Supporting Information of the manuscript entitled:

Transformation of the *cyclo*-P_4 ligand in [Cp'''Co(η^4-P_4)]

Content

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(η^4-P_4)] (**1**)[1], $LiCH_2SiMe_3$[2] and K[CpFe$(CO)_2$][3] were prepared according to literature procedures. 2,2,2-cryptand, NaOH and ^{t}BuLi were purchased commercially.

The NMR spectra were recorded with a Bruker Avance 400 spectrometer (^{1}H: 400.13 MHz, ^{31}P: 161.976 MHz). The chemical shifts are given in ppm referenced to external $SiMe_4$ (^{1}H) and H_3PO_4 (^{31}P). 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 $[K(dme)]_2[(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}P_8)]$ (2a)

A solution of $K[CpFe(CO)_2]$ (260 mg, 1.201 mmol, 1 eq) in dme was added to a stirred solution of **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 $[CpFe(CO)_2]_2$ (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}H NMR (thf-d_8, 25 °C): δ [ppm] = 3.96 (s, 4H, $C_5H_2{}^tBu_3$), 3.58 (s, 6H, dme), 3.28 (s, 8.5H, dme), 1.31 (s, 36H, $C_5H_2{}^tBu_3$), 1.22 (s, 18H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (thf-d_8, 25 °C): δ [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}P NMR (thf-d_8, 25 °C): δ [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 $^{31}P\{^1H\}$ NMR spectrum).

ESI-MS (dme): *m/z* = 1279.14 (50 %, $[(Cp'''Co)_3P_{13}]^-$), 1217.20 (100 %, $[(Cp'''Co)_3P_{11}]^-$), 955.97 (23 %, $[(Cp'''Co)_2P_{12}]^-$), 895.07 (21 %, $[(Cp'''Co)_2P_{10}H]^-$), 833.12 (23%, $[(Cp'''Co)_2P_8H]$).

EA $C_{42}H_{78}O_4K_2P_8Co_2$: calc [%]: C 46.24; H 7.21; found [%]: C 46.11; H 7.04.

1.2 Synthesis of $[K(2,2,2\text{-crypt})]_2[(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}P_8)]$ (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_3CN, 25 °C): δ [ppm] = 3.94 (s, 4H, $C_5H_2{}^tBu_3$), 3.56 (s, 24H, 2,2,2-cryptand), 3.52 (t, 24H, 2,2,2-cryptand, $^1J_{HH}$ = 4.7 Hz), 2.53 (t, 24H, 2,2,2-cryptand, $^1J_{HH}$ = 4.7 Hz), 1.28 (s, 36H, $C_5H_2{}^tBu_3$), 1.21 (s, 18H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (CD_3CN, 25 °C): δ [ppm] = 91.6 (m, 6P, P_8), -124.1 (m, 2P, P_8).

^{31}P NMR (CD_3CN, 25 °C): δ [ppm] = 91.6 (m, 6P, P_8), -124.1 (m, 2P, P_8).

ESI-MS (dme): *m/z* = 1279.14 (100 %, $[(Cp'''Co)_3P_{13}]^-$), 1217.20 (82 %, $[(Cp'''Co)_3P_{11}]^-$).

EA $C_{70}H_{130}O_{12}N_4K_2P_8Co_2$: 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(η^3-P$_4$^{t}Bu)] (4)

a) A solution of ^{t}BuLi 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 C_6D_6 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 %).

^{1}H NMR (thf-d$_8$, 25 °C): δ [ppm] = 4.90 (s, 2H, $C_5H_2{}^t Bu_3$), 3.70 (s, 12H, 2,2,2-crypt), 3.64 (pt, $^3J_{HH}$ = 5.1 Hz, 12H, 2,2,2-crypt), 2.72 (pt, $^3J_{HH}$ = 5.1 Hz, 12H, 2,2,2-crypt), 1.47(s, 9H, $P_4{}^tBu$), 1.36, 1.35, 1.34 (three overlapping singlets, 27H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (thf-d$_8$, 25 °C): δ [ppm] = 94.1 (t, $^1J_{PP}$ = 255.63 Hz, $^2J_{PP}$ = 2.48 Hz, 1P, P_A), 88.7 (t, $^1J_{PP}$ = 186.23 Hz, $^2J_{PP}$ = 3.97 Hz, 1P, P_M), -25.9 (dd, $^1J_{PP}$ = 255.63 Hz, $^1J_{PP}$ = 186.23 Hz, 2P, P_X, $P_{X'}$) (coupling constants obtained from the simulation, cf. Figure S4).

^{31}P NMR (thf-d$_8$, 25 °C): δ [ppm] = 94.1 (t, $^1J_{PP}$ = 255.60 Hz, $^2J_{PP}$ = 1.49 Hz, $^5J_{PH}$ = 0.77 Hz, 1P, P_A), 88.7 (tdec, $^1J_{PP}$ = 186.26 Hz, $^2J_{PP}$ = -0.30 Hz, $^3J_{PH}$ = 9.12 Hz 1P, P_M), -26.0 (dd, $^1J_{PP}$ = 255.60 Hz, $^1J_{PP}$ = 186.26 Hz, $^4J_{PH}$ = -1.12 Hz, 2P, P_X, $P_{X'}$) (coupling constants obtained from the simulation, cf. Figure S4).

EA $C_{39}H_{74}N_2O_6P_4CoLi$: 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 ^{t}BuLi 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-d$_8$ were recorded showing a mixture of **3**, **4**, **5** and **6**.

Compound **5**:

^{31}P{^{1}H} NMR (thf-d$_8$, 25 °C): δ [ppm] = 231.9 (m, $^1J_{PP}$ = 470.35 Hz, $^1J_{PP}$ = 441.32 Hz, $^2J_{PP}$ = -1.21 Hz, $^2J_{PP}$ = 13.24 Hz, 1P, P_A), 130.9 (ddd, $^1J_{PP}$ = 346.33 Hz, $^1J_{PP}$ = 363.12 Hz, $^2J_{PP}$ = 14.02 Hz, $^2J_{PP}$ = -4.69 Hz, $^2J_{PP}$ = 69.86 Hz, $^3J_{PP}$ = -1.52 Hz, 2P, P_M), 74.7 (dddd, $^1J_{PP}$ = 470.35 Hz, $^1J_{PP}$ = 358.96 Hz, $^2J_{PP}$ = -4.69 Hz, $^2J_{PP}$ = 69.86 Hz, $^2J_{PP}$ = -16.59 Hz, $^2J_{PP}$ = -14.40, $^3J_{PP}$ = 1.02 Hz, 2P, P_N), 1.34 (dt, $^1J_{PP}$ = 441.32 Hz, $^1J_{PP}$ = 346.33 Hz, $^2J_{PP}$ = -14.40 Hz, $^2J_{PP}$ = 6.80 Hz, 1P, P_O), -123.9 (t, $^1J_{PP}$ = 363.12 Hz, $^1J_{PP}$ = 358.96 Hz, $^2J_{PP}$ = 6.80 Hz, $^3J_{PP}$ = -1.52 Hz, $^3J_{PP}$ = 1.02 Hz, $^4J_{PP}$ = 20.96 Hz, 2P, P_X) (coupling constants obtained from the simulation, cf. Figure S8).

^{31}P NMR (thf-d$_8$, 25 °C): δ [ppm] = 231.9 (m, 1P, P_A), 130.9 (m, 2P, P_M), 74.7 (m, 2P, P_N), 1.34 (m, 1P, P_O), -123.9 (m, 2P, P_X) (signals 231.9 and 1.34 ppm show further broadening caused by proton coupling, too bad resolved for simulation).

Compound **6**:

^{31}P{^{1}H} NMR (thf-d$_8$, 25 °C): δ [ppm] = 106.8 (ddd, $^1J_{PP}$ = 400.71 Hz, $^1J_{PP}$ = 342.90 Hz, $^2J_{PP}$ = 65.46 Hz, $^2J_{PP}$ = 5.97 Hz, 1P, P_A), 98.9 (tdd, $^1J_{PP}$ = 352.77 Hz, $^1J_{PP}$ = 348.39, $^2J_{PP}$ = 65.46 Hz, $^2J_{PP}$ = 12.84 Hz, 1P, P_B), 77.7 (dddd, $^1J_{PP}$ = 352.77 Hz, $^1J_{PP}$ = 322.67 Hz, $^2J_{PP}$ = 5.97 Hz, $^2J_{PP}$ = 10.00 Hz, 1P, P_C), 31.3 (dddd, $^1J_{PP}$ = 400.71 Hz, $^1J_{PP}$ = 322.67 Hz, $^2J_{PP}$ = 12.84, $^2J_{PP}$ = 7.23 Hz, 1P, P_M), -146.9 (t, $^1J_{PP}$ = 342.90 Hz, $^1J_{PP}$ = 348.39 Hz, $^2J_{PP}$ = 10.00 Hz, $^2J_{PP}$ = 7.23 Hz, 1P, P_X) coupling constants obtained from the simulation, cf. Figure S9).

^{31}P NMR (thf-d_8, 25 °C): δ [ppm] = 106.8 (m, 1P, P_A), 98.9 (m, 1P, P_B), 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-$P_4CH_2SiMe_3$)] and [Li(12-c-4)$_2$][Cp'''Co(η³-$P_4CH_2SiMe_3$)]

a) Reaction with 2,2,2-cryptand: A solution of $LiCH_2SiMe_3$ 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-d_8 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-d_8 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**:

^{1}H NMR (thf-d_8, 25 °C): δ [ppm] = 4.80 (s, 2H, $C_5H_2{}^tBu_3$), 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), 2.20 (s, 2H, CH_2SiMe_3), 1.48 (s, 9H, $C_5H_2{}^tBu_3$), 1.34 (s, 18H, $C_5H_2{}^tBu_3$), 0.02 (s, 9H, CH_2SiMe_3).

^{31}P{^{1}H} NMR (thf-d_8, 25 °C): δ [ppm] = 52.3 (td, $^1J_{PP}$ = 260.89 Hz, $^2J_{PP}$ = 10.95 Hz, 1P, P_A), 45.9 (td, $^1J_{PP}$ = 152.24 Hz, $^2J_{PP}$ = 10.95 Hz, 1P, P_M), 18.8 (dd, $^1J_{PP}$ = 260.89 Hz, $^1J_{PP}$ = 152.24 Hz, $^2J_{PP}$ = -8.00 Hz, 2P, $P_{XX'}$), (coupling constants obtained from the simulation, cf. Figure S12).

^{31}PNMR (thf-d_8, 25 °C): δ [ppm] = 52.3 (td, $^1J_{PP}$ = 260.89 Hz, $^2J_{PP}$ = 10.95 Hz, 1P, P_A), 45.9 (td, $^1J_{PP}$ = 152.24 Hz, $^2J_{PP}$ = 10.95 Hz, 1P, P_M), 18.8 (dd, $^1J_{PP}$ = 260.89 Hz, $^1J_{PP}$ = 152.24 Hz, $^2J_{PP}$ = -8.00 Hz, 2P, $P_{XX'}$), (coupling constants obtained from the simulation of the ^{31}P{^{1}H}, no further coupling observed, cf. Figure S12).

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

^{1}H NMR (thf-d_8, 25 °C): δ [ppm] = 4.75 (s, 2H, $C_5H_2{}^tBu_3$), 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), 1.36 (s, 18H, $C_5H_2{}^tBu_3$), 1.31 (s, 2H, CH_2SiMe_3), 1.26 (s, 9H, $C_5H_2{}^tBu_3$), -0.07 (s, 9H, CH_2SiMe_3).

^{31}P{^{1}H} NMR (thf-d_8, 25 °C): δ [ppm] = 39.4 (td, $^1J_{PP}$ = 135.82 Hz, $^2J_{PP}$ = 14.38 Hz, 1P, P_A), 3.8 (dd, $^1J_{PP}$ = 276.36 Hz, $^1J_{PP}$ = 135.82 Hz, $^2J_{PP}$ = -84.01 Hz, 2P, $P_{MM'}$), -78.2 (td, $^1J_{PP}$ = 276.36 Hz, $^2J_{PP}$ = 14.38 Hz, 1P, P_X), (coupling constants obtained from the simulation, cf. Figure S12).

^{31}P NMR (thf-d_8, 25 °C): δ [ppm] = 39.4 (td, $^1J_{PP}$ = 135.82 Hz, $^2J_{PP}$ = 14.38 Hz, 1P, P_A), 3.8 (dd, $^1J_{PP}$ = 276.36 Hz, $^1J_{PP}$ = 135.82 Hz, $^2J_{PP}$ = -84.01 Hz, 2P, $P_{MM'}$), -78.2 (td, $^1J_{PP}$ = 276.36 Hz, $^2J_{PP}$ = 14.38 Hz, 1P, P_X), (coupling constants obtained from the simulation of the ^{31}P{^{1}H}, 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 $LiCH_2SiMe_3$ 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-d_8 were recorded revealing the formation two isomers **7a** and **7b** in a ratio of 1:1.33 beside other products. The residue was dissolved in a small amount thf and precipitated with pentane. The NMR spectra of the precipitated solid reveals a clean mixture of **7a** and **7b** in a ratio of 1:1.78. 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 $[Li(12\text{-}c\text{-}4)_2]$**7a**:

^{1}H NMR (thf-d_8, 25 °C): δ [ppm] = 4.83 (s, 2H, $C_5H_2{}^tBu_3$), 3.77 (s, 32H, 12-c-4), 2.20 (s, 2H, CH_2SiMe_3), 1.48 (s, 9H, $C_5H_2{}^tBu_3$), 1.34 (s, 18H, $C_5H_2{}^tBu_3$), 0.02 (s, 9H, CH_2SiMe_3).

^{31}P{^{1}H} NMR (thf-d_8, 25 °C): δ [ppm] = 50.1 (td, $^1J_{PP}$ = 259.18 Hz, $^2J_{PP}$ = 10.53 Hz, 1P, P_A), 46.5 (td, $^1J_{PP}$ = 152.95 Hz, $^2J_{PP}$ = 10.53 Hz, 1P, P_M), 17.42 (dd, $^1J_{PP}$ = 259.18 Hz, $^1J_{PP}$ = 152.95 Hz, $^2J_{PP}$ = -8.00 Hz, 2P, $P_{XX'}$), (coupling constants obtained from the simulation, cf. Table S8).

^{31}PNMR (thf-d_8, 25 °C): δ [ppm] = 50.1 (td, $^1J_{PP}$ = 259.18 Hz, $^2J_{PP}$ = 10.53 Hz, 1P, P_A), 46.5 (td, $^1J_{PP}$ = 152.95 Hz, $^2J_{PP}$ = 10.53 Hz, 1P, P_M), 17.42 (dd, $^1J_{PP}$ = 259.18 Hz, $^1J_{PP}$ = 152.95 Hz, $^2J_{PP}$ = -8.00 Hz, 2P, $P_{XX'}$), (coupling constants obtained from the simulation of the ^{31}P{^{1}H}, no further coupling observed, cf. Table S8).

Compound $[Li(12\text{-}c\text{-}4)_2]$**7b**:

^{1}H NMR (thf-d_8, 25 °C): δ [ppm] = 4.79 (s, 2H, $C_5H_2{}^tBu_3$), 3.77 (s, 32H, 12-c-4), 1.36 (s, 18H, $C_5H_2{}^tBu_3$), 1.32 (s, 2H, CH_2SiMe_3), 1.26 (s, 9H, $C_5H_2{}^tBu_3$), -0.07 (s, 9H, CH_2SiMe_3).

^{31}P{^{1}H} NMR (thf-d_8, 25 °C): δ [ppm] = 38.93 (td, $^1J_{PP}$ = 135.34 Hz, $^2J_{PP}$ = 13.76 Hz, 1P, P_A), 2.8 (dd, $^1J_{PP}$ = 273.40 Hz, $^1J_{PP}$ = 135.34 Hz, $^2J_{PP}$ = -84.00 Hz, 2P, $P_{MM'}$), -79.9 (td, $^1J_{PP}$ = 273.40 Hz, $^2J_{PP}$ = 13.76 Hz, 1P, P_X), (coupling constants obtained from the simulation, cf. Table S8).

^{31}P NMR (thf-d_8, 25 °C): δ [ppm] = 38.93 (td, $^1J_{PP}$ = 135.34 Hz, $^2J_{PP}$ = 13.76 Hz, 1P, P_A), 2.8 (dd, $^1J_{PP}$ = 273.40 Hz, $^1J_{PP}$ = 135.34 Hz, $^2J_{PP}$ = -84.00 Hz, 2P, $P_{MM'}$), -79.9 (td, $^1J_{PP}$ = 273.40 Hz, $^2J_{PP}$ = 13.76 Hz, 1P, P_X), (coupling constants obtained from the simulation of the ^{31}P{^{1}H}, no further coupling observed, cf. Table S8).

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

EA $C_{37}H_{72}O_8P_4CoLiSi$: 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 $[Li(dme)_3][(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}P_8CH_2SiMe_3)]$ (8)

A solution of $LiCH_2SiMe_3$ (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, $C_5H_2{}^t Bu_3$), 4.15 (s, 2H, $C_5H_2{}^t Bu_3$), 3.43 (s, 12H, Li(*dme*)$_3$), 3.27 (s, 12H, Li(*dme*)$_3$), 1.80 (br, 2H, $P_8CH_2SiMe_3$), 1.34 (s, 18H, $C_5H_2{}^t Bu_3$), 1.31 (s, 18H, $C_5H_2{}^t Bu_3$), 1.29 (s, 18H, $C_5H_2{}^t Bu_3$), 0.32 (s, 9H, $P_8CH_2SiMe_3$).

^{1}H{^{31}P} NMR (thf-d_8, 300 K, decoupled at -114 ppm): δ [ppm] = 4.53 (d, $^3J_{HH}$ = 2.2 Hz, 2H, $C_5H_2{}^t Bu_3$), 4.15 (d, d, $^3J_{HH}$ = 2.2 Hz, 2H, $C_5H_2{}^t Bu_3$), 3.43 (s, 12H, Li(*dme*)$_3$), 3.27 (s, 12H, Li(*dme*)$_3$), 1.80 (d, $^2J_{PH}$ = 8.5 Hz, 2H, $P_8CH_2SiMe_3$), 1.34 (s, 18H, $C_5H_2{}^t Bu_3$), 1.31 (s, 18H, $C_5H_2{}^t Bu_3$), 1.29 (s, 18H, $C_5H_2{}^t Bu_3$), 0.32 (s, 9H, $P_8CH_2SiMe_3$).

^{1}H{^{31}P} NMR (thf-d_8, 300 K, decoupled at +71 ppm): δ [ppm] = 4.53 (d, $^3J_{HH}$ = 2.2 Hz, 2H, $C_5H_2{}^t Bu_3$), 4.15 (d, d, $^3J_{HH}$ = 2.2 Hz, 2H, $C_5H_2{}^t Bu_3$), 3.43 (s, 12H, Li(*dme*)$_3$), 3.27 (s, 12H, Li(*dme*)$_3$), 1.80 (s, 2H, $P_8CH_2SiMe_3$), 1.34 (s, 18H, $C_5H_2{}^t Bu_3$), 1.31 (s, 18H, $C_5H_2{}^t Bu_3$), 1.29 (s, 18H, $C_5H_2{}^t Bu_3$), 0.32 (s, 9H, $P_8CH_2SiMe_3$).

^{31}P{^{1}H} NMR (thf-d_8, 193 K): δ [ppm] = 187.9 (q, $^1J_{PP}$ = 448.32 Hz, $^1J_{PP}$ = 424.01 Hz, $^2J_{PP}$ = -2.44 Hz, $^2J_{PP}$ = 12.49 Hz, 1P, P_A), 102.8 (td, $^1J_{PP}$ = 351.60 Hz, $^1J_{PP}$ = 366.96 Hz, $^2J_{PP}$ = -2.44 Hz, $^2J_{PP}$ = 6.65 Hz, $^2J_{PP}$ = 62.41 Hz, $^2J_{PP}$ = -12.85 Hz, $^3J_{PP}$ = 0.20 Hz, 2P, P_M), 72.5 (ddd, $^1J_{PP}$ = 448.32 Hz, $^1J_{PP}$ = 369.36 Hz, $^2J_{PP}$ = 62.41 Hz, $^2J_{PP}$ = -12.85 Hz, $^2J_{PP}$ = -3.66 Hz, $^2J_{PP}$ = -17.34 Hz, $^3J_{PP}$ = 0.87 Hz, 2P, P_N), 40.5 (dt, $^1J_{PP}$ = 424.01 Hz, $^1J_{PP}$ = 351.60 Hz, $^2J_{PP}$ = -17.34 Hz, $^2J_{PP}$ = 7.69 Hz, 1P, P_O), -118.8 (t, $^1J_{PP}$ = 366.96 Hz, $^1J_{PP}$ = 369.36 Hz, $^2J_{PP}$ = 12.49 Hz, $^2J_{PP}$ = 7.69 Hz, $^3J_{PP}$ = 0.20 Hz, $^3J_{PP}$ = 0.87 Hz, $^4J_{PP}$ = 19.47 Hz, 2P, P_X). (coupling constants obtained from the simulation, cf. Figure S13).

^{31}P NMR (thf-d_8, 193 K): δ [ppm] = 187.9 (m, 1P, P_A), 102.8 (m, 2P, P_M), 72.5 (m, 2P, P_N), 40.5 (m, 1P, P_O), -118.8 (m, 2P, P_X). (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 [Na(dme)$_2$][Cp'''Co(η^3-P$_4$(O)H)] (10)

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 %).

^{1}H NMR (thf-d$_8$, 300 K): δ [ppm] = 7.78 (dtd, $^1J_{PH}$ = 356.77 Hz, $^2J_{PH}$ = 20.56 Hz, $^3J_{PH}$ = 5.12 Hz, 1H, P$_4$(O)*H*), 4.95 (s, 2H, C$_5$*H*$_2$^{t}Bu$_3$), 3.43 (s, 8H, dme), 3.27 (s, 12H, dme), 1.36 (s, 18H, C$_5$H$_2$^{t}*Bu*$_3$), 1.34 (s, 9H, C$_5$H$_2$^{t}*Bu*$_3$).

^{1}H{^{31}P} NMR (thf-d$_8$, 300 K): δ [ppm] = 7.78 (s, 1H, P$_4$(O)*H*), 4.95 (s, 2H, C$_5$*H*$_2$^{t}Bu$_3$), 3.43 (s, 8H, dme), 3.27 (s, 12H, dme), 1.36 (s, 18H, C$_5$H$_2$^{t}*Bu*$_3$), 1.34 (s, 9H, C$_5$H$_2$^{t}*Bu*$_3$).

^{31}P{^{1}H} NMR (thf + C$_6$D$_6$ capillary, 25 °C): δ [ppm] = 74.8 (dd, $^1J_{PP}$ = 262.67 Hz, $^1J_{PP}$ = 246.57 Hz, $^2J_{PP}$ = -9.00 Hz, 2P, P_A), 29.0 (ddd, $^1J_{PP}$ = 262.67 Hz, $^2J_{PP}$ = 4.92Hz, 1P, P_M), -21.8 (t, $^1J_{PP}$ = 246.57 Hz, $^2J_{PP}$ = 4.92 Hz, 1P, P_X) (coupling constants obtained from the simulation, cf. Figure S17).

^{31}P NMR (thf + C$_6$D$_6$ capillary, 25 °C): δ [ppm] = 74.8 (dd, $^1J_{PP}$ = 262.71 Hz, $^1J_{PP}$ = 246.64 Hz, $^2J_{PH}$ = 20.56 Hz, 2P, P_A), 29.0 (dddd, $^1J_{PP}$ = 262.67 Hz, $^2J_{PP}$ = 4.92Hz, $^1J_{PH}$ = 356.77 Hz, 1P, P_M), -21.8 (t, $^1J_{PP}$ = 246.57 Hz, $^2J_{PP}$ = 4.92 Hz, $^3J_{PH}$ = 5.12 Hz, 1P, P_X) (coupling constants obtained from the simulation, cf. Figure S17).

ESI-MS (anion, dme): *m/z* = 867.2 (100 %. [2M+H]$^-$), 433.0 (12 %, [M]$^-$).

EA C$_{25}$H$_{50}$O$_5$P$_4$CoNa: calc [%]: C 47.18; H 7.92; found [%]: C 46.94; H 7.87.

2. NMR spectroscopic investigations

2.1 $[K(dme)]_2[(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}P_8)]$ (2a)

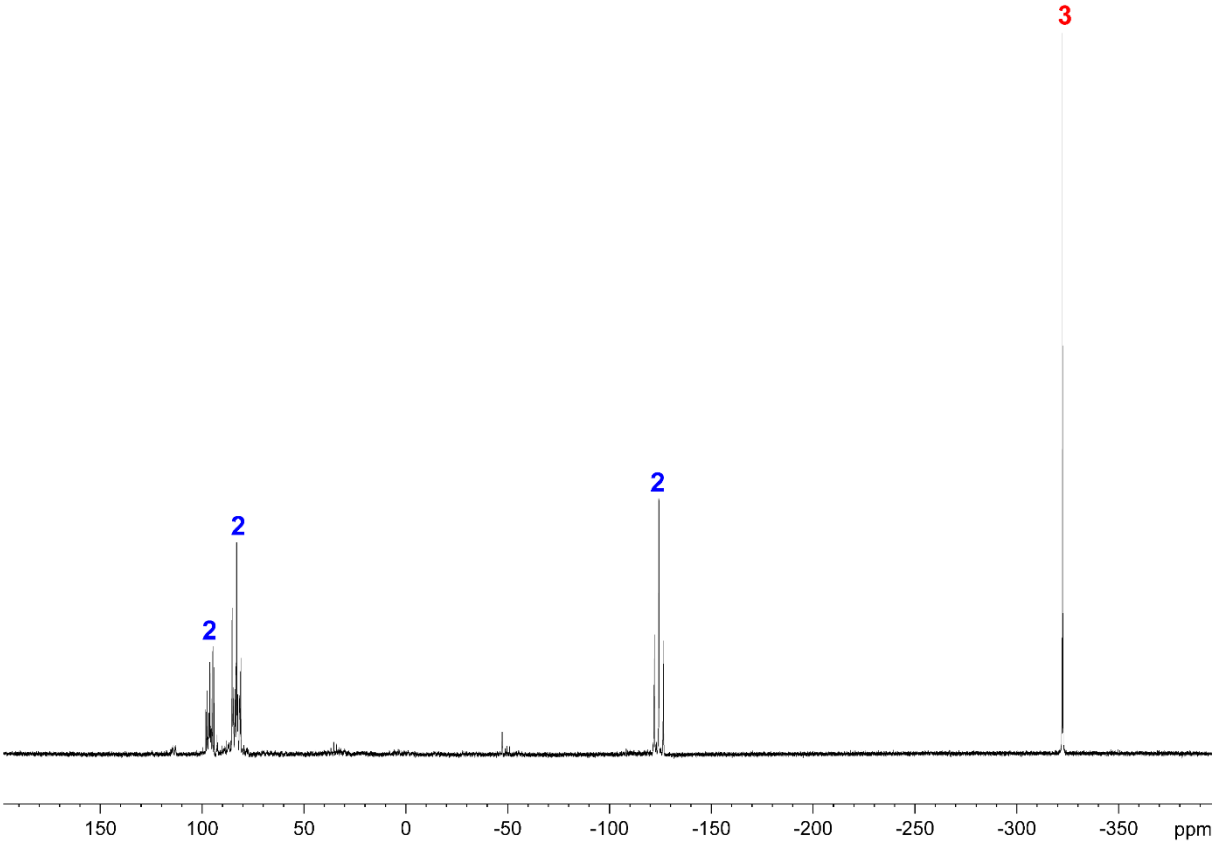


Figure S1: $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture from the reaction of **1** with KC_8 in thf-d_8 at room temperature.

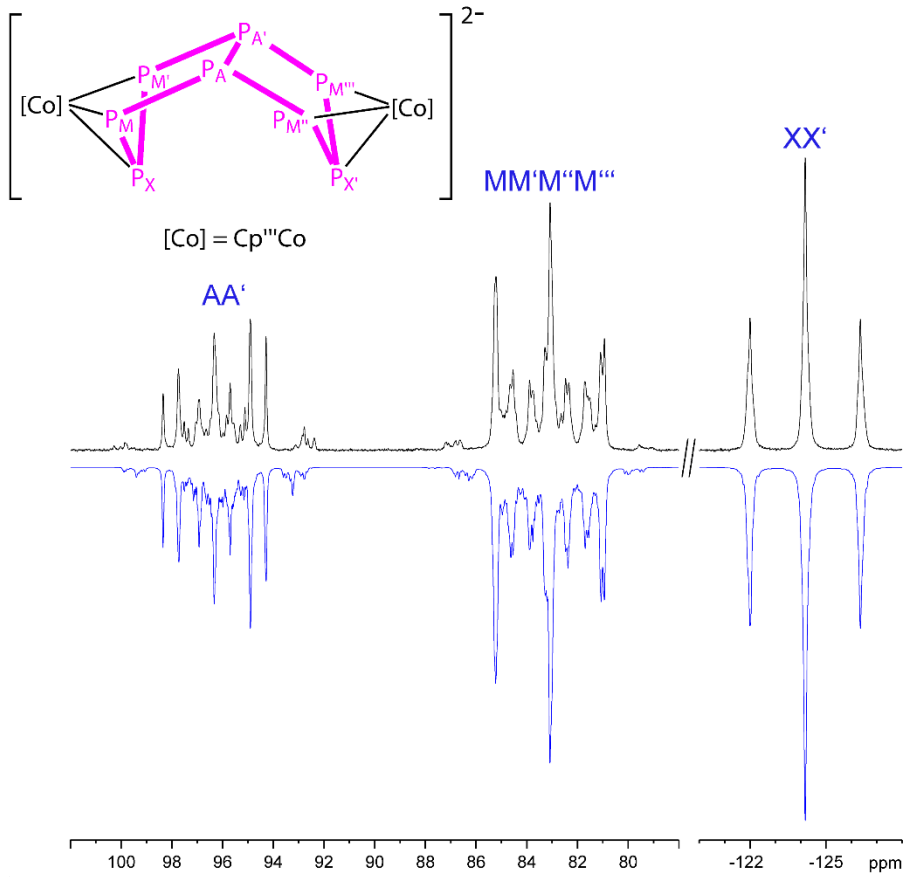


Figure S2: $^{31}P\{^{1}H\}$ NMR spectrum of **2a** in thf-d_8 at room temperature (experimental (black) and simulated (blue)).

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

coupling constants [Hz]

$^{1}J_{P_AP_{A'}}$	309.44	$^{2}J_{P_{A'}P_{M''}}$	23.96
$^{1}J_{P_AP_M}$	330.75	$^{2}J_{P_{A'}P_X}$	-4.96
$^{1}J_{P_AP_{M''}}$	301.97	$^{2}J_{P_{A'}P_{X'}}$	4.28
$^{1}J_{P_{A'}P_{M'}}$	292.35	$^{2}J_{P_MP_{M'}}$	-57.81
$^{1}J_{P_{A'}P_{M'''}}$	343.58	$^{2}J_{P_MP_{M''}}$	-20.81
$^{1}J_{P_MP_X}$	351.21	$^{2}J_{P_{M'}P_{M'''}}$	-11.67
$^{1}J_{P_{M'}P_X}$	359.89	$^{2}J_{P_{M''}P_{M'''}}$	44.81
$^{1}J_{P_{M''}P_{X'}}$	355.82	$^{3}J_{P_MP_{M'''}}$	-11.83
$^{1}J_{P_{M'''}P_{X'}}$	362.15	$^{3}J_{P_MP_{X'}}$	8.65
$^{2}J_{P_AP_{M'}}$	21.49	$^{3}J_{P_{M'}P_{M''}}$	19.83
$^{2}J_{P_AP_{M'''}}$	-10.88	$^{3}J_{P_{M'}P_{X'}}$	-5.40
$^{2}J_{P_AP_X}$	9.55	$^{3}J_{P_{M''}P_X}$	-1.67
$^{2}J_{P_AP_{X'}}$	-0.66	$^{3}J_{P_{M'''}P_X}$	-15.65
$^{2}J_{P_{A'}P_M}$	11.96	$^{4}J_{P_XP_{X'}}$	21.50

chemical shifts [ppm]

$P_{AA'}$	96.16		
$P_{MM'M''M'''}$	83.32	R value	1.56 %
$P_{XX'}$	-124.17		

2.2 $[K(2,2,2\text{-crypt})]_2[(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}P_8)]$ (2b)

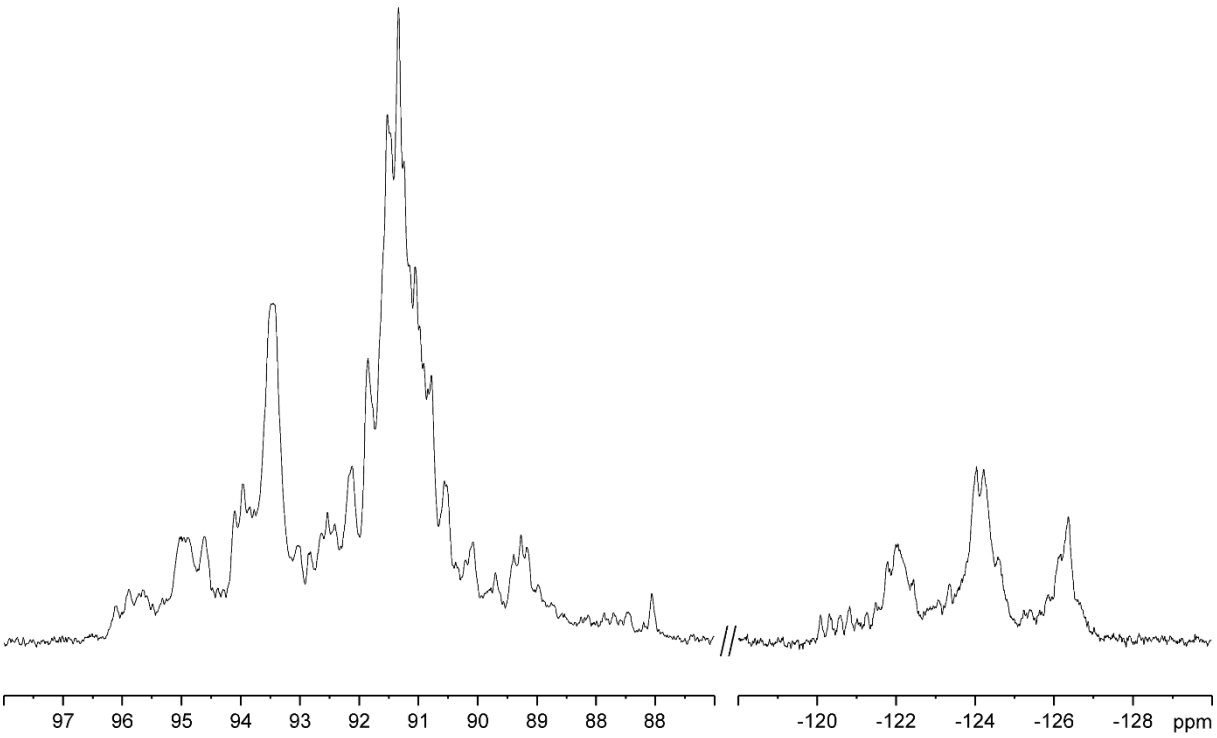


Figure S3: $^{31}P\{^1H\}$ NMR spectrum of **2b** in CD_3CN at room temperature.

2.3 [Li(2,2,2-crypt)][Cp'''Co(η³-P₄ᵗBu)] (4)

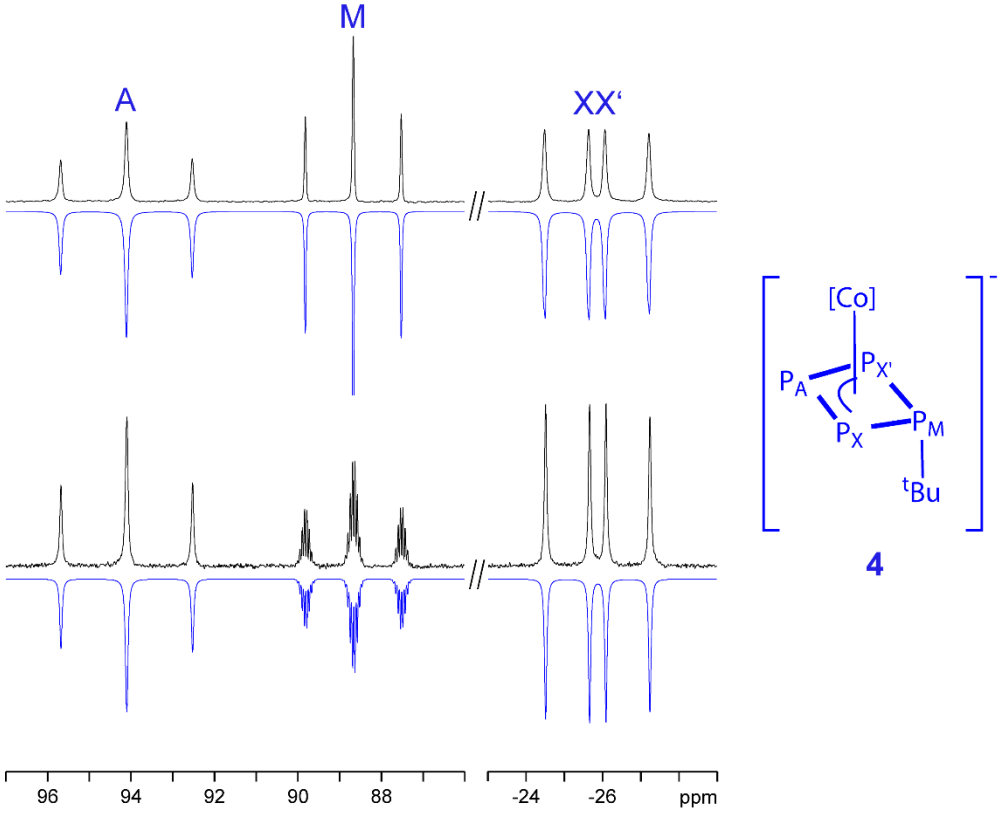


Figure S4: $^{31}P\{^{1}H\}$ (top) and ^{31}P (bottom) NMR spectrum of **4** thf with C_6D_6 capillary at room temperature (experimental (black) and simulated (blue)).

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]	
$^{1}J_{P_AP_X} = {}^{1}J_{P_AP_X'}$	255.63	P_A	94.13
$^{1}J_{P_MP_X} = {}^{1}J_{P_MP_X'}$	186.23	P_M	88.64
$^{2}J_{P_AP_M}$	2.48	P_X	-25.92
$^{2}J_{P_XP_X'}$	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]	
$^{1}J_{P_AP_X} = {}^{1}J_{P_AP_X'}$	255.60	P_A	94.11
$^{1}J_{P_MP_X} = {}^{1}J_{P_MP_X'}$	186.26	P_M	88.62
$^{2}J_{P_AP_M}$	1.49	P_X	-25.95
$^{2}J_{P_XP_X'}$	-0.30	$P_{X'}$	-25.95
$^{3}J_{P_MH}$	9.12		
$^{4}J_{P_XH} = {}^{4}J_{P_X'H}$	-1.12		
$^{5}J_{P_AH}$	0.77		
R value		0.24%	

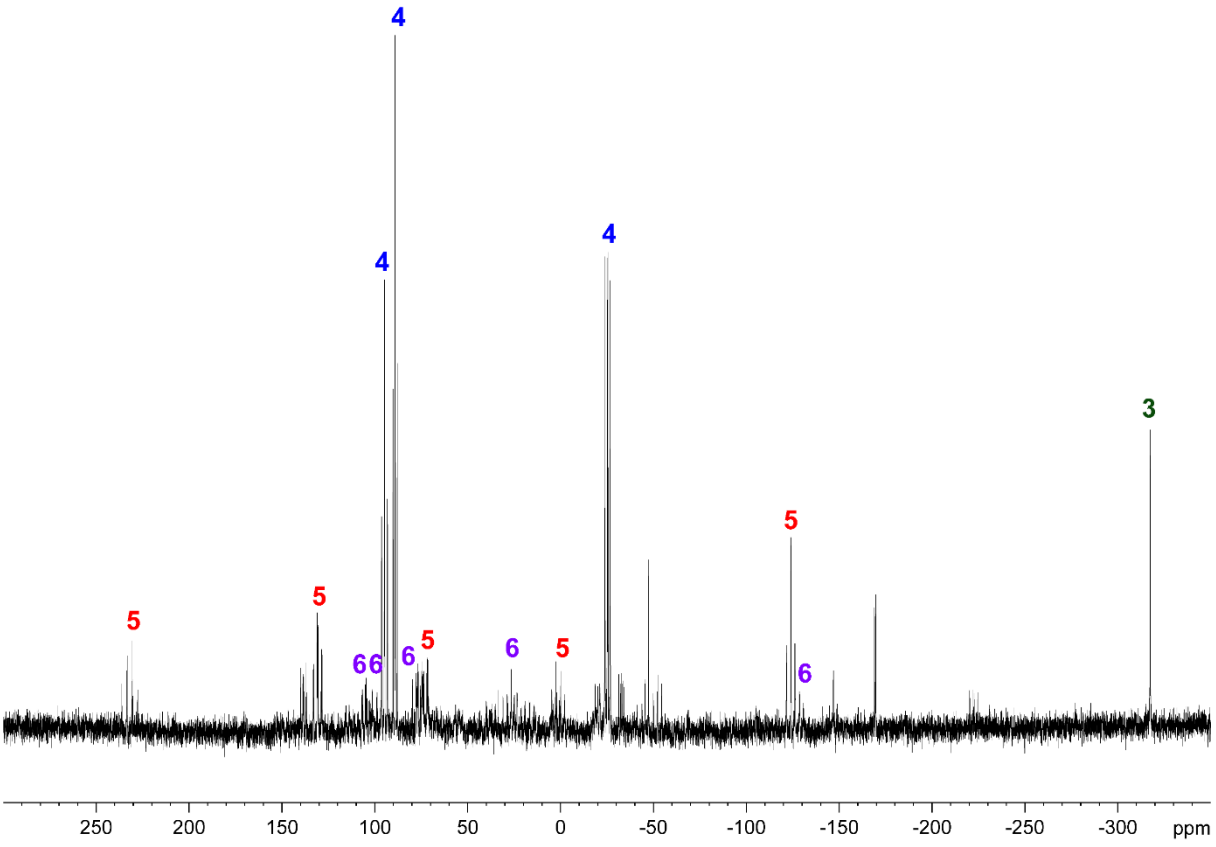


Figure S5: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **1** with ^{t}BuLi at room temperature thf-d_8 at room temperature (large sweep).

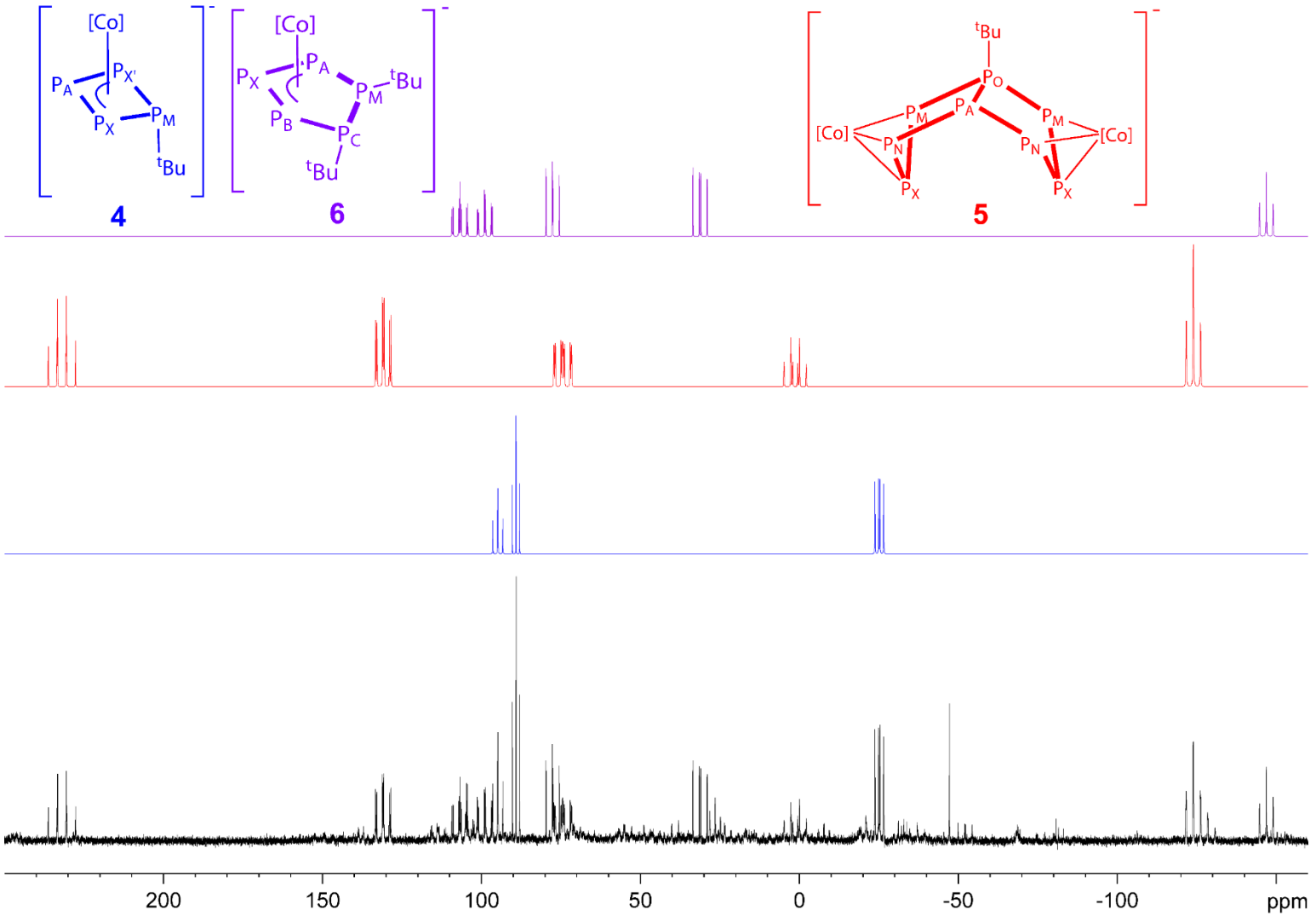


Figure S6: Part of the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **1** with ^{t}BuLi at room temperature thf-d_8 at room temperature and the simulated spectra of **4** (blue), **5** (red) and **6** (purple).

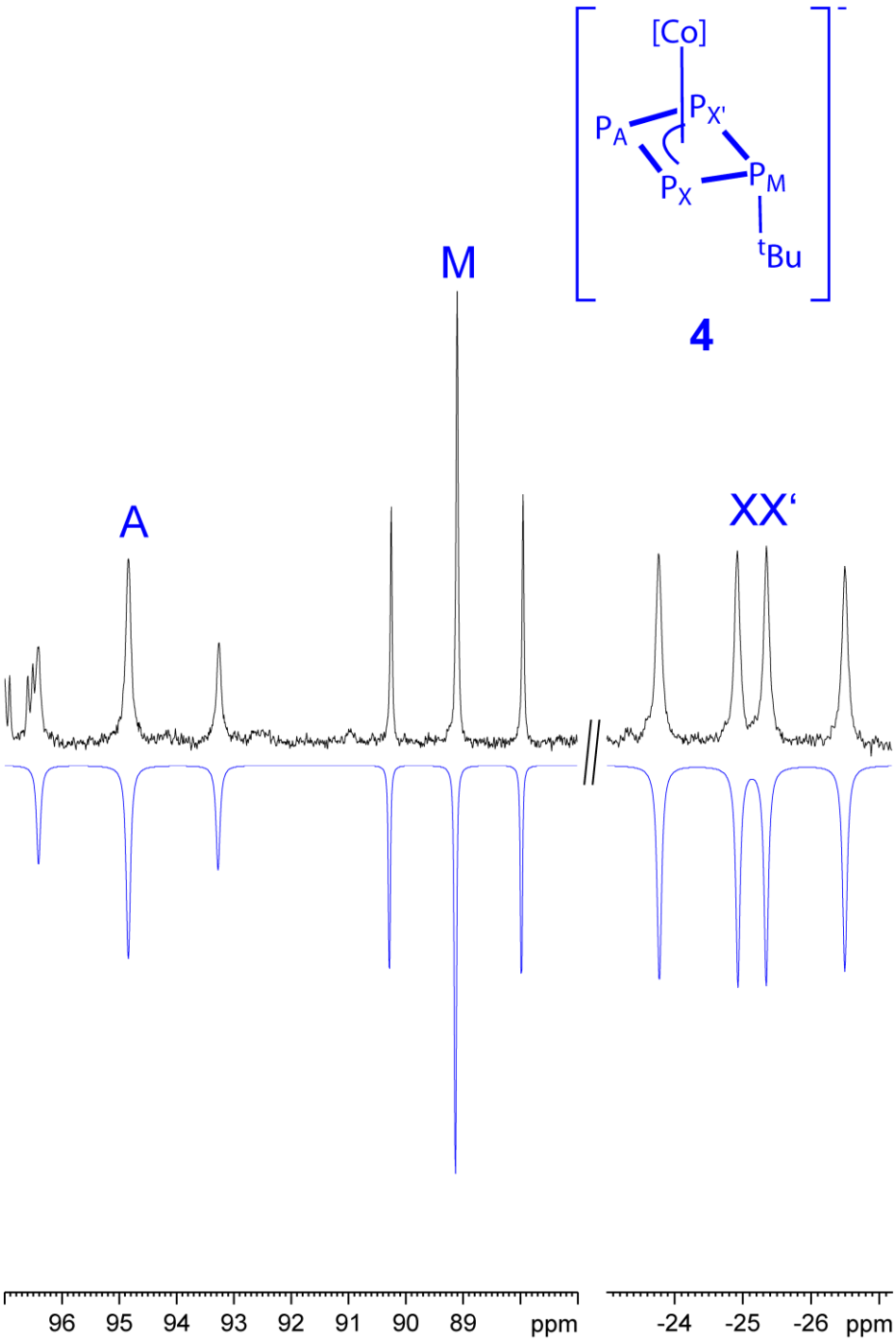


Figure S7: Part of the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **1** with ^{t}BuLi at room temperature thf-d_8 at room temperature and the simulated spectrum of **4** (blue).

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]	
$^{1}J_{P_AP_X} = {}^{1}J_{P_AP_{X'}}$	253.71	P_A	94.83
$^{1}J_{P_MP_X} = {}^{1}J_{P_MP_{X'}}$	186.61	P_M	89.13
$^{2}J_{P_AP_M}$	2.99	P_X	-25.13
$^{2}J_{P_XP_{X'}}$	4.01	$P_{X'}$	-25.13

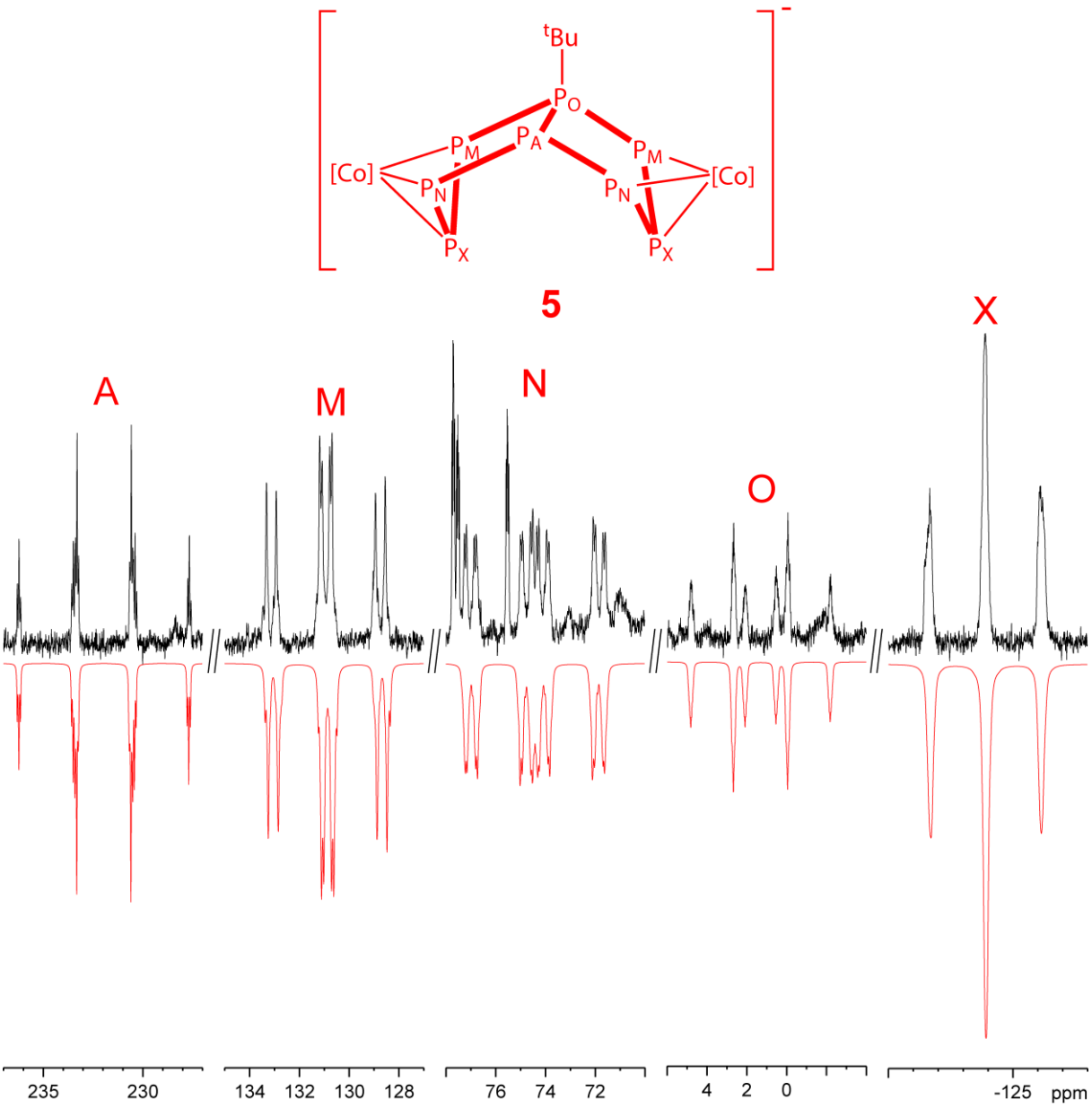


Figure S8: Part of the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **1** with ^{t}BuLi at room temperature thf-d_8 at room temperature and the simulated spectrum of **5** (red).

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

coupling constants [Hz]			
$^{1}J_{P_AP_N}$	470.35	$^{2}J_{P_MP_N}$	-4.69
$^{1}J_{P_AP_O}$	441.32	$^{2}J_{P_MP_N}$	69.86
$^{1}J_{P_MP_O}$	346.33	$^{2}J_{P_NP_N}$	-16.59
$^{1}J_{P_MP_X}$	363.12	$^{2}J_{P_NP_O}$	-14.40
$^{1}J_{P_NP_X}$	358.96	$^{2}J_{P_OP_X}$	6.80
$^{2}J_{P_AP_M}$	-1.21	$^{3}J_{P_MP_X}$	-1.52
$^{2}J_{P_AP_X}$	13.24	$^{3}J_{P_NP_X}$	1.02
$^{2}J_{P_MP_M}$	14.02	$^{4}J_{P_XP_X}$	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

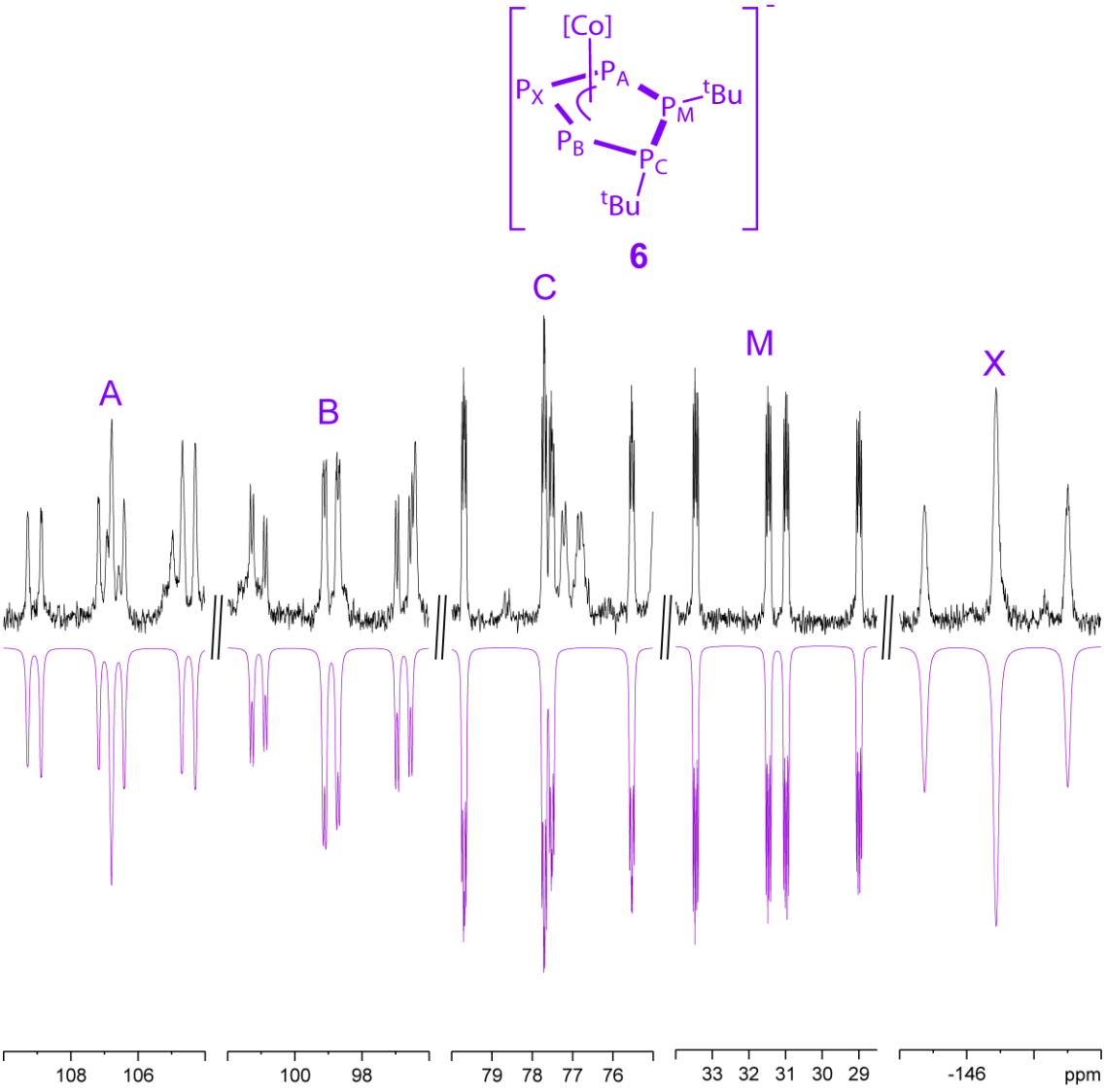


Figure S9: Part of the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **1** with ^{t}BuLi at room temperature thf-d_8 at room temperature and the simulated spectrum of **6** (purple).

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

coupling constants [Hz]

$^{1}J_{P_AP_M}$	400.71	$^{2}J_{P_AP_B}$	65.46
$^{1}J_{P_AP_X}$	342.90	$^{2}J_{P_AP_C}$	5.97
$^{1}J_{P_BP_C}$	352.77	$^{2}J_{P_BP_M}$	12.84
$^{1}J_{P_BP_X}$	348.39	$^{2}J_{P_CP_X}$	10.00
$^{1}J_{P_CP_M}$	322.67	$^{2}J_{P_MP_X}$	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(η^3-$P_4CH_2SiMe_3$)] (7)

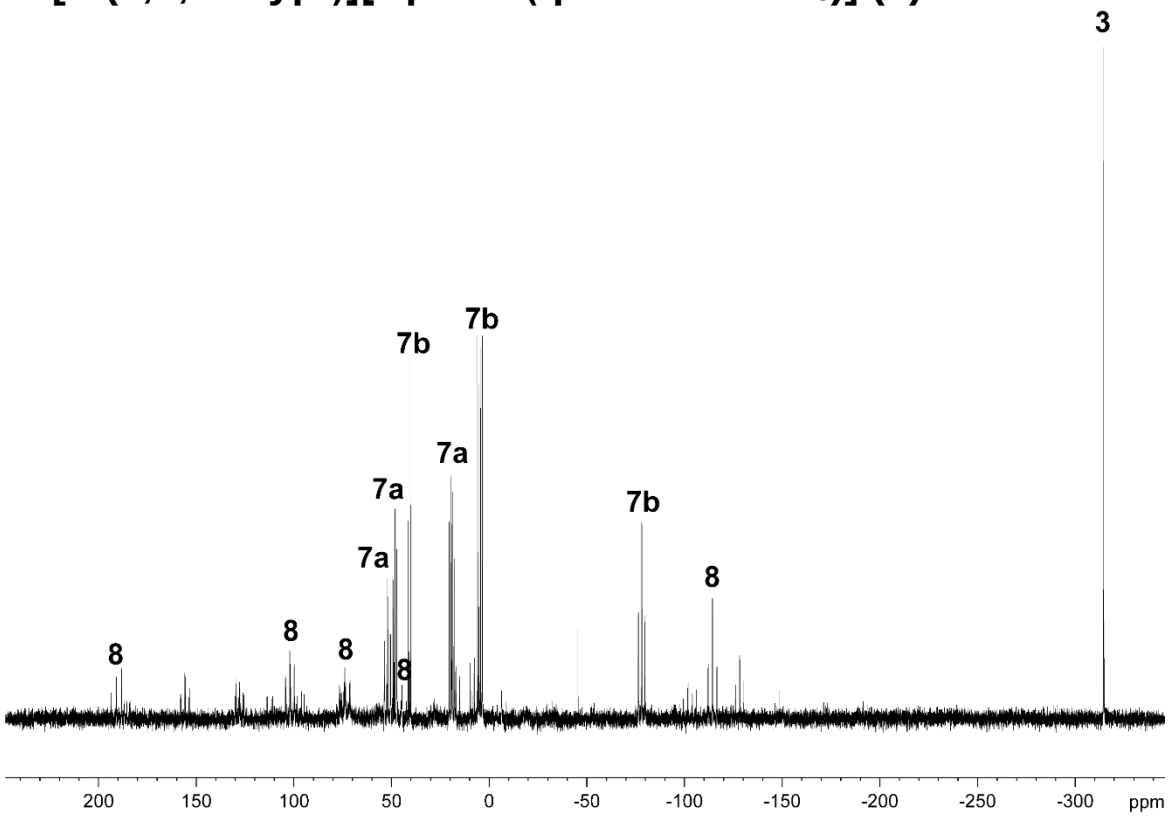


Figure S10: $^{31}P\{^1H\}$ NMR spectrum in thf-d_8 of the reaction of $LiCH_2SiMe_3$ with **1** after addition of 12-c-4.

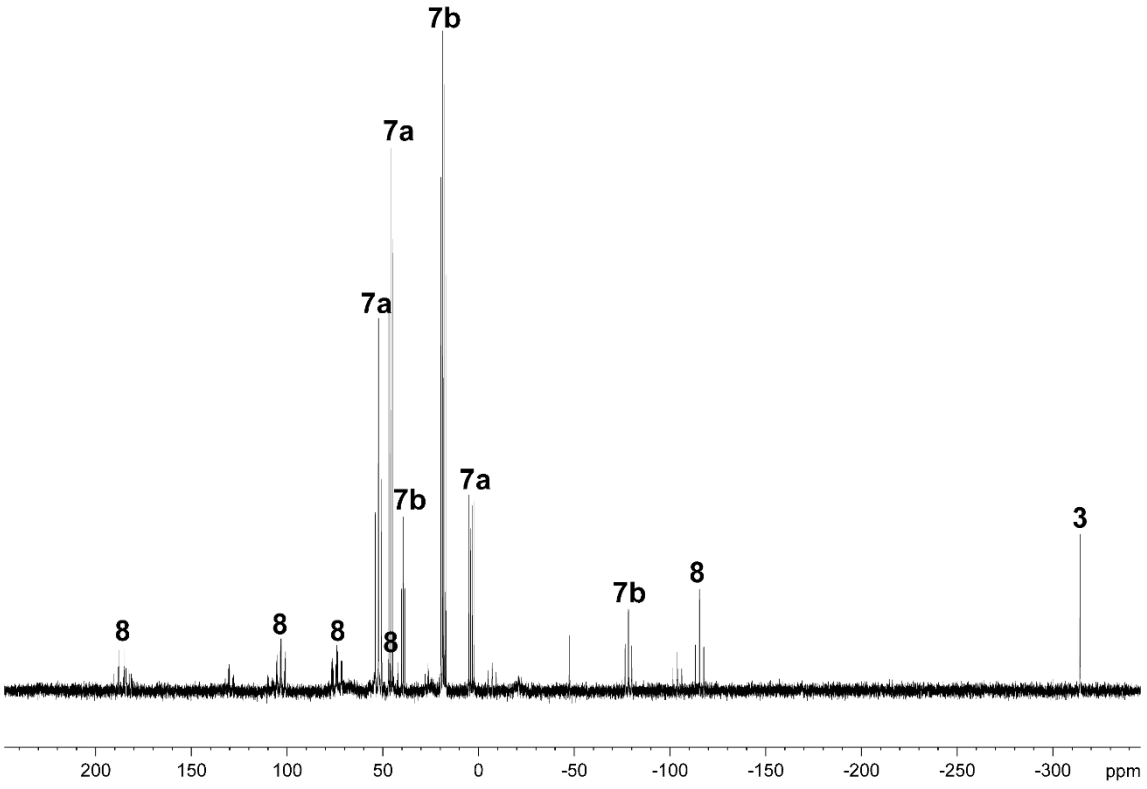


Figure S11: $^{31}P\{^1H\}$ NMR spectrum in thf-d_8 of the reaction of $LiCH_2SiMe_3$ with **1** after addition of 2,2,2-cryptand.

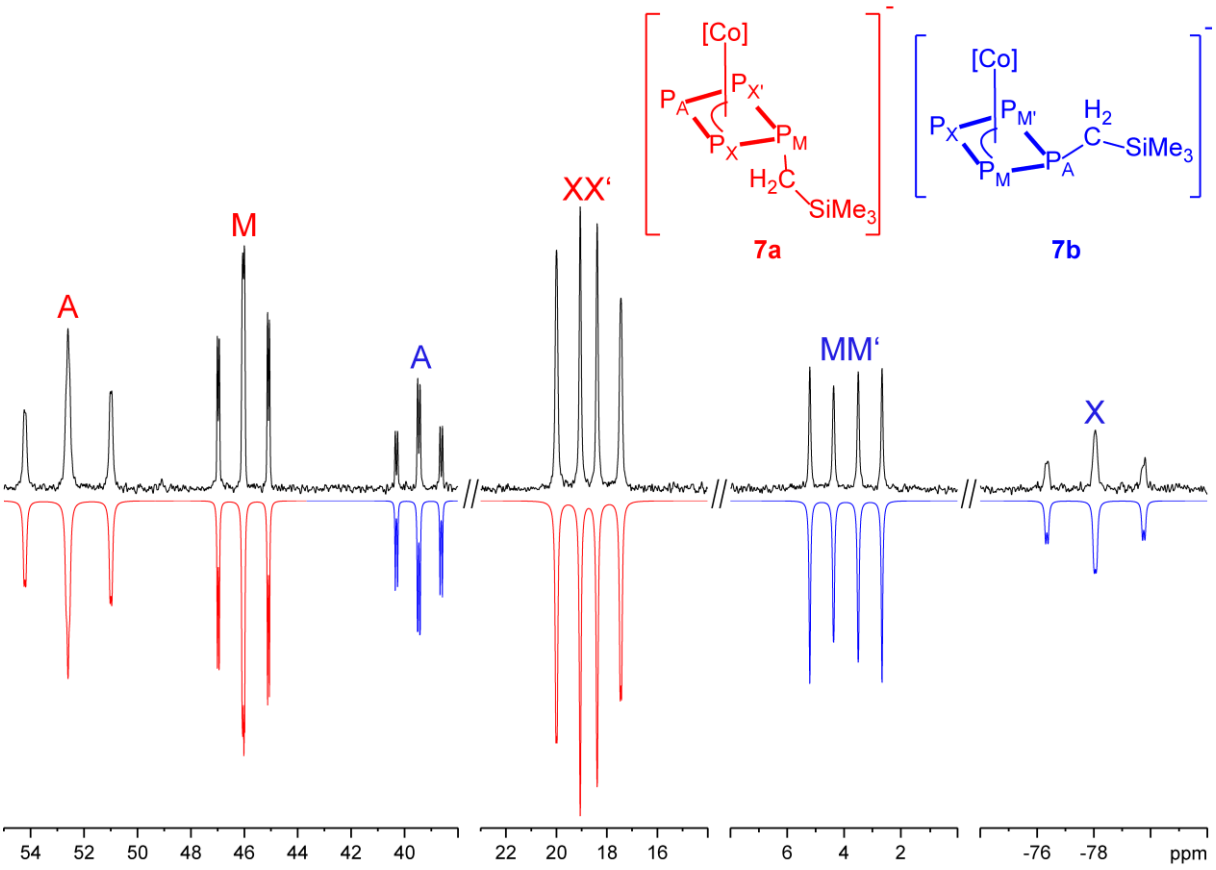


Figure S12: $^{31}P\{^{1}H\}$ NMR spectrum of the [Li(2,2,2-crypt)]**7a**/**7b** in thf-d_8 (experimental (black) and simulated (blue, red)).

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

coupling constants [Hz]			
7a		**7b**	
$^{1}J_{P_AP_X} = {}^{1}J_{P_AP_X'}$	260.89	$^{1}J_{P_AP_M} = {}^{1}J_{P_AP_M'}$	135.82
$^{1}J_{P_MP_X} = {}^{1}J_{P_MP_X'}$	152.24	$^{1}J_{P_MP_X} = {}^{1}J_{P_M'P_X}$	276.36
$^{2}J_{P_AP_M}$	10.95	$^{2}J_{P_AP_X}$	14.38
$^{2}J_{P_XP_X'}$	-8.00	$^{2}J_{P_MP_M'}$	-84.01
chemical shifts [ppm]		chemical shifts [ppm]	
P_A	52.29	P_A	39.39
P_M	45.93	P_M	3.78
P_X	18.48	$P_{M'}$	3.78
$P_{X'}$	18.48	P_X	-78.24
R value	0.53 %		

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

coupling constants [Hz]			
7a		**7b**	
$^{1}J_{P_AP_X} = {}^{1}J_{P_AP_X'}$	259.18	$^{1}J_{P_AP_M} = {}^{1}J_{P_AP_M'}$	135.34
$^{1}J_{P_MP_X} = {}^{1}J_{P_MP_X'}$	152.95	$^{1}J_{P_MP_X} = {}^{1}J_{P_M'P_X}$	273.40

$^2J_{P_AP_M}$	10.53	$^2J_{P_AP_X}$	13.76
$^2J_{P_XP_X'}$	-8.00	$^2J_{P_MP_M'}$	-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	$P_{M'}$	2.84
$P_{X'}$	17.42	P_X	-79.93
R value	1.69 %		

2.5 $[Li(dme)_3][(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}P_8CH_2SiMe_3)]$ (8)

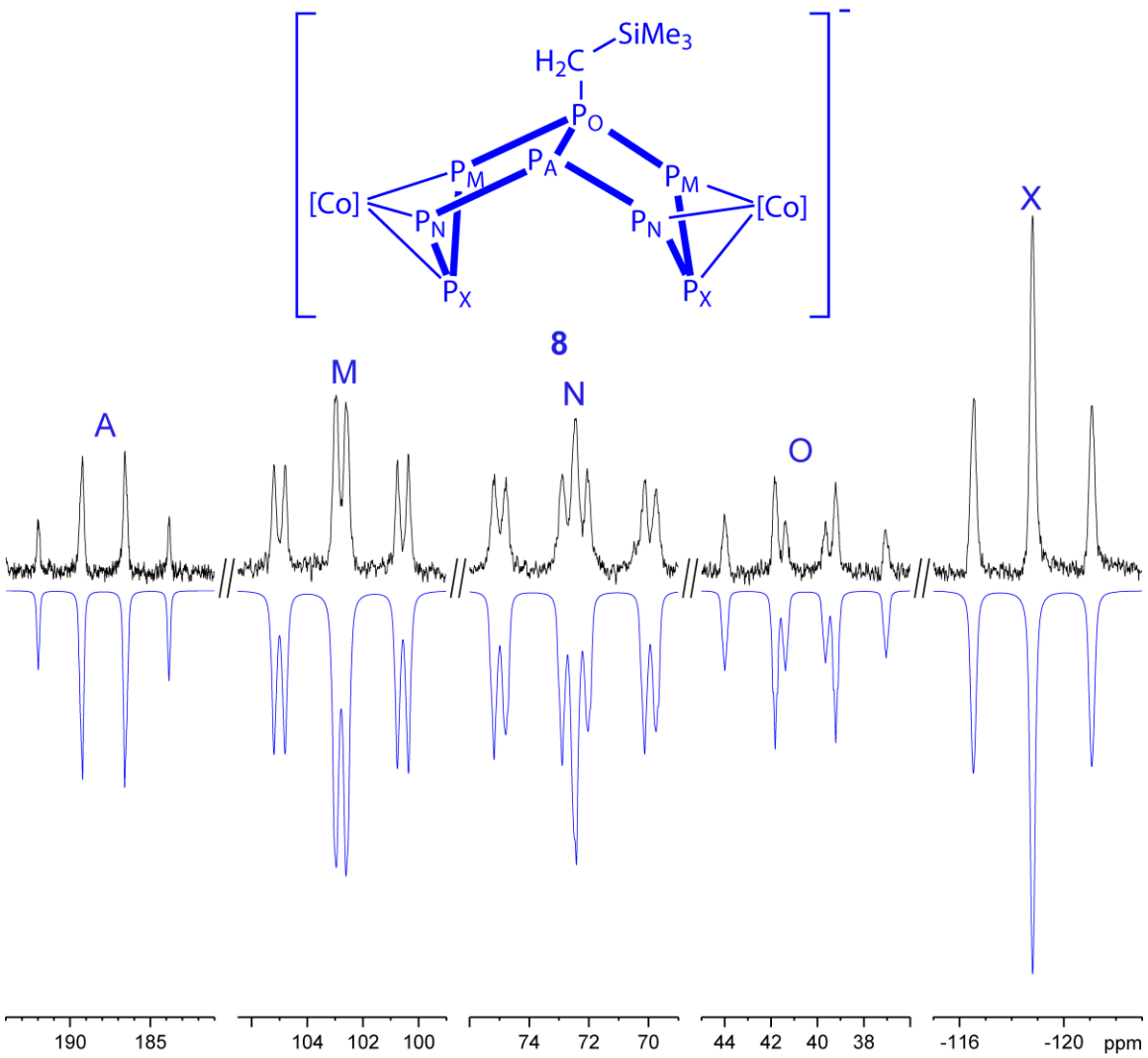


Figure S13: $^{31}P\{^1H\}$ NMR spectrum of **8** in thf-d_8 at 193 K (experimental (black) and simulated (blue)).

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

coupling constants [Hz]			
$^1J_{P_AP_N}$	448.32	$^2J_{P_MP_N}$	62.41
$^1J_{P_AP_O}$	424.01	$^2J_{P_MP_N}$	-12.85
$^1J_{P_MP_O}$	351.60	$^2J_{P_NP_N}$	-3.66
$^1J_{P_MP_X}$	366.96	$^2J_{P_NP_O}$	-17.34
$^1J_{P_NP_X}$	369.36	$^2J_{P_OP_X}$	7.69
$^2J_{P_AP_M}$	-2.44	$^3J_{P_MP_X}$	0.20
$^2J_{P_AP_X}$	12.49	$^3J_{P_NP_X}$	0.87
$^2J_{P_MP_M}$	6.65	$^4J_{P_XP_X}$	19.47
chemical shifts [ppm]			
P_A	187.87		
P_M	102.75	R value	1.53 %
P_N	74.48		
P_O	40.57		
P_X	-118.80		

2.6 1 + $LiCH_2SiMe_3$ VT-NMR

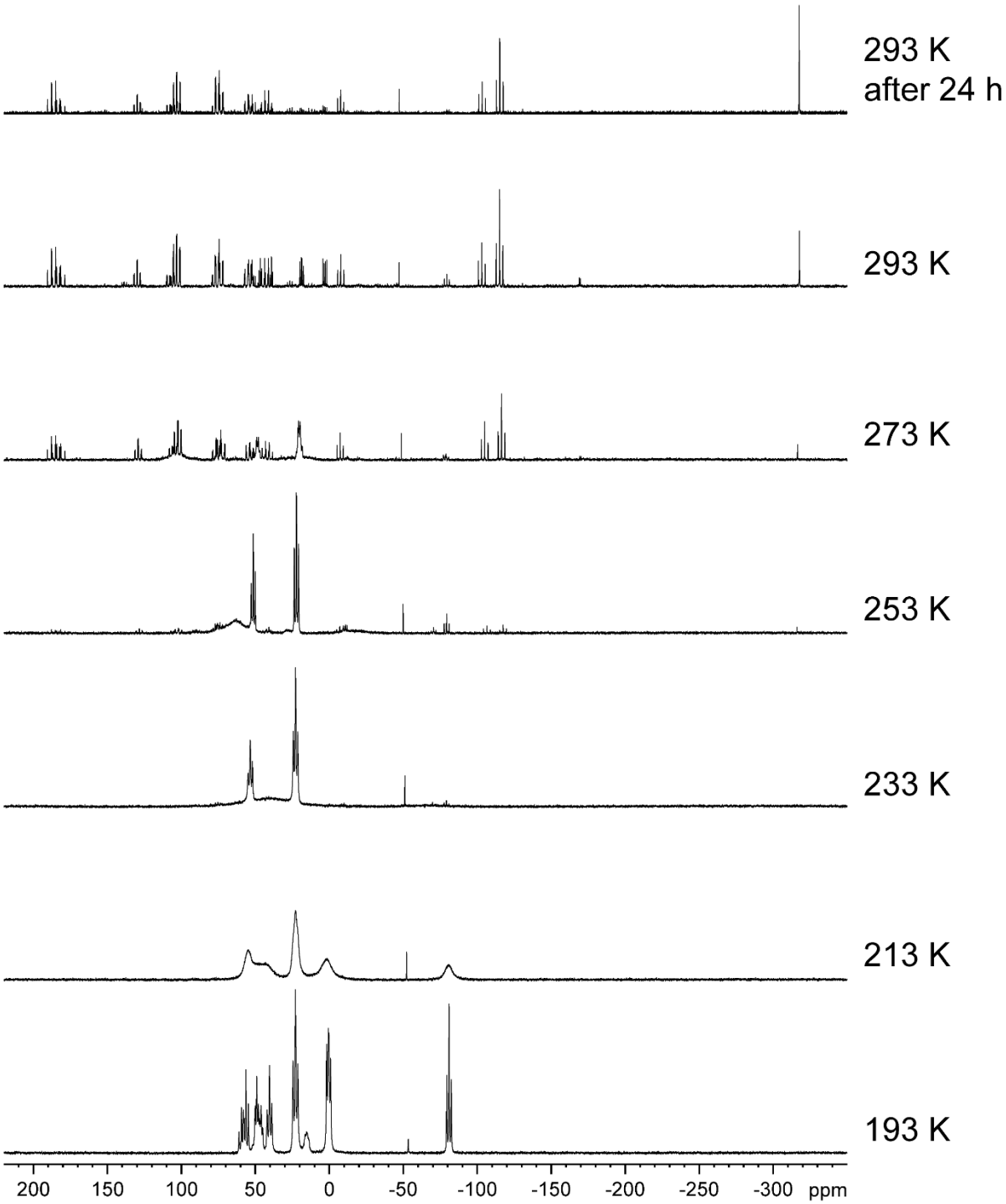


Figure S14: $^{31}P\{^1H\}$ VT NMR spectra of the reaction of **1** with LiCH2SiMe3 in thf-d_8 between 193 and 293 K and after 24 h at room temperature.

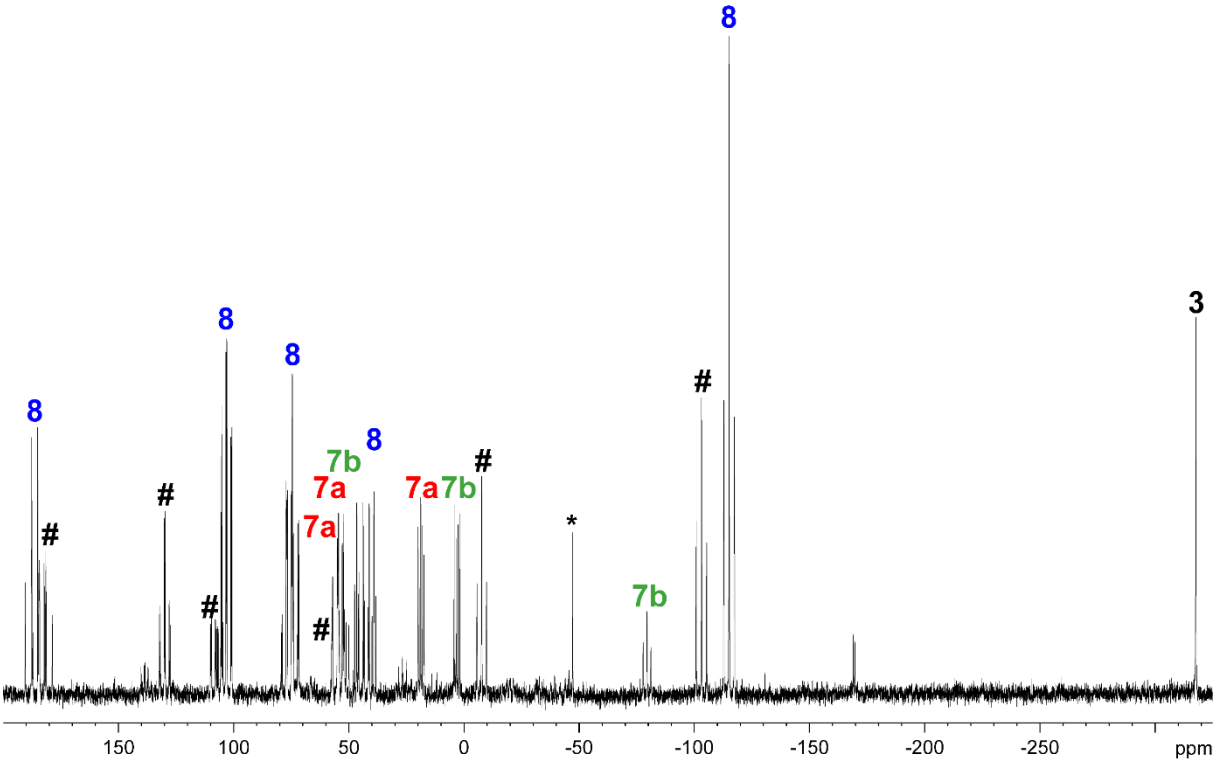


Figure S15: $^{31}P\{^{1}H\}$ NMR spectrum of the VT-NMR (S14) at 293 K (# unknown compound, * $[(Cp'''Co)_2(P_2)_2]$).

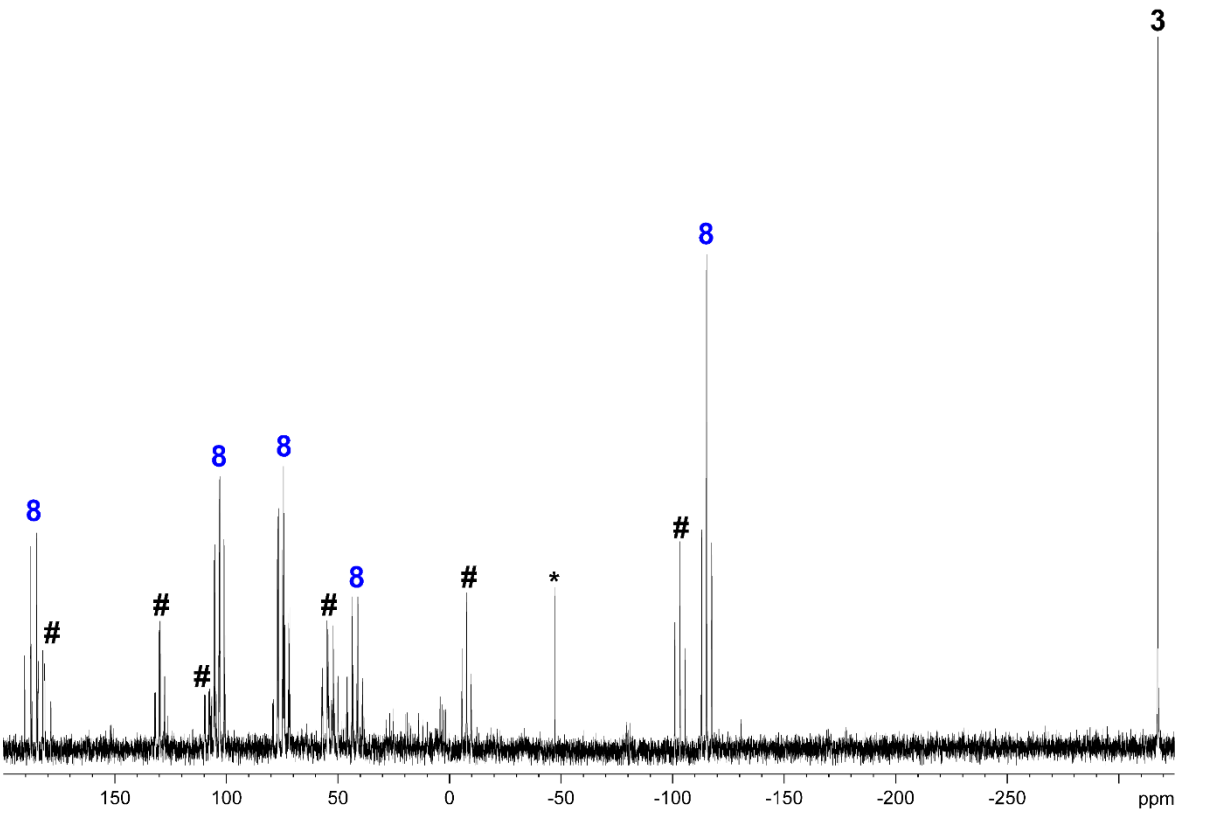


Figure S16: $^{31}P\{^{1}H\}$ NMR spectrum of the VT-NMR (S14) at 293 K after 24 h (# unknown compound, * $[(Cp'''Co)_2(P_2)_2]$).

2.7 [Na(dme)$_2$][Cp'''Co(η^3-P$_4$(O)H)] (10)

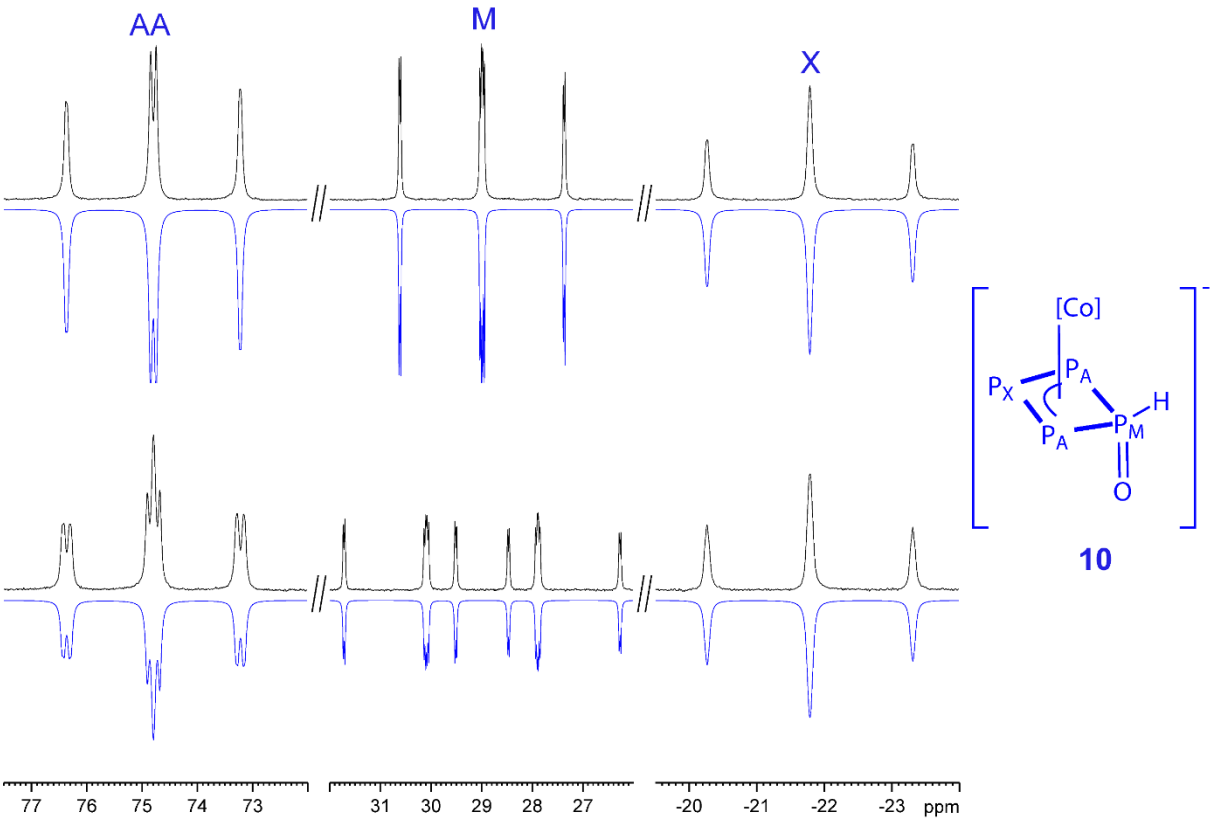


Figure S17: $^{31}P\{^1H\}$ (top) and ^{31}P (bottom) NMR spectrum of **10** thf-d$_8$ at room temperature (experimental (black) and simulated (blue)).

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

coupling constants [Hz]		chemical shifts [ppm]	
$^1J_{P_AP_M}$	262.67	P$_A$	74.78
$^1J_{P_AP_X}$	246.57	P$_M$	29.02
$^2J_{P_AP_A}$	-9.00	P$_X$	-21.77
$^2J_{P_MP_X}$	4.92		
R value		1.23 %	

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

coupling constants [Hz]		chemical shifts [ppm]	
$^1J_{P_AP_M}$	262.71	P$_A$	74.77
$^1J_{P_AP_X}$	246.64	P$_M$	29.02
$^2J_{P_AP_A}$	0.00	P$_X$	-21.78

$^{2}J_{P_M P_X}$	4.98		
$^{1}J_{P_M H}$	356.77		
$^{2}J_{P_A H}$	20.56		
$^{3}J_{P_X H}$	5.12		
R value		0.41 %	

3. Cyclic voltammogram of 1

The measurement was conducted in 5 ml dme with 500 mg conducting salt [^{n}Bu$_4$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 in 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 detected within the blank measurement of the pure solvent. A measurement in CH_2Cl_2 (5 ml, 750 mg conducting salt [^{n}Bu$_4$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.

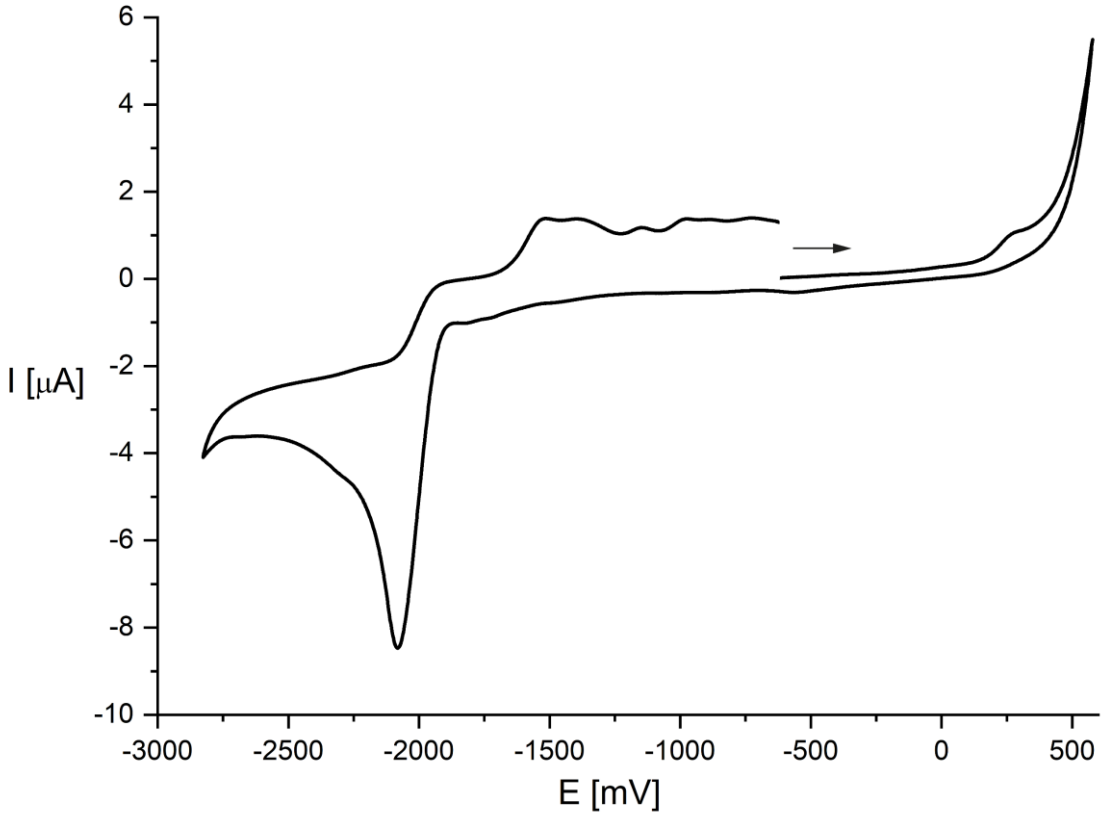


Figure S18_1. Cyclic voltammogram of **1** in dme against [Cp$_2$Fe]/[Cp$_2$Fe]$^+$ (electrolyte ^{n}Bu$_4$NPF$_6$, scan rate: 100 mV/s. temperature: r.t.).

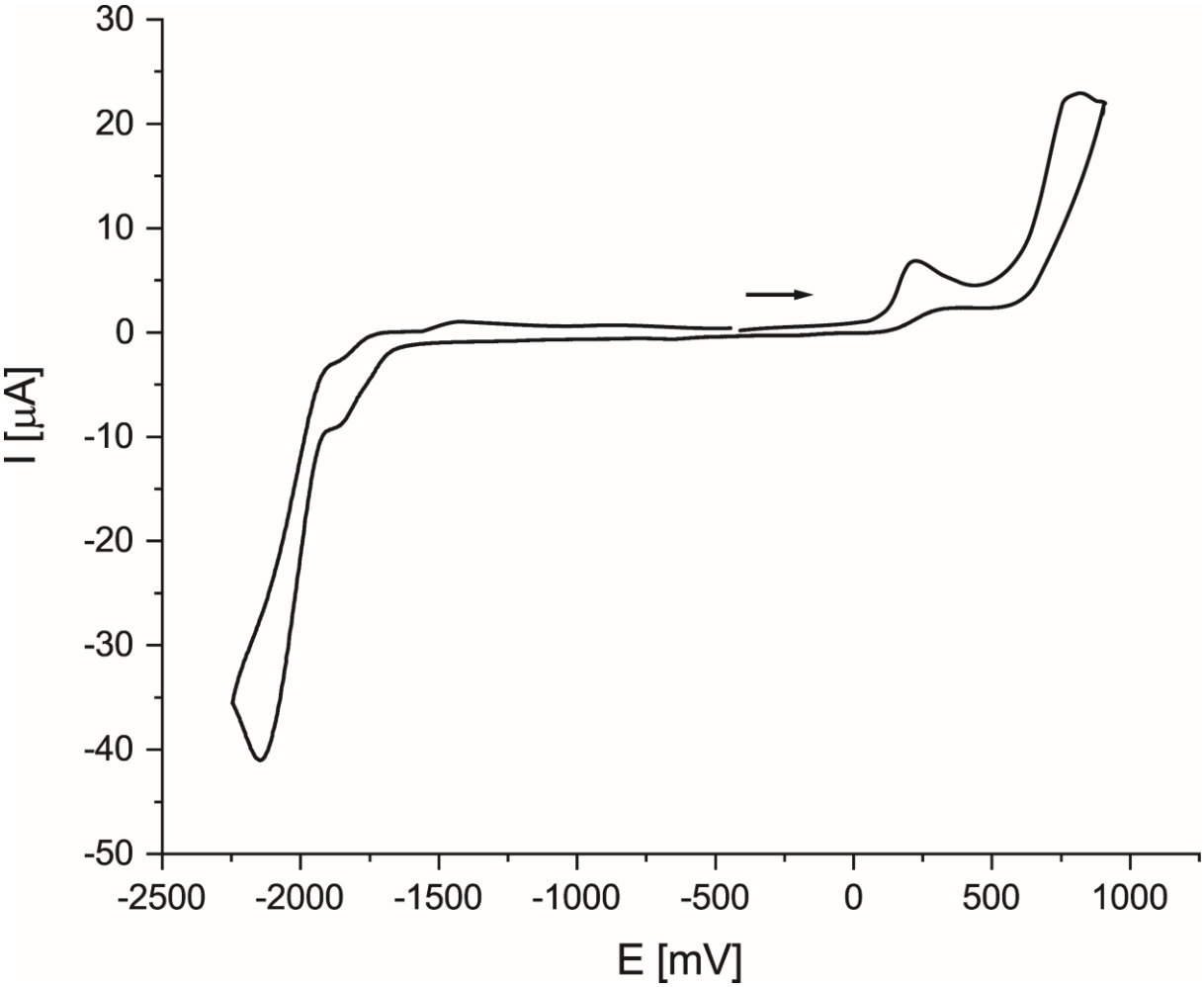


Figure S18_2. Cyclic voltammogram of **1** in CH_2Cl_2 against $[Cp_2Fe]/[Cp_2Fe]^+$ (electrolyte $^nBu_4NPF_6$, scan rate: 100 mV/s. temperature: r.t.).

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-K*α* radiation (λ = 1.54178 Å) (**2b**, **4**), a GV 50 diffractometer (Rigaku, formerly Agilent Technologies) with TitanS2 detector from applying Cu-K*α* radiation (λ = 1.54178 Å) (**6**, **9**) or SuperNova (Agilent Technologies) with an Atlas detector applying Cu-K*α* 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 harmonicsas 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 harmonicsas 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 $[K(dme)]_2[(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}P_8)]$ (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 **2**a 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.

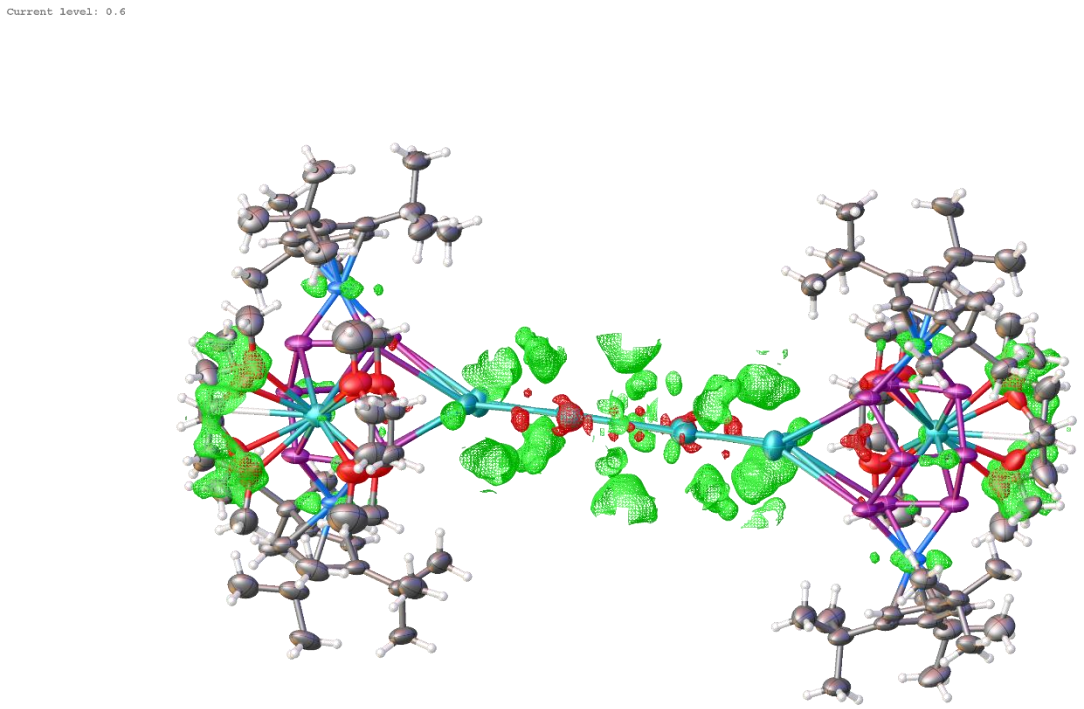


Figure S19. Part of the molecular structure of **2a** in solid state. Depicted is the unfished refinement with the electron density map.

4.2 $[K(2,2,2\text{-crypt})]_2[(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}P_8)]$ (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 $P\bar{1}$. 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.

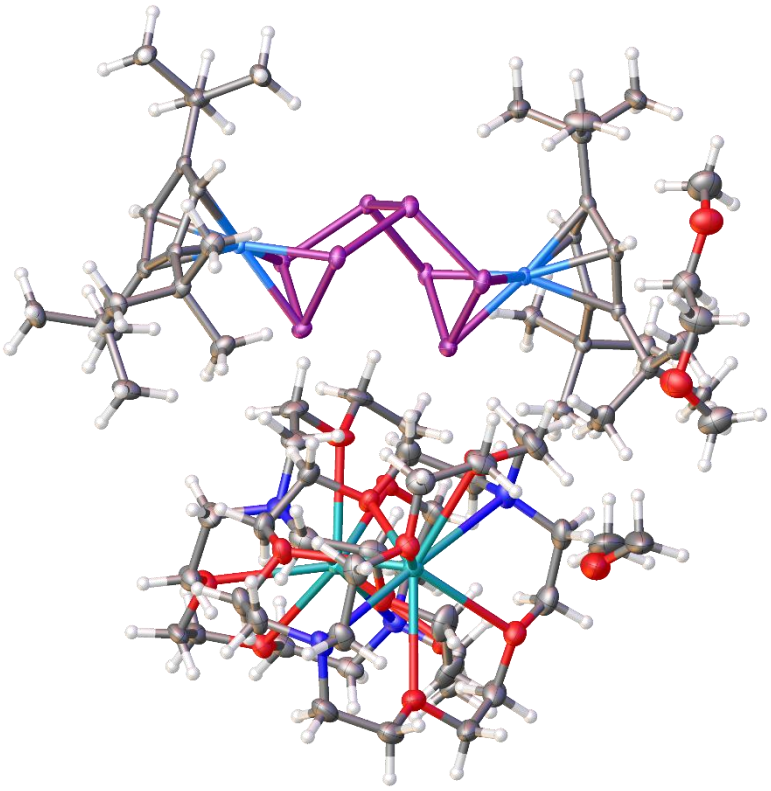


Figure S20: Molecular structure of **2b** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

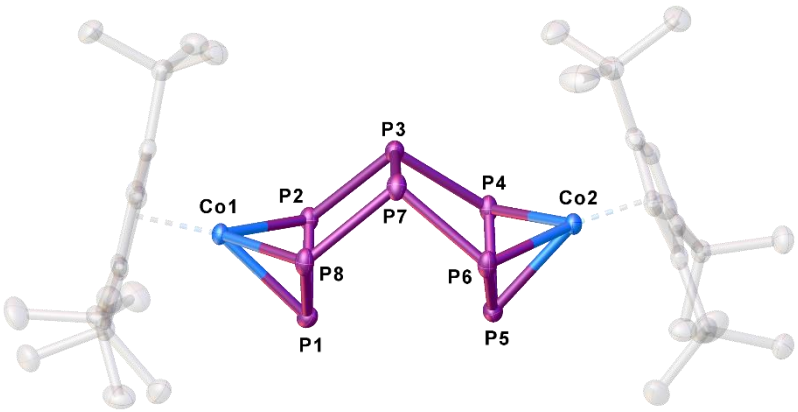


Figure S21: Molecular structure of the dianion in **2b** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.1554(6), P1-P5 3.4607(6), P1-P8 2.1577(6), P2-P3 2.2152(6), P3-P4 2.2151(6), P3-P7 2.1947(6), P4-P5 2.1519(6), P5-P6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

4.5 [Li(2,2,2-crypt)][Cp’’’Co(η^3-P$_4$^{t}Bu)] (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.

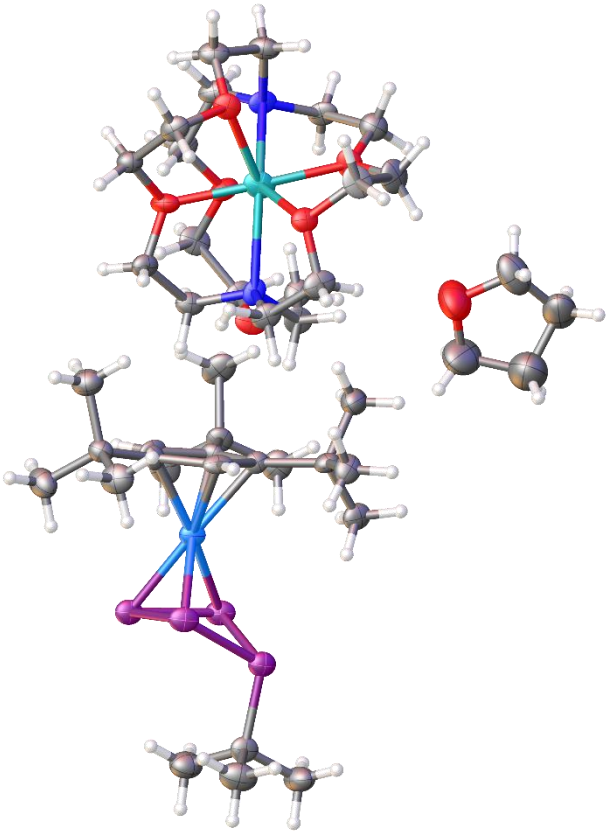


Figure S22: Molecular structure of **4** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

4.6 $[Li(thf)_3][(Cp'''Co)_2(\mu,\eta^3{:}\eta^3\text{-}P_8{}^tBu)]$ (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 *P2₁/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.

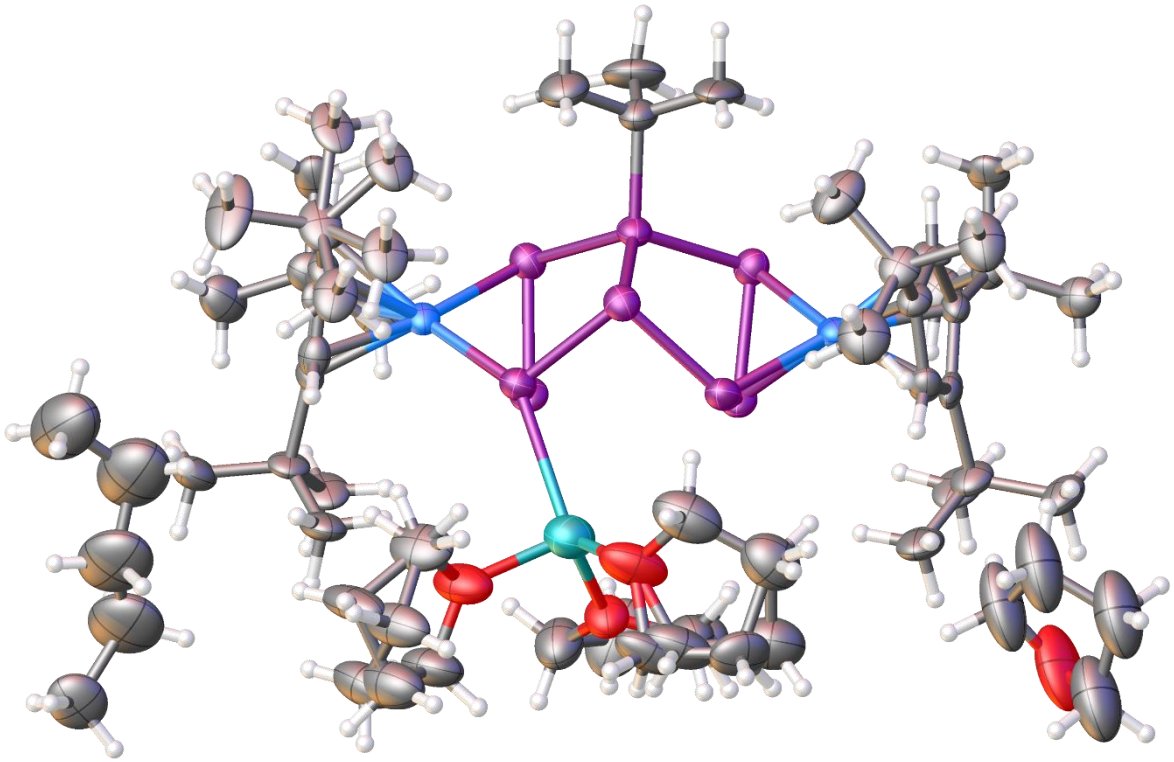


Figure S23: Molecular structure of **5** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

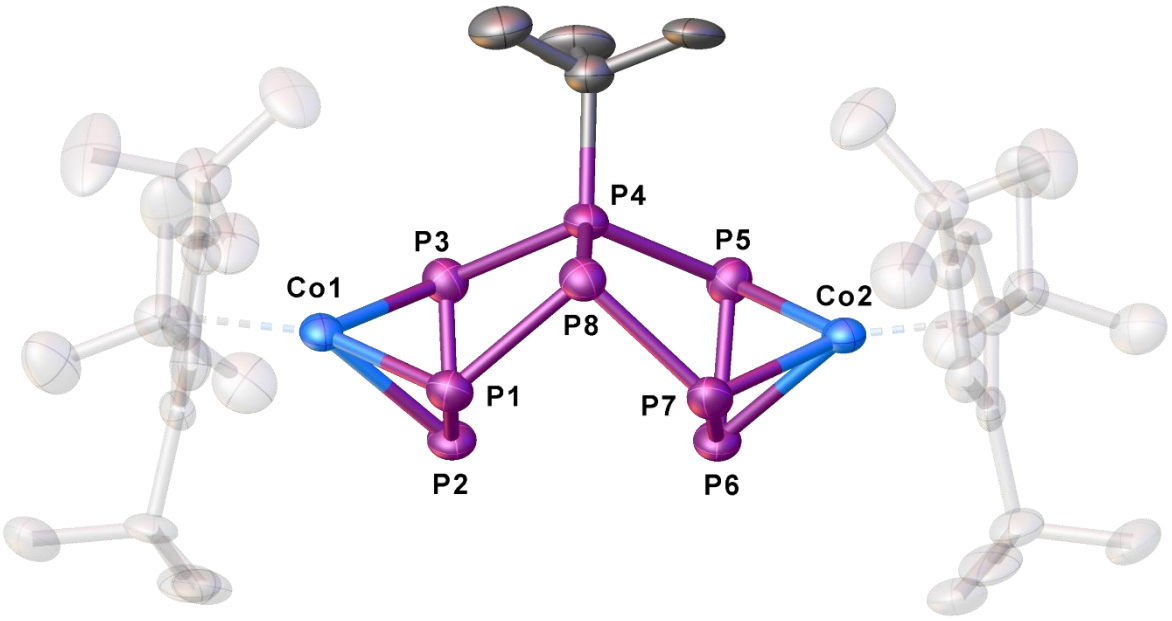


Figure 24 Molecular structure of the anion in **5** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.165(3), P1-P8 2.232(3), P2-P3 2.161(3), P2-P6 3.385(3), P3-P4 2.205(3), P4-P5 2.190(3), P4-P8 2.166(3), P5-P6 2.155(3), P6-P7 2.166(3), P7-P8 2.233(3).

4.6 $[Li(12\text{-}c\text{-}4)_2][Cp'''Co(\eta^3\text{-}P_5{}^tBu_2)]$ (6)

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

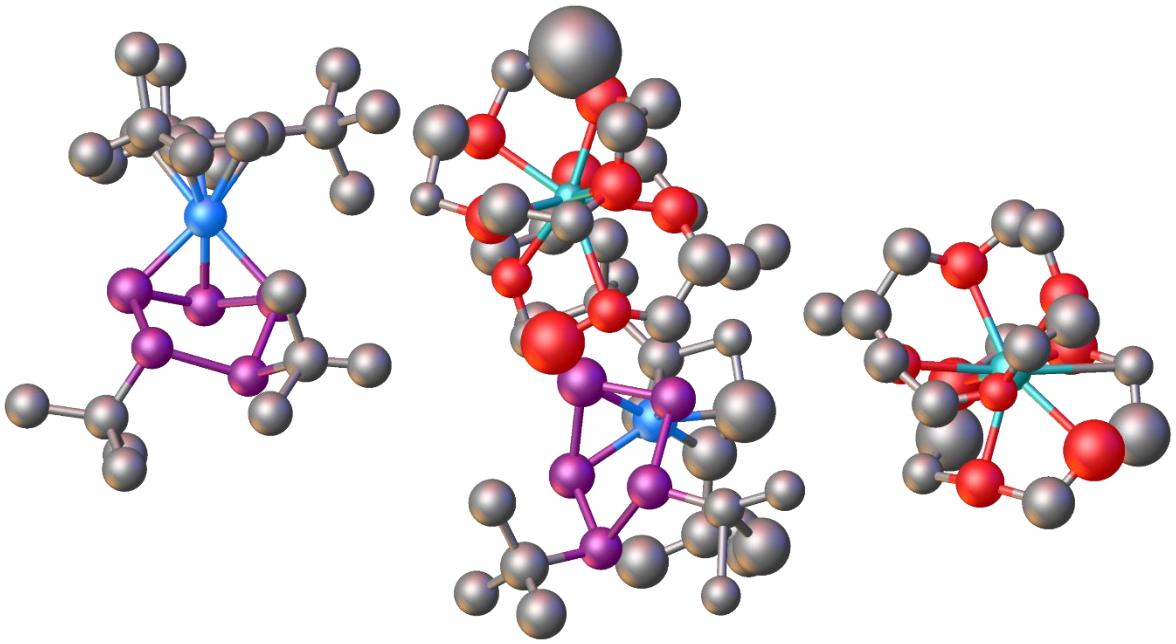


Figure S25: Molecular structure of **7** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

4.3 [Li(2,2,2-crypt)][Cp'''Co(η^3-$P_4CH_2SiMe_3$)] (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 -30 °C. Compound **7a** crystallizes in form of dark brown plates in the triclinic space group $P\bar{1}$. 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.

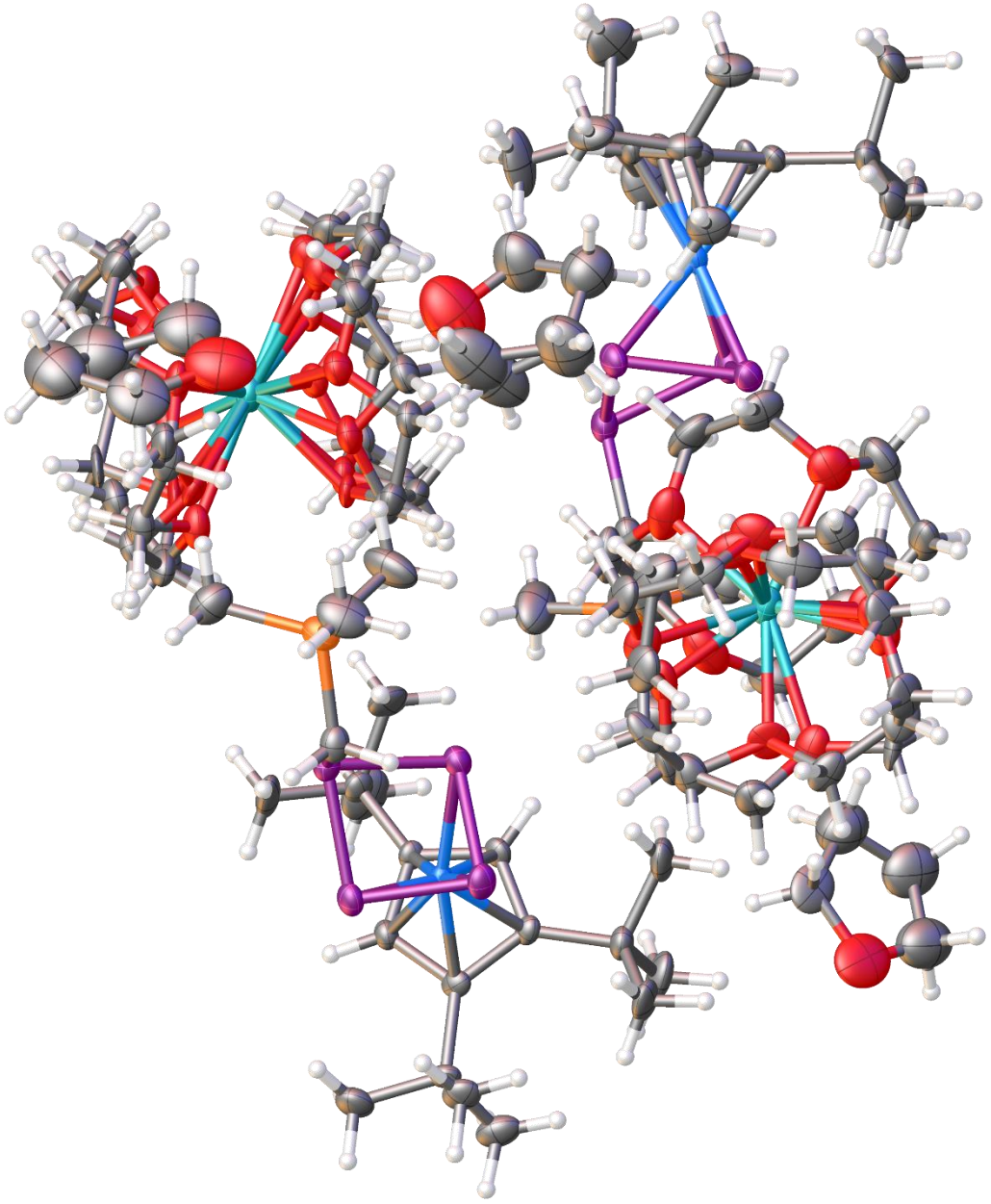


Figure S26: Molecular structure of **7a** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

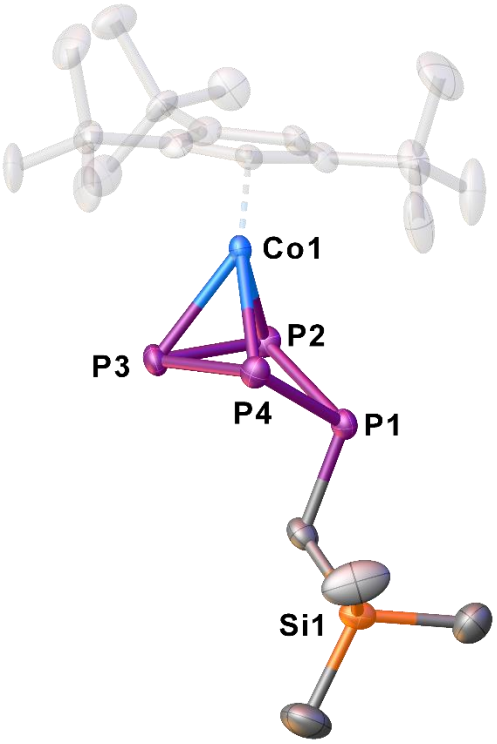


Figure S27: Molecular structure of one anion in **7a** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms, cations and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°] of both anions: P1-P2 2.2283(16), P1-P4 2.2229(19), P2-P3 2.1877(17), 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 $[Li(dme)_3][(Cp'''Co)_2(\mu,\eta^3{:}\eta^3\text{-}P_8CH_2SiMe_3)]$ (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 $P\bar{1}$. 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.

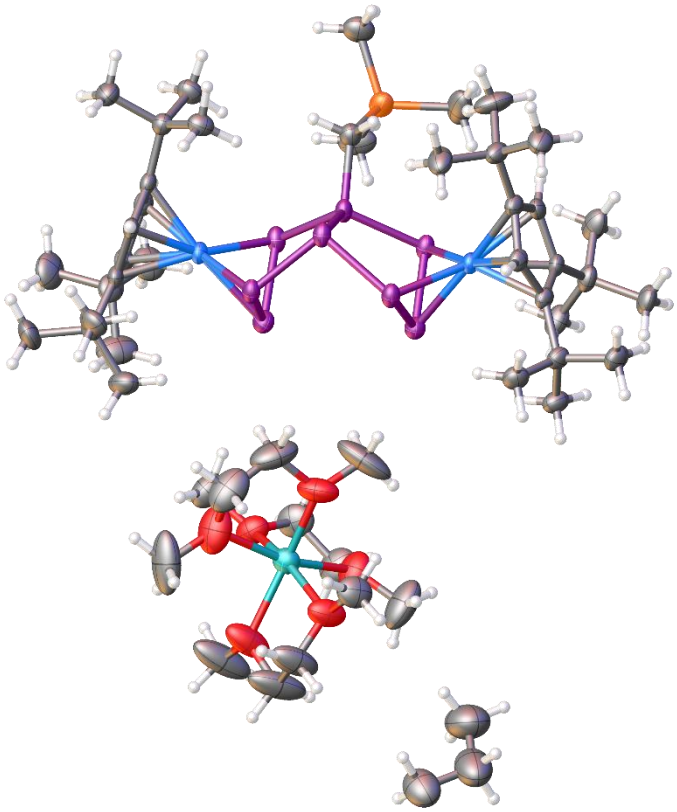


Figure S28. Asymmetric unit of **8** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

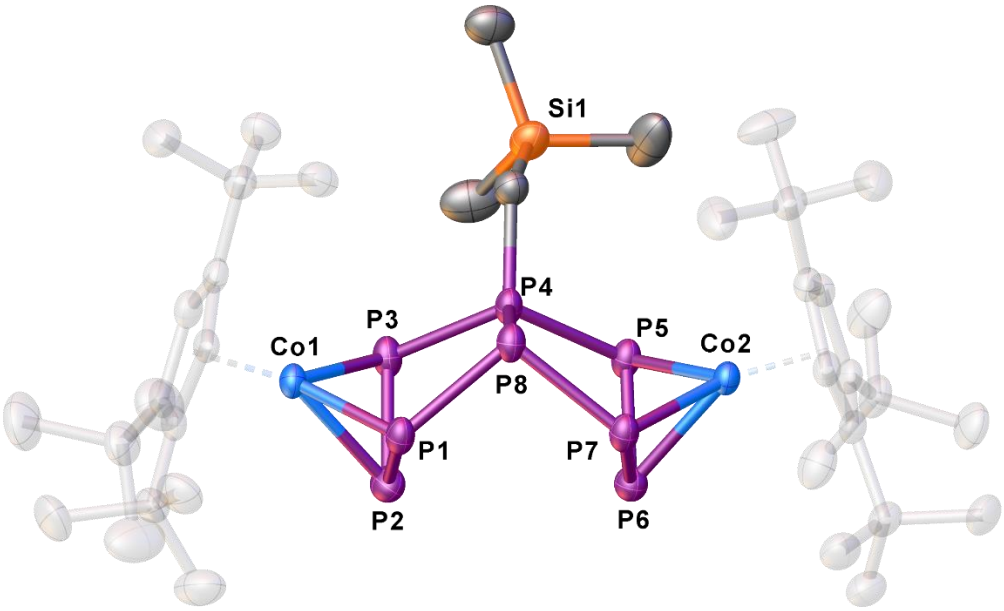


Figure S29: Molecular structure of the anion in **8** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.1643(11), P1-P8 2.2176(10), P2-P3 2.1574(11), P2-P6 3.7294(11), P3-P4 2.1948(10), P4-P5 2.1829(10), P4-P8 2.1738(10), P5-P6 2.1494(11), P6-P7 2.1575(11), P7-P8 2.2174(10).

3.6 $[Na(dme)_2][Cp'''Co(\eta^3\text{-}P_4(O)H)]$ (10)

Crystals suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution of **10** in a in dme layered with n-hexane at -30 °C. Compound **10** crystallizes in form of dark brown blocks in the triclinic space group $P\bar{1}$. 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.

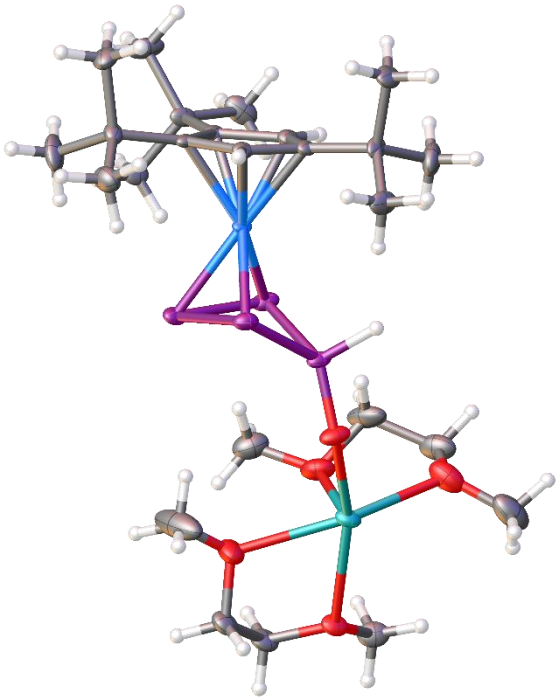


Figure S30: Molecular structure of **10** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

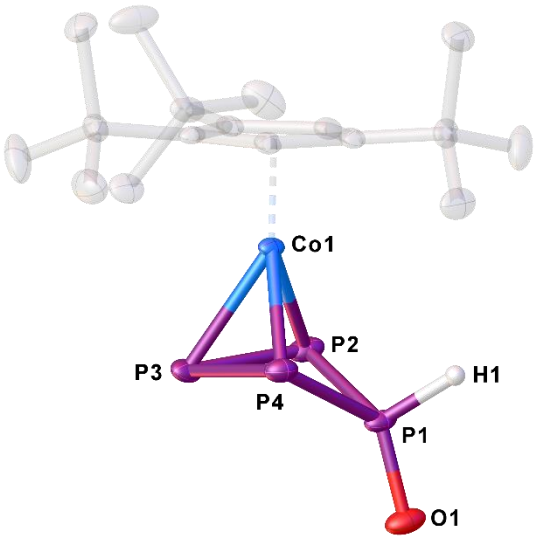


Figure S31: Molecular structure of the anion in **10** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.1659(7), P2-P3 2.1984(8), P3-P4 2.1938(8), P1-P4 2.1676(7), P1-H1 1.30(3), P1-O1 1.5200(15).

3.7 Crystallographic information

Table S12: Crystallographic data for all compounds

	2a	**2b**	**4**	**5**
CCDC		1984450	1984451	1984452
Formula		$C_{76}H_{144}Co_2K_2N_4O_{15}P_8$	$C_{43}H_{82}CoLiN_2O_7P_4$	$C_{53.5}H_{99}Co_2LiO_{3.25}P_8$
$D_{calc.}$/ g cm^{-3}		1.287	1.229	1.231
μ/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	0.63×0.38×0.32	0.23×0.16×0.05	0.67×0.12×0.06	0.32×0.13×0.10
T/K	123	123	123(1)	123(1)
Crystal System	orthorhombic	triclinic	orthorhombic	monoclinic
Space Group	*Cmce*	*P*-1	*Pbca*	$P2_1/c$
a/Å	27.1353(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)
α/°	90	74.8590(10)	90	90
β/°	90	78.8180(10)	90	91.670(8)
γ/°	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_α	Cu K_α	Mo K_α
θ_{min}/°		3.386	3.544	3.242
θ_{max}/°		73.012	40.147	25.156
Measured Refl.		34504	13776	19403
Independent Refl.		17809	3009	19403
Reflections with I > 2(I)		16566	2723	9021
R_{int}		0.0252	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_1 (all data)		0.0344	0.0503	0.1377
R_1		0.0311	0.0459	0.0745

	6	**7a**	**8**	**10**
CCDC		1984453	1984454	1984455
Formula		$C_{80}H_{156}Co_2Li_2O_{17.5}P_8Si_2$	$C_{53}H_{106}Co_2LiO_6P_8Si$	$C_{25}H_{50}O_5NaP_4Co$
$D_{calc.}$/ 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 green	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(4)	10.6602(3)
c/Å	15.467(5)	19.7326(6)	18.2337(5)	17.7138(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
Z'		1	1	1
Wave length/Å	1.54184	0.71073	1.54184	1.54184
Radiation type		Mo K_α	Cu K_α	Cu K_α
θ_{min}/°		3.307	3.462	2.542
θ_{max}/°		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_{int}		.	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.[9] Density functional theory (DFT) in form of Becke's three-parameter hybrid functioncal B3LYP[10] with def2-TZVP all electron basis set[11] was employed. For solvents effects has been accounted by using continuous polarizable continuum model (CPM).[12] The dielectric constant of thf (ε = 7.4257) has been used in the calculations. The Natural Bond Orbital (NBO) analysis has been performed with the NBO6 program.[13] The long range dispersion correction GD3BJ was applied.[14] The figures for the energy schemata were created using OLEX2.[7] The figures for the supporting information concerning the DFT calculations were created with Chemcraft.[15]

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

	total energy [Ha]
1 [Cp'''Co(η^4-P_4)]	-3414.10100308
2 [(Cp'''Co)$_2$(μ,η^3:η^3-P_8)]$^{2-}$	-6328.46309287
3 [Cp'''Co(η^3-P_3)]$^-$	-3072.8032350
4a [Cp'''Co(η^3-$P_4{}^t$Bu)]$^-$ (axial isomer)	-3572.14117871
4b [Cp'''Co(η^3-$P_4{}^t$Bu)]$^-$ (equatorial isomer)	-3572.13664123
5 [(Cp'''Co)$_2$(μ,η^3:η^3-$P_8{}^t$Bu)]$^-$	-6986.30353930
6 [Cp'''Co(η^3-$P_5{}^t$Bu$_2$)]$^-$	-4071.49911149
7a [Cp'''Co(η^3-$P_4CH_2SiMe_3$)]$^-$ (axial isomer)	-3862.92310537
7b [Cp'''Co(η^3-$P_4CH_2SiMe_3$)]$^-$ (equatorial isomer)	-3862.92275672
8 [(Cp'''Co)$_2$(μ,η^3:η^3-$P_8CH_2SiMe_3$)]$^-$	-7277.08151112
I-8 [Cp'''Co(η^3-P_5(CH_2SiMe_3)$_2$)]$^-$	-4653.06490984
10 [Cp'''Co(η^3-P_4(O)H)]$^-$	-3490.11025036

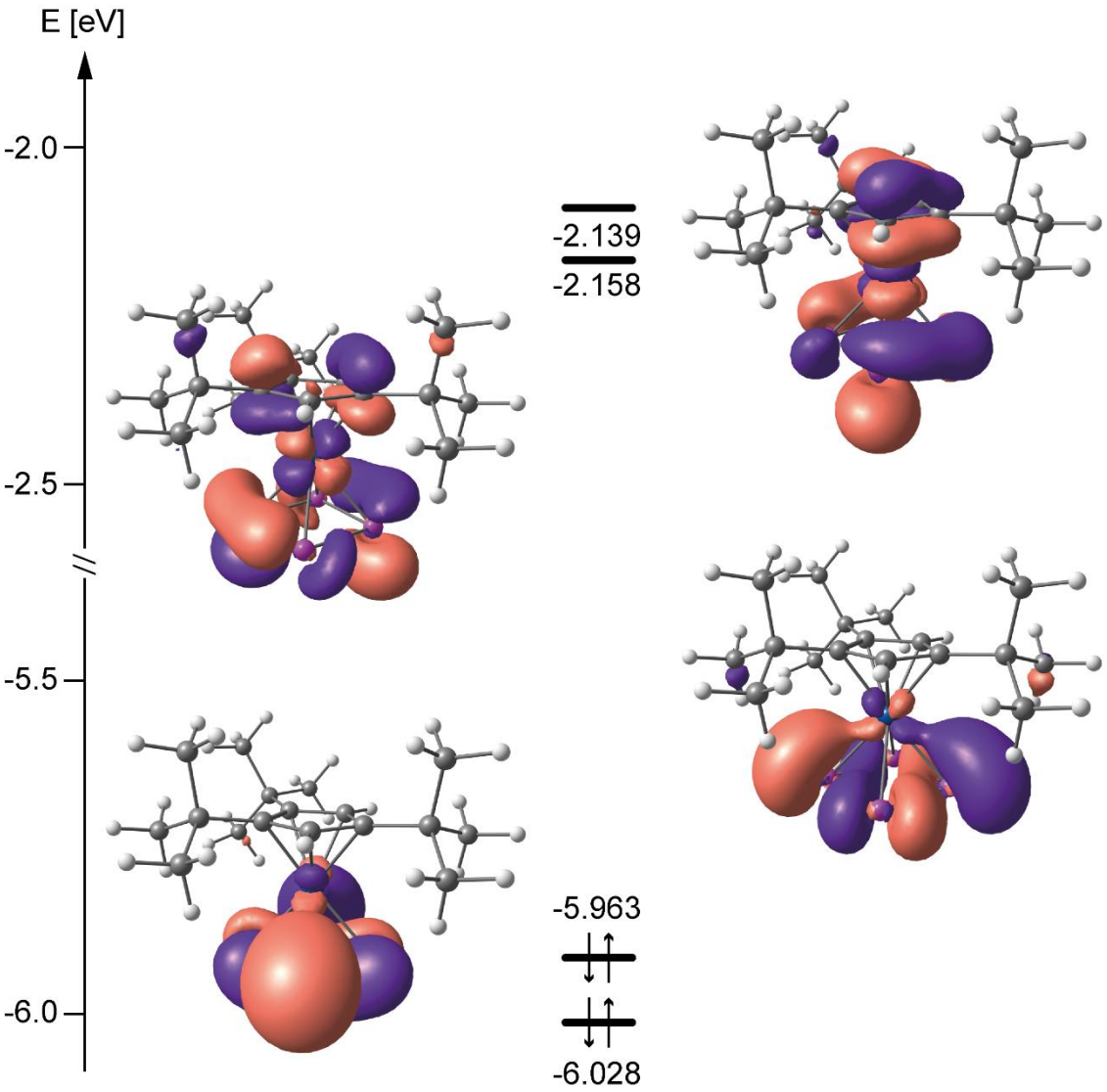
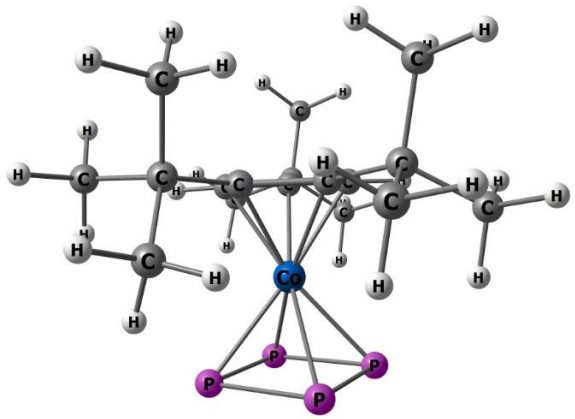
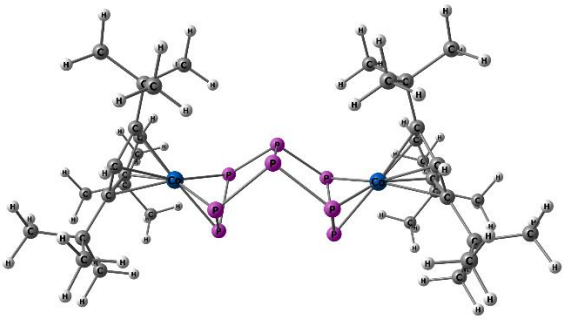


Figure S32: Molecular frontier orbitals of **1** (B3LYP/def2-TZVP level of theory.

Table S14: Optimized geometries of **1** (left), **2** (right). XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.

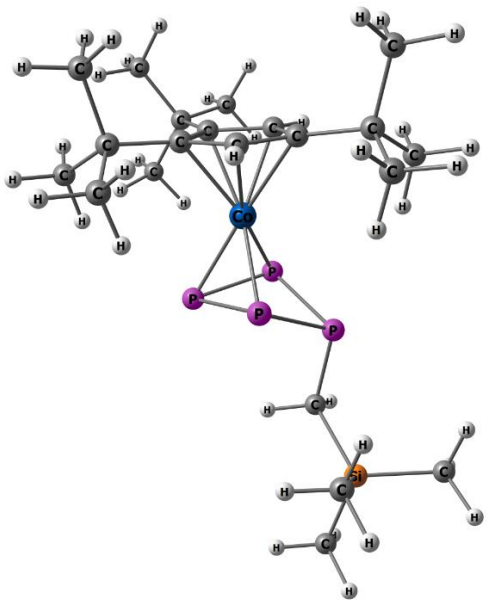


Co	-0.408168000	-0.538547000	-0.006352000	H	-1.830566000	3.780242000	-1.019022000
P	-2.337380000	-1.800346000	0.373219000	H	-2.866629000	1.660822000	-2.025728000
P	-0.515162000	-2.411411000	1.364220000	H	-4.308544000	1.998929000	-1.070804000
P	0.458579000	-2.616151000	-0.563909000	H	-3.524587000	0.420284000	-0.953829000
P	-1.365614000	-1.980853000	-1.552651000	H	-3.315378000	0.673198000	1.595764000
C	-1.101610000	1.425695000	0.083090000	H	-4.197911000	2.193416000	1.409185000
C	-0.283568000	1.113922000	1.197778000	H	-2.661424000	2.174354000	2.269712000
C	1.033190000	0.739624000	0.774553000	H	1.205984000	1.649673000	3.418163000
C	1.028263000	0.805612000	-0.680731000	H	2.388615000	0.453636000	3.941663000
C	-0.290187000	1.219186000	-1.058320000	H	0.790053000	-0.075582000	3.425335000
C	-2.490896000	2.020085000	0.098716000	H	2.041631000	-1.652965000	2.068764000
C	-2.310609000	3.544405000	-0.067907000	H	3.624139000	-0.953968000	2.410182000
C	-3.343566000	1.489436000	-1.060441000	H	3.098376000	-1.186951000	0.745906000
C	-3.203834000	1.744160000	1.426576000	H	3.756258000	1.496308000	0.689520000
C	2.142548000	0.494508000	1.802036000	H	3.951723000	1.502158000	2.437386000
C	1.585083000	0.644575000	3.229595000	H	2.773681000	2.576462000	1.675371000
C	2.765784000	-0.909096000	1.736642000	H	3.079865000	2.559767000	-1.072830000
C	3.221191000	1.581998000	1.630553000	H	1.811175000	2.826230000	-2.268772000
C	2.105389000	0.720236000	-1.766013000	H	3.374779000	2.169083000	-2.770359000
C	2.624373000	2.159882000	-1.977602000	H	3.951069000	-0.198254000	-2.351825000
C	3.289607000	-0.207270000	-1.484116000	H	2.953231000	-1.231732000	-1.330312000
C	1.493290000	0.234507000	-3.095074000	H	3.881021000	0.100562000	-0.628319000
H	-0.613699000	1.135785000	2.218566000	H	2.280255000	0.180624000	-3.848039000
H	-0.621333000	1.351209000	-2.070833000	H	0.726619000	0.904717000	-3.478843000
H	-1.696146000	3.954249000	0.735443000	H	1.058225000	-0.758704000	-2.986451000
H	-3.282948000	4.039853000	-0.042681000				

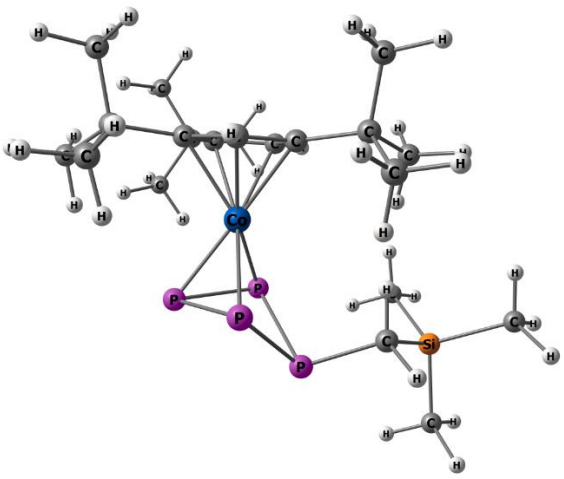


Co	-3.312766000	-0.098603000	-0.053425000	H	-3.913640000	-2.647455000	1.898689000
Co	3.312381000	-0.101957000	-0.041461000	C	-5.546422000	-1.008108000	3.185789000
P	-1.746035000	-0.106960000	-1.677834000	H	-4.493251000	-0.825748000	3.398501000
P	0.017755000	1.010734000	-0.940406000	H	-5.898903000	-1.780338000	3.872499000
P	1.727521000	-0.209689000	-1.641879000	H	-6.108237000	-0.094493000	3.389018000
P	-1.944336000	-1.883204000	-0.453992000	C	-5.129825000	4.016330000	0.473416000
P	-1.743203000	-0.795805000	1.414439000	H	-5.807183000	3.922292000	-0.378177000
P	1.756994000	-0.721101000	1.482858000	H	-4.834272000	5.065544000	0.560146000
P	-0.016459000	0.582211000	1.225777000	H	-5.681247000	3.741266000	1.374943000
P	1.945466000	-1.911916000	-0.321124000	C	5.780995000	-1.369573000	1.797055000
C	-4.370499000	1.684132000	0.178202000	C	7.278957000	-1.660930000	1.597439000
C	5.341243000	-0.310357000	-0.691722000	H	7.477728000	-2.205185000	0.678985000
C	-4.661684000	0.795642000	1.241166000	H	7.653412000	-2.266984000	2.426206000
H	-4.430712000	0.990529000	2.271161000	H	7.851962000	-0.731725000	1.569746000
C	5.955771000	-1.220365000	-1.759498000	C	-5.993624000	-1.101623000	-1.798157000
C	4.681824000	0.878773000	1.171211000	C	3.209669000	3.502178000	-1.241809000
H	4.468169000	1.144577000	2.189374000	H	3.891894000	3.400000000	-2.087711000
C	-5.262051000	-0.411910000	0.756946000	H	2.875854000	4.542156000	-1.208068000
C	-4.800836000	1.012176000	-0.996628000	H	2.342020000	2.867699000	-1.421632000
H	-4.696475000	1.405580000	-1.990593000	C	-5.368338000	-0.745951000	-3.161826000
C	4.783386000	0.945581000	-1.077894000	H	-5.592423000	0.281116000	-3.456887000
H	4.659809000	1.270881000	-2.093680000	H	-5.788412000	-1.398363000	-3.929939000
C	5.278874000	-0.356663000	0.758910000	H	-4.286405000	-0.876642000	-3.149072000
C	-5.352406000	-0.267288000	-0.685756000	C	-7.493676000	-0.747680000	-1.880318000
C	5.306533000	-0.945705000	-3.131171000	H	-8.019285000	-0.978940000	-0.955910000
H	4.223118000	-1.057299000	-3.087379000	H	-7.970930000	-1.303850000	-2.692082000
H	5.700822000	-1.653940000	-3.862592000	H	-7.619727000	0.318430000	-2.079084000
H	5.529883000	0.055950000	-3.497895000	C	-2.966509000	3.288115000	1.501129000
C	3.892197000	3.128355000	0.078950000	H	-3.475386000	3.033927000	2.432745000
C	4.372391000	1.694419000	0.055534000	H	-2.636313000	4.327271000	1.575322000
C	-3.892004000	3.114203000	0.291527000	H	-2.087363000	2.650365000	1.412264000
C	-7.247292000	-1.757329000	1.563800000	C	5.121413000	4.037779000	0.281009000
H	-7.811945000	-0.824741000	1.627294000	H	5.618905000	3.813949000	1.227032000
H	-7.600709000	-2.423638000	2.354769000	H	4.826438000	5.090706000	0.291114000
H	-7.480833000	-2.226289000	0.612218000	H	5.846078000	3.894038000	-0.523466000
C	7.456678000	-0.886633000	-1.893288000	C	4.980761000	-2.683798000	1.801529000
H	7.587523000	0.165965000	-2.151944000	H	3.947825000	-2.487533000	2.085016000
H	7.910728000	-1.490177000	-2.684297000	H	5.415189000	-3.377859000	2.527313000
H	8.001257000	-1.072874000	-0.969854000	H	4.963367000	-3.167605000	0.832557000
C	-3.144057000	3.549584000	-0.973862000	C	-5.830293000	-2.617363000	-1.638868000
H	-2.261649000	2.931289000	-1.135161000	H	-4.776995000	-2.878892000	-1.536478000
H	-2.826192000	4.590979000	-0.880584000	H	-6.226108000	-3.118825000	-2.525196000
H	-3.779086000	3.474619000	-1.858415000	H	-6.367714000	-3.008470000	-0.780716000
C	5.781655000	-2.721366000	-1.500852000	C	2.905631000	3.359373000	1.229376000
H	6.328500000	-3.062129000	-0.627258000	H	2.015625000	2.743350000	1.107028000
H	6.159068000	-3.282625000	-2.358984000	H	2.600895000	4.408596000	1.258671000
H	4.727852000	-2.965249000	-1.364799000	H	3.353325000	3.114908000	2.194064000
C	-5.741266000	-1.492810000	1.736760000	C	5.638898000	-0.782731000	3.214227000
C	-4.956302000	-2.812079000	1.631603000	H	6.217536000	0.135381000	3.331068000
H	-4.971812000	-3.233961000	0.634413000	H	6.007316000	-1.509104000	3.941404000
H	-5.379679000	-3.546589000	2.323127000	H	4.596889000	-0.571056000	3.452930000

Table S15: Optimized geometries of **7a** (left), **7b** (right). XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.

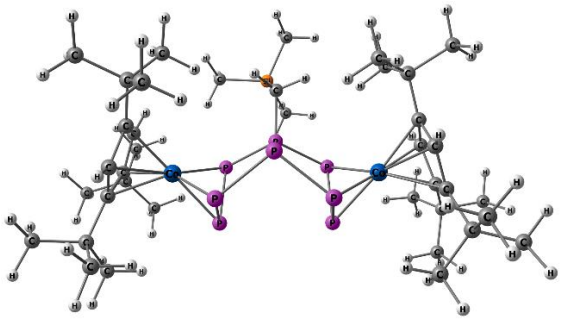


Co	-0.669106000	-0.047351000	-0.081384000	H	6.892250000	-2.089224000	-0.957118000
P	0.417185000	-1.994302000	-0.017222000	C	-2.055103000	4.258415000	0.234348000
P	0.721325000	-0.685682000	-1.765458000	H	-2.723350000	4.175456000	-0.625065000
P	2.446838000	0.324146000	-0.764081000	H	-1.655324000	5.275573000	0.259941000
P	1.287570000	-0.275137000	1.048524000	H	-2.646457000	4.100868000	1.138623000
Si	5.369635000	-0.436958000	0.126659000	C	-3.454595000	-0.198446000	-3.009866000
C	-2.074253000	1.172977000	-0.996390000	H	-3.941716000	0.776890000	-2.962800000
H	-1.989262000	1.519476000	-2.009140000	H	-3.999537000	-0.812841000	-3.729152000
C	-1.534829000	1.846498000	0.124253000	H	-2.440986000	-0.063444000	-3.387948000
C	3.842555000	-0.914448000	-0.858686000	C	0.014689000	3.399766000	1.348490000
H	3.473902000	-1.897687000	-0.551220000	H	-0.525582000	3.280379000	2.289128000
H	4.135078000	-0.989410000	-1.912639000	H	0.453865000	4.400069000	1.341897000
C	-2.557663000	-0.144604000	0.836095000	H	0.818838000	2.664534000	1.324277000
C	-1.844639000	1.025349000	1.241781000	C	-3.167600000	-2.578855000	1.466035000
H	-1.547539000	1.239341000	2.251419000	H	-3.900172000	-2.743782000	0.682596000
C	-2.711662000	-0.049674000	-0.607946000	H	-3.465879000	-3.189266000	2.321468000
C	-4.933561000	-1.066117000	-1.241209000	H	-2.197443000	-2.928428000	1.113987000
H	-5.059866000	-1.641362000	-0.329165000	C	6.158000000	1.090864000	-0.638305000
H	-5.482230000	-1.578363000	-2.035297000	H	6.437307000	0.906972000	-1.678883000
H	-5.394748000	-0.088537000	-1.086195000	H	7.060374000	1.382614000	-0.094807000
C	-0.913739000	3.225756000	0.141017000	H	5.464857000	1.934602000	-0.623615000
C	-2.802782000	-2.277686000	-1.879008000	C	-4.465054000	-0.626720000	2.366998000
H	-1.805819000	-2.142919000	-2.298564000	H	-4.402424000	0.392726000	2.751979000
H	-3.400573000	-2.852696000	-2.592114000	H	-4.847630000	-1.269969000	3.163889000
H	-2.697900000	-2.860318000	-0.972246000	H	-5.186583000	-0.632028000	1.551015000
C	-2.139805000	-1.100023000	3.127666000	C	4.936254000	-0.074772000	1.918299000
H	-1.120055000	-1.353765000	2.837333000	H	4.239186000	0.762257000	1.990598000
H	-2.486785000	-1.836166000	3.855309000	H	5.833990000	0.176149000	2.489644000
H	-2.123234000	-0.132802000	3.627913000	H	4.459602000	-0.936282000	2.390113000
C	-3.455821000	-0.905064000	-1.640703000	C	-0.110295000	3.485038000	-1.140175000
C	-3.076615000	-1.112985000	1.903104000	H	0.720705000	2.784746000	-1.224646000
C	6.609938000	-1.854560000	0.072223000	H	0.292334000	4.500981000	-1.129488000
H	6.187673000	-2.758930000	0.517086000	H	-0.733394000	3.384593000	-2.030260000
H	7.521231000	-1.603737000	0.621713000				

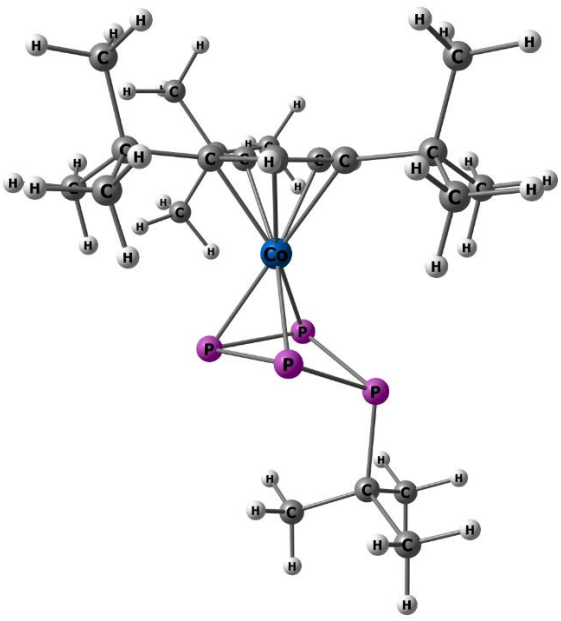


Co	0.588261000	-0.289588000	-0.319910000	H	-6.000836000	1.743961000	-0.531792000
P	0.568812000	-2.429698000	-0.925538000	C	0.478914000	4.263758000	-0.076754000
P	-0.903372000	-1.752966000	0.566166000	H	0.919095000	4.324837000	0.920439000
P	-2.360910000	-1.654171000	-1.140221000	H	-0.187318000	5.120204000	-0.210923000
P	-0.493262000	-0.984535000	-2.195092000	H	1.285747000	4.340668000	-0.807912000
Si	-4.640146000	-0.100799000	0.453867000	C	1.784847000	-0.152604000	3.523064000
C	0.935633000	1.118693000	1.177437000	H	1.807948000	0.912892000	3.757060000
H	0.330297000	1.201971000	2.060079000	H	2.187771000	-0.693925000	4.381184000
C	0.679896000	1.804020000	-0.032063000	H	0.746427000	-0.458020000	3.393669000
C	-3.323348000	-0.081196000	-0.885275000	C	-0.880123000	2.902345000	-1.668852000
H	-2.629882000	0.734925000	-0.684247000	H	-0.092717000	2.965823000	-2.421361000
H	-3.821724000	0.143023000	-1.835893000	H	-1.557566000	3.746304000	-1.820293000
C	2.573902000	0.445460000	-0.302390000	H	-1.426174000	1.977508000	-1.843331000
C	1.691299000	1.373135000	-0.931284000	C	4.317267000	-1.435341000	-0.690466000
H	1.768931000	1.693949000	-1.953915000	H	4.673991000	-1.494916000	0.332618000
C	2.089314000	0.277784000	1.059289000	H	5.155333000	-1.697378000	-1.340525000
C	4.064648000	-0.029446000	2.596501000	H	3.531458000	-2.177233000	-0.828832000
H	4.769510000	-0.284753000	1.810635000	C	-5.884511000	-1.469451000	0.118641000
H	4.410893000	-0.501724000	3.519251000	H	-6.343878000	-1.347657000	-0.865441000
H	4.098308000	1.053229000	2.735345000	H	-6.681804000	-1.467693000	0.866236000
C	-0.293645000	2.939672000	-0.251763000	H	-5.400359000	-2.447905000	0.140458000
C	2.564545000	-2.013035000	2.124418000	C	4.941154000	0.988049000	-0.850879000
H	1.527000000	-2.333376000	2.028320000	H	4.627472000	1.976506000	-1.191243000
H	2.989735000	-2.491022000	3.011701000	H	5.832158000	0.698973000	-1.414607000
H	3.099216000	-2.373555000	1.254874000	H	5.215551000	1.067324000	0.200427000
C	3.506783000	-0.095727000	-2.577386000	C	-3.872634000	-0.353332000	2.149443000
H	2.645733000	-0.734818000	-2.774724000	H	-3.373769000	-1.321366000	2.217585000
H	4.370809000	-0.502905000	-3.106146000	H	-4.637939000	-0.303158000	2.928639000
H	3.304817000	0.889095000	-2.996553000	H	-3.124262000	0.413795000	2.359846000
C	2.628426000	-0.483664000	2.277101000	C	-1.426107000	2.898536000	0.781274000
C	3.810330000	-0.039467000	-1.066686000	H	-1.927567000	1.932473000	0.776757000
C	-5.526824000	1.561601000	0.435774000	H	-2.166231000	3.671722000	0.564564000
H	-4.824425000	2.377489000	0.622978000	H	-1.047130000	3.073195000	1.789689000
H	-6.303227000	1.603437000	1.204236000				

Table S16: Optimized geometries of **8** (left), **4a** (right). XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.

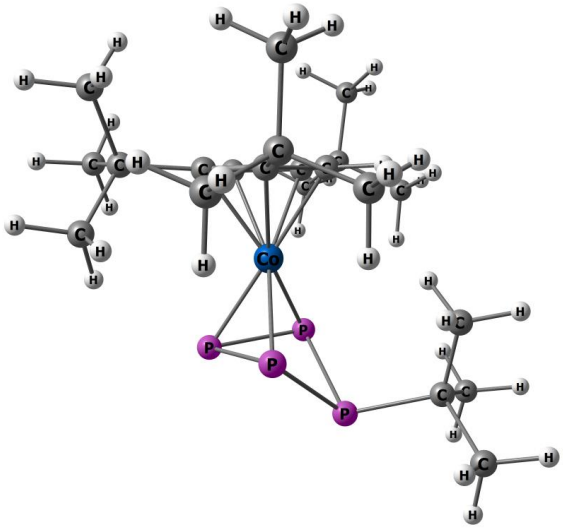


Co	-3.358929000	-0.512317000	0.140542000	H	3.124363000	3.134954000	0.093180000
Co	3.447489000	-0.356650000	0.027198000	C	5.717591000	-2.625471000	1.007728000
P	0.001954000	0.872673000	-0.249667000	C	6.020644000	-0.816833000	-2.099669000
P	0.061479000	-0.374700000	1.583816000	C	-7.287224000	-2.919154000	0.410801000
P	1.861258000	-1.626012000	1.051570000	H	-7.469509000	-2.541907000	1.429717000
P	1.872749000	0.466951000	-1.409020000	H	-7.645089000	-3.962505000	0.365774000
P	-1.895711000	-1.793449000	-1.101041000	H	-7.899801000	-2.322122000	-0.279120000
P	2.000419000	-1.708503000	-1.149531000	C	-4.967029000	-0.604417000	-3.160628000
P	-1.880148000	0.390656000	-1.340870000	H	-3.960022000	-0.162522000	-3.168769000
P	-1.677586000	-1.727370000	1.087201000	H	-5.419325000	-0.438514000	-4.154363000
Si	-0.335352000	4.038495000	-1.086255000	H	-4.846583000	-1.682290000	-3.017755000
C	4.713379000	1.057225000	0.942222000	C	-5.704650000	1.575806000	3.458463000
C	-4.610011000	0.463885000	1.527458000	H	-6.423550000	2.064413000	2.780925000
C	-5.333016000	-0.199090000	-0.625828000	H	-5.577899000	2.219169000	4.346631000
C	-4.891093000	0.895223000	0.201183000	H	-6.150520000	0.623852000	3.788200000
H	-4.779091000	1.916679000	-0.146083000	C	-5.828394000	1.572492000	-2.376675000
C	5.063498000	0.886165000	-0.431850000	H	-6.476218000	2.139367000	-1.689627000
H	5.023686000	1.673949000	-1.177167000	H	-6.200498000	1.738647000	-3.400741000
C	-4.855981000	-0.942768000	1.519668000	H	-4.813250000	1.991316000	-2.323739000
H	-4.713151000	-1.594788000	2.375865000	C	5.545642000	-2.771764000	2.539039000
C	5.452625000	-0.466753000	-0.704402000	H	6.187179000	-2.071196000	3.096785000
C	4.871280000	-0.226808000	1.530720000	H	5.827540000	-3.793678000	2.840833000
H	4.662590000	-0.452067000	2.571254000	H	4.501414000	-2.613164000	2.845552000
C	4.432662000	2.365658000	1.672159000	C	4.846772000	-3.737327000	0.378856000
C	5.331019000	-1.191422000	0.563411000	H	3.805948000	-3.651536000	0.723488000
C	-0.023905000	2.672615000	0.216314000	H	5.226536000	-4.727343000	0.687178000
H	0.942817000	2.875375000	0.705694000	H	4.833264000	-3.706253000	-0.714384000
H	-0.793349000	2.781844000	0.999370000	C	0.634402000	3.766813000	-2.681938000
C	-5.304275000	-1.386423000	0.230001000	H	1.718708000	3.710948000	-2.496560000
C	-5.545079000	-3.457605000	-1.332373000	H	0.445840000	4.595629000	-3.386191000
H	-6.133671000	-2.963966000	-2.114788000	H	0.340305000	2.823518000	-3.168038000
H	-5.845854000	-4.518568000	-1.324876000	C	-3.382101000	0.653598000	3.737715000
H	-4.482285000	-3.403510000	-1.611337000	H	-3.759825000	-0.328092000	4.063084000
C	5.740607000	2.822112000	2.363953000	H	-3.255370000	1.275528000	4.640422000
H	6.079204000	2.076448000	3.100807000	H	-2.393282000	0.494666000	3.283140000
H	5.594565000	3.781087000	2.891208000	C	7.213290000	-2.890637000	0.714255000
H	6.550218000	2.956509000	1.628410000	H	7.431852000	-2.938409000	-0.360263000
C	-4.347736000	1.336806000	2.750614000	H	7.520087000	-3.855005000	1.153721000
C	-5.777677000	-2.849415000	0.063608000	H	7.846532000	-2.102118000	1.152894000
C	3.340687000	2.176811000	2.742863000	C	-3.758741000	2.698263000	2.340656000
H	2.401416000	1.818784000	2.296722000	H	-2.821222000	2.563158000	1.782270000
H	3.145585000	3.126581000	3.269431000	H	-3.546537000	3.310371000	3.232811000
H	3.642032000	1.435054000	3.498976000	H	-4.453156000	3.269624000	1.704298000
C	-5.838697000	0.056558000	-2.068686000	C	5.402776000	0.105436000	-3.179507000
C	-7.309484000	-0.399762000	-2.213919000	H	4.304224000	0.045837000	-3.179886000
H	-7.423663000	-1.487955000	-2.134896000	H	5.765351000	-0.199207000	-4.174807000
H	-7.704068000	-0.099894000	-3.199760000	H	5.685629000	1.159979000	-3.045174000
H	-7.943225000	0.063137000	-1.440089000	C	7.548004000	-0.552487000	-2.085548000
C	0.230090000	5.663315000	-0.278682000	H	7.758937000	0.494958000	-1.817169000
H	-0.312230000	5.850123000	0.663534000	H	7.983369000	-0.743753000	-3.081908000
H	0.045337000	6.521914000	-0.946900000	H	8.069771000	-1.191950000	-1.359817000
H	1.308097000	5.643469000	-0.047267000	C	-2.180645000	4.175142000	-1.474447000
C	-5.036091000	-3.771555000	1.062620000	H	-2.552620000	3.240030000	-1.922580000
H	-3.944341000	-3.687171000	0.959704000	H	-2.368711000	4.999848000	-2.183142000
H	-5.322331000	-4.819632000	0.877410000	H	-2.768469000	4.370718000	-0.562312000
H	-5.294653000	-3.550104000	2.108639000	C	5.755999000	-2.258185000	-2.572878000
C	3.995830000	3.459891000	0.680429000	H	6.261495000	-3.008907000	-1.954003000
H	4.801627000	3.706848000	-0.029012000	H	6.134798000	-2.381142000	-3.601467000
H	3.732834000	4.386627000	1.217263000	H	4.678012000	-2.477813000	-2.575718000



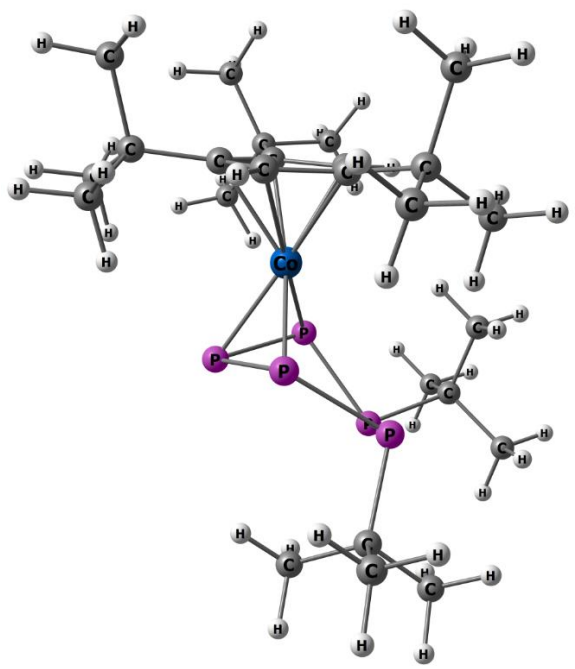
Co	0.183195000	-0.025855000	-0.063508000	H	2.905830000	0.357849000	3.415995000
P	-0.835209000	-1.921200000	-0.596456000	H	2.836201000	-1.321048000	3.957458000
P	-1.435415000	-0.941347000	1.283013000	H	1.357619000	-0.502533000	3.457986000
P	-2.914145000	0.355589000	0.243174000	C	-0.335889000	3.563416000	-1.102223000
P	-1.598568000	-0.065154000	-1.499012000	H	0.285089000	3.489663000	-1.996389000
C	1.401926000	1.049864000	1.221712000	H	-0.736708000	4.579045000	-1.058443000
H	1.143422000	1.263618000	2.241462000	H	-1.164895000	2.864338000	-1.207802000
C	1.062948000	1.871122000	0.123489000	C	2.934407000	-2.368391000	-1.494142000
C	2.202106000	-0.031280000	-0.656065000	H	3.507264000	-2.650400000	-0.616824000
C	1.555910000	1.189264000	-1.022293000	H	3.395594000	-2.860393000	-2.353628000
H	1.433502000	1.536663000	-2.031246000	H	1.919553000	-2.749305000	-1.382675000
C	2.102247000	-0.127028000	0.791099000	C	4.357363000	-0.334478000	-1.870882000
C	4.189412000	-1.253557000	1.657909000	H	4.358906000	0.728384000	-2.119575000
H	4.476982000	-1.712219000	0.716566000	H	4.882159000	-0.871690000	-2.665361000
H	4.595113000	-1.870028000	2.463810000	H	4.919099000	-0.462509000	-0.946602000
H	4.664836000	-0.271790000	1.709805000	C	-0.447514000	3.434924000	1.385224000
C	0.469093000	3.261830000	0.168323000	H	-1.293037000	2.749029000	1.332532000
C	1.990799000	-2.504427000	1.747963000	H	-0.833819000	4.456573000	1.418590000
H	0.939735000	-2.416739000	2.023407000	H	0.087271000	3.252526000	2.318718000
H	2.474333000	-3.186317000	2.453462000	C	-4.544842000	-0.614700000	0.015324000
H	2.032070000	-2.945670000	0.760070000	C	-5.351831000	0.152037000	-1.036783000
C	2.210611000	-0.658334000	-3.094035000	H	-5.514672000	1.189507000	-0.736132000
H	1.155746000	-0.925354000	-3.027157000	H	-4.834999000	0.156690000	-1.999165000
H	2.684086000	-1.298343000	-3.840929000	H	-6.331434000	-0.315908000	-1.183058000
H	2.283030000	0.367185000	-3.453501000	C	-5.267280000	-0.570220000	1.365085000
C	2.663373000	-1.122288000	1.814170000	H	-6.246325000	-1.056705000	1.291793000
C	2.911279000	-0.855034000	-1.734836000	H	-4.692876000	-1.090152000	2.135309000
C	1.634809000	4.266472000	0.270782000	H	-5.425081000	0.457933000	1.698291000
H	2.218860000	4.089577000	1.176170000	C	-4.369711000	-2.063398000	-0.427025000
H	1.259514000	5.292820000	0.300098000	H	-5.349588000	-2.539066000	-0.550612000
H	2.304222000	4.171894000	-0.586729000	H	-3.836022000	-2.125268000	-1.375292000
C	2.421610000	-0.605112000	3.245100000	H	-3.801753000	-2.636188000	0.306183000

Table S17: Optimized geometries of **4b** (left), **5** (right). XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



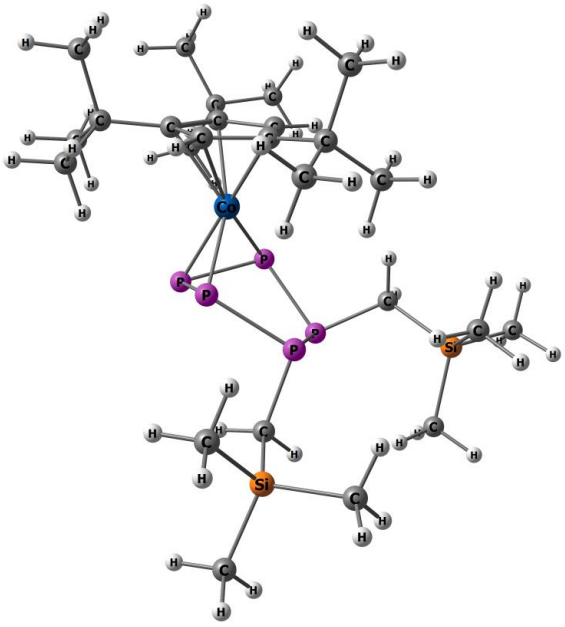
Co	-0.112579000	0.054051000	-0.506496000	H	-4.170450000	1.354418000	-1.745252000	Co	-3.340828000	-0.109571000	-0.273906000	C	7.310250000	-1.746266000	-1.873725000
P	0.418883000	-0.736931000	-2.513824000	H	-4.577232000	-0.063367000	-2.713443000	Co	3.350333000	-0.115579000	-0.258184000	H	7.499301000	-0.793763000	-2.371588000
P	1.766942000	0.737444000	-1.597718000	H	-2.956459000	0.625029000	-2.809807000	P	1.831262000	-0.873167000	1.242095000	H	7.682022000	-2.547596000	-2.517105000
P	3.037660000	-1.025433000	-1.080453000	C	1.210066000	3.169407000	1.226399000	P	-1.804194000	-0.916626000	1.186583000	H	7.883735000	-1.760552000	-0.947994000
P	0.999303000	-1.915377000	-0.742473000	H	1.190758000	2.689776000	2.206064000	P	0.001761000	0.328226000	1.106867000	C	-4.746663000	-2.568722000	2.153656000
C	-1.734022000	1.402031000	-0.493921000	H	1.586395000	4.186293000	1.361379000	P	1.703901000	0.215768000	-1.739673000	H	-4.709068000	-3.233128000	1.300667000
H	-2.036403000	1.983046000	-1.344356000	H	1.907686000	2.623582000	0.593259000	P	0.018586000	1.356313000	-0.820141000	H	-5.159066000	-3.125044000	2.999502000
C	-0.781294000	1.819974000	0.463722000	C	-2.114114000	-2.824007000	1.389097000	P	1.815857000	-1.722906000	-0.754180000	H	-3.723059000	-2.289970000	2.397185000
C	-1.535561000	-0.316555000	1.029510000	H	-3.085894000	-2.810363000	0.907508000	P	-1.701877000	0.284339000	-1.753646000	C	-7.297252000	-1.797593000	-1.839402000
C	-0.656424000	0.759042000	1.391145000	H	-2.152508000	-3.581472000	2.175345000	P	-1.802916000	-1.688842000	-0.839656000	H	-7.505501000	-0.847880000	-2.334858000
H	-0.024079000	0.774343000	2.258688000	H	-1.365025000	-3.132859000	0.660406000	C	-4.700775000	1.478137000	-0.492884000	H	-7.858836000	-1.819352000	-0.906573000
C	-2.226501000	0.095007000	-0.174418000	C	-2.820278000	-1.050709000	3.021807000	C	-5.208561000	-0.499761000	0.663727000	H	-7.666089000	-2.604175000	-2.477897000
C	-4.603198000	-0.755932000	-0.126729000	H	-2.516806000	-0.142908000	3.546491000	C	-4.982035000	0.444465000	-1.424643000	C	-5.781619000	-1.961985000	-1.597177000
H	-4.449294000	-1.495876000	0.652795000	H	-2.978494000	-1.837592000	3.764288000	H	-4.942899000	0.563406000	-2.490446000	C	4.803172000	-2.547635000	2.147957000
H	-5.437338000	-1.095794000	-0.745551000	H	-3.771291000	-0.850082000	2.531484000	C	5.234695000	-0.478230000	0.656496000	H	5.220004000	-3.098785000	2.995028000
H	-4.896993000	0.179464000	0.354126000	C	-0.093369000	3.899713000	-0.774288000	C	4.829024000	0.898512000	0.779503000	H	4.767295000	-3.215368000	1.297327000
C	-0.184226000	3.206217000	0.590007000	H	0.536941000	3.328814000	-1.455949000	H	4.661529000	1.405420000	1.711380000	H	3.778695000	-2.272472000	2.392885000
C	-2.947649000	-1.854126000	-1.694685000	H	0.336927000	4.897216000	-0.658366000	C	4.968199000	0.463672000	-1.428225000	C	-5.083974000	-1.951396000	-2.973019000
H	-2.202925000	-1.647816000	-2.462313000	H	-1.078662000	4.014652000	-1.228701000	H	4.913057000	0.582406000	-2.493369000	H	-5.389543000	-2.834324000	-3.537306000
H	-3.822101000	-2.304188000	-2.173426000	C	3.887028000	-0.656601000	0.584270000	C	4.679394000	1.491955000	-0.492613000	H	-4.000596000	-1.971860000	-2.857677000
H	-2.520630000	-2.581213000	-1.016073000	C	4.727276000	-1.890175000	0.934041000	C	-4.824648000	0.884221000	0.781131000	H	-5.350271000	-1.079634000	-3.568692000
C	-0.443960000	-1.745809000	2.811806000	H	4.095420000	-2.771338000	1.070070000	H	-4.660124000	1.396446000	1.710576000	C	5.085329000	-1.928952000	-2.979905000
H	0.362455000	-2.044183000	2.145164000	H	5.452635000	-2.114303000	0.149258000	C	-5.310777000	-0.771232000	-0.755471000	H	4.003816000	-1.965909000	-2.851678000
H	-0.625048000	-2.557181000	3.519873000	H	5.276311000	-1.725552000	1.867793000	C	7.136826000	-1.658871000	1.789899000	H	5.396951000	-2.806467000	-3.549293000
H	-0.116563000	-0.880256000	3.385045000	C	2.932181000	-0.347923000	1.731723000	H	7.473733000	-2.113362000	2.724593000	H	5.330930000	-1.052538000	-3.577601000
C	-3.352977000	-0.541743000	-1.001076000	H	3.496603000	-0.055797000	2.625341000	H	7.744546000	-0.771010000	1.603902000	C	-5.513357000	-3.345247000	-0.999548000
C	-1.732619000	-1.477259000	2.012608000	H	2.245814000	0.454331000	1.474281000	H	7.328552000	-2.368840000	0.989897000	H	-6.074387000	-3.525169000	-0.087747000
C	-1.121842000	4.023641000	1.502448000	H	2.330955000	-1.219553000	1.985147000	C	-5.866531000	3.644759000	-0.569734000	H	-4.451166000	-3.476508000	-0.794132000
H	-2.127423000	4.070275000	1.080272000	C	4.808086000	0.543558000	0.338548000	H	-6.644556000	3.203911000	-1.196122000	H	-5.815552000	-4.108174000	-1.719974000
H	-0.749954000	5.045091000	1.618354000	H	5.418353000	0.740477000	1.226521000	H	-5.794912000	4.708307000	-0.810201000	C	5.556792000	-3.318731000	-1.014284000
H	-1.191560000	3.569450000	2.492715000	H	5.484009000	0.365065000	-0.501325000	H	-6.176209000	3.548569000	0.472440000	H	6.126345000	-3.491469000	-0.106529000
C	-3.783592000	0.410745000	-2.132824000	H	4.231605000	1.444464000	0.120169000	C	-4.512176000	2.946180000	-0.805985000	H	5.865462000	-4.076253000	-1.737718000
								C	-5.597257000	-1.310715000	1.908825000	H	4.497994000	-3.466023000	-0.802211000
								C	4.457010000	2.955999000	-0.802790000	C	-4.094028000	3.153570000	-2.266030000
								C	5.323304000	-0.747376000	-0.764400000	H	-3.165606000	2.624394000	-2.483161000
								C	5.646253000	-1.286173000	1.895432000	H	-3.941575000	4.217246000	-2.460358000
								C	-0.035699000	1.454309000	2.615047000	H	-4.859276000	2.796043000	-2.957047000
								C	-7.087130000	-1.691453000	1.822168000	C	5.496112000	-0.423150000	3.162130000
								H	-7.701856000	-0.808230000	1.637222000	H	4.462958000	-0.106210000	3.307112000
								H	-7.411224000	-2.142010000	2.763283000	H	6.131665000	0.463109000	3.130399000
								H	-7.283127000	-2.407878000	1.028811000	H	5.789074000	-1.013763000	4.031923000
								C	-5.434299000	-0.446059000	3.172852000	C	-3.455794000	3.575890000	0.104070000
								H	-4.402251000	-0.117061000	3.297985000	H	-3.707631000	3.451526000	1.157463000
								H	-5.703733000	-1.040242000	4.047766000	H	-3.373597000	4.646595000	-0.097368000
								H	-6.080684000	0.432669000	3.153743000	H	-2.485665000	3.113909000	-0.069275000
								C	5.797500000	3.684309000	-0.578077000	C	-1.270423000	2.351659000	2.551054000
								H	6.579559000	3.260727000	-1.211362000	H	-1.335560000	2.944514000	3.468029000
								H	6.118389000	3.594706000	0.461325000	H	-2.185388000	1.769874000	2.448621000
								H	5.700793000	4.746172000	-0.817243000	H	-1.210255000	3.035836000	1.707459000
								C	5.800076000	-1.931088000	-1.612796000	C	4.021570000	3.155011000	-2.258938000
								C	1.226855000	2.314238000	2.645403000	H	3.843215000	4.215089000	-2.450847000
								H	1.224125000	2.926842000	3.551616000	H	3.103533000	2.605292000	-2.468857000
								H	1.265832000	2.979277000	1.785869000	H	4.788843000	2.815657000	-2.956841000
								H	2.130720000	1.705737000	2.644119000	C	3.394807000	3.561892000	0.116873000
								C	-0.095144000	0.569170000	3.867987000	H	3.655269000	3.434978000	1.167929000
								H	0.769741000	-0.090950000	3.934352000	H	2.431196000	3.084869000	-0.054598000
								H	-0.994170000	-0.046613000	3.882642000	H	3.292870000	4.632269000	-0.077232000
								H	-0.104820000	1.211428000	4.753188000				

Table S18: Optimized geometries of **6** (left), **3** (right). XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.

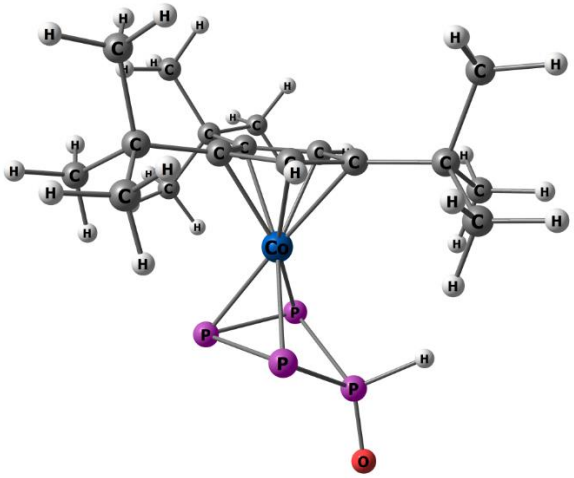


Co	-0.753770000	-0.214316000	-0.150979000	H	-5.601990000	-0.683893000	-0.255186000	Co	10.613423000	3.991815000	9.769552000	H	10.923191000	-0.109333000	10.851724000
P	2.766237000	-0.744432000	0.231409000	H	-5.743229000	-2.179817000	-1.185224000	P	10.696768000	3.024863000	7.725082000	C	8.951259000	0.821485000	12.552582000
P	0.137632000	-0.576432000	-2.204139000	H	-4.990562000	-2.194700000	0.416671000	P	11.944618000	4.763784000	8.109731000	H	9.856266000	0.645345000	13.132270000
P	0.890937000	-1.697901000	-0.477341000	H	-4.490578000	-1.313567000	-3.159921000	P	9.791237000	4.994193000	7.914428000	H	8.385435000	-0.113181000	12.512375000
P	0.516882000	1.321192000	-1.241063000	H	-4.473872000	0.267941000	-2.404821000	C	10.125568000	4.975987000	11.538103000	H	8.350751000	1.560714000	13.085858000
P	2.701079000	1.156898000	-0.894596000	H	-2.959039000	-0.454827000	-2.966943000	C	9.733429000	6.420167000	11.764371000	C	8.325543000	6.699207000	11.226067000
C	-4.749443000	2.022502000	-0.200595000	H	-3.074970000	-3.406335000	-0.623509000	C	10.016612000	2.652666000	11.239206000	H	8.274299000	6.488319000	10.157640000
C	-5.099767000	-1.617924000	-0.503284000	H	-3.715732000	-3.233729000	-2.249510000	C	11.432831000	4.440307000	11.610665000	H	8.063717000	7.747405000	11.387850000
C	-0.374224000	-2.443596000	3.005815000	H	-2.093546000	-2.630021000	-1.871362000	H	12.320381000	5.029117000	11.749831000	H	7.576243000	6.087960000	11.732349000
C	-3.721645000	-1.368967000	-1.152475000	H	-5.175921000	2.998004000	-0.447293000	C	9.263221000	3.866435000	11.324956000	C	13.127243000	1.532827000	10.230399000
C	-0.852409000	-0.989244000	3.081732000	H	-5.199365000	1.288753000	-0.864031000	H	8.196868000	3.935557000	11.216525000	H	12.376924000	0.854860000	9.841740000
C	3.034859000	2.517381000	0.399602000	H	-5.038450000	1.772371000	0.822281000	C	11.416211000	3.017402000	11.431059000	H	14.054011000	0.970056000	10.376127000
C	-2.153225000	-1.399945000	0.847558000	H	-3.061799000	1.632848000	-2.486268000	C	9.274092000	1.317546000	11.127833000	H	13.298044000	2.297570000	9.473098000
C	-1.501883000	-0.556610000	1.785171000	H	-3.345467000	3.325961000	-2.092332000	C	12.706371000	2.196263000	11.553296000	C	13.879018000	3.110685000	11.956610000
C	2.091102000	2.488377000	1.597667000	H	-1.750936000	2.598250000	-1.841994000	C	9.751877000	6.696184000	13.280422000	H	14.070728000	3.872788000	11.200864000
C	-3.216264000	2.070554000	-0.335550000	H	-3.170873000	4.178368000	0.130144000	H	9.054170000	6.037496000	13.801828000	H	14.783905000	2.508390000	12.057464000
C	-3.919709000	-0.660966000	-2.495558000	H	-3.046238000	3.158059000	1.564071000	H	9.466561000	7.730609000	13.489648000	H	13.696391000	3.606001000	12.911474000
C	-2.822661000	2.417499000	-1.780522000	H	-1.651850000	3.357049000	0.488079000	H	10.748326000	6.526703000	13.692883000	C	12.580900000	1.144760000	12.670500000
C	-1.918040000	-0.872328000	4.190610000	H	4.286262000	-3.107051000	1.010275000	C	7.936697000	1.512024000	10.385215000	H	12.304317000	1.621333000	13.613381000
C	0.338435000	-0.095422000	3.432581000	H	3.200964000	-3.658143000	-0.269899000	H	7.255603000	2.172923000	10.919354000	H	13.537384000	0.636280000	12.815717000
H	0.755439000	-0.385564000	4.400169000	H	4.953206000	-3.726269000	-0.507570000	H	7.437931000	0.546065000	10.282730000	H	11.835517000	0.386566000	12.450245000
H	1.115436000	-0.189812000	2.676471000	H	2.973863000	-2.299379000	-2.422473000	H	8.106755000	1.921592000	9.389170000	C	10.723303000	7.365126000	11.069222000
H	0.049018000	0.954310000	3.494123000	H	3.913538000	-0.824906000	-2.638699000	C	10.013244000	0.217146000	10.358841000	H	11.739224000	7.221628000	11.440176000
C	2.887769000	3.854124000	-0.339653000	H	4.729889000	-2.397263000	-2.644044000	H	10.266177000	0.560985000	9.356171000	H	10.444490000	8.406010000	11.251969000
C	4.138903000	-3.137926000	-0.071576000	H	5.507515000	-0.046278000	-0.813525000	H	9.362566000	-0.655844000	10.270076000	H	10.729661000	7.183516000	9.994522000
C	4.479322000	2.364586000	0.884861000	H	5.647381000	-0.958222000	0.693752000								
C	3.921620000	-1.816650000	-2.185296000	H	6.291352000	-1.631569000	-0.810968000								
C	-2.847396000	-0.631924000	-0.131670000	H	1.048896000	2.562628000	1.287967000								
C	-3.107032000	-2.743652000	-1.487117000	H	2.206160000	1.563336000	2.157748000								
C	5.471403000	-1.046590000	-0.380493000	H	2.311119000	3.325016000	2.270400000								
C	-2.613406000	0.761701000	0.194309000	H	4.615124000	1.427284000	1.426223000								
C	-2.736863000	3.256714000	0.522470000	H	5.184899000	2.380363000	0.051811000								
C	4.131969000	-1.728057000	-0.674716000	H	4.734868000	3.187666000	1.560865000								
C	-1.777794000	0.762801000	1.366428000	H	-1.205491000	-3.128923000	2.831397000								
H	-2.110457000	-2.472108000	0.867849000	H	0.346640000	-2.571985000	2.198403000								
H	-1.415414000	1.645724000	1.857654000	H	0.100105000	-2.729423000	3.947352000								
H	-2.785064000	-1.495569000	3.962368000	H	3.554099000	3.907983000	-1.203041000								
H	-1.508847000	-1.193991000	5.151813000	H	1.866316000	3.999316000	-0.694295000								
H	-2.260088000	0.159340000	4.291474000	H	3.136245000	4.680814000	0.334162000								

Table S19: Optimized geometries of **I-8** (left), **10** (right). XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



Co	-1.428363000	-0.144152000	-0.188670000	H	-6.346540000	2.009108000	-1.147389000
P	2.130523000	-0.539791000	-0.206261000	H	-6.099236000	0.341095000	-0.645377000
P	-0.810339000	-1.176093000	-2.119326000	H	-5.862535000	1.644136000	0.515036000
P	0.219154000	-1.653207000	-0.243352000	H	-4.239015000	0.048075000	-2.602822000
P	-0.432503000	0.944405000	-1.901906000	H	-4.753580000	1.677188000	-3.034269000
P	1.778450000	1.005871000	-1.752271000	H	-3.045753000	1.325254000	-2.734031000
C	-5.726920000	1.354805000	-0.529208000	H	-4.554001000	3.538695000	-1.547943000
C	-5.443841000	-1.933256000	1.082535000	H	-4.071649000	3.390972000	0.143422000
C	-0.133554000	-0.423564000	3.423852000	H	-2.875162000	3.178379000	-1.147565000
C	-4.221937000	-1.912321000	0.141022000	H	-0.840834000	-1.141681000	3.842526000
C	-0.848192000	0.825838000	2.896376000	H	0.422571000	-0.916206000	2.626388000
C	2.017042000	2.611014000	-0.825045000	H	0.566502000	-0.145378000	4.214798000
C	-2.415177000	-0.777779000	1.531350000	Si	3.732662000	2.913375000	-0.097483000
C	-1.793878000	0.476999000	1.769076000	Si	4.251373000	-2.824803000	0.035563000
C	-4.248607000	1.489677000	-0.938020000	C	4.092796000	4.760592000	-0.198126000
C	-4.696432000	-1.996993000	-1.312450000	H	3.327351000	5.337068000	0.327662000
C	-4.062267000	1.099140000	-2.414541000	H	5.060029000	4.998465000	0.252162000
C	-1.682476000	1.443900000	4.036333000	H	4.112305000	5.100531000	-1.236636000
C	0.205089000	1.838571000	2.437769000	C	5.059749000	1.990654000	-1.057859000
H	0.831342000	2.139312000	3.280860000	H	4.960786000	0.912586000	-0.924124000
H	0.847038000	1.401607000	1.675972000	H	4.998620000	2.200937000	-2.127580000
H	-0.254501000	2.737918000	2.025056600	H	6.053261000	2.283189000	-0.707864000
C	-3.374117000	-0.682616000	0.481433000	C	3.810706000	2.388863000	1.703681000
C	-3.411662000	-3.200018000	0.392687000	H	3.108972000	2.963003000	2.312051000
C	-3.364476000	0.700482000	0.037533000	H	3.559688000	1.332505000	1.805024000
C	-3.909338000	2.990447000	-0.858419000	H	4.815711000	2.548115000	2.103655000
C	3.273204000	-1.711542000	-1.119365000	C	5.390160000	-1.754373000	1.083380000
C	-2.385405000	1.370285000	0.845479000	H	4.812722000	-1.056263000	1.692203000
H	-2.169739000	-1.683407000	2.053231000	H	5.999515000	-2.367228000	1.752283000
H	-2.123512000	2.407181000	0.750525000	H	6.064832000	-1.168688000	0.453930000
H	-2.456730000	0.749776000	4.369767000	C	5.294676000	-4.011573000	-0.989278000
H	-1.046966000	1.684263000	4.892565000	H	5.897963000	-4.660861000	-0.349458000
H	-2.171724000	2.361793000	3.704898000	H	4.662484000	-4.647627000	-1.613616000
H	-6.072357000	-1.054433000	0.945553000	H	5.973535000	-3.464765000	-1.648283000
H	-6.052580000	-2.820950000	0.892288000	C	3.117164000	-3.814791000	1.157796000
H	-5.122084000	-1.957152000	2.125160000	H	2.435558000	-4.437598000	0.574992000
H	-5.206972000	-2.950147000	-1.466887000	H	3.698533000	-4.465021000	1.816783000
H	-5.397843000	-1.210691000	-1.573432000	H	2.506901000	-3.155312000	1.777343000
H	-3.845145000	-1.949352000	-1.991087000	H	1.264935000	2.728031000	-0.042507000
H	-3.154673000	-3.332953000	1.442662000	H	1.828899000	3.397162000	-1.563135000
H	-4.007511000	-4.064194000	0.092461000	H	3.993152000	-1.101863000	-1.672726000
H	-2.488710000	-3.194950000	-0.186875000	H	2.712326000	-2.289929000	-1.857890000



Co	-0.315892000	-0.232194000	-0.045065000	C	2.400116000	-0.458586000	1.808786000
P	-3.288776000	-0.999549000	0.089992000	C	2.032009000	0.008303000	3.230104000
H	-3.643393000	0.355208000	0.362992000	H	2.191043000	1.079928000	3.359187000
P	-1.595078000	-1.458850000	1.395359000	H	2.662867000	-0.514502000	3.951196000
P	-0.698515000	-2.392695000	-0.396654000	H	0.993714000	-0.221803000	3.469772000
P	-1.866177000	-0.930903000	-1.568138000	C	3.888550000	-0.115499000	1.615981000
O	-4.544823000	-1.834623000	0.057133000	H	4.287745000	-0.484849000	0.676277000
C	1.584522000	0.357807000	-0.680786000	H	4.478391000	-0.556970000	2.422556000
C	1.543962000	0.281728000	0.773154000	H	4.036960000	0.966056000	1.640518000
C	0.523246000	1.196396000	1.190513000	C	2.188050000	-1.981975000	1.798751000
H	0.222970000	1.346969000	2.209994000	H	1.166275000	-2.214219000	2.099051000
C	-0.072132000	1.840979000	0.080915000	H	2.869127000	-2.454218000	2.511998000
C	0.592001000	1.315035000	-1.059282000	H	2.351223000	-2.424219000	0.824143000
H	0.357562000	1.579257000	-2.073598000	C	-1.076838000	2.970762000	0.113567000
C	2.496974000	-0.241918000	-1.754024000	C	-1.993659000	2.933831000	-1.115269000
C	1.755183000	-0.308863000	-3.103676000	H	-1.423079000	3.004255000	-2.042383000
H	0.836707000	-0.889443000	-3.014937000	H	-2.690404000	3.774665000	-1.087749000
H	2.397246000	-0.789873000	-3.843662000	H	-2.566184000	2.007558000	-1.142903000
H	1.500582000	0.677979000	-3.487913000	C	-1.937097000	2.903881000	1.381179000
C	2.985303000	-1.667281000	-1.475056000	H	-2.478086000	1.959157000	1.432999000
H	3.625134000	-1.734084000	-0.601436000	H	-2.663639000	3.719196000	1.382856000
H	3.566505000	-2.019149000	-2.330143000	H	-1.329839000	2.999119000	2.282598000
H	2.138475000	-2.339308000	-1.335984000	C	-0.291605000	4.297796000	0.111794000
C	3.710030000	0.694913000	-1.932693000	H	0.368997000	4.356841000	0.979024000
H	3.379864000	1.698784000	-2.206170000	H	-0.974942000	5.150097000	0.142402000
H	4.362811000	0.322624000	-2.726354000	H	0.321759000	4.383300000	-0.787285000
H	4.297784000	0.773960000	-1.019498000				

5. References

[1] F. Dielmann, A. Timoshkin, M. Piesch, G. Balázs, M. Scheer, *Angew. Chem.* **2017**, *129*, 1693.

[2] J. W. Connolly, G. Urry, *Inorg. Chem.* **1963**, *2*, 645.

[3] K. Inkrott, R. Goetze, S. G. Shore, *J. Organomet. Chem.* **1978**, *154*, 337.

[4] R. C. Clark, J. S. Reid, *Acta Cryst.* **1995**, *A51*, 887.

[5] CrysAlisPro Software system, Agilent Technologies UK Ltd, Yarnton, Oxford, UK (2014).

[6] G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3.

[7] O. V. Dolomanov, l. J. Bourhis, R. J. Gildea, Howard, J. A. K., H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339.

[8] G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3.

[9] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

[10] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[11] a) D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chim. Acta* **1990**, *77*, 123; b) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

[12] a) G. Scalmani, M. J. Frisch, *J. Chem. Phys.* **2010**, *132*, 114110; b) J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, *105*, 2999.

[13] NBO 6.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, and F. Weinhold (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2013), http://nbo6.chem.wisc.edu.

[14] a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comp. Chem.* **2011**, *32*, 1456.

[15] Chemcraft - graphical software for visualization of quantum chemistry computations. https://www.chemcraftprog.com.