SOMO of $(^{H}L)Co_3(PMe_3)_3$, is antibonding, (π*) for Co-Co, antibonding (σ*) for Co-N, and bonding (π) for $N\text{-}C_{aryl}$. This description is supported by the change in bond length upon oxidation in both X-ray data and the calculated structures: Co-Co contracts by 0.029 Å (calc. 0.020 Å); $Co\text{-}N_1$ contracts by 0.024 Å (calc. 0.026 Å); $Co\text{-}N_2$ contracts by 0.032 Å (calc. 0.027 Å); $N_1\text{-}C_1$ expands by 0.029 Å (calc. 0.020 Å); $N_2\text{-}C_2$ distance expands by 0.023 Å (calc. 0.015 Å).

Table S5. Average Experimental and Calculated Bond Lengths (Å)



Bond	X-Ray		Calculated		Cation LUMO
	$({}^{H}L)Co_3(PMe_2Ph)_3$	$[({}^{H}L)Co_3(PMe_2Ph)_3]^+$	$({}^{H}L)Co_3(PMe_3)_3$	$[({}^{H}L)Co_3(PMe_3)_3]^+$	
Co-Co	2.385	2.366	2.387	2.377	π*
Co-P	2.221	2.259	2.218	2.249	-
Co-N_1	2.020	1.988	2.017	1.990	σ*
Co-N_2	2.003	1.979	2.008	1.981	σ*
N_1-C_1	1.406	1.435	1.407	1.427	π
N_2-C_2	1.406	1.429	1.403	1.418	π
C_1-C_2	1.388	1.395	1.401	1.396	π*
C_2-C_3	1.415	1.411	1.436	1.424	π*
C_3-C_4	1.405	1.418	1.420	1.423	π
C_4-C_5	1.377	1.378	1.404	1.400	π*
C_5-C_6	1.407	1.425	1.419	1.422	π
C_6-C_1	1.389	1.384	1.402	1.396	π*

Table S6. DFT Coordinates

Optimized Coordinates for $(^{H}L)Co_3(PMe_3)_3$				**Optimized Coordinates for $[(^{H}L)Co_3(PMe_3)_3]^+$**			
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Co	0.67768	1.189809	4.665109	Co	0.676113	1.187432	4.65299
Co	-1.390878	-0.003269	4.651991	Co	-1.383822	-0.000406	4.65147
Co	0.677615	-1.195011	4.659397	Co	0.676855	-1.186947	4.653089
P	1.786379	3.103189	4.837132	P	1.808225	3.126255	4.808908
P	-3.602539	-0.003289	4.810172	P	-3.624799	-0.001067	4.817814
P	1.808435	-3.098317	4.812296	P	1.809837	-3.125263	4.809528
N	1.719012	0.001178	3.425262	N	1.694056	0.000469	3.437658
N	-0.869912	1.491362	3.420583	N	-0.859202	1.473605	3.436337
N	-0.868669	-1.495858	3.416922	N	-0.858226	-1.474101	3.436371
N	1.804694	-0.007268	5.833826	N	1.76603	0.000694	5.820357
N	-0.930595	1.564901	5.828618	N	-0.898733	1.535385	5.818921
N	-0.926819	-1.575769	5.824255	N	-0.897772	-1.535861	5.818956
C	0.002624	0.001813	-0.001143	C	-0.005887	0.000025	-0.001091
C	-0.000625	-0.000097	1.54882	C	-0.006228	0.000037	1.548509
C	1.487154	0.000751	1.990682	C	1.476271	0.000504	1.99666
C	-0.745524	1.289605	1.986709	C	-0.746378	1.285251	1.995672
C	-0.743491	-1.292006	1.983481	C	-0.745546	-1.285651	1.995701
C	2.005708	3.61618	6.599243	C	2.075832	3.606743	6.56672
C	-4.163045	-0.016636	6.570461	C	-4.170328	-0.001079	6.577226
C	2.248615	-3.506341	6.560234	C	2.073717	-3.607253	6.567526
C	3.521669	3.224941	4.220871	C	3.512427	3.227077	4.121885
C	-4.575406	1.416128	4.144072	C	-4.574971	1.414988	4.128217
C	1.036534	-4.684105	4.269928	C	1.082012	-4.662867	4.107511
C	1.091173	4.651558	4.111363	C	1.077911	4.664153	4.110102
C	-4.578354	-1.409925	4.121547	C	-4.574082	-1.417818	4.128438
C	3.456011	-3.256586	3.992911	C	3.515746	-3.224349	4.126617
C	3.054303	0.000342	3.867781	C	3.05006	0.000881	3.883258
C	-1.532432	2.652974	3.858963	C	-1.530921	2.651756	3.88136
C	-1.533881	-2.657182	3.853184	C	-1.529134	-2.652711	3.88139
C	4.241499	0.006372	3.12144	C	4.230994	0.001085	3.139125
C	-2.113851	3.6855	3.109629	C	-2.114708	3.678119	3.13724
C	-2.116501	-3.687661	3.101983	C	-2.112256	-3.679449	3.13727
C	5.487366	-0.007474	3.800562	C	5.473304	0.001786	3.830671
C	-2.729821	4.770977	3.785668	C	-2.729498	4.758193	3.8287
C	-2.745404	-4.76702	3.775858	C	-2.726238	-4.759984	3.828732
C	5.537116	-0.027107	5.203609	C	5.511881	0.002285	5.230203
C	-2.759717	4.815985	5.188532	C	-2.74893	4.792228	5.228088
C	-2.787126	-4.807819	5.178432	C	-2.74554	-4.794094	5.228119
C	3.103837	-0.01196	5.303328	C	3.088143	0.001198	5.307213
C	-1.56526	2.696549	5.294114	C	-1.55133	2.684948	5.305159
C	-1.571775	-2.700608	5.287948	C	-1.549481	-2.685937	5.305189
C	4.338298	-0.029209	5.965629	C	4.307196	0.001984	5.987122
C	-2.173917	3.772307	5.953562	C	-2.15371	3.744801	5.984924
C	-2.196594	-3.768206	5.945429	C	-2.151036	-3.746259	5.984953
H	0.524033	-0.896071	-0.403013	H	0.513251	-0.898335	-0.403183
H	0.521218	0.902308	-0.400799	H	0.512772	0.898658	-0.403194
H	-1.035041	0.000708	-0.404727	H	-1.043515	-0.000256	-0.403085
H	1.9787	0.89762	1.533024	H	1.974874	0.897609	1.552412
H	-1.765081	1.270213	1.522786	H	-1.770387	1.273184	1.54653
H	-0.204713	-2.162562	1.528821	H	-0.212591	-2.163207	1.552927
H	1.97944	-0.897124	1.535383	H	1.975473	-0.896149	1.552182
H	-0.208442	2.161504	1.532784	H	-0.21398	2.163175	1.552954
H	-1.762765	-1.273445	1.518971	H	-1.769576	-1.274245	1.546591
H	4.21721	0.017252	2.019628	H	4.21615	0.000814	2.037699
H	-2.096741	3.663579	2.007777	H	-2.107065	3.665012	2.035747
H	-2.094095	-3.666617	2.000155	H	-2.104664	-3.666311	2.035779

H	6.422888	-0.004474	3.215302	H	6.412646	0.001987	3.253282
H	-3.187569	5.585026	3.197888	H	-3.193694	5.574567	3.25096
H	-3.20547	-5.578611	3.186492	H	-3.1899	-5.576662	3.250993
H	6.510714	-0.039325	5.722964	H	6.481236	0.002875	5.755921
H	-3.240322	5.664391	5.705311	H	-3.228108	5.634966	5.753663
H	-3.279044	-5.650744	5.693545	H	-3.224087	-5.63719	5.753695
H	4.377075	-0.039989	7.069738	H	4.339389	0.002293	7.090433
H	-2.198412	3.805685	7.057623	H	-2.169893	3.772099	7.088244
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H	1.777279	-0.015819	6.865479	H	1.72464	0.0008	6.85241
H	-0.924069	1.540006	6.86041	H	-0.876104	1.499323	6.851028
H	-0.920905	-1.552453	6.85602	H	-0.875223	-1.499745	6.851063
H	2.56396	4.576273	6.685315	H	2.641932	4.561943	6.644225
H	-5.273825	-0.011153	6.651655	H	-5.28063	-0.001536	6.655356
H	2.813366	-4.463585	6.632049	H	2.639658	-4.562518	6.645467
H	1.006001	3.736119	7.069211	H	1.092132	3.731201	7.067608
H	-3.768501	-0.926563	7.071762	H	-3.77586	-0.904005	7.090764
H	2.87219	-2.686481	6.97727	H	2.642038	-2.809918	7.092333
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H	-3.757893	0.879043	7.088703	H	-3.776631	0.902324	7.09052
H	1.31785	-3.588475	7.16205	H	1.089011	-3.732124	7.06633
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H	-5.660657	1.273674	4.35097	H	-5.661476	1.273813	4.324307
H	1.719164	-5.537532	4.485514	H	1.757025	-5.524014	4.312303
H	1.760833	5.51414	4.331321	H	1.752357	5.525668	4.315231
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H	4.164597	2.458304	4.701576	H	4.177231	2.475655	4.595363
H	-4.23366	2.369609	4.597984	H	-4.242536	2.370956	4.582622
H	0.06822	-4.843538	4.788282	H	0.085214	-4.868682	4.548549
H	0.079201	4.856141	4.518172	H	0.08151	4.86834	4.55279
H	-4.240298	-2.370891	4.562267	H	-4.241009	-2.373504	4.582967
H	4.163382	-2.498908	4.388722	H	4.178646	-2.472341	4.60187
H	3.5387	3.040905	3.125646	H	3.488205	3.026542	3.02972
H	-4.420687	1.488926	3.046387	H	-4.412378	1.478511	3.031369
H	0.834274	-4.64748	3.178559	H	0.960696	-4.557065	3.008547
H	0.999601	4.536797	3.010105	H	0.955214	4.559836	3.011152
H	-4.422065	-1.466829	3.023113	H	-4.411486	-1.481374	3.031592
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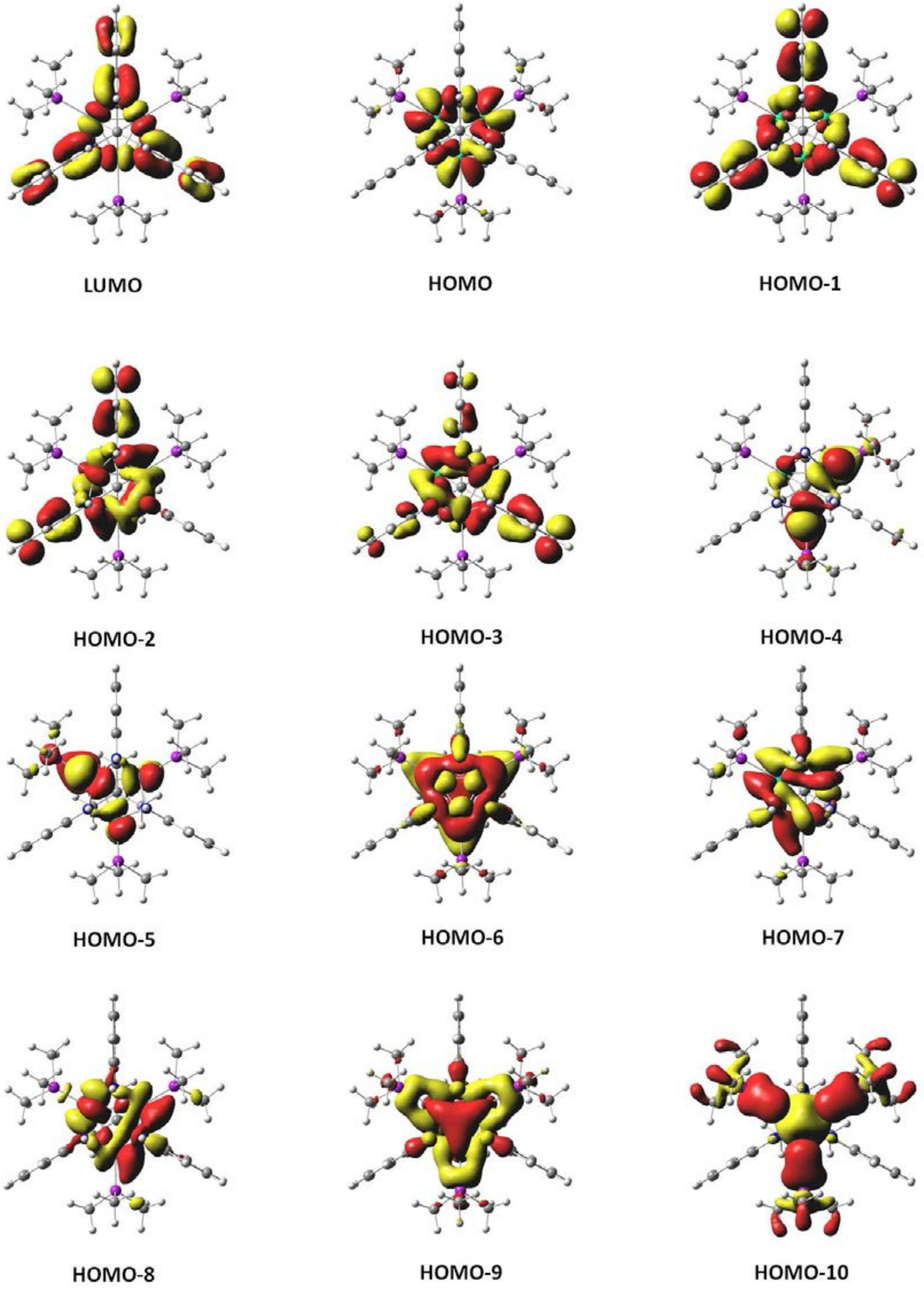

LUMO HOMO HOMO-1

HOMO-2 HOMO-3 HOMO-4

HOMO-5 HOMO-6 HOMO-7

HOMO-8 HOMO-9 HOMO-10

Figure S10. Molecular orbitals for $(^{H}L)Co_3(PMe_3)_3$ (**4a**).

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