

Probing the limits of alkaline earth–transition metal bonding: an experimental and computational study

Supporting Information

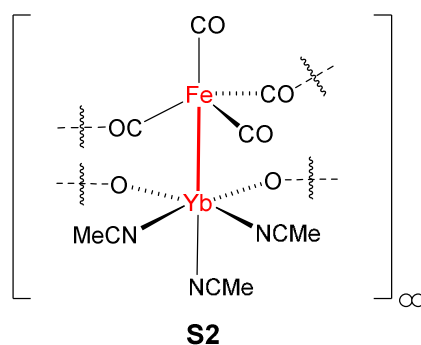
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Discussion of reactions with other Group 8 carbonylate anions.

The $[\text{CpRu}(\text{CO})_2]^-$ (Rp^-) anion has been used successfully for the synthesis of both Ln–TM and An–TM bonded complexes.¹ In particular, Kempe has reported² the ytterbium complexes $[\text{YbRp}_2(\text{THF})_2]_\infty$ and $\text{YbRp}_2(4\text{-NC}_5\text{H}_4^t\text{Bu})_3$, both of which contain Yb–Ru bonds. Reaction of Rp_2 with Ca/Hg in THF afforded a mixture of compounds as judged by the ^1H NMR spectrum of the crude product in $\text{THF-}d_8$. Attempted crystallization afforded small amounts of an unusual cubane-like structure $[\text{CaRp}(\mu_3\text{-OH})(\text{THF})]_4$ (**S1**) characterized only by X-ray crystallography as shown in Fig. S3; bulk purification was not possible. Reactions of CaI_2 with NaRp in THF, or reduction of Fp_2 with Ca in liquid ammonia were also unsuccessful. Although **S1** appears to be the product of adventitious hydrolysis it contains the first examples of Ca–TM bonds for a $4d$ transition metal. The structure is quite interesting and formally comprises a $[\text{Ca}_4(\mu_3\text{-OH})_4(\text{THF})_4]^{4+}$ core with pairs of Ca atoms on four of the six faces bridged by $\mu(\text{Ru},\text{O})$ -bound Rp^- moieties. The average Ca–Ru bond length of 3.118 Å (range 3.0916(10) – 3.1728(10) Å) is comparable to the sum of the covalent radii (3.22(12) Å)³ and falls within the range of Yb–Ru bond distances in Kempe’s compounds mentioned above (3.0129(4) – 3.1808(7) Å).



The $[\text{Fe}(\text{CO})_4]^{2-}$ dianion is found in Shore's landmark complex $[\{(\text{MeCN})_3\text{Yb}\{\text{Fe}(\text{CO})_4\}_2\cdot\text{MeCN}\}]_\infty$ (**S2**, the first structurally authenticated example of a Ln–TM bond) prepared from $\text{Fe}_3(\text{CO})_{12}$ and Yb in liquid ammonia followed by treatment with MeCN.⁴ Unfortunately, as described in this SI, attempts to form an analogous calcium analogue lead to a number of products, depending on the reducing conditions (e.g. liquid ammonia or amalgam) and Lewis bases present (THF, MeCN, HMPA). These included isocarbonyl-bonded $[\text{Fe}(\text{CO})_4]^{2-}$ units but also partially reduced species like $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ and $[\text{Fe}_2(\text{CO})_8]^{2-}$ despite their being an excess of calcium metal present. These structures are shown in Figs. S4 – S7 and further experimental details are given below.

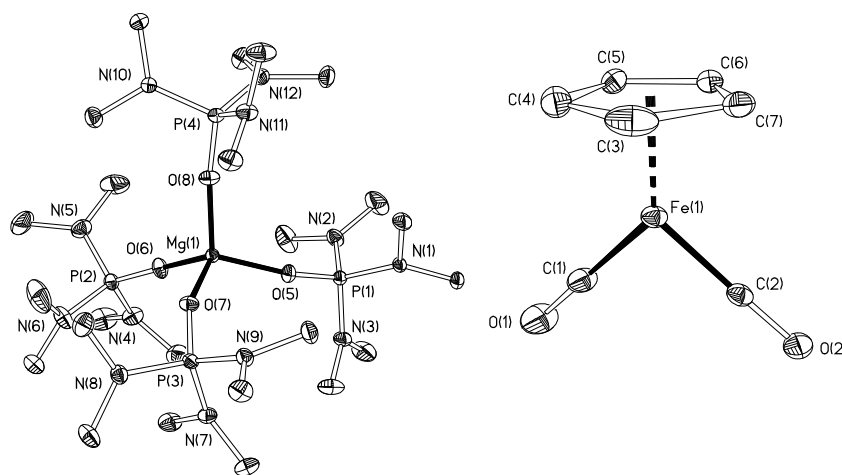


Figure S1. Displacement ellipsoid plots of $[\text{Mg}(\text{HMPA})_4]^{2+}$ (left) and one of the Fp^- anions (right) of $[\text{Mg}(\text{HMPA})_4][\text{Fp}]_2$ (**10**). H atoms omitted. Selected distances (Å) and angles (°): Mg(1)–O(av.(range)) 1.897 (1.887(2) - 1.908(2)), Fe(1)–C(1) 1.711(3), Fe(1)–C(2) 1.706(3), Fe(1)–C_{pcent} 1.731, C(1)–Fe(1)–C(2) 91.25(16), C_{pcent}–Fe(1)–C(1) 135.5, C_{pcent}–Fe(1)–C(1) 133.3.

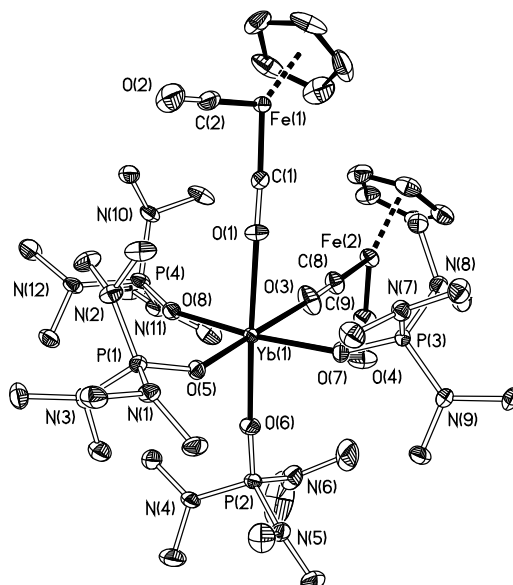


Figure S2. Displacement ellipsoid plot of $\text{YbFp}_2(\text{HMPA})_4$ (**12**). H atoms omitted.

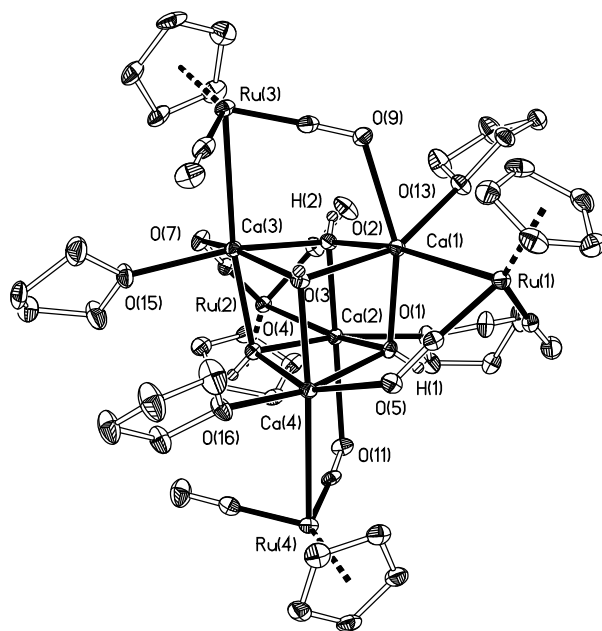


Figure S3. Displacement ellipsoid plot of $[\text{CaRp}(\mu_3\text{-OH})(\text{THF})]_4$ (**S1**). C-bound H atoms omitted. $\text{Ca}(1)\text{--Ru}(1) = 3.1728(10) \text{ \AA}$. Average $\text{Ca--Ru} = 3.118 \text{ \AA}$ (range $3.0916(10) - 3.1728(10) \text{ \AA}$)

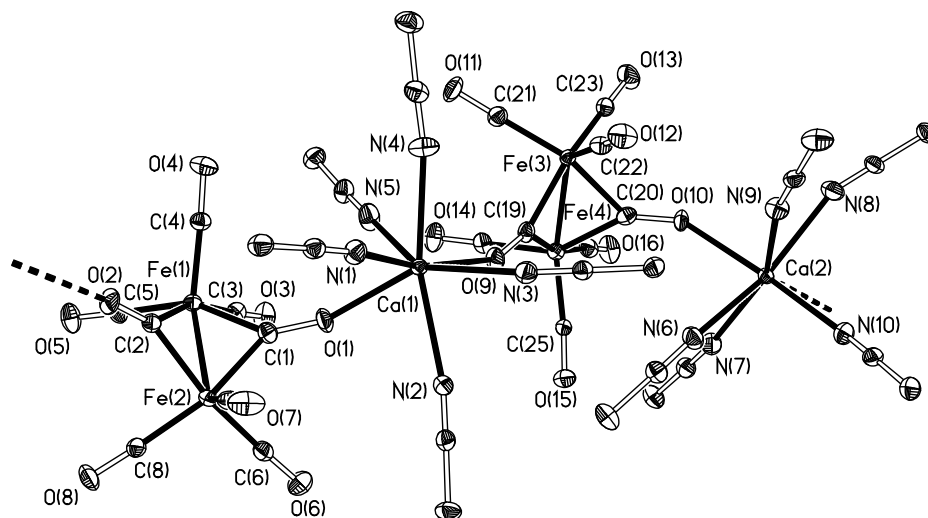


Figure S4. Displacement ellipsoid plot of the asymmetric unit of $[\text{Ca}\{\text{Fe}_2(\text{CO})_8\}(\text{MeCN})_5]_\infty$ (**S3**). H atoms omitted. Ca(2) and O(2) connect to O(2A) and Ca(2B) in the neighbouring asymmetric units by the symmetry operators $x, y-1, z$ and $x, y+1, z$ respectively.

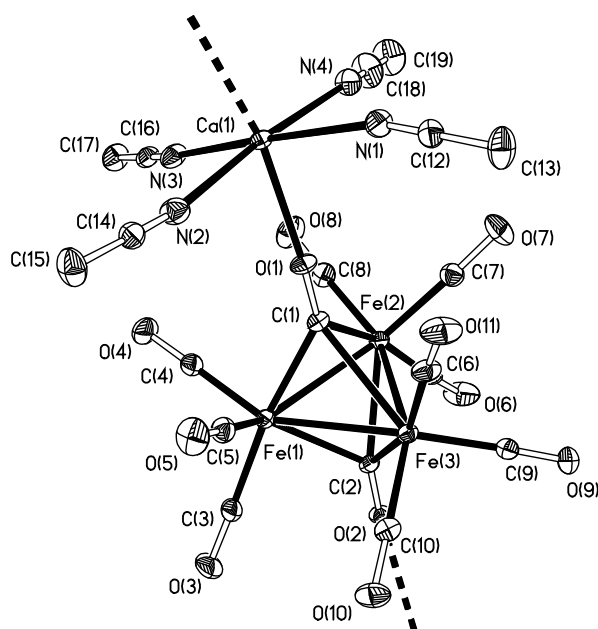


Figure S5. Displacement ellipsoid plot of the asymmetric unit of $[\text{Ca}\{\text{Fe}_3(\text{CO})_{11}\}(\text{MeCN})_4]_\infty$ (**S4**). H atoms omitted. Ca(1) and O(2) connect to O(2B) and Ca(1A) in the neighbouring asymmetric units by the symmetry operators $-x+3/2, y+1/2, 3/2-z$ and $-x+3/2, y-1/2, 3/2-z$ respectively.

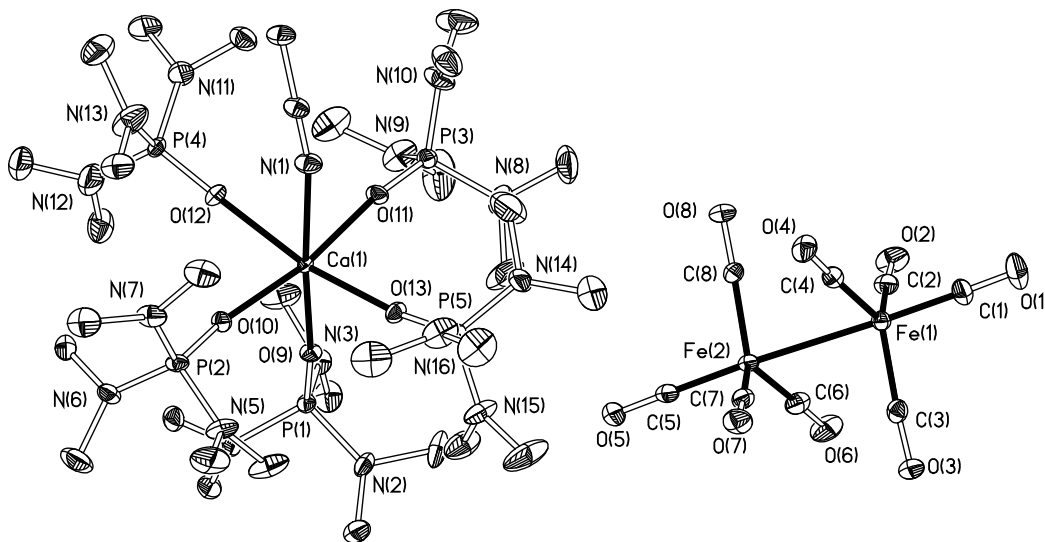


Figure S6. Displacement ellipsoid plot of the ion pair $[\text{Ca}(\text{HMPA})_5(\text{MeCN})][\text{Fe}_2(\text{CO})_8]$ (**S5**). H atoms omitted

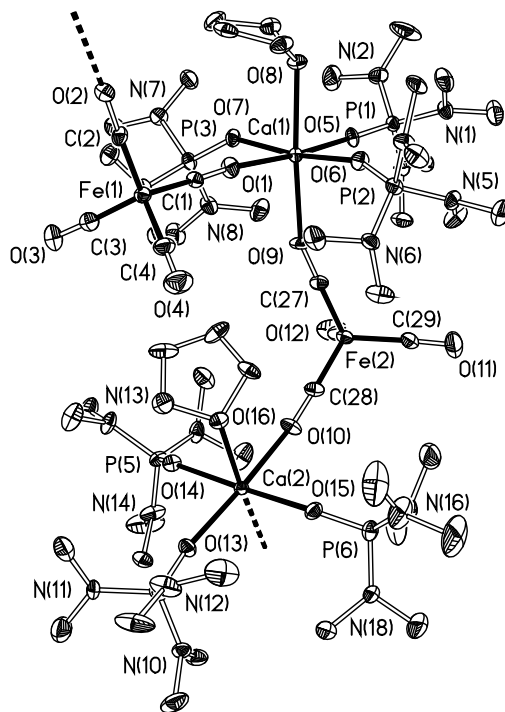


Figure S7. Displacement ellipsoid plot of the asymmetric unit of $[\text{Ca}\{\text{Fe}(\text{CO})_4\}(\text{HMPA})_3(\text{THF})]_\infty$ (**S6**). H atoms omitted for clarity. Ca(2) and O(2) connect to O(2B) and Ca(2A) in the neighbouring asymmetric units by the symmetry operators $x, y-1, z$ and $x, y+1, z$ respectively.

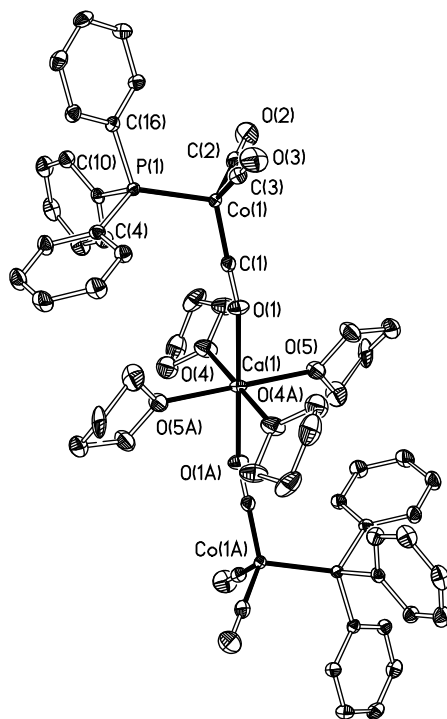


Figure S8. Displacement ellipsoid plot of $\text{Ca}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_4$ (**16**). H atoms omitted.

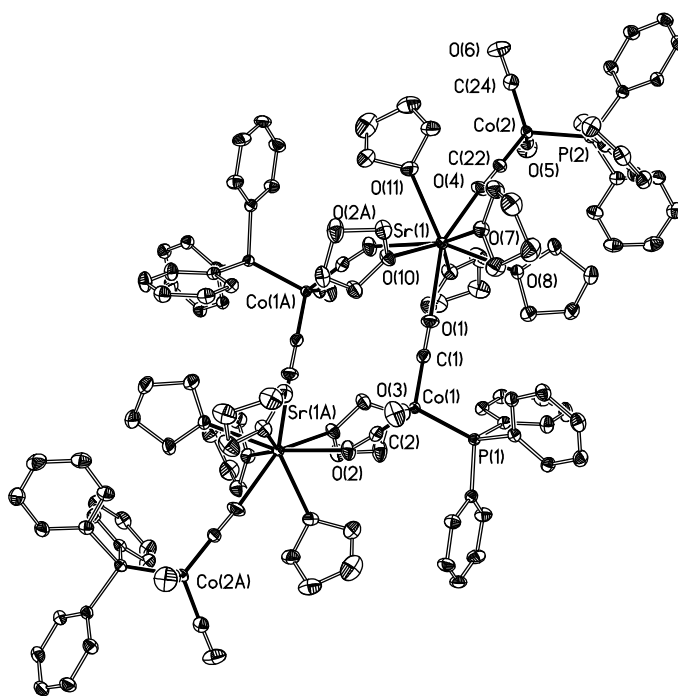


Figure S9. Displacement ellipsoid plot of $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_5]_2$ (**17**). H atoms omitted.

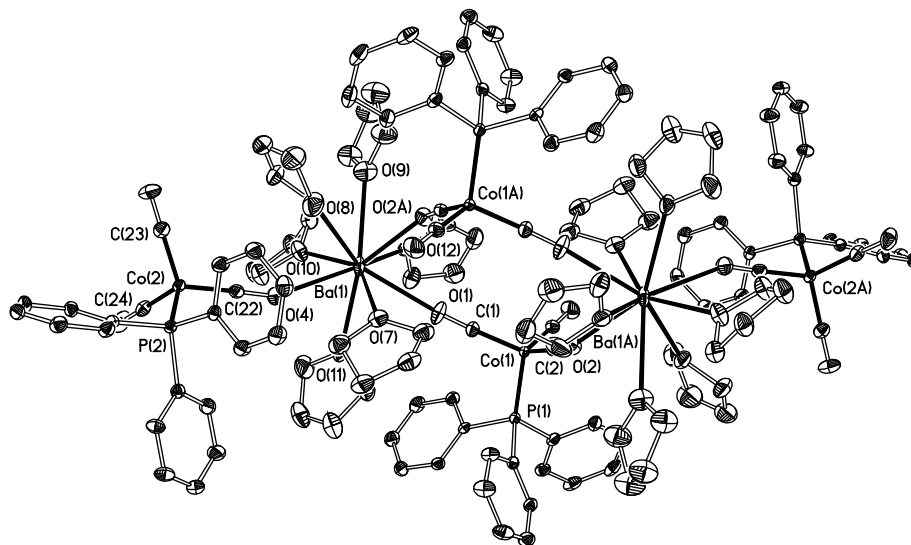


Figure S10. Displacement ellipsoid plot of $[\text{Ba}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_6]_2$ (**18**). H atoms omitted.

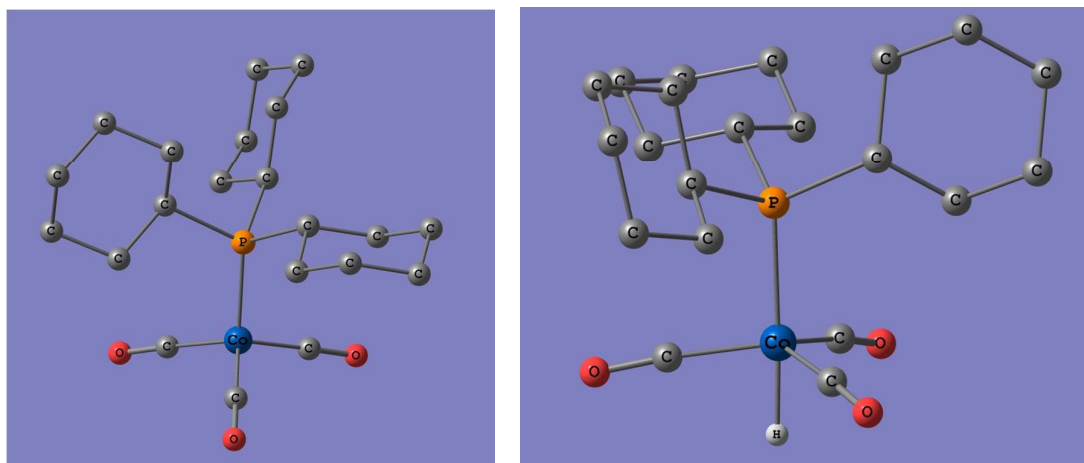


Figure S11. DFT structure of $[\text{Co}(\text{CO})_3(\text{PCy}_3)]^-$ (**S7Q**, left, $\Sigma(\text{P}-\text{Co}-\text{CO}) = 324.3^\circ$) and $\text{Co}(\text{CO})_3(\text{PCy}_3)\text{H}$ (**S8Q**, right, $\Sigma(\text{P}-\text{Co}-\text{CO}) = 295.6^\circ$). H atoms except the Co-H hydride omitted.

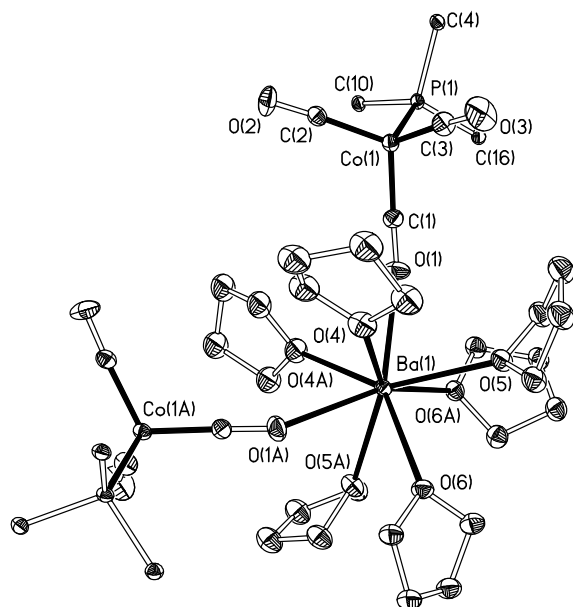


Figure S12. Displacement ellipsoid plot of $\text{Ba}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_6$ (**23**), H atoms and cyclohexyl methylene carbons omitted.

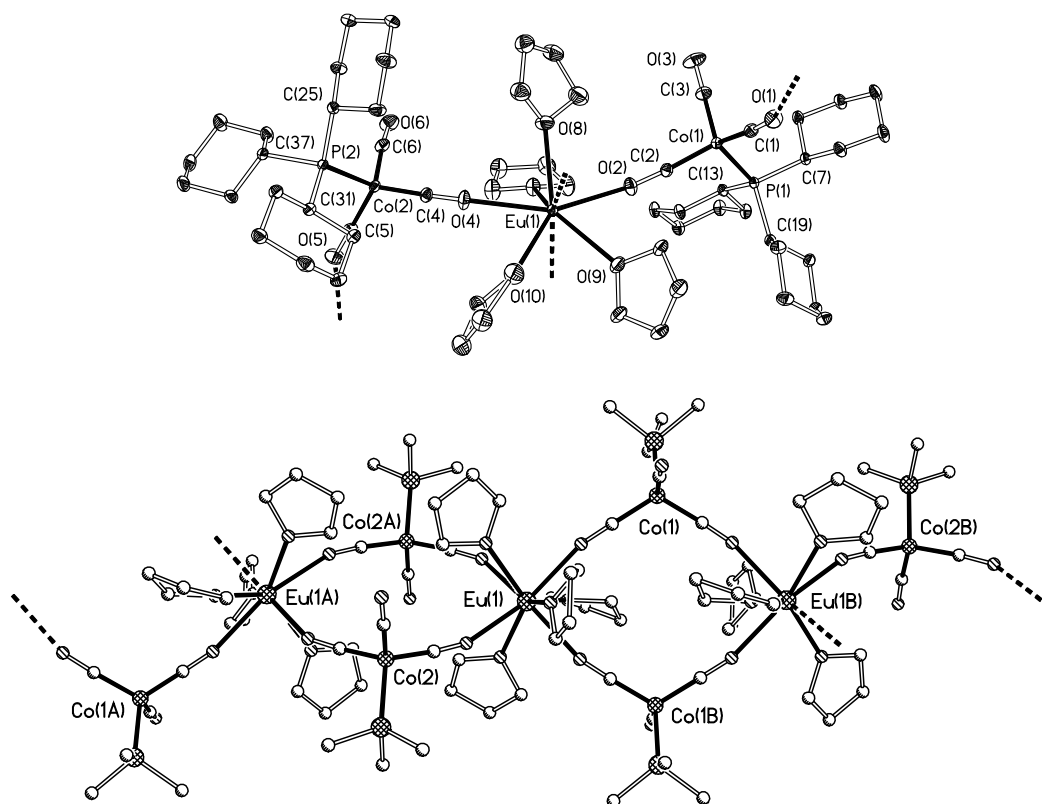


Figure S13. Displacement ellipsoid plot of the asymmetric unit (top) and ball and stick plot (bottom) of a portion of the infinite chain of $[\text{Eu}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_4]_\infty$ (**25·THF**). H atoms and cyclohexyl methylene groups omitted.

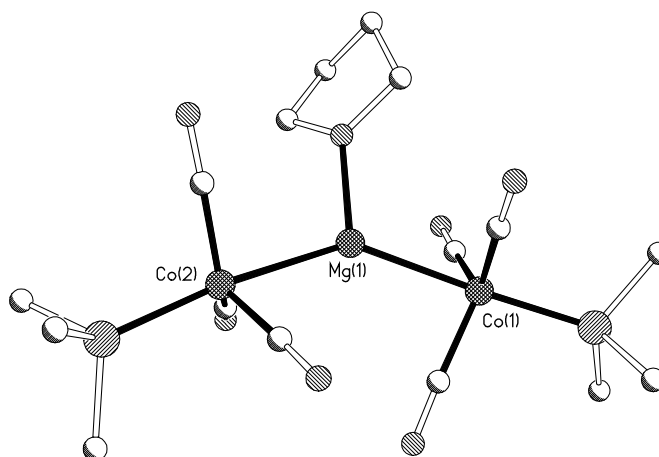


Figure S14. DFT structure of $\text{Mg}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}_2(\text{THF})$ (**19_monoQ**). H atoms omitted. See Table 2 of the main text for further details.

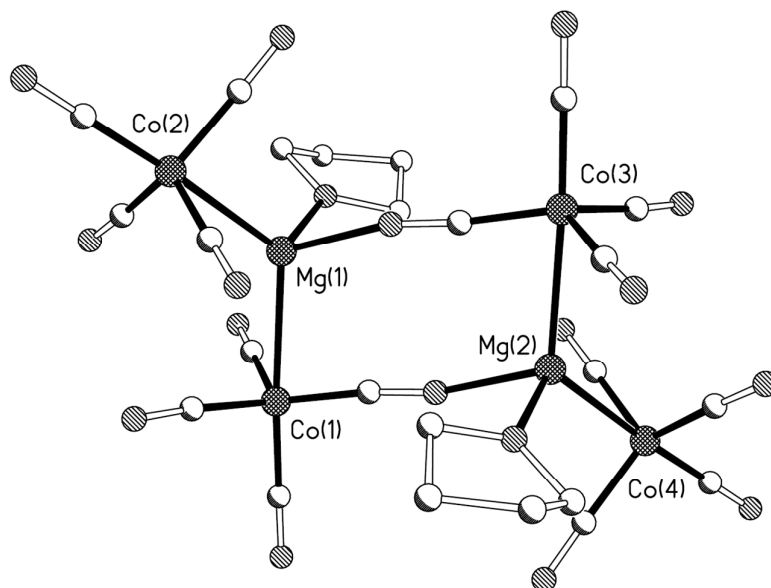


Figure S15. DFT structure of $[\text{Mg}\{\text{Co}(\text{CO})_4\}_2(\text{THF})]_2$ (**28Q**). H atoms omitted. See Table 2 of the main text for further details.

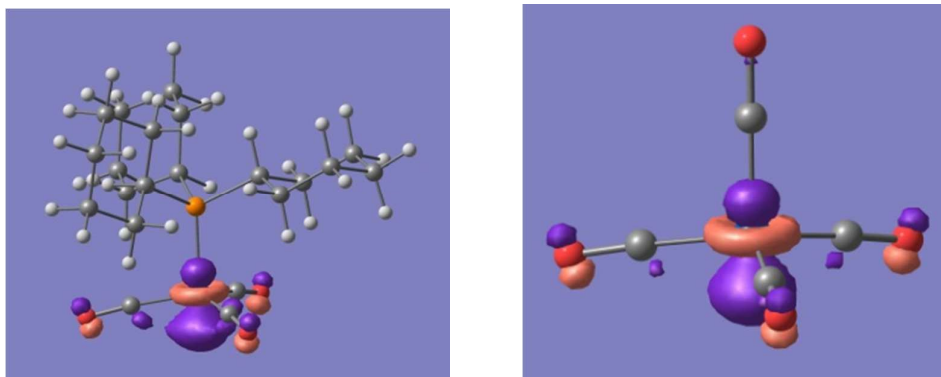


Figure S16. Isosurfaces of the HOMO of the $[\text{Co}(\text{CO})_3(\text{L})]^-$ anion for $\text{L} = \text{PCy}_3$ (**S9Q**, left, $E = 0.63$ eV) and CO (**S11Q**, right, $E = 0.24$ eV) calculated in the geometry of the optimized corresponding $\text{Co}(\text{H})(\text{CO})_3(\text{L})$.

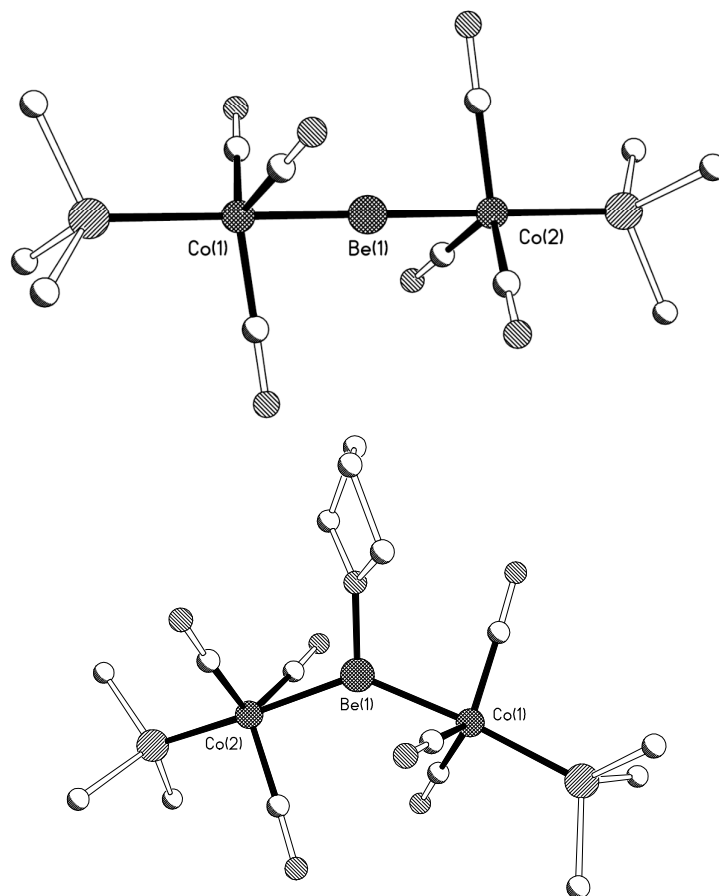


Figure S17. DFT structure of $\text{Be}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}_2$ (**31Q**, top) and $\text{Be}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}_2(\text{THF})$ (**30Q**, bottom). See Table S1 and Table 2 of the main text for further details.

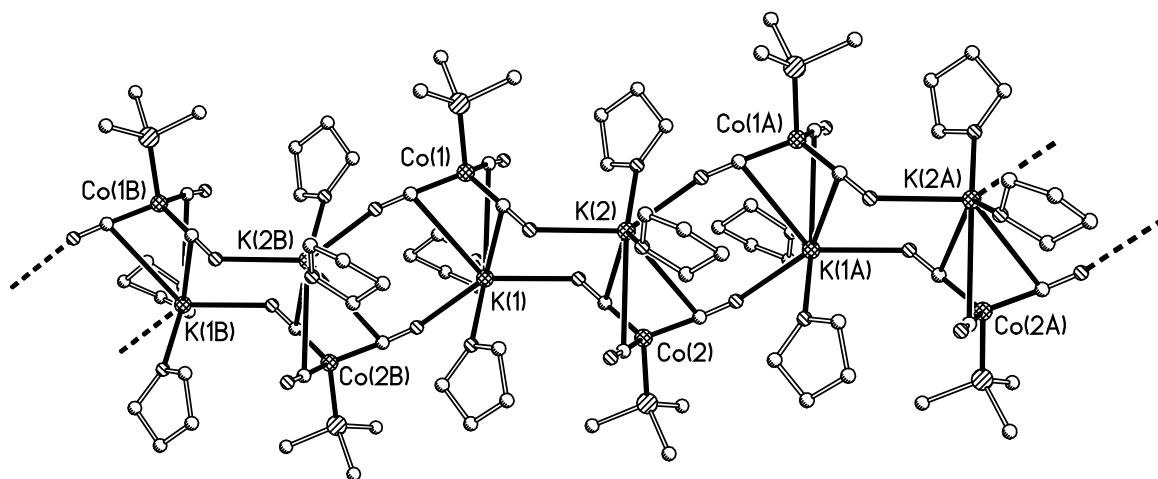


Figure S18. Ball and stick plot of a portion of the infinite chain of $\text{K}[\text{Co}(\text{CO})_3(\text{PCy}_3)](\text{THF})_2$ (**22**). H atoms and cyclohexyl methylene groups omitted.

Table S1. Selected computational results for Be{Co(CO)₃(PMe₃)₂}₂ (**31Q**). All BCP data are given in atomic units.

Be–Co(1)) (Å)	2.020
Be–Co(2)) (Å) ^a	2.020
Sum of OC–Co(1)–PMe ₃ (°)	298.4
Sum of OC–Co(2)–PMe ₃ (°)	298.4
Charge Be	0.47
Charge Co(1)	-0.44
Charge Co(2)	-0.44
electron density (ρ) Be–Co(1)	0.064
electron density (ρ) Be–Co(2)	0.064
electron density Laplacian ($\nabla^2\rho$) Be–Co(1)	0.044
electron density Laplacian ($\nabla^2\rho$) Be–Co(2)	0.044
energy density (H) Be–Co(1)	-0.033
energy density (H) Be–Co(2)	-0.033

Experimental Details

General methods and instrumentation. All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were either degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent (DME, pentane and hexanes) or refluxed over sodium (toluene) or potassium (THF) and distilled. Deuterated solvents were dried over sodium (toluene-*d*₈) or potassium (C₆D₆, THF-*d*₈), distilled under reduced pressure and stored under argon in Teflon valve ampoules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ¹H and ¹³C{¹H} spectra were recorded on a Bruker AVC 500 spectrometer fitted with a ¹³C cryoprobe or Varian Mercury-VX 300. ³¹P{¹H} spectra were recorded on Varian Mercury-VX 300. ¹H and ¹³C{¹H} spectra are referenced internally to residual protio-solvent (¹H) or solvent (¹³C) resonances, and are reported relative to tetramethylsilane ($\delta = 0$ ppm). ³¹P{¹H} spectra were referenced externally to an 85% H₃PO₄ solution. Assignments were confirmed as necessary with the use of two-dimensional ¹H-¹H and ¹³C-¹H NMR correlation experiments. IR spectra were recorded on a Perkin Elmer Paragon 1000 FTIR or Thermo Scientific Nicolet iS5 FTIR spectrometer and samples prepared in a dry-box as Nujol mulls between NaCl plates or as a solution (THF or toluene) in a NaCl cell. Mass spectra were recorded by the mass spectrometry service of Oxford University's Department of Chemistry.

Elemental analyses were carried out by the Elemental Analysis Service at London Metropolitan University.

Starting materials. $[\text{Co}(\text{CO})_3(\text{PPh}_3)]_2$ (**14**)⁵ and $[\text{Co}(\text{CO})_3(\text{PCy}_3)]_2$ (**15**)⁶ were synthesised according to published procedures. Metals and other reagents were purchased from Strem Chemicals, Sigma Aldrich or Alfa Aesar and either used as received or purified according to standard procedures.

$[\text{MgFp}_2(\text{THF})]_2$ (9**) and $\text{MgFp}_2(\text{THF})_4$ (**8**).** To a stirring Mg amalgam (0.343 g, 14.1 mmol Mg; 10 mL Hg) was added a solution of Fp_2 (1.00 g, 2.83 mmol) in THF (20 mL). The red solution was stirred over the amalgam for 16 h at RT. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was washed with pentane (2 x 10 mL) then dried *in vacuo* to afford “ $\text{MgFp}_2(\text{THF})_{1.6}$ ” as a yellow solid. Yield: 1.18 g (84%). Diffraction-quality crystals of **9** were grown from benzene layered with pentane at RT. When crystallized from a THF solution diffraction-quality crystals of $\text{MgFp}_2(\text{THF})_4$ (**8**) were obtained. ^1H NMR (THF- d_8 , 299.9 MHz): δ 4.35 (20 H, s, Cp). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5 MHz): δ 78.7 (Cp) ($\delta(\text{CO})$ not observed). IR (NaCl plates, Nujol mull, cm^{-1}): 1912 (s, $\nu(\text{CO})$), 1855 (s, $\nu(\text{CO})$), 1775 (m, $\nu(\text{CO})$), 1261 (w), 1015 (m), 870 (m), 817 (w), 805 (w). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1875 (br, s), 1703 (s). Anal. found (calcd. for $\text{C}_{41.2}\text{H}_{46.4}\text{Fe}_4\text{Mg}_2\text{O}_{11.3}$): C, 49.97 (49.76); H, 4.49 (4.70)%.

$[\text{Mg}(\text{HMPA})_4][\text{Fp}]_2$ (10**).** To a stirring solution of $\text{MgFp}_2(\text{THF})_4$ (**8**) (formed *in situ* from as-prepared “ $\text{MgFp}_2(\text{THF})_{1.6}$ ” (0.300 g, 0.604 mmol)) in THF (10 mL) was added HMPA (0.43 mL, 2.47 mmol). The red solution was stirred for 16 h at RT then volatiles were removed under reduced pressure. The resulting solid was washed with pentane (2 x 10 mL) to afford **10** as a red solid. Yield: 0.451 g (68 %). Diffraction-quality crystals were grown from THF at RT. ^1H NMR (THF- d_8 , 299.9 MHz): δ 4.20 (10 H, s, Cp), 2.65 (72 H, d, $^3J = 8.9$ Hz, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5 MHz): δ 76.8 (s, Cp), 37.1 (d, $^2J = 4.5$ Hz, Me), ($\delta(\text{CO})$ not observed). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8 , 121.6 MHz): δ 24.1 (s). IR (NaCl plates, Nujol mull, cm^{-1}): 1863 (s, $\nu(\text{CO})$), 1789 (s, $\nu(\text{CO})$), 1304 (s), 1186 (s), 1165 (s), 1104 (w), 1068 (m), 994 (s), 801 (w), 759 (s), 672 (m). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1865 (m), 1787 (m). Anal. found (calcd. for $\text{C}_{38}\text{H}_{82}\text{Fe}_2\text{MgN}_{12}\text{O}_8\text{P}_4$): C, 41.53 (41.68); H, 7.40 (7.55); N, 15.50 (15.35)%.

$\text{CaFp}_2(\text{HMPA})_4$ (11**).** To a stirring Ca amalgam (0.283 g, 7.06 mmol Ca; 10 mL Hg) was added a solution of HMPA (2.06 mL, 11.9 mmol) in THF (10 mL). The colorless solution was stirred over the amalgam for 10 min at RT then a solution of Fp_2 (0.500 g, 1.41 mmol) in THF (10 mL) added. The red solution was stirred for 16 h at RT. The red solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting gummy red solid was washed with benzene (2 x 10 mL) and dried *in vacuo* to afford **11** as a red solid. Yield: 1.14 g (73%). ^1H NMR (THF- d_8 , 299.9 MHz): δ 4.16 (10 H, s, Cp), 2.67 (72 H, d, $^3J = 9.4$ Hz, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5

MHz): δ 229.7 (s, CO), 76.7 (s, Cp), 37.2 (d, $^2J = 4.4$ Hz, Me). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8 , 121.6 MHz): δ 23.7 (s). IR (NaCl plates, Nujol mull, cm^{-1}): 1864 (s, $\nu(\text{CO})$), 1781 (s, $\nu(\text{CO})$), 1753 (s, $\nu(\text{CO})$), 1299 (s), 1196 (s), 1174 (s), 1105 (w), 1070 (s), 987 (s), 776 (m), 754 (s), 676 (w). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1787 (s), 1742 (s). Anal. found (calcd. for $\text{C}_{38}\text{H}_{82}\text{CaFe}_2\text{N}_{12}\text{O}_8\text{P}_4$): C, 40.92 (41.09); H, 7.28 (7.44); N, 14.72 (15.13)%.

YbFp₂(HMPA)₄ (12). To a stirring Yb amalgam (4.89 g, 28.3 mmol Yb; 20 mL Hg) was added a solution of HMPA (8.26 mL, 47.4 mmol) in THF (10 mL). The colorless solution was stirred over the amalgam for 10 min at RT then a solution of Fp₂ (2.00 g, 5.65 mmol) in THF (20 mL) added. The red solution was stirred over the amalgam for 16 h at RT. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting red solid was washed with pentane (2 x 10 mL) then dried *in vacuo* to afford **12** as an orange solid. Yield: 6.93 g (99%). Diffraction-quality crystals were grown from THF at RT. ^1H NMR (THF- d_8 , 299.9 MHz): δ 4.24 (10 H, s, Cp), 2.66 (72 H, d, $^3J = 8.2$ Hz, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5 MHz): δ 230.0 (s, CO), 76.7 (s, Cp), 37.2 (d, $^2J = 4.1$ Hz, Me). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8 , 121.6 MHz): δ 26.6 (s). IR (NaCl plates, Nujol mull, cm^{-1}): 1863 (s, $\nu(\text{CO})$), 1749 (s, br, $\nu(\text{CO})$), 1300 (s), 1194 (s), 1169 (s), 1104 (m), 1068 (m), 985 (s), 803 (w), 752 (s), 671 (m). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1790 (m), 1746 (m). Anal. found (calcd. for $\text{C}_{38}\text{H}_{82}\text{Fe}_2\text{N}_{12}\text{O}_8\text{P}_4\text{Yb}_1$): C, 36.51 (36.70); H, 6.47 (6.65); N, 13.39 (13.51)%.

SrFp₂ (13). To a stirring Sr amalgam (1.24 g, 14.1 mmol Sr; 15 mL Hg) was added a solution of Fp₂ (1.00 g, 2.83 mmol) in THF (20 mL). The red solution was stirred over the amalgam for 16 h at RT. The solution was filtered away from the amalgam and volatiles removed under reduced pressure to give a brown solid. The solid was washed with pentane (2 x 10 mL) and dried *in vacuo* to afford **13** as a dark orange solid (1.20 g). ^1H NMR (THF- d_8 , 299.9 MHz): δ 4.29 (s, Cp). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5 MHz): δ 229.6 (CO), 78.0 (Cp). IR (NaCl plates, Nujol mull, cm^{-1}): 1871 (s, br, $\nu(\text{CO})$), 1808 (m, $\nu(\text{CO})$), 1749 (m, $\nu(\text{CO})$), 1590 (w), 1260 (m), 1170 (w), 1107 (m), 1032 (m), 1011 (m), 797 (s), 673 (m). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1878 (s), 1712 (s). A satisfactory elemental analysis could not be obtained due to the extreme sensitivity of the product.

Reaction of Fe₃(CO)₁₂ with Ca in liquid ammonia. NH_{3(g)} was condensed (20 mL) onto elemental Ca (0.637 g, 0.16 mmol) and Fe₃(CO)₁₂ (2.00 g, 3.97 mmol) at -78 °C to give a blue solution and formation of a yellow mirror on the wall of the vessel. The material was stirred at -78 °C for 5 h then allowed to gradually warm to RT, allowing evaporation of NH₃, then was then dried *in vacuo*. To the resultant grey solid was added MeCN (40 mL) and the resulting red mixture was stirred for 16 h at RT. The solution was filtered and volatiles removed under reduced pressure. The resulting solid was washed with pentane (2 x 5 mL) then dried *in vacuo* to afford [Ca{Fe₂(CO)₈}(MeCN)₅]_∞ (**S3**) as a yellow solid. Yield: 0.644 g (18%). Diffraction-quality crystals were grown from MeCN at RT.

$^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5 MHz): δ 230.1 (CO). EI-MS: m/z = 196 (70%) $[\text{Fe}(\text{CO})_5]^+$, 168 (100%) $[\text{Fe}(\text{CO})_4]^+$, 140 (70%) $[\text{Fe}(\text{CO})_3]^+$, 112 (80%) $[\text{Fe}(\text{CO})_2]^+$, 84 (100%) $[\text{Fe}(\text{CO})]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 2304 (m), 2279 (s), 2208 (w), 2003 (sh, $\nu(\text{CO})$), 1945 (s, br, $\nu(\text{CO})$), 1881 (s, br, $\nu(\text{CO})$), 1580 (s, br), 1261 (m), 1092 (w), 1035 (m), 931 (w), 799 (w), 695 (m), 650 (m), 620 (m), 578 (m). A satisfactory elemental analysis could not be obtained.

Reaction of $\text{Fe}_3(\text{CO})_{12}$ with Ca amalgam.

Method 1. To a stirring Ca amalgam (2.39 g, 59.6 mmol; 20 mL Hg) was added a suspension of $\text{Fe}_3(\text{CO})_{12}$ (2.00 g, 3.97 mmol) in THF (30 mL). An immediate color change from teal to red was observed. The mixture was stirred over the amalgam for 16 h at RT. The red suspension was decanted away from the amalgam. The amalgam was washed with THF (20 mL) and the washings combined with the red suspension. Volatiles were removed under reduced pressure. To the resulting brown solid was added MeCN (20 mL) and the resulting red solution was stirred for 16 h at RT. The solution was filtered and volatiles were removed under reduced pressure. The resulting solid was dried *in vacuo* to afford $[\text{Ca}\{\text{Fe}_3(\text{CO})_{11}\}(\text{MeCN})_4]_\infty$ (**S4**) as a dark red-black microcrystalline solid. Yield: 1.94 g (72%). Diffraction-quality crystals were grown from MeCN at RT. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 75.5 MHz): δ 232.8 (CO), 225.3 (CO). IR (NaCl plates, Nujol mull, cm^{-1}): 2303 (m), 2272 (s), 2203 (w), 2000 (sh, $\nu(\text{CO})$), 1933 (s, br, $\nu(\text{CO})$), 1879 (s, br, $\nu(\text{CO})$), 1619 (w), 1562 (w), 1302 (w), 1261 (w), 1155 (w), 1080 (w), 1029 (m), 929 (w), 798 (m), 722 (m), 684 (m), 619 (m). Anal. found (calcd. for $\text{C}_{19}\text{H}_{12}\text{CaFe}_3\text{N}_4\text{O}_{11}$): C, 33.36 (33.56); H, 1.67 (1.78); N, 8.05 (8.24)%.

Method 2. To a stirring Ca amalgam (1.19 g, 29.8 mmol; 20 mL Hg) was added a solution of HMPA (4.15 mL, 23.8 mmol) in THF (10 mL). The colorless solution was stirred over the amalgam for 10 min at RT then a suspension of $\text{Fe}_3(\text{CO})_{12}$ (1.00 g, 1.99 mmol) in THF (20 mL) was added. An immediate color change from teal to purple was observed followed by a gradual transition to brown. The suspension was stirred over the amalgam for 16 h at RT. The suspension was decanted away from the amalgam and filtered, isolating a brown solid. To the solid was added MeCN (40 mL) and the resulting red solution was stirred for 16 h at RT. The solution was filtered and volatiles removed under reduced pressure. The resulting solid was washed with pentane (2 x 10 mL) and dried *in vacuo* to afford $[\text{Ca}(\text{HMPA})_5(\text{MeCN})][\text{Fe}_2(\text{CO})_8]$ (**S5**) as a red solid. Yield: 2.68 g (66%). Diffraction-quality crystals were grown from MeCN at RT. ^1H NMR (CD_3CN , 299.9 MHz): δ 2.60 (d, $^3J = 9.5$ Hz, 90 H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 75.5 MHz): δ 236.4 (CO), 225.6 (CO), 225.4 (CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN , 121.6 MHz): δ 23.8 (s). IR (NaCl plates, Nujol, cm^{-1}): Broad band from 2000-1600 with maxima at 1905 (s, br, $\nu(\text{CO})$), 1851 (s, br, $\nu(\text{CO})$), 1801 (s, br, $\nu(\text{CO})$) 1764 (s, br, $\nu(\text{CO})$). Other bands at 1300 (s), 1193 (s), 1165 (s), 1067 (m), 986 (s), 799 (w), 749 (s), 698 (m). A satisfactory elemental analysis could not be obtained.

Following filtration, the THF solution produced in the synthesis of **S5** was under reduced pressure to give a black viscous oil. Reduced pressure (to 10^{-2} mbar) was maintained for a further 5 h to afford a waxy green solid. The material was washed with pentane (2 x 10 mL) and dried *in vacuo* to afford $[\text{Ca}\{\text{Fe}(\text{CO})_4\}(\text{HMPA})_3(\text{THF})]_\infty$ (**S6**) as a green solid. Yield: 0.458 g (8%). Diffraction-quality crystals were grown from THF at RT. ^1H NMR (THF- d_8 , 299.9 MHz): δ 2.63 (s, 72 H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5 MHz): δ 250.2 (CO), 37.4 (Me). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8 , 121.6 MHz): δ 25.5 (s). IR (NaCl plates, Nujol, cm^{-1}): 1877 (s, br, $\nu(\text{CO})$), 1745 (s, $\nu(\text{CO})$), 1686 (s, $\nu(\text{CO})$), 1300 (s), 1261 (m), 1194 (s), 1068 (m), 987 (s), 890 (w), 801 (m), 747 (s). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1875 (s). A satisfactory elemental analysis could not be obtained.

$\text{Ca}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_4$ (16). To a stirring Ca amalgam (0.124 g, 3.08 mmol Ca; 10 mL Hg) was added a red suspension of $[\text{Co}(\text{CO})_3(\text{PPh}_3)]_2$ (0.500 g, 0.617 mmol) in THF (30 mL). The suspension was stirred over the amalgam for 16 h at RT to give a green solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was washed with hexanes (2 x 10 mL) and dried *in vacuo* to afford **16** as a pale green solid. Yield: 0.501 g (71%). Diffraction-quality crystals were grown from THF at RT. ^1H NMR (THF- d_8 , 299.9 MHz): δ 7.49 (24 H, s, 2,6- C_6H_5), 7.19 (32 H, s, 4- & 3,5- C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5 MHz): δ 142.9 (d, $^1J = 29.4$ Hz, 1- C_6H_5), 134.3 (d, $^2J = 13.8$ Hz, 2,6- C_6H_5), 128.8 (s, 4- C_6H_5), 128.2 (d, $^4J = 8.8$ Hz, 3,5- C_6H_5) ($\delta(\text{CO})$ not observed). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8 , 121.4 MHz): δ 63.6 (br s). IR (NaCl plates, Nujol mull, cm^{-1}): 1935 (s, $\nu(\text{CO})$), 1861 (s, $\nu(\text{CO})$), 1729 (s, $\nu(\text{CO})$), 1584 (w), 1297 (w), 1261 (w), 1180 (w), 1090 (m), 1026 (m), 918 (w), 872 (m), 801 (w), 746 (m), 696 (m). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1937 (m), 1874 (s), 1721 (s). Anal. found (calcd. for $\text{C}_{58}\text{H}_{62}\text{CaCo}_2\text{O}_{10}\text{P}_2$): C, 61.29 (61.16); H, 5.69 (5.49)%.

$[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_5]_2$ (17). To a stirring Sr amalgam (0.270 g, 3.08 mmol Sr; 10 mL Hg) was added a red suspension of $[\text{Co}(\text{CO})_3(\text{PPh}_3)]_2$ (0.500 g, 0.617 mmol) in THF (30 mL). The suspension was stirred over the amalgam for 16 h at RT to give a yellow solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was washed with hexanes (2 x 10 mL) and dried *in vacuo* to afford **17** as a yellow solid. Yield: 0.604 g (78%). Diffraction-quality crystals were grown from THF at RT. ^1H NMR (THF- d_8 , 299.9 MHz): δ 7.54 (24 H, s, 2,6- C_6H_5), 7.21 (32 H, s, 4- & 3,5- C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5 MHz): δ 143.3 (d, $^1J = 28.7$ Hz, 1- C_6H_5), 134.3 (d, $^2J = 14.1$ Hz, 2,6- C_6H_5), 128.8 (s, 4- C_6H_5), 128.2 (d, $^4J = 8.8$ Hz, 3,5- C_6H_5) ($\delta(\text{CO})$ not observed). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8 , 121.4 MHz): δ 64.1 (br s). IR (NaCl plates, Nujol mull, cm^{-1}): 1930 (s, $\nu(\text{CO})$), 1855 (m, $\nu(\text{CO})$), 1816 (s, br, $\nu(\text{CO})$), 1746 (s, br, $\nu(\text{CO})$), 1585 (w), 1261 (m), 1179 (w), 1089 (m), 1029 (s), 918 (w), 875 (w), 801 (w), 744 (m), 696 (s). IR (NaCl

cell, THF, $\nu(\text{CO})$, cm^{-1}): 1932 (m), 1874 (s), 1737 (s). Anal. found (calcd. for $\text{C}_{124}\text{H}_{140}\text{Co}_4\text{O}_{22}\text{P}_4\text{Sr}_2$): C, 58.91 (59.16); H, 5.48 (5.61)%.

[Ba{Co(CO)₃(PPh₃)₂(THF)₆]₂ (18). To a stirring Ba amalgam (0.847 g, 6.17 mmol Ba; 20 mL Hg) was added a red suspension of $[\text{Co}(\text{CO})_3(\text{PPh}_3)]_2$ (1.00 g, 1.24 mmol) in THF (50 mL). The suspension was stirred over the amalgam for 16 h at RT to give a green solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was washed with hexanes (2 x 10 mL) and dried *in vacuo* to afford **18** as a dark green solid. Yield: 1.51 g (89%). Diffraction-quality crystals were grown from THF at RT. ^1H NMR (THF-*d*₈, 299.9 MHz): δ 7.50 (24 H, s, 2,6- C_6H_5), 7.18 (32 H, s, 4- & 3,5- C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF-*d*₈, 75.5 MHz): δ 143.3 (d, $^1J = 28.6$ Hz, 1- C_6H_5), 134.3 (d, $^2J = 13.9$ Hz, 2,6- C_6H_5), 128.8 (s, 4- C_6H_5), 128.2 (d, $^4J = 8.8$ Hz, 2,6- C_6H_5) ($\delta(\text{CO})$ not observed). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF-*d*₈, 121.4 MHz): δ 64.3 (br s). IR (NaCl plates, Nujol mull, cm^{-1}): 1924 (s, $\nu(\text{CO})$), 1818 (s, br, $\nu(\text{CO})$), 1780 (s, br, $\nu(\text{CO})$), 1260 (m), 1168 (w), 1087 (m), 1026 (m), 875 (w), 800 (m), 694 (m). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1931 (m), 1872 (s), 1747 (s). Anal. found (calcd. for $\text{C}_{132}\text{H}_{156}\text{Ba}_2\text{Co}_4\text{O}_{24}\text{P}_4$): C, 57.31 (57.42); H, 5.60 (5.70)%.

[Mg{Co(CO)₃(PCy₃)₂(THF)₂]₂ (19). To a stirring magnesium amalgam (0.0574 g, 2.36 mmol Mg; 10 mL mercury) was added a red solution of $[\text{Co}(\text{CO})_3(\text{PCy}_3)]_2$ (**15**) (0.400 g, 0.472 mmol) in THF (30 mL). The solution was stirred over the amalgam for 16 h at RT to give a dark dichroic red/green solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure to give a white solid. The solid was washed with hexanes (2 x 10 mL) and dried *in vacuo* to afford **2** as a white solid. Yield: 0.410 g (87%). Diffraction-quality crystals were grown from toluene layered with pentane at RT. ^1H NMR (C_6D_6 , 500.3 MHz): 3.91 (14 H, br s, OCH_2), 2.26 (24 H, m, 2,6- C_6H_{11}), 2.10 (12 H, m, 1- C_6H_{11}), 1.82 (24 H, m, 3,5- C_6H_{11}), 1.77-1.58 (36 H, m centered at 1.71 & 1.64, overlapping 4 & 2,6- C_6H_{11}), 1.44 (14 H, br s, OCH_2CH_2), 1.28 (36 H, m, 4 & 3,5- C_6H_{11}). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz): 210.4 (s, CO), 69.2 (s, OCH_2), 37.7 (d, $^1J = 16.6$ Hz, 1- C_6H_{11}), 30.4 (s, 2,6- C_6H_{11}), 28.2 (d, $^3J = 10.2$ Hz, 3,5- C_6H_{11}), 27.0 (s, 4- C_6H_{11}), 25.5 (s, OCH_2CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.4 MHz): 68.6 (br s). IR (NaCl plates, Nujol mull, cm^{-1}): 1935 (s, $\nu(\text{CO})$), 1861 (s, $\nu(\text{CO})$), 1720 (s, $\nu(\text{CO})$), 1261 (w), 1171 (w), 1026 (m), 918 (w), 882 (w), 850 (w), 801 (w). IR (NaCl plates, toluene, cm^{-1}): 1905 (s, $\nu(\text{CO})$), 1842 (m, $\nu(\text{CO})$), 1701 (m, $\nu(\text{CO})$). Anal. found (calcd. for $\text{C}_{98}\text{H}_{160}\text{Co}_4\text{Mg}_2\text{O}_{15.5}\text{P}_4$ (**2**·1.5(THF)): C, 58.75 (59.01); H, 7.93 (8.09)%.

[Ca{Co(CO)₃(PCy₃)₂(THF)₂]_∞ (20). To a stirring calcium amalgam (0.118 g, 2.95 mmol Ca; 10 mL mercury) was added a red solution of $[\text{Co}(\text{CO})_3(\text{PCy}_3)]_2$ (**15**) (0.500 g, 0.590 mmol) in THF (30 mL). The solution was stirred over the amalgam for 16 h at RT to give a dark dichroic red/green solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was dried *in vacuo* to afford **20** as a white solid. Yield: 0.512 g (84%).

Diffraction-quality crystals were grown from toluene layered with pentane at RT. ^1H NMR (C_6D_6 , 500.3 MHz): 4.00 (8 H, br s, OCH_2), 2.21 (12 H, m, 2,6- C_6H_{11}), 1.97 (6 H, m, 1- C_6H_{11}), 1.86 (12 H, m, 3,5- C_6H_{11}), 1.76-1.53 (26 H, m centered at 1.71 & 1.65 and br s at 1.59, overlapping 4 & 2,6- C_6H_{11} and OCH_2CH_2), 1.33 (18 H, m, 4 & 3,5- C_6H_{11}). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz): 217.4 (s, CO), 69.2 (s, OCH_2), 37.4 (d, $^1J = 14.9$ Hz, 1- C_6H_{11}), 30.5 (s, 2,6- C_6H_{11}), 28.3 (d, $^3J = 10.0$ Hz, 3,5- C_6H_{11}), 27.2 (s, 4- C_6H_{11}), 25.7 (s, OCH_2CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.4 MHz): 71.2 (br s). IR (NaCl plates, Nujol mull, cm^{-1}): 1929 (s, $\nu(\text{CO})$), 1844 (s, $\nu(\text{CO})$), 1743 (s, $\nu(\text{CO})$), 1718 (s, $\nu(\text{CO})$), 1261 (w), 1028 (m), 876 (w), 803 (w). IR (NaCl plates, toluene, cm^{-1}): 1913 (s, $\nu(\text{CO})$), 1838 (m, $\nu(\text{CO})$), 1755 (s, $\nu(\text{CO})$), 1718 (s, $\nu(\text{CO})$). Anal. found (calcd. for $\text{C}_{50}\text{H}_{82}\text{CaCo}_2\text{O}_8\text{P}_2$): C, 58.08 (58.24); H, 7.92 (8.02)%.

$[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PCy}_3)_2(\text{THF})_3\}]_\infty$ (21). To a stirring strontium amalgam (0.207 g, 2.36 mmol Sr; 10 mL mercury) was added a red solution of $[\text{Co}(\text{CO})_3(\text{PCy}_3)_2]$ (**15**) (0.400 g, 0.472 mmol) in THF (30 mL). The solution was stirred over the amalgam for 16 h at RT to give a dark dichroic red/green solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure to give a white solid. The solid was washed with hexanes (2 x 10 mL) and dried *in vacuo* to afford **21** as a white solid. Yield: 0.381 g (70%). Diffraction-quality crystals were grown from pentane at RT. ^1H NMR (C_6D_6 , 500.3 MHz): 4.05 (12 H, br s, OCH_2), 2.21 (12 H, m, 2,6- C_6H_{11}), 2.05-1.81 (18 H, m centered at 1.96 & 1.89, overlapping 1- C_6H_{11} & 3,5- C_6H_{11}), 1.79-1.52 (30 H, m centered at 1.73 & 1.67 and br s at 1.60, overlapping 4 & 2,6- C_6H_{11} and OCH_2CH_2), 1.34 (18 H, m, 4 & 3,5- C_6H_{11}). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz): 217.8 (s, CO), 69.0 (s, OCH_2), 37.5 (d, $^1J = 14.9$ Hz, 1- C_6H_{11}), 30.5 (s, 2,6- C_6H_{11}), 28.4 (d, $^3J = 10.1$ Hz, 3,5- C_6H_{11}), 27.2 (s, 4- C_6H_{11}), 25.7 (s, OCH_2CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.4 MHz): 71.7 (br s). IR (NaCl plates, Nujol mull, cm^{-1}): 1916 (m, $\nu(\text{CO})$), 1821 (s, $\nu(\text{CO})$), 1787 (s, $\nu(\text{CO})$), 1743 $\nu(\text{CO})$, 1260 (w), 1036 (m), 886 (w), 851 (w), 800 (w). IR (NaCl plates, toluene, cm^{-1}): 1913 (s, $\nu(\text{CO})$), 1837 (s, $\nu(\text{CO})$), 1755 (s, $\nu(\text{CO})$), 1717 (m, $\nu(\text{CO})$). Anal. found (calcd. for $\text{C}_{54}\text{H}_{90}\text{Co}_2\text{O}_9\text{P}_2\text{Sr}$): C, 56.13 (56.36); H, 8.08 (7.88)%.

$\text{K}[\text{Co}(\text{CO})_3(\text{PCy}_3)](\text{THF})_2$ (22). To a stirring K amalgam (0.231 g, 5.90 mmol K; 10 mL Hg) was added a red solution of $[\text{Co}(\text{CO})_3(\text{PCy}_3)_2]$ (1.00 g, 1.18 mmol) in THF (40 mL). The solution was stirred over the amalgam for 16 h at RT to give a pale-yellow solution which was filtered, and volatiles were removed under reduced pressure. The resulting solid was washed with pentane (2 x 10 mL) and dried *in vacuo* to afford **22** as a white solid. Yield: 1.09 g (76%). Diffraction-quality crystals were grown from THF at RT (see Fig. S18). ^1H NMR ($\text{THF}-d_8$, 500.3 MHz): δ 1.98 (6 H, m, 2,6- C_6H_{11}), 1.73 (overlapping with THF resonance, m, 3,5- C_6H_{11}), 1.64 (6 H, m, overlapping 1- & 4- C_6H_{11}), 1.39 (6 H, m, 2,6- C_6H_{11}), 1.22 (9 H, m, overlapping 4- & 3,5- C_6H_{11}). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF}-d_8$, 125.8 MHz): δ 38.4 (d, $^1J = 11.7$ Hz, 1- C_6H_{11}), 31.1 (d, $^2J = 3.4$ Hz, 2,6- C_6H_{11}), 29.1 (d, $^3J = 9.9$ Hz, 3,5- C_6H_{11}), 28.0 (s, 4- C_6H_{11}) ($\delta(\text{CO})$ not observed). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{THF}-d_8$, 121.4 MHz): δ 74.7 (br

s). IR (NaCl plates, Nujol mull, cm^{-1}): 1921 (s, $\nu(\text{CO})$), 1822 (s, br, $\nu(\text{CO})$), 1756 (s, br, $\nu(\text{CO})$), 1264 (w), 1198 (w), 1173 (w), 1111 (w), 1040 (w), 1005 (w), 916 (w), 851 (w). IR (NaCl cell, **[22]** = 0.33 mmol L^{-1} , THF, $\nu(\text{CO})$, cm^{-1}): 1914 (s), 1839 (s), 1788 (s). Anal. found (calcd. for $\text{C}_{29}\text{H}_{49}\text{CoKO}_5\text{P}$): C, 56.95 (57.41); H, 7.96 (8.14)%.

Ba{Co(CO)₃(PCy₃)₂(THF)₆ (23). To a stirring barium amalgam (0.407 g, 2.95 mmol Ba; 20 mL mercury) was added a red solution of $[\text{Co}(\text{CO})_3(\text{PCy}_3)_2]$ (**15**, 0.500 g, 0.590 mmol) in THF (40 mL). The solution was stirred over the amalgam for 16 h at RT to give a dark dichroic red/green solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure to give an off-white solid. The solid was washed with pentane (2 x 10 mL) and dried *in vacuo* to afford **23** as a white solid. Yield: 0.444 g (53%). Diffraction-quality crystals were grown from THF at RT. ^1H NMR (THF-*d*₈, 500.3 MHz): 1.97 (12 H, m, 2,6-C₆H₁₁), 1.75 (overlapping with THF resonance, m, 3,5-C₆H₁₁), 1.66 (12 H, m, overlapping 1 & 4-C₆H₁₁), 1.38 (12 H, m, 2,6-C₆H₁₁), 1.23 (18 H, m, overlapping 4 & 3,5-C₆H₁₁). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF-*d*₈, 125.8 MHz): 220.9 (s, CO), 38.10 (d, $^1J = 12.8$ Hz, 1-C₆H₁₁), 31.1 (s, 2,6-C₆H₁₁), 29.0 (d, $^3J = 10.0$ Hz, 3,5-C₆H₁₁), 27.9 (s, 4-C₆H₁₁). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF-*d*₈, 121.4 MHz): 76.6 (br s). IR (NaCl plates, Nujol mull, cm^{-1}): 1953 (s, $\nu(\text{CO})$), 1813 (s br, $\nu(\text{CO})$), 1755 (s br, $\nu(\text{CO})$), 1294 (w), 1261 (w), 1194 (w), 1172 (w), 1107 (w), 1039 (m), 1005 (w), 917 (w), 886 (m), 851 (m), 818 (w). IR (NaCl plates, THF, cm^{-1}): 1921 (s, $\nu(\text{CO})$), 1857 (s, $\nu(\text{CO})$), 1737 (s, $\nu(\text{CO})$). Anal. found (calcd. for $\text{C}_{66}\text{H}_{114}\text{BaCo}_2\text{O}_{12}\text{P}_2$): C, 55.69 (55.95); H, 7.89 (8.11)%.

[Yb{Co(CO)₃(PCy₃)₂(THF)₃]₂ (24). To a stirring Yb amalgam (0.409 g, 2.36 mmol Yb; 10 mL Hg) was added a red solution of $[\text{Co}(\text{CO})_3(\text{PCy}_3)_2]$ (0.400 g, 0.472 mmol) in THF (30 mL). The solution was stirred over the amalgam for 16 h at RT to give a yellow solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was washed with pentane (2 x 10 mL) and dried *in vacuo* to afford **24** as a yellow solid. Yield: 0.360 g (62%). Diffraction-quality crystals were grown from pentane at RT. ^1H NMR (C₆D₆, 500.3 MHz): δ 3.84 (24 H, br s, OCH₂), 2.20 (24 H, m, 2,6-C₆H₁₁), 1.98 (12 H, m, 1-C₆H₁₁), 1.82 (24 H, m, 3,5-C₆H₁₁), 1.66 (36 H, m, overlapping 4- & 2,6-C₆H₁₁), 1.50 (24 H, br s, OCH₂CH₂), 1.30 (36 H, m, 4- & 3,5-C₆H₁₁). $^{13}\text{C}\{^1\text{H}\}$ NMR (C₆D₆, 125.8 MHz): δ 217.0 (s, CO), 68.7 (s, OCH₂), 37.5 (d, $^1J = 15.3$ Hz, 1-C₆H₁₁), 30.5 (s, 2,6-C₆H₁₁), 28.3 (d, $^3J = 10.1$ Hz, 3,5-C₆H₁₁), 27.2 (s, 4-C₆H₁₁), 25.7 (s, OCH₂CH₂). $^{31}\text{P}\{^1\text{H}\}$ NMR (C₆D₆, 121.4 MHz): δ 71.6 (br s). IR (NaCl plates, Nujol mull, cm^{-1}): 1914 (s, $\nu(\text{CO})$), 1853 (s, $\nu(\text{CO})$), 1783 (s, $\nu(\text{CO})$), 1757 (s, $\nu(\text{CO})$), 1295 (w), 1262 (w), 1171 (w), 1109 (w), 1028 (s), 915 (w), 884 (m), 850 (w). IR (NaCl cell, toluene, $\nu(\text{CO})$, cm^{-1}): 1897 (s), 1838 (s), 1754 (s), 1718 (m $\nu(\text{CO})$). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1924 (m), 1862 (m), 1712 (s). Anal. found (calcd. for $\text{C}_{108}\text{H}_{180}\text{Co}_4\text{O}_{18}\text{P}_4\text{Yb}_2$): C, 52.21 (52.47); H, 7.13 (7.34)%.

[Eu{Co(CO)₃(PCy₃)₂(THF)₃]_∞ (25). To a stirring Eu amalgam (1.40 g, 9.21 mmol Eu; 20 mL Hg)

was added a red solution of $[\text{Co}(\text{CO})_3(\text{PCy}_3)]_2$ (**15**, 1.56 g, 1.84 mmol) in THF (40 mL). The solution was stirred over the amalgam for 16 h at RT to give a dark dichroic red-green solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was dried *in vacuo* to afford **25** as a light silver-green solid. Yield: 1.67 g (75%). Diffraction-quality crystals of **25** were grown from pentane at RT. Diffraction-quality crystals of $[\text{Eu}\{\text{Co}(\text{CO})_3(\text{PCy}_3)_2(\text{THF})_4\}]_\infty$ (**25·THF**) were grown from THF at RT. Interpretable NMR data could not be obtained for this compound due to its extreme paramagnetism. IR (NaCl plates, Nujol mull, cm^{-1}): 1918 (s, $\nu(\text{CO})$), 1797 (s, br $\nu(\text{CO})$), 1746 (s, br, $\nu(\text{CO})$), 1293 (w), 1261 (w), 1172 (w), 1109 (w), 1040 (m), 915 (w), 887 (m), 850 (m), 801 (w). IR (NaCl cell, toluene, $\nu(\text{CO})$, cm^{-1}): 1892 (s), 1837 (s), 1755 (s), 1718 (m). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1922 (m), 1860 (m), 1720 (s). Anal. found (calcd. for $\text{C}_{54}\text{H}_{90}\text{Co}_2\text{EuO}_9\text{P}_2$): C, 53.19 (53.38); H, 7.31 (7.47)%.

Sm{Co(CO)₃(PCy₃)₂(THF)₃ (26). To a stirring Sm amalgam (0.887 g, 5.90 mmol Sm; 20 mL Hg) was added a red solution of $[\text{Co}(\text{CO})_3(\text{PCy}_3)]_2$ (**15**, 1.00 g, 1.18 mmol) in THF (40 mL). The solution was stirred over the amalgam for 16 h at RT to give a dark solution which was filtered away from the amalgam and volatiles removed under reduced pressure to afford **26** as a dark green solid. Yield: 1.19 g (83%). Diffraction-quality crystals of $\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_6$ (**26·3THF**) were grown from THF at 5 °C. ^1H NMR (THF-*d*₈, 500.3 MHz): δ 2.53 (12 H, br s, 2,6- C_6H_{11}), 2.09-1.64 (m centered at 1.92 & 1.76, overlapping 2,6-, 3,5-, 1- & 4- C_6H_{11} overlapping with THF resonance) 1.56-1.19 (18 H, m centered at 1.46 & 1.38, overlapping 3,5- & 4- C_6H_{11}). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF-*d*₈, 125.8 MHz): δ 36.2 (d, $^1J = 12.4$ Hz, 1- C_6H_{11}), 30.5 (s, 2,6- C_6H_{11}), 28.8 (d, $^3J = 10.0$ Hz, 3,5- C_6H_{11}), 27.8 (s, 4- C_6H_{11}) ($\delta(\text{CO})$ not observed). EI-MS: $m/z = 280$ (40%) $[\text{PCy}_3]^+$, 198 (100%) $[\text{HPCy}_2]^+$, 143 (35%) $[\text{Co}(\text{CO})_3]^+$, 117 (100%) $[\text{H}_3\text{PCy}]^+$, 83 (80%) $[\text{C}_6\text{H}_{11}]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 1917 (s, $\nu(\text{CO})$), 1859 (m, $\nu(\text{CO})$), 1801 (s, $\nu(\text{CO})$), 1750 (s, $\nu(\text{CO})$), 1340 (w), 1293 (w), 1261 (w), 1196 (w), 1171 (w), 1109 (w), 1041 (m), 915 (w), 888 (m), 851 (m), 817 (w), 727 (w). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1921 (m), 1861 (m), 1712 (s). Anal. found (calcd. for $\text{C}_{54}\text{H}_{90}\text{Co}_2\text{O}_9\text{P}_2\text{Sm}$): C, 54.10 (53.45); H, 9.77 (7.48)%. The higher than expected %C,H may reflect retention of additional THF despite prolonged drying *in vacuo*; the paramagnetic nature of Sm(II) prevented accurate NMR integration of the sample to test this hypothesis.

Sm{Co(CO)₃(PCy₃)₃(THF)₃ (27). $\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3$ (450 mg, 0.371 mmol, prepared as above) was dissolved in benzene (10 mL) to give a dark red-black solution. This was filtered away from the grey, insoluble residue (believed to be elemental Sm) which was extracted with a further aliquot of benzene (10 mL). Volatiles were removed from the combined solution under reduced pressure to afford **27** as a dark red-black solid which was dried *in vacuo*. Yield: 348 mg (86% based on $\text{Co}(\text{CO})_3(\text{PCy}_3)$). Diffraction-quality crystals were grown from pentane at RT. ^1H NMR (C_6D_6 , 500.3 MHz): δ 3.61 (12 H, br s, OCH_2), 1.87 (12 H, br s, 2,6- C_6H_{11}), 2.05-1.54 (18 H, br s centered at

1.73 & 1.67, overlapping 3,5- & 4-C₆H₁₁) 1.41 (12 H, br s, 2,6-C₆H₁₁), 1.22 (18 H, br s, 4- & 3,5-C₆H₁₁), 0.25 (6 H, br s, 1-C₆H₁₁), -0.33 (12 H, br s, OCH₂CH₂). ¹³C{¹H} NMR (C₆D₆, 125.8 MHz): δ 31.1 (d, ¹J = 14.7 Hz, 1-C₆H₁₁), 28.1 (d, ³J = 9.8 Hz, 3,5-C₆H₁₁), 27.7 (s, 2,6-C₆H₁₁ & OCH₂), 22.3 (s, 4-C₆H₁₁), 22.2 (s, OCH₂CH₂) (δ(CO) not observed). EI-MS: *m/z* = 280 (40%) [PCy₃]⁺, 198 (100%) [HPCy₂]⁺, 143 (30%) [Co(CO)₃]⁺, 117 (100%) [H₃PCy]⁺, 83 (80%) [C₆H₁₁]⁺. IR (NaCl plates, Nujol mull, cm⁻¹): 1917 (s, ν(CO)), 1861 (s, br, ν(CO)), 1766 (s, br, ν(CO)), 1342 (w), 1295 (w), 1262 (m), 1198 (w), 1172 (m), 1111 (m), 1035 (m), 1006 (m), 916 (w), 887 (m), 851 (m), 818 (m), 728 (m). IR (NaCl cell, toluene, ν(CO), cm⁻¹): 1893 (s), 1837 (s), 1755 (s), 1717 (m). A satisfactory analysis could not be obtained: anal. found (calcd. for C₇₅H₁₂₃Co₃O₁₂P₃Sm): C, 48.71 (55.03); H, 6.85 (7.57)%.

Alternative synthesis of Sm{Co(CO)₃(PCy₃)₃}(THF)₃ (27). To SmI₂ (167 mg, 0.412 mmol) and K[Co(CO)₃(PCy₃)](THF)₂ (**22**, 0.500 g, 0.824 mmol) was added THF (20 mL). The resulting blue solution was stirred for 24 h at RT, filtered and volatiles were removed under reduced pressure to give crude **26** (contaminated with unreacted SmI₂ and **22**) as a green solid (yield: 561 mg). This was extracted into benzene (20 mL) to give a dark red-purple solution which was filtered and the volatiles removed under reduced pressure to afford **27** as a dark red-black solid. Yield: 298 mg (71%). IR (NaCl plates, Nujol mull, cm⁻¹): identical to that for Sm{Co(CO)₃(PCy₃)₃}(THF)₃ (**27**) when synthesised *via* Sm{Co(CO)₃(PCy₃)₂}(THF)₃ (**26**) prepared from Sm amalgam and [Co(CO)₃(PCy₃)₂]₂ (**15**).

Diffusion NMR measurements. Samples of [Co(CO)₃(PCy₃)₂]₂ (**15**), [Mg{Co(CO)₃(PCy₃)₂}(THF)]₂ (**19**), [Sr{Co(CO)₃(PCy₃)₂}(THF)₃]_∞ (**21**) and [Yb{Co(CO)₃(PCy₃)₂}(THF)₃]₂ (**24**) were prepared with a concentration of 0.01 mol L⁻¹ in toluene-*d*₈. Diffusion NMR spectra were collected on a Bruker AVII500 spectrometer equipped with a ¹H/¹³C/¹⁹F TXI probe regulated at 298 K with an air flow of 800 L h⁻¹. Samples were equilibrated in the probe for at least 30 min prior to data collection. The bipolar LED stimulated echo sequence⁷ was used with a diffusion time Δ of 100 ms and 4 ms gradient pulses (applied as sine-bell shaped bipolar pairs of 2 ms each). Signal attenuation was monitored over 16 experiments with gradients strengths ranging from 2-60% of maximum (53.5 G cm⁻¹). Signal decays were fitted to the Stejskal-Tanner equation using the Bruker *T₁/T₂ Relaxation* module within TOPSPIN 2.1. For all samples the residual toluene solvent signal was used as an internal reference signal to monitor for possible viscosity differences between sample preparations.

Diffusion coefficients *D* were used to calculate hydrodynamic radii *r_s* according to the Stokes-Einstein equation (*r_s* = *kT*/6π*ηD*) assuming solvent viscosity to be that of the pure (protio) solvent (0.56 mPa.s at 298 K).⁸ Effective molecule volumes were then derived from these radii as spherical volumes. Molecular volumes derived from crystal structures were determined using Accelrys

Discovery Studio Visualiser 2.5.5⁹ based on a solvent accessible surface area determined using a 1.4 Angstrom probe.

X-ray data collection and processing procedures. Crystals were mounted on glass fibres using perfluoropolyether oil and cooled rapidly in a stream of cold N₂ using an Oxford Cryosystems Cryostream unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer or Agilent Technologies Supernova diffractometer using Mo-K α or Cu-K α , respectively. As appropriate, absorption and decay corrections were applied to the data and equivalent reflections merged.^{10,11} The structures were solved using SIR92¹² or Superflip¹³ and further refinements and all other crystallographic calculations were performed using the CRYSTALS program suite.¹⁴ *The CIF supporting information file contains specific details for the refinements of the individual structures.*

Computational Details. Gradient-corrected density functional theory calculations were carried out using the PBE functional,¹⁵ as implemented in the Amsterdam Density Functional 2012.01¹⁶ (ADF) and the Gaussian 09 Rev. C.01 (G09)¹⁷ quantum chemistry codes. Atoms-in-molecules analyses were performed using the AIMALL programme,¹⁸ using wavefunction or formatted G09 checkpoint files as input.

Geometry optimisations were carried out in G09, without symmetry constraints. The cc-pVDZ basis set of Dunning *et al.* was used for all atoms except Sr, for which a 28 electron pseudopotential was used, in conjunction with a (6s6p5d)/[4s4p2d] valence basis set.¹⁹ The ultrafine grid was employed, together with default geometry convergence criteria. The SCF convergence criterion was set to 10⁻⁶ in all cases. Frequencies calculations were performed at all optimised geometries, yielding no imaginary frequencies in all cases, and were used in the calculation of ΔG for the described reactions (SCF total energies modified with zero point energies, thermal corrections to 298.15 K, and entropic corrections).

Single point calculations were performed in the ADF code using the Zeroth Order Regular Approximation (ZORA) Hamiltonian. Slater Type Orbital ZORA basis sets of TZP quality were used for all atoms bar H, for which a DZP ZORA basis set was employed. The frozen core approximation was employed for all atoms; Mg(1s), P(2p), Ca(2p), Co(2p), Sr(3p) and 1s for all other atoms except H. The default SCF convergence criteria were used, together with an integration grid of 4.5. Ziegler-Rauk bond energy decomposition analyses were performed.²⁰ The orbital mixing (and hence total energy) terms were corrected for basis set superposition error *via* the counterpoise method. Quoted Mulliken charges are from ADF.

DFT Converged Cartesian atomic coordinates and total SCF energies (Hartree)

The coordinates for the following structures are provided as a separate .XYZ file elsewhere in the Supporting Information. The total SCF energies (Hartree) are given in brackets below after each compound.

THF	[-232.157623377]
[Mg{Co(CO) ₃ (PMe ₃) ₂ (THF)} ₂ (19Q)	[-9597.1319236]
Mg{Co(CO) ₃ (PMe ₃) ₂ (THF)} (19_monoQ)	[-4798.5461836]
[Mg{Co(CO) ₄ } ₂ (THF)] ₂ (28Q)	[-8206.9222514]
Be{Co(CO) ₃ (PMe ₃) ₂ } (31Q)	[-4381.09182122]
[Be{Co(CO) ₃ (PMe ₃) ₂ } ₂ (29Q)	[-8762.19702862]
Be{Co(CO) ₃ (PMe ₃) ₂ (THF)} (30Q)	[-4613.27390717]
[Ca{Co(CO) ₃ (PMe ₃) ₂ (THF) ₂ } ₂ (20Q)	[-11016.3908483]
[Ca{Co(CO) ₃ (PMe ₃) ₂ (THF) ₃ } ₂ (20·THFQ)	[-11480.7266808]
[Sr{Co(CO) ₃ (PMe ₃) ₂ (THF) ₃ } ₂ (21Q)	[-10187.4140963]
[Sr{Co(CO) ₃ (PMe ₃) ₂ (THF) ₄ } ₂ (21·THFQ)	[-10651.7339004]
[Co(CO) ₃ (PCy ₃)] ⁻ (relaxed geometry) (S7Q)	[-2757.7374053]
Co(CO) ₃ (PCy ₃)H (S8Q)	[-2758.2582538]
[Co(CO) ₃ (PCy ₃)] ⁻ (S9Q)	[-2757.7216005]
[Co(CO) ₃ (CO)] ⁻ (S11Q)	[-1835.677053]

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