Supporting Information of the manuscript entitled:

Transformation of the cyclo-P₄ ligand in [Cp””Co(η⁴-P₄)]

Content
1. Synthetic procedures and experimental details ................................................................. 2
   1.1 Synthesis of [K(dme)]₂[(Cp””Co)(µ,η³:η³-P₆)] (2a) ...................................................... 3
   1.2 Synthesis of [K(2,2,2-crypt)]₂[(Cp””Co)(µ,η³:η³-P₆)] (2b) ............................................. 4
   1.3 Synthesis of [Li(2,2,2-crypt)][Cp””Co(η²-P₄Bu)] (4) ................................................... 5
   1.4 Synthesis of [Li(2,2,2-crypt)][Cp””Co(η³-P₄CH₂SiMe₃)] and [Li(12-c-4)]₂[Cp””Co(η³-P₄CH₂SiMe₃)] ............................................................ 7
   1.5 Synthesis of [Li(dme)]₂[(Cp””Co)(µ,η³:η³-P₆CH₂SiMe₃)] (8) ........................................... 9
   1.6 Synthesis of [Na(dme)]₂[Cp””Co(η³-P₄(OH))] (10) .................................................... 10
2. NMR spectroscopic investigations ....................................................................................... 11
   2.1 [K(dme)]₂[(Cp””Co)(µ,η³:η³-P₆)] (2a) ........................................................................... 11
   2.2 [K(2,2,2-crypt)]₂[(Cp””Co)(µ,η³:η³-P₆)] (2b) ................................................................. 13
   2.3 [Li(2,2,2-crypt)][Cp””Co(η³-P₄Bu)] (4) ................................................................. 14
   2.4 [Li(2,2,2-crypt)][Cp””Co(η²-P₄CH₂SiMe₃)] (7) ........................................................... 21
   2.5 [Li(dme)]₂[(Cp””Co)(µ,η³:η³-P₆CH₂SiMe₃)] (8) .............................................................. 24
   2.6 1 + LiCH₂SiMe₃ VT-NMR .......................................................................................... 25
   2.7 [Na(dme)]₂[Cp””Co(η³-P₄(OH))] (10) ......................................................................... 27
3. Cyclic voltammogram of 1 ................................................................................................. 28
4. Details on single crystal X-ray structure analysis .............................................................. 30
   4.1 [K(dme)]₂[(Cp””Co)(µ,η³:η³-P₆)] (2a) ........................................................................... 31
   4.2 [K(2,2,2-crypt)]₂[(Cp””Co)(µ,η³:η³-P₆)] (2b) ................................................................. 32
   4.5 [Li(2,2,2-crypt)][Cp””Co(η³-P₄Bu)] (4) ................................................................. 33
   4.6 [Li(thf)]₂[(Cp””Co)(µ,η³:η³-P₆Bu)] (5) ......................................................................... 34
   4.6 [Li(12-c-4)]₂[Cp””Co(η³-P₄Bu)] (6) ........................................................................... 36
   4.3 [Li(2,2,2-crypt)][Cp””Co(η³-P₄CH₂SiMe₃)] (7a) ............................................................. 37
   4.4 [Li(dme)]₂[(Cp””Co)(µ,η³:η³-P₆CH₂SiMe₃)] (8) .............................................................. 39
   3.6 [Na(dme)]₂[Cp””Co(η³-P₄(OH))] (10) ......................................................................... 41
3.7 Crystallographic information ............................................................................................ 42
4. Computational Details ........................................................................................................ 44
5. References .......................................................................................................................... 52
1. Synthetic procedures and experimental details

**Synthetic Procedures:** All manipulations were performed under an atmosphere of dry argon using standard glove-box and Schlenk techniques. All solvents were degassed and purified by standard procedures. The compounds [Cp'''Co(η⁴-P₄)] (1)[¹], LiCH₂SiMe₃[²] and K[CpFe(CO)₂][³] were prepared according to literature procedures. 2,2,2-cryptand, NaOH and 'BuLi were purchased commercially.

The NMR spectra were recorded with a Bruker Avance 400 spectrometer (¹H: 400.13 MHz, ³¹P: 161.976 MHz). The chemical shifts are given in ppm referenced to external SiMe₄ (¹H) and H₃PO₄ (³¹P). Elemental analyses were determined with an Elementar Vario EL III apparatus. The ESI-MS spectra were acquired on a ThermoQuest Finnigan MAT TSQ 7000 mass spectrometer.
1.1 Synthesis of \([\text{K(dme)}_2[(\text{Cp'''Co})_2(\mu,\eta^3:\eta^3-P_8)]\) (2a)

A solution of \([\text{K(CpFe(CO)}_2]\) (260 mg, 1.201 mmol, 1 eq) in dme was added to a stirred solution of \(\text{I}\) (500 mg, 1.201 mmol, 1 eq) in dme at -50 °C while the color changed from dark red to purple. The reaction mixture was warmed to room temperature and after 2 h a color change from purple to brown to green was observed. The solvent was removed in vacuo. The residue was washed with n-hexane to remove \([\text{CpFe(CO)}_2]\) (brown solution). n-Hexane was added and dme was added slowly until complete dissolution. After storage at -30 °C overnight, 2a could be obtained as dark green blocks. The supernatant was decanted off, washed with n-hexane and the crystals dried in vacuo.

Yield: 260 mg (40%)

\(^1\text{H NMR}\) (thf-d8, 25 °C): \(\delta\) [ppm] = 3.96 (s, 4H, \(\text{C}_5\text{H}_2\text{tBu}_3\)), 3.58 (s, 6H, dme), 3.28 (s, 8.5H, dme), 1.31 (s, 36H, \(\text{C}_5\text{H}_2\text{tBu}_3\)), 1.22 (s, 18H, \(\text{C}_5\text{H}_2\text{tBu}_3\)).

\(^{31}\text{P}\{^1\text{H}\}\) NMR (thf-d8, 25 °C): \(\delta\) [ppm] = 96.2 (m, 2P, \(P_A, P_A'\)), 83.1 (m, 4P, \(P_M, P_M, P_M', P_M''\)), -124.2 (m, 2P, \(P_X, P_X'\)) (coupling constants given in table S1).

\(^{31}\text{P NMR}\) (thf-d8, 25 °C): \(\delta\) [ppm] = 96.2 (m, 2P, \(P_A, P_A'\)), 83.1 (m, 4P, \(P_M, P_M, P_M', P_M''\)), -124.2 (m, 2P, \(P_X, P_X'\)) (coupling constants taken from simulation of \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum).

\(\text{ESI-MS}\) (dme): \(m/z = 1279.14\) (50 %, \([\text{Cp'''Co)}_3\text{P}_{13}]\)), 1217.20 (100 %, \([\text{Cp'''Co)}_3\text{P}_{11}]\)), 955.97 (23 %, \([\text{Cp'''Co)}_2\text{P}_{12}]\)), 895.07 (21 %, \([\text{Cp'''Co)}_2\text{P}_{10}\text{H}]\)), 833.12 (23%, \([\text{Cp'''Co)}_2\text{P}_{9}\text{H}]\)).

\(\text{EA C}_{42}\text{H}_{78}\text{O}_{3}\text{K}_2\text{P}_{8}\text{Co}_2\): calc [%]: C 46.24; H 7.21; found [%]: C 46.11; H 7.04.
1.2 Synthesis of [K(2,2,2-crypt)]$_2$[(Cp”’Co)$_2$(μ,η$^3$-η$^3$-P$_8$)] (2b)

A solution of K[CpFe(CO)$_2$] (101.7 mg, 0.47 mmol, 1 eq) in dme was added to a stirred solution of I (196 mg, 0.47 mmol, 1 eq) in dme at -50 °C while the color changed from dark red to purple. The reaction mixture was warmed to room temperature and after 2 h a color change from purple to brown to green was observed. The solvent was removed in vacuo. The residue was washed with n-hexane to remove [CpFe(CO)$_2$]$_2$ (brown solution). The residue was dissolved in dme (dark green) and 2,2,2-cryptand (177.2 mg, 0.47 mmol, 1 eq) in dme was added. After stirring for 5 minutes some green precipitate was formed. Acetonitrile was added dropwise until complete dissolution. After storage at -30 °C, 2b can be obtained as dark green plates. The supernatant was decanted off, washed with n-hexane and the crystals dried in vacuo.

Yield: 94 mg (24 %).

$^1$H NMR (CD$_3$CN, 25 °C): δ [ppm] = 3.94 (s, 4H, C$_5$H$_2$Bu$_3$), 3.56 (s, 24H, 2,2,2-cryptand), 3.52 (t, 24H, 2,2,2-cryptand, $^1$J$_{HH}$ = 4.7 Hz), 2.53 (t, 24H, 2,2,2-cryptand, $^1$J$_{HH}$ = 4.7 Hz), 1.28 (s, 36H, C$_5$H$_2$Bu$_3$), 1.21 (s, 18H, C$_5$H$_2$Bu$_3$).

$^{31}$P($^1$H) NMR (CD$_3$CN, 25 °C): δ [ppm] = 91.6 (m, 6P, $P_6$), -124.1 (m, 2P, $P_6$).

$^{31}$P NMR (CD$_3$CN, 25 °C): δ [ppm] = 91.6 (m, 6P, $P_6$), -124.1 (m, 2P, $P_6$).

ESI-MS (dme): m/z = 1279.14 (100 %, [(Cp”’Co)$_3$P$_{13}$]), 1217.20 (82 %, [(Cp”’Co)$_3$P$_{11}$]).

EA C$_{70}$H$_{130}$O$_{12}$N$_4$K$_2$P$_8$Co$_2$: calc [%]: C 50.54; H 7.88; N 3.37; found [%]: C 49.86; H 7.68; N 3.09.
1.3 Synthesis of [Li(2,2,2-crypt)][Cp''''Co(η³-P₄Bu)] (4)

a) A solution of tBuLi in pentane (0.96 ml, 0.249 mol/L, 0.24 mmol, 1 eq) was added to a stirred solution of I (100 mg, 0.24 mmol, 1 eq) in thf at -80 °C while the color changed immediately from red to brown. After five minutes a solution of 2,2,2-cryptand (90.4 mg, 0.24 mmol, 1 eq) in thf was added and the reaction mixture warmed to room temperature. The solvent was reduced in vacuo and NMR spectra with a CsDs capillary was recorded revealing the clean formation of 4. The thf solution was layered with n-hexane at room temperature. After a few days, 4 can be obtained as brown flat rods. The supernatant was decanted off and the obtained crystals dried in vacuo.

Yield: 98 mg (48 %).

1H NMR (thf-d₈, 25 °C): δ [ppm] = 4.90 (s, 2H, C₈H₂Bu₃), 3.70 (s, 12H, 2,2,2-crypt), 3.64 (pt, 2Jₚₜ = 5.1 Hz, 12H, 2,2,2-crypt), 2.72 (pt, 2Jₚₜ = 5.1 Hz, 12H, 2,2,2-crypt), 1.47 (s, 9H, P₈Bu), 1.36, 1.35, 1.34 (three overlapping singlets, 27H, CsH₂Bu₃).

31P{1H} NMR (thf-d₈, 25 °C): δ [ppm] = 94.1 (t, 1JPP = 255.73 Hz, 2JPP = 2.48 Hz, 1P, P₈Bu), 88.7 (t, 1JPP = 186.23 Hz, 2JPP = 3.97 Hz, 1P, P₈Bu), -25.9 (dd, 1JPP = 255.63 Hz, 1JPP = 186.23 Hz, 2P, P₈Bu, P₈Bu) (coupling constants obtained from the simulation, cf. Figure S4).

31P NMR (thf-d₈, 25 °C): δ [ppm] = 94.1 (t, 1JPP = 255.73 Hz, 2JPP = 1.49 Hz, 5Jₚₜ = 0.77 Hz, 1P, P₈Bu), 88.7 (t, 1JPP = 186.23 Hz, 2JPP = -0.30 Hz, 5Jₚₜ = 9.12 Hz 1P, P₈Bu), -26.0 (dd, 1JPP = 255.63 Hz, 1JPP = 186.23 Hz, 2Jₚₜ = -1.12 Hz, 2P, P₈Bu, P₈Bu) (coupling constants obtained from the simulation, cf. Figure S4).

EA C₃₉H₃₄N₂O₆P₄CoLi: calc [%]: C 54.67; H 8.71; N 3.27; found [%]: C 54.35; H 8.42; N 3.27.

Despite of several attempts it was not possible to obtain a proper mass spectrum (ESI), due to the extreme redox sensitivity of 4.

b) A solution of tBuLi in pentane (0.96 ml, 0.249 mol/L, 0.24 mmol, 1 eq) was added to a stirred solution of I (100 mg, 0.24 mmol, 1 eq) in thf at -80 °C while the color changed immediately from red to brown. The reaction mixture was warmed to room temperature. The solvent was reduced in vacuo and NMR spectra in thf-d₈ were recorded showing a mixture of 3, 4, 5 and 6.

Compound 5:

31P{1H} NMR (thf-d₈, 25 °C): δ [ppm] = 231.9 (m, 1JPP = 470.35 Hz, 1JPP = 441.32 Hz, 2JPP = -1.21 Hz, 2JPP = 13.24 Hz, 1P, P₈Bu), 130.9 (ddd, 1JPP = 346.33 Hz, 1JPP = 363.12 Hz, 2JPP = 14.02 Hz, 2JPP = -4.69 Hz, 2JPP = 69.86 Hz, 3JPP = 1.52 Hz, 2P, P₈Bu), 74.7 (ddd, 1JPP = 255.73 Hz, 3JPP = 358.96 Hz, 3JPP = -4.69 Hz, 3JPP = 69.86 Hz, 3JPP = -16.59 Hz, 3JPP = -14.40, 3JPP = 1.02 Hz, 2P, P₈Bu), 1.34 (dt, 1JPP = 441.32 Hz, 1JPP = 358.96 Hz, 2JPP = -1.52 Hz, 3JPP = 1.02 Hz, 4JPP = 20.96 Hz, 2P, P₈Bu) (coupling constants obtained from the simulation, cf. Figure S8).

31P NMR (thf-d₈, 25 °C): δ [ppm] = 231.9 (m, 1P, P₈Bu), 130.9 (m, 2P, P₈Bu), 74.7 (m, 2P, P₈Bu), 1.34 (m, 1P, P₈Bu), -123.9 (m, 2P, P₈Bu) (signals 231.9 and 1.34 ppm show further broadening caused by proton coupling, too broad resolved for simulation).

Compound 6:

31P{1H} NMR (thf-d₈, 25 °C): δ [ppm] = 106.8 (ddd, 1JPP = 400.71 Hz, 1JPP = 342.90 Hz, 2JPP = 65.46 Hz, 2JPP = 5.97 Hz, 1P, P₈Bu), 98.9 (ddd, 1JPP = 352.77 Hz, 1JPP = 348.39, 2JPP = 65.46 Hz, 2JPP = 12.84 Hz, 1P, P₈Bu), 77.7 (ddd, 1JPP = 352.77 Hz, 1JPP = 322.67 Hz, 2JPP = 5.97 Hz, 2JPP = 10.00 Hz, 1P, P₈Bu), 31.3 (ddd, 1JPP = 400.71 Hz, 1JPP = 322.67 Hz, 2JPP = 12.84, 2JPP = 7.23 Hz, 1P, P₈Bu), -146.9 (t, 1JPP = 342.90 Hz, 1JPP = 348.39 Hz, 2JPP = 10.00 Hz, 2JPP = 7.23 Hz, 1P, P₈Bu) coupling constants obtained from the simulation, cf. Figure S9).
$^{31}$P NMR (thf-d$_8$, 25 °C): $\delta$ [ppm] = 106.8 (m, 1P, $P_A$), 98.9 (m, 1P, $P_9$), 77.7 (m, 1P, $P_C$), 31.3 (m, 1P, $P_M$), -146.9 (m, 1P, $P_X$) (signals 77.7 and 31.3 ppm show further broadening caused by proton coupling, too bad resolved for simulation).

Despite of several attempts it was not possible to obtain proper mass spectra (ESI) of 5 and 6, probably due to the extreme redox sensitivity. No elemental analysis could be conducted since compound 5 and 6 were obtained as a mixture of compounds.
1.4 Synthesis of [Li(2,2,2-crypt)][Cp””Co(η³-P₄CH₂SiMe₃)] and [Li(12-c-4)₂][Cp””Co(η³-P₄CH₂SiMe₃)]

a) Reaction with 2,2,2-cryptand: A solution of LiCH₂SiMe₃ in thf (22.6 mg, 0.24 mmol, 1 eq) was added to a stirred solution of 1 (100 mg, 0.24 mmol, 1 eq) in thf at -80 °C while the color changed immediately from red to brown. After five minutes a solution of 2,2,2-cryptand (90.4 mg, 0.24 mmol, 1 eq) in thf was added and the reaction mixture warmed to room temperature. The solvent was reduced in vacuo and NMR spectra in thf-d₈ were recorded revealing the formation two isomers 7a and 7b in a ratio of 1:0.25 beside other products. The residue was dissolved in a small amount thf and precipitated with pentane (brown oily solid). The NMR spectra in thf-d₈ of the obtained oil reveals a clean mixture of 7a and 7b in a ratio of 1:0.36.

Compound [Li(2,2,2-crypt)]7a:

1H NMR (thf-d₈, 25 °C): δ [ppm] = 4.80 (s, 2H, C₆H₂Bu₃), 3.75 (s, 12H, 2,2,2-crypt), 3.56 (t, 3J_HH = 4.9 Hz, 12H, 2,2,2-crypt), 2.77 (t, 3J_HH = 4.9 Hz, 12H, 2,2,2-crypt), 2.40 (s, 2H, CH₂SiMe₃), 1.43 (s, 9H, C₆H₂Bu₃), 1.33 (s, 18H, C₆H₂Bu₃), 0.02 (s, 9H, CH₂SiMe₃).

31P{1H} NMR (thf-d₈, 25 °C): δ [ppm] = 52.3 (td, 1J_pP = 260.89 Hz, 2J_pP = 10.95 Hz, 1P, P₄), 45.9 (td, 1J_pP = 152.24 Hz, 2J_pP = 10.95 Hz, 1P, P₄), 18.8 (dd, 1J_pP = 260.89 Hz, 1J_pP = 152.24 Hz, 2J_pP = -8.00 Hz, 2P, Pₓₓ), (coupling constants obtained from the simulation, cf. Figure S12).

31PNMR (thf-d₈, 25 °C): δ [ppm] = 52.3 (td, 1J_pP = 260.89 Hz, 2J_pP = 10.95 Hz, 1P, P₄), 45.9 (td, 1J_pP = 152.24 Hz, 2J_pP = 10.95 Hz, 1P, P₄), 18.8 (dd, 1J_pP = 260.89 Hz, 1J_pP = 152.24 Hz, 2J_pP = -8.00 Hz, 2P, Pₓₓ), (coupling constants obtained from the simulation of the 31P{1H}, no further coupling observed, cf. Figure S12).

Compound [Li(2,2,2-crypt)]7b:

1H NMR (thf-d₈, 25 °C): δ [ppm] = 4.75 (s, 2H, C₆H₂Bu₃), 3.73 (s, 12H, 2,2,2-crypt), 3.67 (t, 3J_HH = 4.9 Hz, 12H, 2,2,2-crypt), 2.75 (t, 3J_HH = 4.9 Hz, 12H, 2,2,2-crypt), 2.00 (s, 2H, CH₂SiMe₃), 1.31 (s, 2H, CH₂SiMe₃), 1.21 (s, 9H, C₆H₂Bu₃), -0.07 (s, 9H, CH₂SiMe₃).

31P{1H} NMR (thf-d₈, 25 °C): δ [ppm] = 39.4 (td, 1J_pP = 135.82 Hz, 2J_pP = 14.38 Hz, 1P, P₄), 3.8 (dd, 1J_pP = 276.36 Hz, 2J_pP = 135.82 Hz, 2J_pP = -84.01 Hz, 2P, Pₓₓ), -78.2 (td, 1J_pP = 276.36 Hz, 2J_pP = 14.38 Hz, 1P, Pₓ), (coupling constants obtained from the simulation, cf. Figure S12).

31P NMR (thf-d₈, 25 °C): δ [ppm] = 39.4 (td, 1J_pP = 135.82 Hz, 2J_pP = 14.38 Hz, 1P, P₄), 3.8 (dd, 1J_pP = 276.36 Hz, 2J_pP = 135.82 Hz, 2J_pP = -84.01 Hz, 2P, Pₓₓ), -78.2 (td, 1J_pP = 276.36 Hz, 2J_pP = 14.38 Hz, 1P, Pₓ), (coupling constants obtained from the simulation of the 31P{1H}, no further coupling observed, cf. Figure S12).

Despite of several attempts it was not possible to obtain proper mass spectrum (ESI) of 7a,b probably due to the extreme redox sensitivity. No elemental analysis could be conducted since compound 7 was only obtained as an oily substance when 2,2,2-cryptand is used.
b) Reaction with 12-c-4: A solution of LiCH₂SiMe₃ in thf (22.6 mg, 0.24 mmol, 1 eq) was added to a stirred solution of 1 (100 mg, 0.24 mmol, 1 eq) in thf at -80 °C while the color changed immediately from red to brown. After five minutes a solution of 12-c-4 in dme (0.60 mL, 0.48 mmol, 0.8102 mol/L, 2 eq) was added and the reaction mixture warmed to room temperature. The solvent was reduced in vacuo and NMR spectra in thf-d₆ were recorded revealing the formation two isomers 7a and 7b in a ratio of 1:1.33 beside other products. The supernatant was decanted off, the residue dissolved in thf and layered with n-hexane at room temperature. After a few days, very few single crystals of 7a could be obtained.

Yield: 20 mg (precipitated solid, 10 %).

**Compound [Li(12-c-4)₂] 7a:**

1H NMR (thf-d₈, 25 °C): δ [ppm] = 4.83 (s, 2H, C₅H₂Bu₃), 3.77 (s, 32H, 12-c-4), 2.20 (s, 2H, CH₂SiMe₃), 1.48 (s, 9H, C₅H₂Bu₃), 1.34 (s, 18H, C₅H₂Bu₃), 0.02 (s, 9H, CH₂SiMe₃).

31P{¹H} NMR (thf-d₆, 25 °C): δ [ppm] = 50.1 (td, JPP = 259.18 Hz, 2JPP = 10.53 Hz, 1P, P₄), 46.5 (td, JPP = 152.95 Hz, 2JPP = 10.53 Hz, 1P, P₄), 17.42 (dd, JPP = 259.18 Hz, JPP = 152.95 Hz, JPP = -8.00 Hz, 2P, PXX), (coupling constants obtained from the simulation, cf. Table S8).

31P{¹H} NMR (thf-d₆, 25 °C): δ [ppm] = 38.93 (td, JPP = 135.34 Hz, 2JPP = 13.76 Hz, 1P, P₄), 2.8 (dd, JPP = 273.40 Hz, JPP = 135.34 Hz, JPP = -84.00 Hz, 2P, PMM), -79.9 (td, JPP = 273.40 Hz, JPP = 13.76 Hz, 1P, P₄), (coupling constants obtained from the simulation, cf. Table S8).

31P NMR (thf-d₆, 25 °C): δ [ppm] = 38.93 (td, JPP = 135.34 Hz, 2JPP = 13.76 Hz, 1P, P₄), 2.8 (dd, JPP = 273.40 Hz, JPP = 135.34 Hz, JPP = -84.00 Hz, 2P, PMM), -79.9 (td, JPP = 273.40 Hz, JPP = 13.76 Hz, 1P, P₄), (coupling constants obtained from the simulation of the 31P{¹H}, no further coupling observed, cf. Table S8).

**Precipitated solid 7a/7b:**

EA C₅H₂O₈P₄CoLiSi: calc [%]: C 51.51; H 8.41; found [%]: C 51.10; H 8.27.

Despite of several attempts it was not possible to obtain a proper mass spectrum (ESI) of 7a,b, probably due to the extreme redox sensitivity.
1.5 Synthesis of [Li(dme)]\([\text{Cp}^\sim\text{Co}]_2(\mu,\eta^3:\eta^3-\text{P}_8\text{CH}_2\text{SiMe}_3)]\) (8)

A solution of LiCH$_2$SiMe$_3$ (11.3 mg, 0.12 mmol, 1 eq) in thf was added to a stirred solution of 1 (100 mg, 0.24 mmol, 1 eq) in thf at -80°C while the color changed from red to brown. The reaction mixture was warmed to room temperature, while the color changed to dark green. The solvent was removed in vacuo. n-Hexane was added to the residue (partial dissolution) and dme dropwise until complete dissolution. After storage at -30 °C 8 can be obtained as dark green blocks. The supernatant was decanted off and washed with cold (-50 °C) n-hexane. The crystals were dried in vacuo.

Yield: 47 mg (33%).

$^1$H NMR (thf-d$_8$, 300 K): δ [ppm] = 4.53 (s, 2H, C$_5$H$_2$Bu$_3$), 4.15 (s, 2H, C$_5$H$_2$Bu$_3$), 3.43 (s, 12H, Li(dme)$_3$), 3.27 (s, 12H, Li(dme)$_3$), 1.80 (br, 2H, P$_8$CH$_2$SiMe$_3$), 1.34 (s, 18H, C$_5$H$_2$Bu$_3$), 1.31 (s, 18H, C$_5$H$_2$Bu$_3$), 1.29 (s, 18H, C$_5$H$_2$Bu$_3$), 0.32 (s, 9H, P$_8$CH$_2$SiMe$_3$).

$^1$H(31P) NMR (thf-d$_8$, 300 K, decoupled at -114 ppm): δ [ppm] = 4.53 (d, $^3$J$_{1P} = 2.2$ Hz, 2H, C$_5$H$_2$Bu$_3$), 4.15 (d, $^3$J$_{1P} = 2.2$ Hz, 2H, C$_5$H$_2$Bu$_3$), 3.43 (s, 12H, Li(dme)$_3$), 3.27 (s, 12H, Li(dme)$_3$), 1.80 (d, $^2$J$_{PP} = 8.5$ Hz, 2H, P$_8$CH$_2$SiMe$_3$), 1.34 (s, 18H, C$_5$H$_2$Bu$_3$), 1.31 (s, 18H, C$_5$H$_2$Bu$_3$), 1.29 (s, 18H, C$_5$H$_2$Bu$_3$), 0.32 (s, 9H, P$_8$CH$_2$SiMe$_3$).

$^3$P(31H) NMR (thf-d$_8$, 193 K): δ [ppm] = 187.9 (q, $^1$J$_{PP} = 448.32$ Hz, $^1$J$_{PP} = 424.01$ Hz, $^2$J$_{PP} = -2.44$ Hz, $^2$J$_{PP} = 12.49$ Hz, 1P, $P_\alpha$), 102.8 (td, $^1$J$_{PP} = 351.60$ Hz, $^1$J$_{PP} = 366.96$ Hz, $^2$J$_{PP} = -2.44$ Hz, $^2$J$_{PP} = 6.65$ Hz, $^2$J$_{PP} = 62.41$ Hz, $^2$J$_{PP} = -12.85$ Hz, $^2$J$_{PP} = 0.20$ Hz, 2P, $P_\delta$), 72.5 (ddd, $^1$J$_{PP} = 448.32$ Hz, $^1$J$_{PP} = 369.36$ Hz, $^2$J$_{PP} = 62.41$ Hz, $^2$J$_{PP} = -12.85$ Hz, $^2$J$_{PP} = -3.66$ Hz, $^2$J$_{PP} = -17.34$ Hz, $^3$J$_{PP} = 0.87$ Hz, 2P, $P_\delta$), 40.5 (dt, $^1$J$_{PP} = 424.01$ Hz, $^1$J$_{PP} = 351.60$ Hz, $^2$J$_{PP} = -17.34$ Hz, $^2$J$_{PP} = 12.49$ Hz, $^2$J$_{PP} = 7.69$ Hz, 1P, $P_\delta$), -118.8 (t, $^1$J$_{PP} = 366.96$ Hz, $^1$J$_{PP} = 369.36$ Hz, $^2$J$_{PP} = 12.49$ Hz, $^2$J$_{PP} = 7.69$ Hz, $^3$J$_{PP} = 0.20$ Hz, $^3$J$_{PP} = 0.87$ Hz, $^3$J$_{PP} = 19.47$ Hz, 2P, $P_\delta$). (coupling constants obtained from the simulation, cf. Figure S13).

$^{31}$P NMR (thf-d$_8$, 193 K): δ [ppm] = 187.9 (m, 1P, $P_\alpha$), 102.8 (m, 2P, $P_\delta$), 72.5 (m, 2P, $P_\delta$), 40.5 (m, 1P, $P_\delta$), -118.8 (m, 2P, $P_\delta$). (no further broadening or splitting of the signals detected).

ESI-MS (anion, dme): $m/z$ = 919.3 (100 %, [M$^+$]).

No proper elemental analysis could be obtained despite of several attempts, even if the EA tube was filled in a glove box with the compound. Maybe the extreme oxidation sensibility of 8 is the reason.
1.6 Synthesis of \([\text{Na(dme)}_2][\text{Cp'''Co(\eta^3-P_4(O)H)}]\) (10)

\[
\text{NaOH (9.6 mg, 0.24 mmol, 1 eq) and 1 (100 mg, 0.24 mmol, 1 eq) were weighed in together, dme was added and stirred for three days. The solvent was reduced in vacuo, layered with n-hexane and stored at -30 °C. After a few days, 10 can be obtained as dark brown blocks. The supernatant was decanted off, washed with n-hexane and dried in vacuo.}
\]

Yield: 84 mg (55 %).

\[\begin{align*}
\text{H NMR (thf-}d_8, 300 K): & \quad \delta [\text{ppm}] = 7.78 (\text{dtd, } J_{PH} = 356.77 \text{ Hz, } J_{PP} = 20.56 \text{ Hz, } J_{PH} = 5.12 \text{ Hz, } 1H, P_4(O)H), 4.95 (\text{s, 2H, C}_5\text{H}_2\text{Bu}_3), 3.43 (\text{s, 8H, dme}), 3.27 (\text{s, 12H, dme}), 1.36 (\text{s, 18H, C}_5\text{H}_2\text{Bu}_3), 1.34 (\text{s, 9H, C}_5\text{H}_2\text{Bu}_3). \\
\text{H}{^31P} \text{ NMR (thf-}d_8, 300 K): & \quad \delta [\text{ppm}] = 7.78 (\text{s, 1H, P}_4\text{(O)H}), 4.95 (\text{s, 2H, C}_5\text{H}_2\text{Bu}_3), 3.43 (\text{s, 8H, dme}), 3.27 (\text{s, 12H, dme}), 1.36 (\text{s, 18H, C}_5\text{H}_2\text{Bu}_3), 1.34 (\text{s, 9H, C}_5\text{H}_2\text{Bu}_3). \\
\text{P}{^31P} \text{NMR (thf + }C_6D_6 \text{ capillary, 25 °C): } & \quad \delta [\text{ppm}] = 74.8 (\text{dd, } J_{PP} = 262.67 \text{ Hz, } J_{PP} = 246.57 \text{ Hz, } J_{PH} = -9.00 \text{ Hz, 2P, P}_{\lambda}), 29.0 (\text{dd, } J_{PP} = 262.67 \text{ Hz, } J_{PP} = 4.92 \text{Hz, 1P, P}_{\lambda}), -21.8 (\text{t, } J_{PP} = 246.57 \text{ Hz, } J_{PP} = 4.92 \text{ Hz, 1P, P}_{\lambda}) \text{ (coupling constants obtained from the simulation, cf. Figure S17).} \\
\text{P}{^31P} \text{NMR (thf + }C_6D_6 \text{ capillary, 25 °C): } & \quad \delta [\text{ppm}] = 74.8 (\text{dd, } J_{PP} = 262.71 \text{ Hz, } J_{PP} = 246.64 \text{ Hz, } J_{PH} = 20.56 \text{ Hz, 2P, P}_{\lambda}), 29.0 (\text{dd, } J_{PP} = 262.67 \text{ Hz, } J_{PP} = 4.92 \text{Hz, 1P, P}_{\lambda}), -21.8 (\text{t, } J_{PP} = 246.57 \text{ Hz, } J_{PP} = 4.92 \text{ Hz, 1P, P}_{\lambda}) \text{ (coupling constants obtained from the simulation, cf. Figure S17).} \\
\text{SI-MS (anion, dme): } & \quad m/z = 867.2 (100. \%, [2M+H]), 433.0 (12. \%, [M]). \\
\text{EA } & \quad C_{25}H_{50}O_5P_4CoNa: \text{ calc } [\%]: C 47.18; H 7.92; \text{ found } [\%]: C 46.94; H 7.87.
\end{align*}\]
2. NMR spectroscopic investigations
2.1 \([\text{K(dme)}]_2[\text{(Cp'''Co)}_2(\mu,\eta^3:\eta^3-P_8)]\) (2a)

**Figure S1**: \(^{31}\text{P}\)\(^{1}\text{H}\) NMR spectrum of the crude reaction mixture from the reaction of 1 with KC₈ in thf-d₈ at room temperature.
**Figure S2**: $^{31}$P{$^1$H} NMR spectrum of 2a in thf-d$_8$ at room temperature (experimental (black) and simulated (blue)).

**Table S1**: Coupling constants and chemical shifts obtained from the simulation.

| Coupling Constants [Hz] | Chemical Shifts [ppm] |
|-------------------------|-----------------------|
| $^1$J$_{PAP'A'}$        | 309.44                | $^2$J$_{PP'M'M''}$        | 23.96 |
| $^1$J$_{PAP'M}$        | 330.75                | $^2$J$_{PAP_X}$           | -4.96 |
| $^1$J$_{PAP'M''}$      | 301.97                | $^2$J$_{PAP_X'}$          | 4.28  |
| $^1$J$_{PAP'M'}$       | 292.35                | $^2$J$_{PMP'M'}$          | -57.81|
| $^1$J$_{PAP'M'''}$     | 343.58                | $^2$J$_{PMP'M''}$         | -20.81|
| $^1$J$_{PMPX}$         | 351.21                | $^2$J$_{PMP'M'''}$        | -11.67|
| $^1$J$_{PMPX'}$        | 359.89                | $^2$J$_{PMP'M'''}$        | 44.81 |
| $^1$J$_{P'M'M''P_X'}$  | 355.82                | $^2$J$_{PMP'M'''}$        | -11.83|
| $^1$J$_{P'M'M'''P_X'}$ | 362.15                | $^3$J$_{PMP'M''''}$       | 8.65  |
| $^2$J$_{PAP'M'}$       | 21.49                 | $^3$J$_{PMP'M'''}$        | 19.83 |
| $^2$J$_{PAP'M''}$      | 9.55                  | $^3$J$_{PMP'M''''}$       | -5.40 |
| $^2$J$_{PAP_X}$        | -10.88                | $^3$J$_{PMP'M''''}$       | 1.67  |
| $^2$J$_{PAP_X'}$       | -0.66                 | $^3$J$_{PMP'M''''P_X}$    | -15.65|
| $^2$J$_{PAP'M}$        | 11.96                 | $^4$J$_{PMP'M''''P_X}$    | 21.50 |

| Chemical Shifts [ppm] | |
|-----------------------|-----------------------|
| $^3$P$_{AA'}$          | 96.16                 | $^3$P$_{MM'M''M'''}$     | 83.32 |
| $^3$P$_{XX'}$          | -124.17               | R value                 | 1.56 %|
2.2 \([K(2,2,2\text{-crypt})]_2[(\text{Cp}''''\text{Co})_2(\mu,\eta^3:\eta^3-P_8)]\) (2b)

**Figure S3:** $^{31}\text{P}^{(1}\text{H})$ NMR spectrum of 2b in CD$_3$CN at room temperature.
2.3 [Li(2,2,2-crypt)][Cp'''Co(η^3-P_4^1Bu)] (4)

Figure S4: $^{31}$P($^1$H) (top) and $^{31}$P (bottom) NMR spectrum of 4 thf with C_6D_6 capillary at room temperature (experimental (black) and simulated (blue)).

Table S2: Coupling constants and chemical shifts obtained from the simulation of the $^{31}$P($^1$H) NMR spectrum.

| coupling constants [Hz] | chemical shifts [ppm] |
|------------------------|------------------------|
| $J_{PA}^P_X$ = $J_{PA}^P_{X'}$ | 255.63 | $P_A$ | 94.13 |
| $J_{PM}^P_X$ = $J_{PM}^P_{X'}$ | 186.23 | $P_M$ | 88.64 |
| $J_{PA}^{PP}$ | 2.48 | $P_X$ | -25.92 |
| $J_{PX}^{PP}$ | 3.97 | $P_{X'}$ | -25.92 |

R value | 0.84 % |

Table S3: Coupling constants and chemical shifts obtained from the simulation of the $^{31}$P NMR spectrum.

| coupling constants [Hz] | chemical shifts [ppm] |
|------------------------|------------------------|
| $J_{PA}^P_X$ = $J_{PA}^P_{X'}$ | 255.60 | $P_A$ | 94.11 |
| $J_{PM}^P_X$ = $J_{PM}^P_{X'}$ | 186.26 | $P_M$ | 88.62 |
| $J_{PA}^{PP}$ | 1.49 | $P_X$ | -25.95 |
| $J_{PX}^{PP}$ | -0.30 | $P_{X'}$ | -25.95 |
| $J_{PM}^{PP}$ | 9.12 |
| $J_{PX}^{PH}$ | -1.12 |
| $J_{PA}^{PH}$ | 0.77 |

R value | 0.24 % |
Figure S5: $^{31}$P($^1$H) NMR spectrum of the reaction of 1 with tBuLi at room temperature thf-d$_8$ at room temperature (large sweep).
Figure S6: Part of the $^{31}$P($^1$H) NMR spectrum of the reaction of 1 with tBuLi at room temperature thf-d$_8$ at room temperature and the simulated spectra of 4 (blue), 5 (red) and 6 (purple).
Figure S7: Part of the $^{31}$P($^1$H) NMR spectrum of the reaction of 1 with $^1$BuLi at room temperature thf-d$_8$ at room temperature and the simulated spectrum of 4 (blue).

Table S4: Coupling constants and chemical shifts obtained from the simulation of 4 from the $^{31}$P($^1$H) NMR spectrum.

| Coupling constants [Hz] | Chemical shifts [ppm] |
|------------------------|-----------------------|
| $^1J_{PA}P_X$          | 253.71 $P_A$          |
| $^1J_{PM}P_X$          | 186.61 $P_M$          |
| $^2J_{PA}P_{M}$        | 2.99 $P_X$            |
| $^2J_{PX}P_{X'}$       | 4.01 $P_{X'}$         |

| Coupling constants [Hz] | Chemical shifts [ppm] |
|------------------------|-----------------------|
| $^1J_{PA}P_X$          | 253.71 $P_A$          |
| $^1J_{PM}P_X$          | 186.61 $P_M$          |
| $^2J_{PA}P_{M}$        | 2.99 $P_X$            |
| $^2J_{PX}P_{X'}$       | 4.01 $P_{X'}$         |
Figure S8: Part of the $^{31}$P-$^1$H NMR spectrum of the reaction of 1 with $^1$BuLi at room temperature thf-$d_8$ at room temperature and the simulated spectrum of 5 (red).

Table S5: Coupling constants and chemical shifts obtained from the simulation of 5 from the $^{31}$P-$^1$H NMR spectrum.

| Coupling Constants [Hz] | 1$^1$J$_{PA}$P$_N$ | 2$^1$J$_{PA}$P$_N$ | 1$^2$J$_{PA}$P$_N$ | 2$^2$J$_{PA}$P$_N$ |
|-------------------------|------------------|------------------|------------------|------------------|
| 1$^1$J$_{PA}$P$_O$      | 441.32           |                  |                  |                  |
| 1$^1$J$_{PM}$P$_O$      | 346.33           |                  |                  |                  |
| 1$^1$J$_{PM}$P$_X$      | 363.12           |                  |                  |                  |
| 1$^1$J$_{PN}$P$_X$      | 358.96           |                  |                  |                  |
| 2$^1$J$_{PA}$P$_M$      | -1.21            |                  |                  |                  |
| 2$^1$J$_{PA}$P$_X$      | 13.24            |                  |                  |                  |
| 2$^1$J$_{PM}$P$_M$      | 14.02            |                  |                  |                  |
| 2$^1$J$_{PM}$P$_X$      | 20.96            |                  |                  |                  |
| chemical shifts [ppm] |       |
|----------------------|-------|
| $P_A$                | 231.93|
| $P_M$                | 130.85|
| $P_N$                | 74.73 |
| $P_O$                | 1.34  |
| $P_X$                | -123.91|
Figure S9: Part of the $^{31}\text{P}({}^1\text{H})$ NMR spectrum of the reaction of 1 with $^t\text{BuLi}$ at room temperature thf-$d_8$ at room temperature and the simulated spectrum of 6 (purple).

Table S6: Coupling constants and chemical shifts obtained from the simulation of 6 from the $^{31}\text{P}({}^1\text{H})$ NMR spectrum.

| Coupling constants [Hz] |  
|-------------------------|
| $^1J_{PA}P_M$ | 400.71 |
| $^1J_{PA}PX$ | 342.90 |
| $^1J_{PB}PC$ | 352.77 |
| $^1J_{PB}PX$ | 348.39 |
| $^1J_{PC}PM$ | 322.67 |
| $^2J_{PA}PB$ | 65.46 |
| $^2J_{PA}PC$ | 5.97 |
| $^2J_{PB}PM$ | 12.84 |
| $^2J_{PC}PX$ | 10.00 |
| $^2J_{PM}PX$ | 7.23 |

| Chemical shifts [ppm] |  
|-----------------------|
| $P_A$ | 106.76 |
| $P_B$ | 98.86 |
| $P_C$ | 77.65 |
| $P_M$ | 31.27 |
| $P_X$ | -146.87 |
2.4 [Li(2,2,2-crypt)][Cp‴Co(η⁴-P₄CH₂SiMe₃)] (7)

Figure S10: $^{31}$P{¹H} NMR spectrum in thf-d₈ of the reaction of LiCH₂SiMe₃ with 1 after addition of 12-c-4.

Figure S11: $^{31}$P{¹H} NMR spectrum in thf-d₈ of the reaction of LiCH₂SiMe₃ with 1 after addition of 2,2,2-cryptand.
Figure S12: $^{31}P$($^1H$) NMR spectrum of the [Li(2,2,2-crypt)]7a/7b in thf-d$_8$ (experimental (black) and simulated (blue, red)).

Table S7: Coupling constants and chemical shifts obtained from the simulation ([Li(2,2,2-crypt)]7a/7b).

|                  | 7a        | 7b        |
|------------------|-----------|-----------|
| $^1J_{PAPX} = ^1J_{PA'PX'}$ | 260.89    | 135.82    |
| $^1J_{PM'PX} = ^1J_{PM'PX'}$ | 152.24    | 143.8     |
| $^2J_{PA'M} = ^2J_{PA'M'}$  | 10.95     | 276.36    |
| $^2J_{PX'} = ^2J_{PX'}$     | -8.00     | -84.01    |

| chemical shifts [ppm] | 7a        | 7b        |
|-----------------------|-----------|-----------|
| P$_A$                 | 52.29     | 39.39     |
| P$_M$                 | 45.93     | 3.78      |
| P$_X$                 | 18.48     | 3.78      |
| P$_X'$                | 18.48     | -78.24    |

R value                  | 0.53 %    |

Table S8: Coupling constants and chemical shifts obtained from the simulation ([Li(12-c-4)$_2$]7a/7b).

|                  | 7a        | 7b        |
|------------------|-----------|-----------|
| $^1J_{PAPX} = ^1J_{PA'PX'}$ | 259.18    | 135.34    |
| $^1J_{PM'PX} = ^1J_{PM'PX'}$ | 152.95    | 273.40    |
| $J_{P_A P_M}$ | 10.53 | $J_{P_A P_X}$ | 13.76 |
| $J_{P_X P_{X'}}$ | -8.00 | $J_{P_M P_{M'}}$ | -84.00 |

| Chemical shifts [ppm] | Chemical shifts [ppm] |
|-----------------------|-----------------------|
| $P_A$ | 50.07 | $P_A$ | 38.93 |
| $P_M$ | 46.54 | $P_M$ | 2.84 |
| $P_X$ | 17.42 | $P_{X'}$ | 2.84 |
| $P_{X'}$ | 17.42 | $P_X$ | -79.93 |

R value | 1.69 %
2.5 [Li(dme)$_3$][(Cp'’Co)$_2$(µ,η$^3$:η$^3$-P$_8$CH$_2$SiMe$_3$)] (8)

Figure S13: $^{31}$P{$^1$H} NMR spectrum of 8 in thf-d$_8$ at 193 K (experimental (black) and simulated (blue)).

Table S9: Coupling constants and chemical shifts obtained from the simulation.

| Coupling constants [Hz] | Chemical shifts [ppm] |
|------------------------|-----------------------|
| $^1J_{PAPN}$ | 448.32 | \( P_A \) | 187.87 |
| $^1J_{PAPO}$ | 424.01 | \( P_M \) | 102.75 |
| $^3J_{PMPM}$ | 351.60 | \( P_N \) | 74.48 |
| $^3J_{PMPX}$ | 366.96 | \( P_O \) | 40.57 |
| $^3J_{PNPX}$ | 369.36 | \( P_X \) | -118.80 |
| $^2J_{PMPN}$ | 62.41 | \( J_{PM} \) | \( R \) value | \( 1.53 \) % |
2.6 1 + LiCH$_2$SiMe$_3$ VT-NMR

Figure S14: $^{31}$P{$^1$H} VT NMR spectra of the reaction of 1 with LiCH$_2$SiMe$_3$ in thf-d$_8$ between 193 and 293 K and after 24 h at room temperature.
Figure S15: $^{31}$P{$^1$H} NMR spectrum of the VT-NMR (S14) at 293 K (# unknown compound, * [(Cp'''Co)$_2$(P$_2$)$_2$]).

Figure S16: $^{31}$P{$^1$H} NMR spectrum of the VT-NMR (S14) at 293 K after 24 h (# unknown compound, * [(Cp'''Co)$_2$(P$_2$)$_2$]).
2.7 [Na(dme)$_2$][Cp”’Co(η$^3$-P$_4$(O)H)] (10)

![Chemical structure](image)

**Figure S17**: $^{31}$P(1H) (top) and $^{31}$P (bottom) NMR spectrum of 10 thf-d$_8$ at room temperature (experimental (black) and simulated (blue)).

**Table S10**: Coupling constants and chemical shifts obtained from the simulation of the $^{31}$P(1H) NMR spectrum.

| coupling constants [Hz] | chemical shifts [ppm] |
|-------------------------|-----------------------|
| $^1J_{PA}P_M$           | 262.67                |
| $^1J_{PA}P_X$           | 246.57                |
| $^2J_{PA}P_A$           | -9.00                 |
| $^2J_{PM}P_X$           | 4.92                  |
| $^3J_{PA}P_A$           | 262.71                |
| $^3J_{PA}P_M$           | 246.64                |
| $^3J_{PA}P_X$           | 0.00                  |

**Table S11**: Coupling constants and chemical shifts obtained from the simulation of the $^{31}$P NMR spectrum.

| coupling constants [Hz] | chemical shifts [ppm] |
|-------------------------|-----------------------|
| $^1J_{PA}P_M$           | 262.71                |
| $^1J_{PA}P_X$           | 246.64                |
| $^2J_{PA}P_A$           | 0.00                  |

R value | 1.23 %
3. Cyclic voltammogram of 1

The measurement was conducted in 5 ml dme with 500 mg conducting salt [\(^n\text{Bu}_4\text{N}\)][PF\(_6\)] and 0.01 mmol of 1 were used. A platinum working electrode, a platinum counter electrode and a silver wire as a reference electrode were used. Ferrocene was added as an internal standard for referencing. The weak oxidation process at +275 mV against [Cp\(_2\)Fe]/[Cp\(_2\)Fe]\(^+\) is a feature of 1 and could not be detected within the blank measurement of the pure solvent. A measurement in CH\(_2\)Cl\(_2\) (5 ml, 750 mg conducting salt [\(^n\text{Bu}_4\text{N}\)][PF\(_6\)], 0.01 mmol 1, cf. Figure S18_2) reveals the oxidation process more clearly separated from the solvent window, while the reduction process can be detected in the shoulder of the solvent window.

![Graph](image.png)

**Figure S18_1.** Cyclic voltammogram of 1 in dme against [Cp\(_2\)Fe]/[Cp\(_2\)Fe]\(^+\) (electrolyte \(^n\text{Bu}_4\text{NPF}_6\), scan rate: 100 mV/s. temperature: r.t.).
Figure S18.2. Cyclic voltammogram of 1 in CH$_2$Cl$_2$ against [Cp$_2$Fe]/[Cp$_2$Fe]$^+$ (electrolyte $^4$Bu$_4$NPF$_6$, scan rate: 100 mV/s. temperature: r.t.).
4. Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on either an Gemini Ultra diffractometer (Oxford diffraction) with an AtlasS2 detector applying Mo radiation (λ = 0.71073 Å) \(2a\, 5\, 7a\) or Cu-Kα radiation (λ = 1.54178 Å) \(2b\, 4\), a GV 50 diffractometer (Rigaku, formerly Agilent Technologies) with TitanS2 detector from applying Cu-Kα radiation (λ = 1.54178 Å) \(6\, 9\) or SuperNova (Agilent Technologies) with an Atlas detector applying Cu-Kα radiation (λ = 1.54178 Å) \(8\). All measurements were performed at 123 K. An analytical numeric absorption correction\(^{[4]}\) using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid using spherical harmonics as implemented in SACLE3 ABSPACK was applied \(2a\, 2b\, 4\, 5\, 7\).\(^{[5]}\) A numerical absorption correction based on gaussian integration over a multifaceted crystal model using CrysAlisPro using spherical harmonics as implemented in SACLE3 ABSPACK was applied \(8\, 9\). All structures were solved by direct methods with ShelXT\(^{[6]}\) and Olex2\(^{[7]}\) and refined by full-matrix least-squares method against \(F^2\) in anisotropic approximation using ShelXL.\(^{[8]}\) Hydrogen atoms were refined in calculated positions using riding on pivot atom model.

CCDC-1984450 \(2b\), CCDC-1984451 \(4\), CCDC-1984452 \(5\), CCDC-1984453 \(7a\), CCDC-1984454 \(8\) and CCDC-1984455 \(10\) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
4.1 [K(dme)]$_2$[(Cp”’Co)$_2$(µ,η$^3$:η$^3$-P$_8$)] (2a)

Crystals suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution in a mixture of n-hexane and dme at -30 °C. Compound 2a crystallizes in the orthorhombic space group Cmce as dark green blocks. Although a very good measurement was conducted (up to a resolution of 0.67 Å) a final refinement of the data was not possible. The anion can be modeled quite well, but the potassium counterions are located over several positions (partially side occupancies below 8 %) surrounded by dme molecules which cannot be modeled properly. The structure in solid state including the electron density map is depicted in Figure S19.

Figure S19. Part of the molecular structure of 2a in solid state. Depicted is the unfinished refinement with the electron density map.
4.2 \( [K(2,2,2\text{-crypt})]_2[(\text{Cp'''}\text{Co})_2(\mu,\eta^3:\eta^3-\text{P}_8)] \) (2b)

Crystals suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution of 2b in a mixture of dme and MeCN at -30 °C. Compound 2b crystallizes in form of dark green plates in the triclinic space group P\(\overline{1}\). The asymmetric unit contains one dianion of 2b, two potassium counterions chelated by 2,2,2-cryptand and 1.5 molecules dme. The structure in solid state is depicted in Figure S20 and S21.

![Figure S20: Molecular structure of 2b in the solid state. Thermal ellipsoids are drawn with 50 % probability level.](image)

![Figure S21: Molecular structure of the dianion in 2b in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.1554(6), P1-P5 3.4607(6), P1-P8 2.1577(6), P2-P3 2.2152(6), P3-P4 2.2151(6), P3-P7 2.1947(6), P4-P5 2.1519(6), P5-P6 2.1580(6), P6-P7 2.2247(6), P7-P8 2.2133(6).](image)
4.5 [Li(2,2,2-crypt)][Cp′′′Co(η³-P₄₄Bu)] (4)

Crystals suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution of 4 in a in thf layered with n-hexane at room temperature. Compound 4 crystallizes in form of brown flat rods in the orthorhombic space group Pbca. The asymmetric unit contains one anion of 4, one lithium counterion chelated by 2,2,2-cryptand and one molecule thf. Since the crystals were only poorly diffracting, only a measurement until a resolution of 1.20 Å was conducted. The structure in solid state is depicted in Figure S22.

Figure S22: Molecular structure of 4 in the solid state. Thermal ellipsoids are drawn with 50 % probability level.
4.6 [Li(thf)$_3$][(Cp""Co)$_2$(μ,η$^3$:η$^3$-P$_8$Bu)] (5)

Crystals suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution of 5 in pentane at -30 °C. Compound 5 crystallizes in form of dark brown blocks in the monoclinic space group $P2_1/c$. The asymmetric unit contains one anion of 5, one lithium counterion chelated by three thf molecules, 0.25 free thf and 0.5 pentane molecules. One tBu group of one Cp"" ligand is disordered over two positions. Two of the coordinating thf molecules are disordered over two positions. The restraints DFIX, SIMU and SADI were applied to describe the disorder and the free solvent molecules properly. The measured crystal was a twin and therefore a HKLF5 refinement was applied. The structure in solid state is depicted in Figure S23 and S24.

![Molecular structure of 5 in the solid state. Thermal ellipsoids are drawn with 50 % probability level.](image-url)
Figure 24 Molecular structure of the anion in 5 in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.165(3), P1-P8 2.232(3), P2-P3 2.161(3), P2-P6 3.385(3), P3-P4 2.205(3), P4-P5 2.190(3), P4-P8 2.166(3), P5-P6 2.155(3), P6-P7 2.166(3), P7-P8 2.233(3).
4.6 $[\text{Li}(12\text{-c-4})_2][\text{Cp}''''\text{Co(}\eta^3\text{-P}_5\text{Bu}_2)]$ (6)

Crystals of very poor quality were obtained from the reaction mixture of 1 and $^1\text{BuLi}$ in thf layered with $n$-hexane at -30 °C. A low resolution measurement gives a hint on the connectivity of 6.

Figure S25: Molecular structure of 7 in solid state. Thermal ellipsoids are drawn with 50 % probability level.
4.3 [Li(2,2,2-crypt)][Cp””Co(η³-P₄CH₂SiMe₃)] (7a)

Crystals suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution of 7a in thf layered with n-hexane at 30 °C. Compound 7a crystallizes in form of dark brown plates in the triclinic space group P1. The asymmetric unit contains two anions of 7a, two lithium atoms each chelated by two 12-c-4 molecules and 1.5 molecules thf. One thf molecule and all 12-c-4 are disordered over several positions. The restraints SIMU and SADI were applied to describe the disorder. The measured crystals was twinned and a HKLF5 refinement was applied. The structure in the solid state is depicted in Figure S26 and S27.

**Figure S26**: Molecular structure of 7a in solid state. Thermal ellipsoids are drawn with 50 % probability level.
Figure S27: Molecular structure of one anion in 7a in solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms, cations and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°] of both anions: P1-P2 2.2283(16), P1-P4 2.2229(19), P2-P3 2.1877(17), P3-P4 2.1895(16), P5-P6 2.240(2), P5-P8 2.2286(16), P6-P7 2.1914(16), P7-P8 2.1898(17).
4.4 [Li(dme)$_3$][(Cp’’’Co)$_2$(μ,η$^3$;η$^3$-P$_8$CH$_2$SiMe$_3$)] (8)

Crystals suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution of 8 in a mixture of n-hexane and dme at -30 °C. Compound 8 crystallizes in form of dark green blocks in the triclinic space group P1. The asymmetric unit contains one anion of 8, one lithium counterion chelated by three molecules dme and 0.5 molecules n-hexane. The structure in solid state is depicted in Figure S28 and S29.

Figure S28. Asymmetric unit of 8 in the solid state. Thermal ellipsoids are drawn with 50 % probability level.
Figure S29: Molecular structure of the anion in 8 in the solid state. Thermal ellipsoids are drawn with 50% probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.1643(11), P1-P8 2.2176(10), P2-P3 2.1574(11), P2-P6 3.7294(11), P3-P4 2.1948(10), P4-P5 2.1829(10), P4-P8 2.1738(10), P5-P6 2.1494(11), P6-P7 2.1575(11), P7-P8 2.2174(10).
3.6 $[\text{Na(dme)}_2][\text{Cp'''Co(\eta^3-P_4(O)H)}]]$ (10)

Crystals suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution of 10 in a dme layered with n-hexane at -30 °C. Compound 10 crystallizes in form of dark brown blocks in the triclinic space group P1̅. The asymmetric unit contains one anion of 10, one sodium counterion chelated by two molecules dme. The structure in solid state is depicted in Figure S30 and S31.

**Figure S30**: Molecular structure of 10 in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

**Figure S31**: Molecular structure of the anion in 10 in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.1659(7), P2-P3 2.1984(8), P3-P4 2.1938(8), P1-P4 2.1676(7), P1-H1 1.30(3), P1-O1 1.5200(15).
3.7 Crystallographic information

Table S12: Crystallographic data for all compounds

|                | 2a                     | 2b                     | 4                      | 5                       |
|----------------|------------------------|------------------------|------------------------|------------------------|
| CCDC           | 1984450                | 1984451                | 1984452                |
| Formula        | C$_{76}$H$_{144}$Co$_2$K$_2$N$_4$O$_3$P$_8$ | C$_{43}$H$_{62}$CoLiN$_4$O$_7$P$_4$ | C$_{53.5}$H$_{99}$Co$_2$LiO$_3$2.25P$_8$ |
| $D_{calc}$ / g cm$^{-3}$ | 1.287                | 1.229                | 1.231                |
| $\mu$/mm$^{-1}$ | 5.379                | 4.248                | 0.768                |
| Formula Weight | 1797.76               | 928.85               | 1166.88               |
| Colour         | dark green            | clear dark green      | clear dark brown       | dark brown             |
| Shape          | block                 | plate                 | needle                 | block                  |
| Size/mm$^3$    | 0.63x0.38x0.32        | 0.23x0.16x0.05        | 0.67x0.12x0.06         | 0.32x0.13x0.10         |
| $T/K$          | 123                   | 123                   | 123(1)                | 123(1)                |
| Crystal System | orthorhombic          | triclinic             | orthorhombic           | monoclinic             |
| Space Group    | Cmce                  | P-1                   | Pbc$a$                | P2$_{1}$/c             |
| a/Å            | 27.135(5)             | 13.7131(2)            | 17.8715(3)            | 31.947(3)             |
| b/Å            | 26.3358(7)            | 15.2042(2)            | 22.5218(4)            | 15.5710(12)           |
| c/Å            | 21.7358(6)            | 25.3794(3)            | 24.9460(5)            | 12.6636(10)           |
| $\alpha^\circ$ | 90                    | 74.8590(10)           | 90                    | 90                    |
| $\beta^\circ$  | 90                    | 78.8180(10)           | 90                    | 91.670(8)             |
| $\gamma^\circ$ | 90                    | 65.9260(10)           | 90                    | 90                    |
| V/Å$^3$        | 15533.0(7)            | 4640.57(11)           | 10040.7(3)            | 6296.8(9)             |
| Z              | 2                     | 8                     | 4                     |
| Z'             | 1                     | 1                     | 1                     |
| Wave length/Å  | 0.71073               | 1.54184               | 1.54184               | 0.71073               |
| Radiation type | CuK$_\alpha$          | Cu K$_\alpha$        | Mo K$_\alpha$         |
| $\theta_{min}^\circ$ | 3.386            | 3.544                | 3.242                |
| $\theta_{max}^\circ$ | 73.012          | 40.147               | 25.156               |
| Measured Refl. | 34504                | 13776                | 19403                |
| Independent Refl. | 17809              | 3009                | 19403                |
| Reflections with I > 2(l) | 16566               | 2723                | 9021                 |
| $R_{int}$      | 0.0252                | 0.0414               | 0.0414               | 0.0414                |
| Parameters    | 985                   | 535                  | 747                  |
| Restraints    | 0                     | 0                    | 277                  |
| Largest Peak   | 0.490                 | 0.433                | 1.250                |
| Deepest Hole   | -0.360                | -0.352               | -0.620               |
| Goof           | 1.022                 | 1.066                | 0.876                |
| wR$_2$ (all data) | 0.0794            | 0.1273               | 0.1886               |
| wR$_2$         | 0.0773                | 0.1223               | 0.1727               |
| $R_I$ (all data) | 0.0344            | 0.0503               | 0.1377               |
| $R_I$          | 0.0311                | 0.0459               | 0.0745               |
|                | 6     | 7a    | 8     | 10    |
|----------------|-------|-------|-------|-------|
| CCDC           | 1984453 | 1984454 | 1984455 |
| Formula        | C_{80}H_{156}Co_{2}Li_{2}O_{17.5}P_{8}Si_{2} | C_{53}H_{108}Co_{2}Li_{2}O_{8}P_{6}Si_{2} | C_{25}H_{50}O_{8}Na_{4}P_{6}Co |
| D_{calc}/ g cm^{-3} | 1.196 | 1.203 | 1.299 |
| μ/mm^{-1}      | 0.531 | 6.043 | 6.376 |
| Formula Weight | 1833.72 | 1240.02 | 636.45 |
| Colour         | dark brown | clear dark brown | clear dark brown |
| Shape          | block | plate | plate | block |
| Size/mm^3      | 0.066×0.082×0.111 | 0.39×0.13×0.04 | 0.13×0.05×0.04 | 0.51×0.20×0.14 |
| T/K            | 122.9 (3) | 123(1) | 123.01(10) | 123.0(2) |
| Crystal System | monoclinic | triclinic | triclinic | triclinic |
| Space Group    | Pn    | P-1   | P-1   | P-1   |
| a/Å            | 13.520(3) | 14.4740(7) | 14.2675(3) | 8.8103(3) |
| b/Å            | 26.875(4) | 18.2968(4) | 15.0423(5) | 17.7138(5) |
| c/Å            | 15.467(5) | 19.7326(6) | 18.2337(5) | 17.166(5) |
| α'             | 90    | 87.037(2) | 102.047(2) | 78.926(2) |
| β'             | 99.51(3) | 77.660(4) | 94.044(2) | 89.741(2) |
| γ'             | 90    | 86.306(3) | 114.602(2) | 85.158(2) |
| V/Å^3          | 5543(2) | 5090.5(3) | 3424.69(16) | 1626.75(9) |
| Z              | 2     | 2     | 2     | 2     |
| Z'             | 1     | 1     | 1     | 1     |
| Wave length/Å  | 1.54184 | 0.71073 | 1.54184 | 1.54184 |
| Radiation type | Mo Kα | Cu Kα | Cu Kα |
| θ_{max}^ρ      | 3.307 | 3.462 | 2.542 |
| θ_{max}^ρ      | 25.125 | 73.444 | 74.291 |
| Measured Refl. | 26773 | 24262 | 10786 |
| Independent Refl. | 26773 | 13133 | 6333 |
| Reflections with I > 2(I) | 15803 | 10990 | 6143 |
| R \_e^{}(all data) | 0.0488 | 0.0425 |
| Parameters     | 1430 | 668 | 342 |
| Restraints     | 1102 | 0 | 0 |
| Largest Peak   | 0.589 | 0.700 | 0.686 |
| Deepest Hole   | -0.437 | -0.486 | -0.609 |
| Goof           | 0.908 | 1.018 | 1.038 |
| wR_2 (all data) | 0.1123 | 0.1321 | 0.1183 |
| wR_2           | 0.1051 | 0.1219 | 0.1169 |
| R_1 (all data) | 0.0967 | 0.0608 | 0.0441 |
| R_1            | 0.0526 | 0.0494 | 0.0432 |
4. Computational Details

Gaussian 09 program package was used throughout. Density functional theory (DFT) in form of Becke’s three-parameter hybrid functional B3LYP with def2-TZVP all electron basis set was employed. For solvents effects has been accounted by using continuous polarizable continuum model (CPM). The dielectric constant of THF (ɛ = 7.4257) has been used in the calculations. The Natural Bond Orbital (NBO) analysis has been performed with the NBO6 program. The long range dispersion correction GD3BJ was applied. The figures for the energy schemata were created using OLEX2. The figures for the supporting information concerning the DFT calculations were created with Chemcraft.

Table S13: Total energies for all optimized geometries (B3LYP/def2-TZVP level of theory).

|          | total energy [Ha] |
|----------|------------------|
| 1 [Cp'''Co(η^4-P_4)] | -3414.1010308 |
| 2 [(Cp'''Co)_2(µ,η^3:η^3-P_8)] | -6328.46309287 |
| 3 [Cp'''Co(η^3-P_9)] | -3072.803250 |
| 4a [Cp'''Co(η^3-P_4'Bu)] (axial isomer) | -3572.14117871 |
| 4b [Cp'''Co(η^3-P_4'Bu)] (equatorial isomer) | -3572.13664123 |
| 5 [(Cp'''Co)_2(µ,η^3:η^3-P_8'Bu)] | -6986.30353930 |
| 6 [Cp'''Co(η^3-P_5'Bu_2)] | -4071.49911149 |
| 7a [Cp'''Co(η^3-P_4'C_2H_2SiMe_3)] (axial isomer) | -3862.92310537 |
| 7b [Cp'''Co(η^3-P_4'C_2H_2SiMe_3)] (equatorial isomer) | -3862.92275672 |
| 8 [(Cp'''Co)_2(µ,η^3:η^3-P_8'C_2H_2SiMe_3)] | -7277.08151112 |
| 9-10 [Cp'''Co(η^2-P_5(CH_2SiMe_3)2)] | -4653.06490984 |
| 10 [Cp'''Co(η^2-P_4(O)H)] | -3490.11025036 |
Figure S32: Molecular frontier orbitals of 1 (B3LYP/def2-TZVP level of theory.)
Table S14: Optimized geometries of 1 (left), 2 (right). XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.
Table S15: Optimized geometries of 7a (left), 7b (right). XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.

|       | X (Å) | Y (Å) | Z (Å) |
|-------|-------|-------|-------|
| 7a    |       |       |       |
| P     | 1.69720000 | 0.62489300 | 0.95725200 |
| C     | 2.36706400 | 2.36706400 | 2.36706400 |
| H     | 2.91250600 | 2.91250600 | 2.91250600 |
| C     | 3.57130600 | 3.57130600 | 3.57130600 |
| H     | 4.18543600 | 4.18543600 | 4.18543600 |
| P     | 4.81050000 | 4.81050000 | 4.81050000 |
| C     | 5.43560000 | 5.43560000 | 5.43560000 |
| H     | 6.05870000 | 6.05870000 | 6.05870000 |
| C     | 6.68180000 | 6.68180000 | 6.68180000 |
| H     | 7.30500000 | 7.30500000 | 7.30500000 |

| 7b    |       |       |       |
| P     | 3.09250000 | 3.09250000 | 3.09250000 |
| C     | 3.70660000 | 3.70660000 | 3.70660000 |
| H     | 4.32170000 | 4.32170000 | 4.32170000 |
| C     | 4.94670000 | 4.94670000 | 4.94670000 |
| H     | 5.56180000 | 5.56180000 | 5.56180000 |
| C     | 6.18700000 | 6.18700000 | 6.18700000 |
| H     | 6.80210000 | 6.80210000 | 6.80210000 |
| C     | 7.41640000 | 7.41640000 | 7.41640000 |
| H     | 8.03150000 | 8.03150000 | 8.03150000 |
| C     | 8.64660000 | 8.64660000 | 8.64660000 |
| H     | 9.26170000 | 9.26170000 | 9.26170000 |

Optimized geometries of 7a (left), 7b (right). XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.
Table S16: Optimized geometries of 8 (left), 4a (right). XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.
Table S17: Optimized geometries of 4b (left), 5 (right). XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.
Table S18: Optimized geometries of 6 (left), 3 (right). XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.
Table S19: Optimized geometries of I-8 (left), 10 (right). XYZ co-ordinated in angstroms. B3LYP/def2-TZVP level of theory.
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