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Supporting Information

Synthesis and Multiple Subsequent Reactivity of Anionic *cyclo*-E_3 Ligand Complexes (E = P, As)

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Supporting Information

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)(Cp'''Ni)(μ,η^3:η^3-P_3)] (**3**),[1] [(Cp'''Co)(Cp'''Ni)(μ,η^3:η^3-As_3)] (**4**),[2] [(^{t}BuN)$_2$CPhSiCl][3] and Tl[TEF][4] were prepared according to literature procedures. K, Ph_2PCl, ^{t}Bu_2PCl, Cy_2PCl, 18-c-6 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 X-Band EPR measurements were carried out with a MiniScope MS400 device with a frequency of 9.44 GHz and a rectangular resonator TE102 of the company Magnettech GmbH. The ESI-MS spectra were acquired on a ThermoQuest Finnigan MAT TSQ 7000 mass spectrometer. The LIFDI-MS spectra were recorded with a Finnigan MAT 95 mass spectrometer.

1.1 Synthesis of [K(thf)$_{0.7}$)][Cp'''Co(η^3-P$_3$)] ([K(thf)$_{0.7}$)][5]) and [K(18-c-6))][Cp'''Co(η^3-P$_3$)] ([K(18-c-6)][5])

Compound **3** (2 g, 2.95 mmol, 1 eq) and elemental potassium (352 mg, 9.00 mmol, 3.05 eq) were stirred together in thf for 2 days, while the color changed from brown to dark red/purple and a large amount of black precipitate was formed. The solution was filtered over diatomaceous earth and the solvent removed *in vacuo*. The obtained dark red solid contains a 1:0.8 mixture of KCp''' and ([K(thf)$_{0.7}$)][**5**]) according to the ^{1}H NMR spectrum in thf-d$_8$ (cf. Figure S1) giving a sum formula of [Cp'''CoP$_3$K(thf)$_{0.7}$]$_{0.444}$[KCp''']$_{0.556}$.

Yield: 1.67 g (2.05 mmol [K(thf)$_{0.7}$)][**5**] within the mixture, 69 %).

^{1}H NMR (thf-d$_8$, 25 °C): *δ* [ppm] = 5.47 (s, 2H, C$_5$*H*$_2$^{t}Bu$_3$ (KCp''')), 4.35 (s, 1.6H, C$_5$*H*$_2$^{t}Bu$_3$ ([K(thf)$_{0.7}$)][**5**])), 3.53 (s, 2.3H, thf (K(thf)$_{0.7}$)), 1.68 (s, 2.3H, thf (K(thf)$_{0.7}$)), 1.30 (s, 18H, C$_5$H$_2$^{t}*Bu*$_3$ (KCp''')), 1.26 (s, 14.4H, C$_5$H$_2$^{t}*Bu*$_3$ ([K(thf)$_{0.7}$)][**5**])), 1.14 (s, 9H, C$_5$H$_2$^{t}*Bu*$_3$ (KCp''')), 1.07 (s, 7.2H, C$_5$H$_2$^{t}*Bu*$_3$ ([K(thf)$_{0.7}$)][**5**])).

^{31}P{^{1}H} NMR (thf-d$_8$, 25 °C): *δ* [ppm] = -313.1 (s, *P*$_3$).

18-c-6 (1.56 g, 5.9 mmol, 2 eq) in thf was added to the mixture above, stirred for 5 minutes and the solvent reduces *in vacuo*. The concentrated thf solution was layered with *n*-hexane at room temperature and after a few days, large crystals of [K(18-c-6)][**5**] and [K(18-c-6)]Cp''' (cf. chapter 3.1) were obtained. The mother liquor was decanted off and the obtained crystals separated under the microscope yielding analytically pure [K(18-c-6)][**5**].

Yield: 468 mg (0.68 mmol, 23 %).

^{1}H NMR (thf-d$_8$, 25 °C): *δ* [ppm] = 4.36 (s, 2H, C$_5$*H*$_2$^{t}Bu$_3$ ([K(18-c-6)][**5**])), 3.63 (s, 24H, 18-c-6), 1.32 (s, 18H, C$_5$*H*$_2$^{t}Bu$_3$ ([K(18-c-6)][**5**])), 1.13 (s, 9H, C$_5$*H*$_2$^{t}Bu$_3$ ([K(18-c-6)][**5**])).

^{31}P{^{1}H} NMR (thf-d$_8$, 25 °C): *δ* [ppm] = -313.1 (s, *P*$_3$).

ESI-MS (dme): *m/z* = 385.09 (100 %, [M]$^-$).

EA C$_{29}$H$_{53}$O$_6$KCoP$_3$: calc [%]: C 50.58; H 7.76; found [%]: C 50.56; H 7.54.

1.2 Synthesis of $[K(thf)_{0.8})][Cp'''Co(\eta^3\text{-}As_3)]$ ($[K(thf)_{0.7})][6]$) and $[K(18\text{-}c\text{-}6))][Cp'''Co(\eta^3\text{-}As_3)]$ ($[K(18\text{-}c\text{-}6)][6]$)

Compound **4** (2 g, 2.47 mmol, 1 eq) and elemental potassium (290 mg, 7.42 mmol, 3.00 eq) were stirred together in thf for 2 days, while the color changed from green to brown and then to green and a large amount of black precipitate was formed. The solution was filtered over diatomaceous earth and the solvent removed *in vacuo*. The obtained dark green solid contains a 1:0.7 mixture of KCp''' and ($[K(thf)_{0.8}][$**6**]) according to the ^{1}H NMR spectrum in thf-d_8 (cf. Figure S4) giving a sum formula of $[Cp'''CoAs_3K(thf)_{0.8}]_{0.412}[KCp''']_{0.588}$.

Yield: 1.57 g (1.56 mmol $[K(thf)_{0.8})][$**6**] within the mixture, 63 %).

^{1}H NMR (thf-d_8, 25 °C): δ [ppm] = 5.46 (s, 2H, $C_5H_2{}^t$Bu$_3$ (KCp''')), 4.40 (s, 1.4H, $C_5H_2{}^t$Bu$_3$ ($[K(thf)_{0.8})][$**6**])), 3.53 (s, 2.3H, thf ($K(thf)_{0.8}$)), 1.67 (s, 2.3H, thf ($K(thf)_{0.7}$)), 1.29 (s, 18H, $C_5H_2{}^tBu_3$ (KCp''')), 1.25 (s, 12.6H, $C_5H_2{}^tBu_3$ ($[K(thf)_{0.8})][$**6**])), 1.14 (s, 9H, $C_5H_2{}^tBu_3$ (KCp''')), 1.07 (s, 7.2H, $C_5H_2{}^tBu_3$ ($[K(thf)_{0.8})][$**6**])).

18-c-6 (1.46 g, 5.54 mmol, 2 eq) in thf was added to the mixture above, stirred for 5 minutes and the solvent reduces *in vacuo*. The concentrated thf solution was layered with *n*-hexane at room temperature and after a few days, large crystals of [K(18-c-6)][**6**] and [K(18-c-6)]Cp''' (cf. chapter 3.1) were obtained. The mother liquor was decanted off and the obtained crystals separated under the microscope yielding analytically pure [K(18-c-6)][**6**].

Yield: 300 mg (0.37 mmol, 15 %).

^{1}H NMR (thf-d_8, 25 °C): δ [ppm] = 4.41 (s, 2H, $C_5H_2{}^t$Bu$_3$ ($[K(18\text{-}c\text{-}6)][$**6**])), 3.62 (s, 24H, 18-c-6), 1.31 (s, 18H, $C_5H_2{}^t$Bu$_3$ ($[K(18\text{-}c\text{-}6)][$**6**])), 1.13 (s, 9H, $C_5H_2{}^t$Bu$_3$ ($[K(18\text{-}c\text{-}6)][$**6**])).

ESI-MS (dme): *m/z* = 516.92 (100 %, $[M]^-$).

EA $C_{29}H_{53}O_6KCoAs_3$ x C_4H_8O: calc [%]: C 44.40; H 6.89; found [%]: C 44.38; H 6.59.

1.3 Reaction of $[K(thf)_{0.7}][5]$ with Ph_2PCl

A mixture of KCp''' and $[K(thf)_{0.7}][\mathbf{5}]$ (300 mg, 0.368 mmol, 1 eq) in thf was cooled to -80 °C and Ph_2PCl in toluene (1.56 ml, 0.39 mmol, 0.25 mol/L, 1.06 eq) was added, while the color changed from dark red to brown. The mixture was allowed to reach room temperature and the solvent was removed *in vacuo*. The residue was extracted with *n*-pentane.

and filtered over diatomaceous earth. The solvent was removed *in vacuo* and NMR spectra in toluene-d_8 were recorded. The $^{31}P\{^1H\}$ NMR spectrum reveals the formation of [Cp'''Co(η^3-P_4Ph_2)] (**7a**) and [Cp'''Co(η^2:η^1-P_4Ph_2)] (**8a**) in a ratio of 1:0.2 beside minor amounts of Ph_3P, $(Ph_2P)_2$ and $(PhP)_5$. The residue was dissolved in toluene and layered with MeCN. After storage at -30 °C for three weeks, **8a** can be obtained in form of red plates. The supernatant was decanted of and the obtained crystals dried *in vacuo*.

Compound **7a**:

^{1}H NMR (C_6D_6, 25 °C): δ [ppm] = 7.82 (m, 2H, P_4Ph_2), 7.32 (m, 2H, P_4Ph_2), 6.99 (m, 6H, P_4Ph_2) 5.17 (s, 2H, $C_5H_2{}^t Bu_3$), 1.39 (s, 18H, $C_5H_2{}^t Bu_3$), 1.28 (s, 9H, $C_5H_2{}^t Bu_3$).

$^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ [ppm] = 32.1 (m, 1P, P_A, P_4Ph_2), -8.2 (m, 2P, $P_M/P_{M'}$, P_4Ph_2), -80.7 (m, 1P, P_X, P_4Ph_2). Coupling constants are obtained from the simulation (cf. Figure S6 and Table S1).

^{31}P NMR (C_6D_6, 25 °C): δ [ppm] = 32.1 (m, 1P, P_A, P_4Ph_2), -8.2 (m, 2P, $P_M/P_{M'}$, P_4Ph_2), -80.7 (m, 1P, P_X, P_4Ph_2).

Compound **8a**:

Yield: 86 mg (0.151 mmol, 41 %)

^{1}H NMR (C_6D_6, 25 °C): δ [ppm] = 7.92 (m, 4H, P_4Ph_2), 7.07 (m, 6H, P_4Ph_2), 4.19 (s, 2H, $C_5H_2{}^t Bu_3$), 1.37 (s, 9H, $C_5H_2{}^t Bu_3$), 1.34 (s, 18H, $C_5H_2{}^t Bu_3$).

$^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ [ppm] = -34.1 (m, 1P, P_A, P_4Ph_2), -73.1 (m, 1P, P_M, P_4Ph_2), -192.6 (m, 2P, P_X /$P_{X'}$, P_4Ph_2). Coupling constants are obtained from the simulation (cf. Figure S19 and Table S5).

^{31}P NMR (C_6D_6, 25 °C): δ [ppm] = -34.1 (m, 1P, P_A, P_4Ph_2), -73.1 (m, 1P, P_M, P_4Ph_2), -192.6 (m, 2P, P_X /$P_{X'}$, P_4Ph_2).

LIFDI-MS (toluene): m/z = 570.13 (100 %, $[M]^{+\cdot}$).

EA $C_{29}H_{39}CoP_4$: calc [%]: C 61.06; H 6.89; found [%]: C 61.25; H 6.77.

1.4 Reaction of $[K(thf)_{0.7}][5]$ with Cy_2PCl

A mixture of KCp''' and $[K(thf)_{0.7}][\mathbf{5}]$ (500 mg, 0.61 mmol, 1 eq) in thf was cooled to -80 °C and Cy_2PCl in toluene (1.33 ml, 0.8 mmol, 0.6 mol/L, 1.31 eq) was added, while the color changed from dark red to brown. The mixture was allowed to reach room temperature and the solvent was removed *in vacuo*. The residue was extracted with *n*-pentane and filtered over diatomaceous earth. The solvent was removed *in vacuo* and NMR spectra in toluene-d_8 were recorded. The $^{31}P\{^1H\}$ NMR spectrum reveals the formation of $[Cp'''Co(\eta^3\text{-}P_4Cy_2)]$ (**7b**) and $[Cp'''Co(\eta^2\text{:}\eta^1\text{-}P_4Cy_2)]$ (**8b**) in a ratio of 1:0.01 beside unused Cy_2PCl. The crude mixture was purified by column chromatography (SiO_2, *n*-hexane, 16 x 3.5 cm). Using *n*-hexane, a weak red fraction of **8b** followed by a strong purple fraction of **7b** was collected. The solvent was removed *in vacuo*. Since **8b** was obtained in a very small amount only NMR spectroscopic investigations were performed. Compound **7b** was dissolved in toluene, layered with MeCN and stored at -30 °C. After a few days, **7b** can be obtained as red blocks. The supernatant was decanted off and the obtained crystals dried *in vacuo*.

Compound **7b**:

Yield: 35 mg (0.06 mmol, 10 %)

^{1}H NMR (C_6D_6, 25 °C): δ [ppm] = 5.16 (s, 2H, $C_5H_2{}^tBu_3$), 2.67 (m. 1H, P_4Cy_2), 2.01 (m. 2H, P_4Cy_2), 1.88 (m. 2H, P_4Cy_2), 1.61 (m. 8H, P_4Cy_2), 1.52 (s, 18H, $C_5H_2{}^tBu_3$), 1.43 (s, 9H, $C_5H_2{}^tBu_3$), 0.96 (m. 9H, P_4Cy_2).

$^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ [ppm] = 62.7 (m, 1P, P_A, P_4Cy_2), -36.1 (m, 2P, $P_M/P_{M'}$, P_4Cy_2), -71.3 (m, 1P, P_X, P_4Cy_2). Coupling constants are obtained from the simulation (cf. Figure S10 and Table S2).

^{31}P NMR (C_6D_6, 25 °C): δ [ppm] = 62.7 (m, 1P, P_A, P_4Cy_2), -36.1 (m, 2P, $P_M/P_{M'}$, P_4Cy_2), -71.3 (m, 1P, P_X, P_4Cy_2).

LIFDI-MS (toluene): *m/z* = 582.23 (100 %, $[M]^{+\cdot}$).

EA $C_{29}H_{51}CoP_4 \cdot (toluene)_{0.1}$: calc [%]: C 60.28; H 8.83; found [%]: C 60.48; H 8.78.

Compound **8b**:

^{1}H NMR (C_6D_6, 25 °C): δ [ppm] = 4.08 (s, 2H, $C_5H_2{}^tBu_3$), 2.56 (m. 2H, P_4Cy_2), 1.90 (m. 2H, P_4Cy_2), 1.81 (m. 2H, P_4Cy_2), 1.63 (m. 9H, P_4Cy_2), 1.49 (s, 18H, $C_5H_2{}^tBu_3$), 1.42 (s, 9H, $C_5H_2{}^tBu_3$), 1.14 (m. 7H, P_4Cy_2).

$^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ [ppm] = -52.9 (m, 1P, P_A, P_4Cy_2), -83.5 (m, 1P, P_M, P_4Cy_2), -199.1 (m, 2P, P_X /$P_{X'}$, P_4Cy_2). Coupling constants are obtained from the simulation (cf. Figure S21 and Table S6).

^{31}P NMR (C_6D_6, 25 °C): δ [ppm] = -52.9 (m, 1P, P_A, P_4Cy_2), -83.5 (m, 1P, P_M, P_4Cy_2), -199.1 (m, 2P, P_X /$P_{X'}$, P_4Cy_2).

1.5 Reaction of [K(thf)$_{0.7}$][5] with ^{t}Bu$_2$PCl

A mixture of KCp''' and [K(thf)$_{0.7}$][**5**] (320 mg, 0.39 mmol, 1 eq) in thf was cooled to -80 °C and ^{t}Bu$_2$PCl in toluene (4.5 ml, 0.5 mmol, 0.112 mol/L, 1.28 eq) was added, while the color changed from dark red to brown. The mixture was allowed to reach room temperature and the solvent was removed *in vacuo*. The residue was extracted with *n*-pentane and filtered over diatomaceous earth. The solvent was removed *in vacuo* and NMR spectra in toluene-d$_8$ were recorded. The ^{31}P{^{1}H} NMR spectrum reveals the formation of [Cp'''Co(η^3-P$_4$^{t}Bu$_2$)] (**7c**) and [Cp'''Co(η^2:η^1-P$_4$^{t}Bu$_2$)] (**8c**) in a ratio of 1:0.01 beside unused ^{t}Bu$_2$PCl. The crude mixture was purified by column chromatography (SiO_2, *n*-hexane, 15 x 3.5 cm). Using a 1:1 mixture of *n*-hexane and toluene, a strong brown-green fraction of **7c** could be eluted. The solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2, layered with MeCN and stored at r.t.. After a few days, **7c** can be obtained as red blocks. The supernatant was decanted off and the obtained crystals dried *in vacuo*.

Compound **7c**:

Yield: 8 mg (0.02 mmol, 4 %).

^{1}H NMR (C_6D_6, 25 °C): δ [ppm] = 5.05 (s, 2H, C_5H_2^{t}Bu$_3$), 1.54 (s, 18H, C_5H_2^{t}Bu$_3$), 1.38 (s, 9H, C_5H_2^{t}Bu$_3$), 1.30 (d. 9H, $^3J_{PH}$ = 13 Hz, P$_4$^{t}Bu$_2$), 1.23 (d. 9H, $^3J_{PH}$ = 13 Hz, P$_4$^{t}Bu$_2$).

^{31}P{^{1}H} NMR (C_6D_6, 25 °C): δ [ppm] = 89.5 (m, 1P, P_A, P_4^{t}Bu$_2$), -30.9 (m, 2P, P_M/$P_{M'}$, P_4^{t}Bu$_2$), -61.4 (m, 1P, P_X, P_4^{t}Bu$_2$). Coupling constants are obtained from the simulation (cf. Figure S14 and Table S3).

^{31}P NMR (C_6D_6, 25 °C): δ [ppm] = 89.5 (m, 1P, P_A, P_4^{t}Bu$_2$), -30.9 (m, 2P, P_M/$P_{M'}$, P_4^{t}Bu$_2$), -61.4 (m, 1P, P_X, P_4^{t}Bu$_2$). Coupling constants are obtained from the simulation (cf. Figure S15 and Table S4).

LIFDI-MS (toluene): *m/z* = 530.20 (100 %, $[M]^{+\cdot}$).

EA $C_{25}H_{47}CoP_4$: calc [%]: C 56.60; H 8.93; found [%]: C 56.62; H 8.82.

Compound **8c**:

^{31}P{^{1}H} NMR (toluene-d$_8$, 25 °C): δ [ppm] = -56.2 (m, 1P, P_A, P_4^{t}Bu$_2$), -80.8 (m, 2P, P_M, P_4^{t}Bu$_2$), -197.8 (m, 2P, P_X,$P_{X'}$, P_4^{t}Bu$_2$). Coupling constants are obtained from the simulation (cf. Figure S22 and Table S7).

1.6 Reaction of $[K(thf)_{0.8}][6]$ with Ph_2PCl

A mixture of KCp''' and $[K(thf)_{0.8}]$[**6**] (650 mg, 0.65 mmol, 1 eq) was dissolved in thf and Ph_2PCl in toluene (2.6 ml, 0.65 mmol, 0.25 mol/L, 1 eq) was added at -80 °C, while the color changed from dark green to red-brown. The solvent was removed *in vacuo*. The residue was extracted with *n*-pentane and filtered over diatomaceous earth. The solvent was removed *in vacuo* and NMR spectra in toluene-d_8 were recorded. The $^{31}P\{^1H\}$ NMR spectrum reveals the formation of $[Cp'''Co(\eta^3\text{-}As_3PPh_2)]$ (**9a**), $[Cp'''Co(\eta^2{:}\eta^1\text{-}As_3PPh_2)]$ (**10a**) and Ph_4P_2 in a ratio of 1:3.45:0.67 beside PPh_3 and other unidentified side products. The ^1H NMR spectrum reveals additionally the formation of $[(Cp'''Co)_2(\mu,\eta^2{:}\eta^2\text{-}As_2)_2]$. The crude mixture was purified by column chromatography (SiO_2, *n*-hexane, 15 x 4 cm). Using *n*-hexane, a first green fraction of $[(Cp'''Co)_2(\mu,\eta^2{:}\eta^2\text{-}As_2)_2]$ was eluted and disposed, followed by a red-brown fraction of **10a** which was collected. The solvent was removed *in vacuo*. Compound **10a** was dissolved in toluene and layered with MeCN at room temperature and stored at -30 °C. After a few days, **10a** can be obtained as dark brown blocks. The supernatant was decanted off and the obtained crystals dried *in vacuo*.

Compound **9a**

$^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ [ppm] = -28.5 (s, $As_3\mathit{P}Ph_2$).

^{31}P NMR (C_6D_6, 25 °C): δ [ppm] = -28.5 (s, $As_3\mathit{P}Ph_2$).

Compound **10a**

Yield: 202 mg (0.288 mmol, 44 %).

^1H NMR (C_6D_6, 25 °C): δ [ppm] = 7.94 (m, 4H, $As_3P\mathit{Ph}_2$), 7.06 (m, 6H, $As_3P\mathit{Ph}_2$) 4.02 (s, 2H, $C_5\mathit{H}_2{}^t\mathrm{Bu}_3$), 1.34 (s, 9H, $C_5H_2{}^{\mathit{t}}\mathit{Bu}_3$), 1.32 (s, 18H, $C_5\mathit{H}_2{}^t\mathrm{Bu}_3$).

$^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ [ppm] = -90.4 (s, $As_3\mathit{P}Ph_2$).

^{31}P NMR (C_6D_6, 25 °C): δ [ppm] = -90.4 (s, $As_3\mathit{P}Ph_2$).

LIFDI-MS (toluene): *m/z* = 1403.92, (0.5 %, $[M]^{2+\cdot}$), 702.01 (100 %, $[M]^{+\cdot}$).

EA $C_{29}H_{39}CoAs_3P$: calc [%]: C 49.60; H 6.60; found [%]: C 50.26; H 5.53.

1.7 Reaction of [K(thf)$_{0.8}$][6] with Cy_2PCl

A mixture of KCp''' and [K(thf)$_{0.8}$][**6**] (500 mg, 0.50 mmol, 1 eq) in thf was cooled to -80 °C and Cy_2PCl in toluene (1.16 ml, 0.7 mmol, 0.6 mol/L, 1.40 eq) was added, while the color changed from dark green to red-brown. The mixture was allowed to reach room temperature and the solvent was removed *in vacuo*. The residue was extracted with *n*-pentane and filtered over diatomaceous earth. The solvent was removed *in vacuo* and NMR spectra in toluene-d_8 were recorded. The $^{31}P\{^1H\}$ NMR spectrum reveals the formation of [Cp'''Co(η^3-As_3PCy_2)] (**9a**) and [Cp'''Co(η^2:η^1-As_3PCy_2)] (**10b**) in a ratio of 1:0.11 beside unused Cy_2PCl. The crude mixture was purified by column chromatography (SiO_2, *n*-hexane, 16 x 3.5 cm). Using *n*-hexane, a red fraction of **10b** followed by a brown fraction of **9b** was collected. The solvent was removed *in vacuo*. The first red fraction contains a 1:3 mixture of **9b** and **10b**, while the second brown one contains clean **9b**. Compound **9b** was dissolved in o-difluorobenzene and layered with MeCN at room temperature, the mixture of **9b** and **10b** was dissolved in toluene, layered with MeCN and stored at -30 °C. After a few days, **9b** can be obtained as dark brown blocks and **10b** as bright red needles. The supernatant was decanted off and the obtained crystals dried *in vacuo*.

Compound **9b**:

Yield: 25 mg (0.035 mmol, 7 %).

^{1}H NMR (C_6D_6, 25 °C): δ [ppm] = 5.10 (s, 2H, $C_5H_2{}^tBu_3$), 2.27 (m. 1H, P_4Cy_2), 1.86 (m. 4H, P_4Cy_2), 1.62 (m. 7H, P_4Cy_2), 1.47 (s, 18H, $C_5H_2{}^tBu_3$), 1.47 (s, 9H, $C_5H_2{}^tBu_3$), 1.27 (m. 2H, P_4Cy_2), 0.98 (m. 8H, P_4Cy_2).

^{31}P NMR (C_6D_6, 25 °C): δ [ppm] = 13.0 (s, As_3PCy_2).

LIFDI-MS (toluene): *m/z* = 883.97 (20 %, $[(Cp'''Co)_2(As_2)_2]^{+\cdot}$), 714.06 (100 %, $[M]^{+\cdot}$).

EA $C_{29}H_{51}CoAs_3P$: calc [%]: C 48.76; H 7.20; found [%]: C 48.96; H 6.85.

Compound **10b**:

Yield: 45 mg (0.063 mmol mixture **9b** and **10b** 1:3, 12 %).

^{1}H NMR (C_6D_6, 25 °C): δ [ppm] = 3.96 (s, 2H, $C_5H_2{}^tBu_3$), 2.57 (m. 2H, P_4Cy_2), 1.86 (m. 4H, P_4Cy_2), 1.62 (m. 8H, P_4Cy_2), 1.48 (s, 18H, $C_5H_2{}^tBu_3$), 1.43 (s, 9H, $C_5H_2{}^tBu_3$), 1.32 (m. 1H, P_4Cy_2), 1.16 (m. 7H, P_4Cy_2).

^{31}P NMR (C_6D_6, 25 °C): δ [ppm] = -61.7 (s, As_3PCy_2).

1.8 Reaction of [K(thf)$_{0.8}$][6] with ^{t}Bu$_2$PCl

A mixture of KCp''' and [K(thf)$_{0.8}$][**6**] (470 mg, 0.469 mmol, 1 eq) in thf was cooled to -80 °C and ^{t}Bu$_2$PCl in toluene (5.4 ml, 0.6 mmol, 0.112 mol/L, 1.28 eq) was added, while the color changed from dark green to brown. The mixture was allowed to reach room temperature and the solvent was removed *in vacuo*. The residue was extracted with *n*-pentane and filtered over diatomaceous earth. The solvent was removed *in vacuo* and NMR spectra in toluene-d$_8$ were recorded. The ^{31}P{^{1}H} NMR spectrum reveals the clean formation of [Cp'''Co(η^3-As$_3$P^{t}Bu$_2$)] (**9c**) beside unused ^{t}Bu$_2$PCl. The crude mixture was purified by column chromatography (SiO$_2$, *n*-hexane, 17 x 3.5 cm). Using *n*-hexane, a strong brown-green fraction of **9c** could be eluted. The solvent was removed *in vacuo*. The residue was dissolved in CH$_2$Cl$_2$, layered with MeCN and stored at r.t.. After a few days, **9c** can be obtained as brown blocks. The supernatant was decanted off and the obtained crystals dried *in vacuo*.

Yield: 20 mg (0.03 mmol, 6 %).

^{1}H NMR (C$_6$D$_6$, 25 °C): *δ* [ppm] = 4.99 (s, 2H, C$_5$*H*$_2$^{t}Bu$_3$), 1.54 (s, 18H, C$_5$H$_2$^{t}*Bu*$_3$), 1.37 (s, 9H, C$_5$*H*$_2$^{t}Bu$_3$), 1.29 (d. 9H, $^{3}J_{PH}$ = 13 Hz, P$_4$^{t}*Bu*$_2$), 1.16 (d. 9H, $^{3}J_{PH}$ = 13 Hz, P$_4$^{t}*Bu*$_2$).

^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C): *δ* [ppm] = 37.1 (s, As$_3$*P*^{t}Bu$_2$).

^{31}P NMR (C$_6$D$_6$, 25 °C): *δ* [ppm] = 37.1 (m, $^{3}J_{PH}$ = 13 Hz, As$_3$*P*^{t}Bu$_2$).

LIFDI-MS (toluene): *m/z* = 883.97 (100 %, [(Cp'''Co)$_2$(As$_2$)$_2$$^{+\cdot}$), 662.03 (10 %, [M]$^{+\cdot}$).

EA C$_{25}$H$_{47}$CoAs$_3$P: calc [%]: C 45.34; H 7.15; found [%]: C 45.59; H 6.89.

1.9 Synthesis of [Cp'''Co(η^3-P$_3$SiL)] (L = (^{t}BuN)$_2$CPh) (11)

A mixture of KCp''' and [K(thf)$_{0.7}$][**5**] (200 mg, 0.245 mmol, 1 eq) in thf was cooled to -80 °C and (^{t}BuN)$_2$CPhSiCl (72 mg, 0.245 mmol, 1 eq) was added, while no change of the color was observed. The mixture was allowed to reach room temperature, while the color changed from dark red to brown-green. The solvent was removed *in vacuo*. The residue was extracted with toluene and filtered over diatomaceous earth. The solvent was removed *in vacuo*, the residue dissolved in *o*-difluorobenzene, layered with *n*-pentane and stored at -30 °C. After a few days, **11** can be obtained as bright green blocks. The supernatant was decanted off and the obtained crystals dried *in vacuo*.

Yield: 45 mg (0.07 mmol, 29 %).

^{1}H NMR (thf-d$_8$, 25 °C): *δ* [ppm] = 7.54 (m, 5H, (^{t}BuN)$_2$C*Ph*SiP$_3$), 4.89 (s, 2H, C$_5$*H*$_2$^{t}Bu$_3$), 1.45 (s, 18H, C$_5$H$_2$^{t}*Bu*$_3$), 1.31 (s, 9H, C$_5$*H*$_2$^{t}Bu$_3$), 1.29 (s, 5H, (^{t}*Bu*N)$_2$CPhSiP$_3$), 1.26 (s, 5H, (^{t}*Bu*N)$_2$CPhSiP$_3$).

^{31}P{^{1}H} NMR (thf-d$_8$, 25 °C): *δ* [ppm] = -66.6 (dd, 1P, $^1J_{PP}$ = 217 Hz, $^1J_{PP}$ = 262 Hz, (^{t}BuN)$_2$CPhSi*P*$_3$), -75.0 (d, 1P, $^1J_{PP}$ = 217 Hz, $^1J_{PSi}$ = 109 Hz, (^{t}BuN)$_2$CPhSi*P*$_3$), -75.0 (d, 1P, $^1J_{PP}$ = 262 Hz, $^1J_{PSi}$ = 109 Hz, (^{t}BuN)$_2$CPhSi*P*$_3$).

^{31}P NMR (thf-d$_8$, 25 °C): *δ* [ppm] = -66.6 (dd, 1P, $^1J_{PP}$ = 217 Hz, $^1J_{PP}$ = 262 Hz, (^{t}BuN)$_2$CPhSi*P*$_3$), -75.0 (d, 1P, $^1J_{PP}$ = 217 Hz, $^1J_{PSi}$ = 109 Hz, (^{t}BuN)$_2$CPhSi*P*$_3$), -75.0 (d, 1P, $^1J_{PP}$ = 262 Hz, $^1J_{PSi}$ = 109 Hz, (^{t}BuN)$_2$CPhSi*P*$_3$).

^{29}Si{^{1}H} NMR (thf-d$_8$, 25 °C): *δ* [ppm] = -24.62 (dt, $^1J_{PSi}$ = 109 Hz, $^2J_{PSi}$ = 12 Hz, (^{t}BuN)$_2$CPh*Si*P$_3$).

LIFDI-MS (toluene): *m/z* = 644.15 (100 %, [M]$^{+\cdot}$).

EA C$_{32}$H$_{52}$N$_2$SiCoP$_3$: calc [%]: C 59.60; H 8.13; N 4.35; found [%]: C 60.07; H 7.66; N 3.99.

1.10 Synthesis of [Cp'''Co(η^3-As$_3$SiL)] (L = (^{t}BuN)$_2$CPh) (12)

A mixture of KCp''' and [K(thf)$_{0.8}$][**6**] (200 mg, 0.199 mmol, 1 eq) in thf was cooled to -80 °C and (^{t}BuN)$_2$CPhSiCl (66 mg, 0.199 mmol, 1 eq) was added, while no change of the color was observed. The mixture was allowed to reach room temperature, while the color changed from dark green to brown-green. The solvent was removed *in vacuo*. The residue was extracted with toluene and filtered over diatomaceous earth. The solvent was removed *in vacuo*, *n*-pentane was added and toluene dropwise until complete dissolution. After storage at -30 °C for one day,**12** can be obtained as dark brown needles. The supernatant was decanted off and the obtained crystals dried *in vacuo*.

Yield: 28 mg (0.036 mmol, 18 %).

^{1}H NMR (C_6D_6, 25 °C): *δ* [ppm] = 6.86 (m, 1H, (^{t}BuN)$_2$C*Ph*SiAs$_3$), 6.76 (m, 2H, (^{t}BuN)$_2$C*Ph*SiAs$_3$), 6.63 (m, 2H, (^{t}BuN)$_2$C*Ph*SiAs$_3$), 5.12 (s, 2H, C$_5$*H*$_2$^{t}Bu$_3$), 1.70 (s, 18H, C$_5$H$_2$^{t}*Bu*$_3$), 1.54 (s, 9H, C$_5$*H*$_2$^{t}Bu$_3$), 1.21 (s, 5H, (^{t}*Bu*N)$_2$CPhSiAs$_3$), 1.19 (s, 5H, (^{t}*Bu*N)$_2$CPhSiAs$_3$).

^{29}Si{^{1}H} NMR (thf-d$_8$, 25 °C): *δ* [ppm] = -51.59 (s, (^{t}BuN)$_2$CPh*Si*As$_3$).

LIFDI-MS (toluene): *m/z* = 883.97 (5 %, [(Cp'''Co)$_2$(As$_2$)$_2$$^{+\cdot}$),776.07 (100 %, [M]$^{+\cdot}$).

EA $C_{32}H_{52}N_2SiCoAs_3$: calc [%]: C 49.49; H 6.75; N 3.60; found [%]: C 49.89; H 6.74; N 3.42.

1.11 Synthesis of [Cp'''Co(η^2:η^1-$As_3P_2Ph_4$)][TEF] (13)

A solution of **10a** (50 mg, 0.043 mmol, 1eq) and Ph_2PCl (0.2 ml, c = 0.25 mol/L in toluene, 0.05 mmol, 1.16 eq) in CH_2Cl_2 was cooled to -80 °C and a solution of Tl[TEF] (49.3 mg, 0.043 mmol, 1 eq) in CH_2Cl_2 was added dropwise. The color changed immediately from dark red to brown while a white precipitate (TlCl) was formed. The reaction mixture was warmed to room temperature and stirred for further 2 h. The reaction mixture was filtered over diatomaceous earth and the solvent removed *in vacuo*. The residue was washed with *n*-pentane. The residue was dissolved in CH_2Cl_2 and layered with *n*-pentane. After a few days, **13** can be obtained as red blocks. The supernatant was decanted off and the obtained crystals dried *in vacuo*.

Yield: 26 mg (0.014 mmol, 33 %).

^{1}H NMR (Cd_2Cl_2, 25 °C): *δ* [ppm] = 8.01 (m, 2H, $As_3P_2Ph_4$), 7.85 (m, 2H, $As_3P_2Ph_4$), 7.61 (m, 4H, $As_3P_2Ph_4$), 7.52 (m, 2H, $As_3P_2Ph_4$), 7.36 (m, 1H, $As_3P_2Ph_4$), 7.18 (m, 4H, $As_3P_2Ph_4$), 7.02 (m, 1H, $As_3P_2Ph_4$), 6.81 (m, 4H, $As_3P_2Ph_4$), 5.05 (d, 1H, $^2J_{HH}$ = 2.5 Hz, $C_5H_2{}^tBu_3$), 4.74 (t, 1H, $^2J_{HH}$ = 2.5 Hz, $^3J_{PH}$ = 2.5 Hz, $C_5H_2{}^tBu_3$), 1.27 (s, 9H, $C_5H_2{}^tBu_3$), 1.24 (s, 9H, $C_5H_2{}^tBu_3$), 1.15 (s, 9H, $C_5H_2{}^tBu_3$).

^{19}F{^{1}H} NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = -75.6 (s, [TEF]).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 2.4 (d,1P, $^2J_{PP}$ = 41 Hz, $As_3P_2Ph_4$), -27.1 (d,1P, $^2J_{PP}$ = 41 Hz, $As_3P_2Ph_4$).

^{31}P NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 2.4 (m,1P, $As_3P_2Ph_4$), -27.1 (m,1P, $As_3P_2Ph_4$).

ESI-MS (CH_2Cl_2): *m/z* = 886.96 (100 %, $[M]^{+\cdot}$).

EA $C_{57}H_{49}CoAs_3P_2AlO_4F_{36}$: calc [%]: C 36.91; H 2.66; found [%]: C 37.14, H 2.70.

2. NMR spectroscopic investigations

2.1 [K(thf)$_{0.7}$][Cp'''Co(η^3-P$_3$)] ([K(thf)$_{0.7}$)][5])

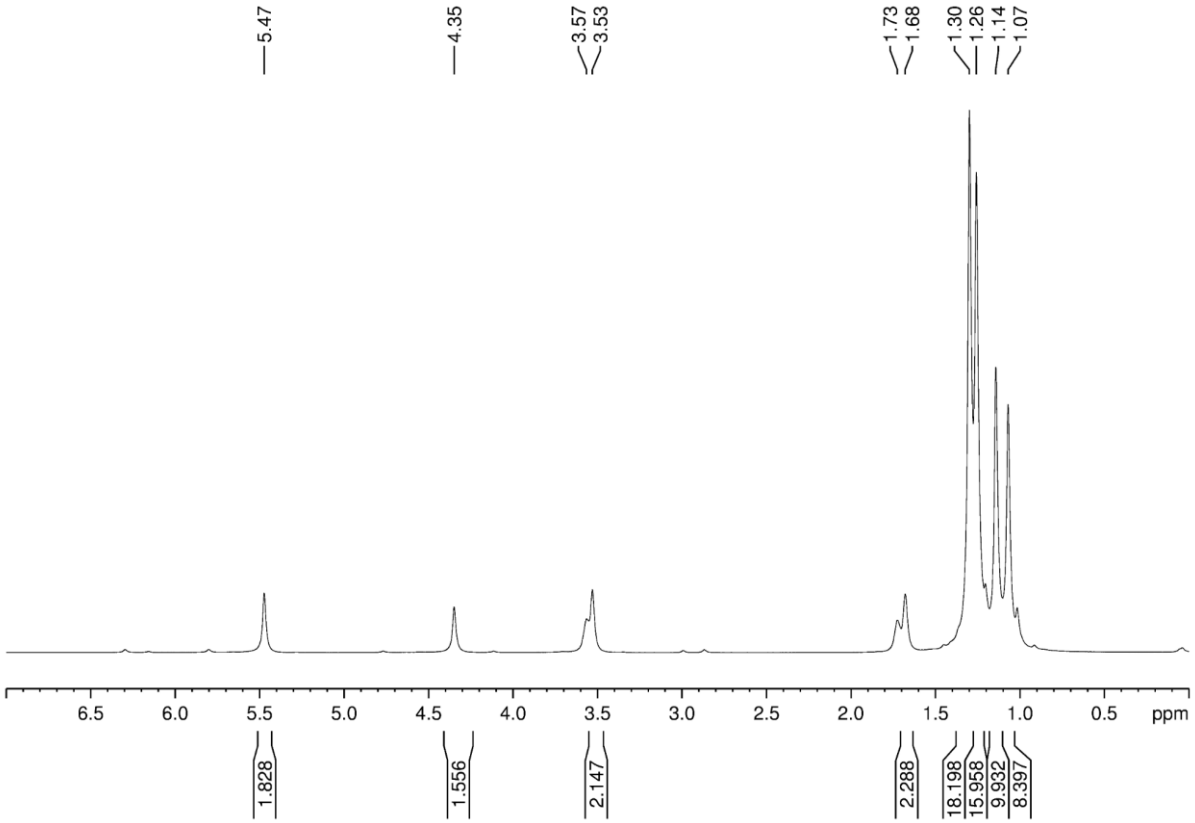


Figure S1. ^{1}H NMR spectrum in thf-d$_8$ of the mixture of [K(thf)$_{0.7}$][**5**] and Cp'''K at room temperature.

2.2 [K(18-c-6)][Cp’’’Co(η^3-P_3)] ([K(18-c-6))][5])

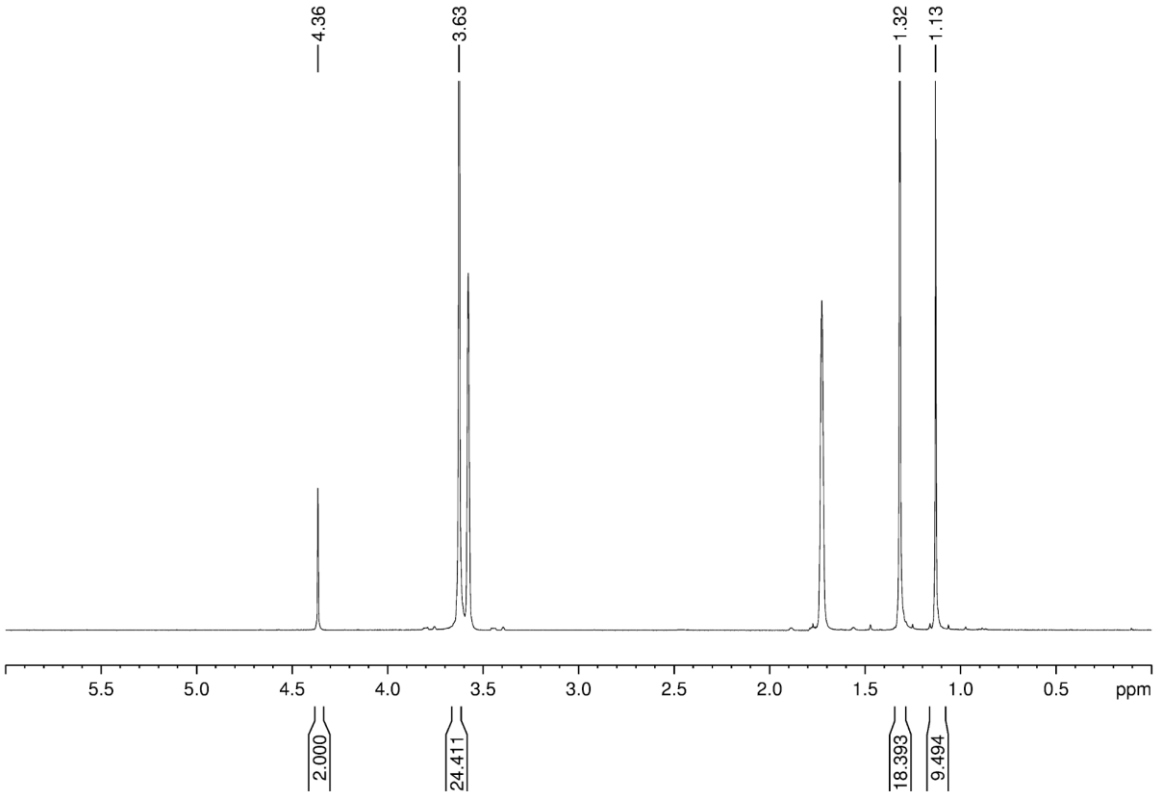


Figure S2. ^{1}H NMR spectrum of [K(18-c-6)][**5**] in thf-d_8 at room temperature.

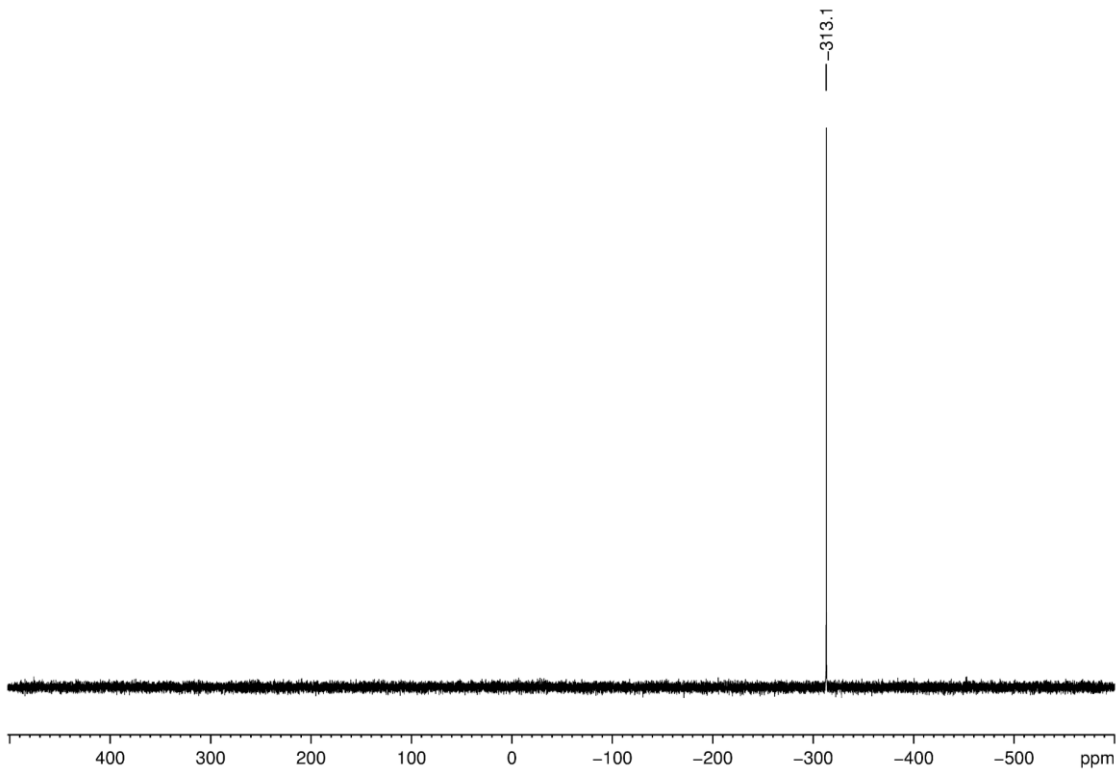


Figure S3. $^{31}P\{^1H\}$ NMR spectrum of [K(18-c-6)][**5**] in thf-d_8 at room temperature.

2.3 $[K(thf)_{0.8}][Cp'''Co(\eta^3\text{-}As_3)]$ ($[K(thf)_{0.8}][\mathbf{6}]$)

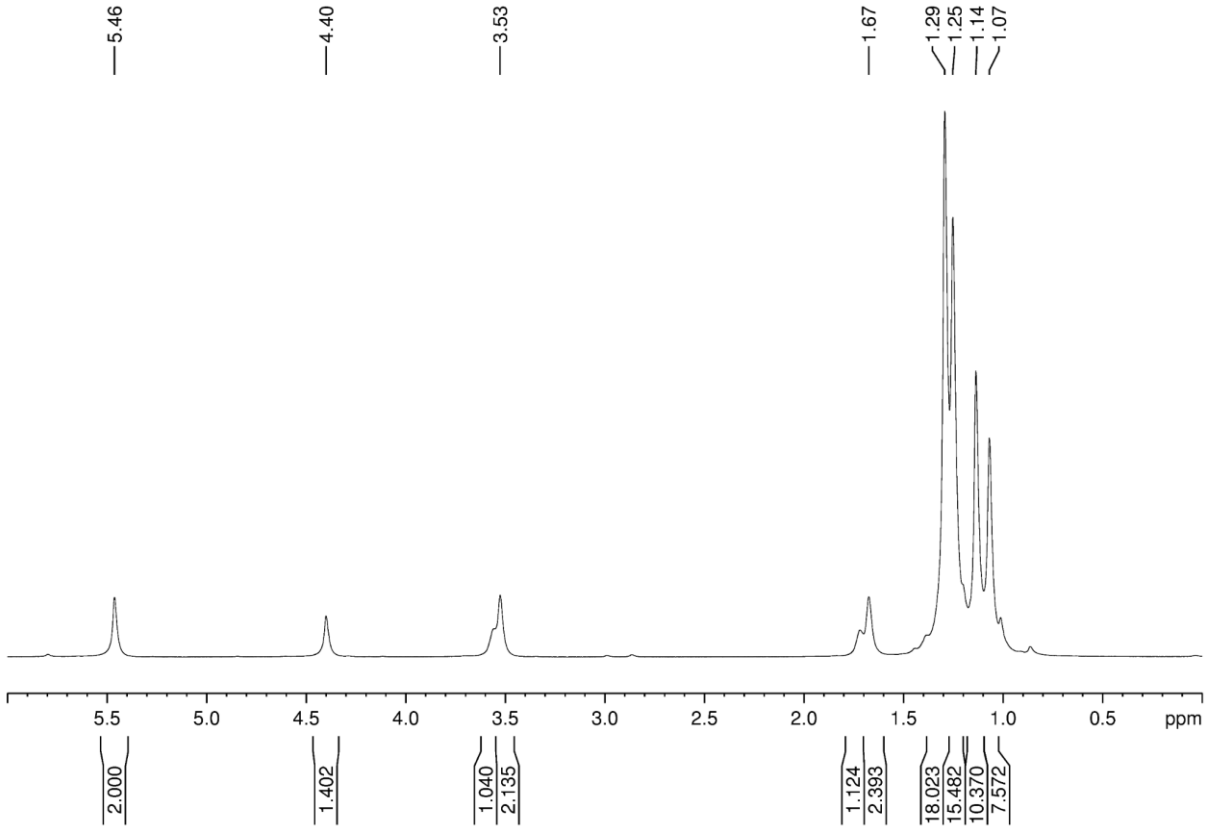


Figure S4. ^{1}H NMR spectrum in thf-d_8 of the mixture of $[K(thf)_{0.8}][\mathbf{6}]$ and Cp'''K at room temperature.

2.4 [K(18-c-6)][Cp'''Co(η^3-As_3)] ([K(18-c-6)][6])

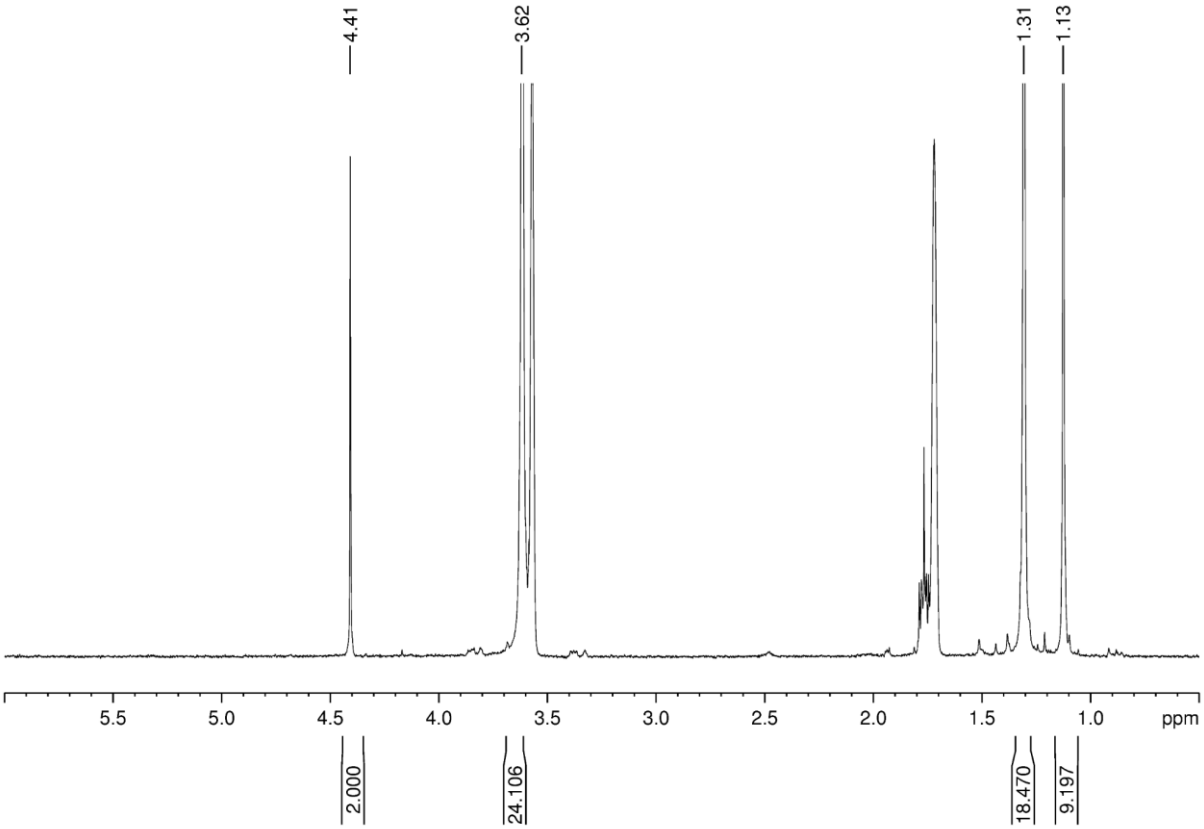


Figure S5. ^{1}H NMR spectrum of [K(18-c-6)][**6**] in thf-d_8 at room temperature.

2.5 [Cp'''Co(η^3-P_4Ph_2)] (7a)

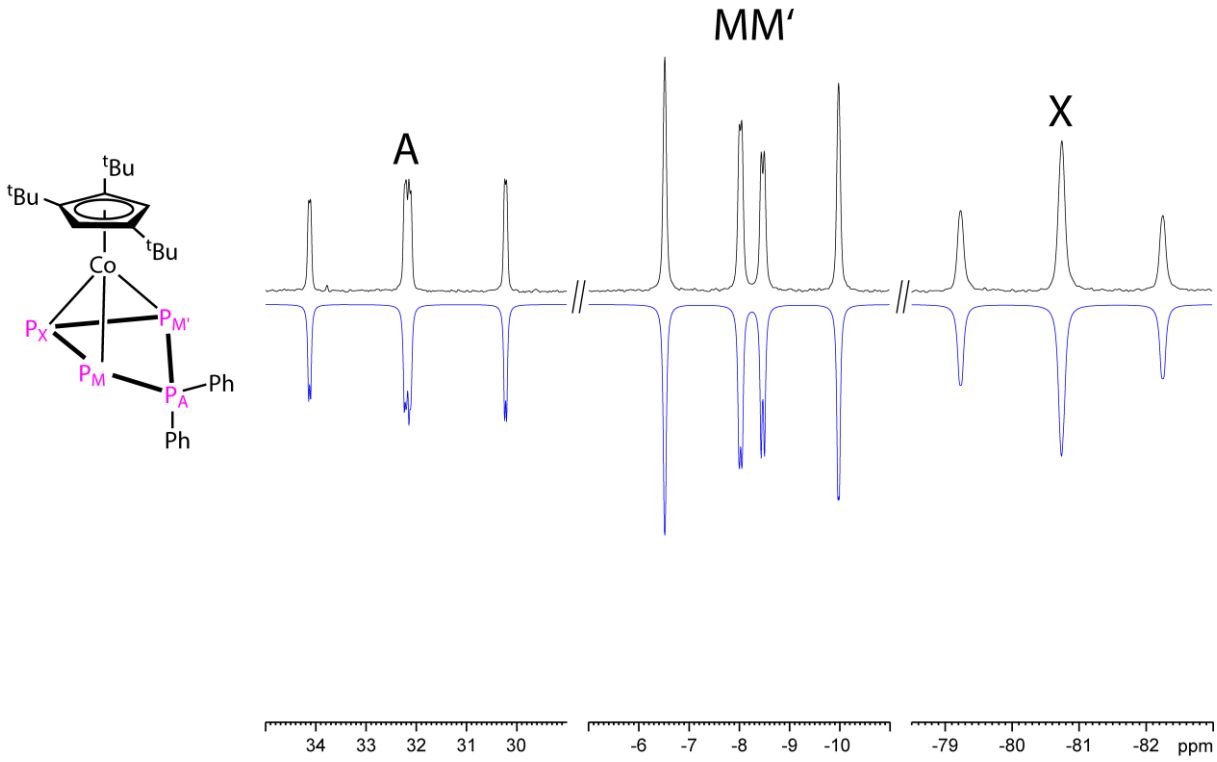


Figure S6: $^{31}P\{^1H\}$ NMR spectrum of **7a** in C_6D_6 at room temperature (experimental (black) and simulated (blue)).

Table S1: Coupling constants and chemical shifts obtained from the simulation of the $^{31}P\{^1H\}$ NMR spectrum.

coupling constants [Hz]		chemical shifts [ppm]	
$^1J_{P_AP_M}$	314.82	P_A	32.13
$^1J_{P_AP_{M'}}$	317.30	P_M	-8.23
$^1J_{P_MP_X}$	244.85	P_M	-8.23
$^1J_{P_MP_{X'}}$	244.10	P_X	-80.72
$^2J_{P_MP_{M'}}$	-9.45		
$^2J_{P_AP_X}$	6.33		
R value		0.51 %	

2.6 Reaction of $[K(thf)_{0.7}][Cp'''Co(\eta^3\text{-}P_3)]$ ($[K(thf)_{0.7}][\mathbf{5}]$) with Ph_2PCl

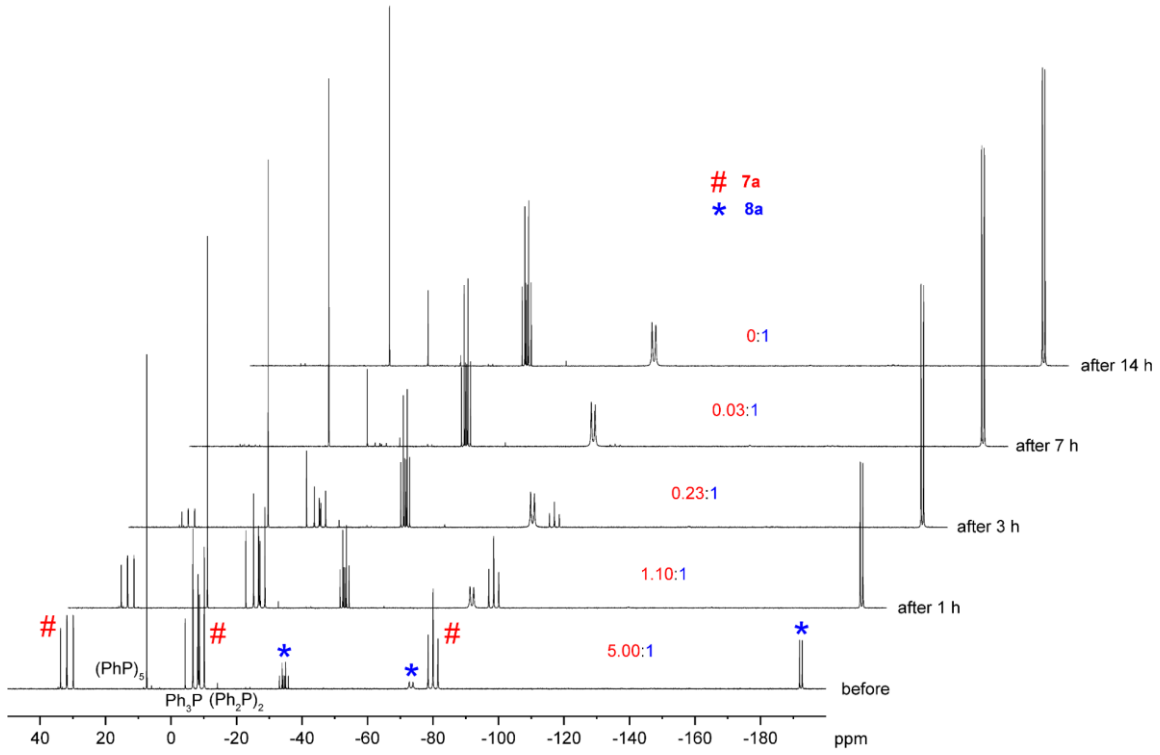


Figure S7: $^{31}P\{^1H\}$ NMR spectra of the reaction of $[K(thf)_{0.7}][\mathbf{5}]$ with Ph_2PCl in toluene-d_8 before thermolysis and after 1, 3, 7 and 14 h at 60 °C.

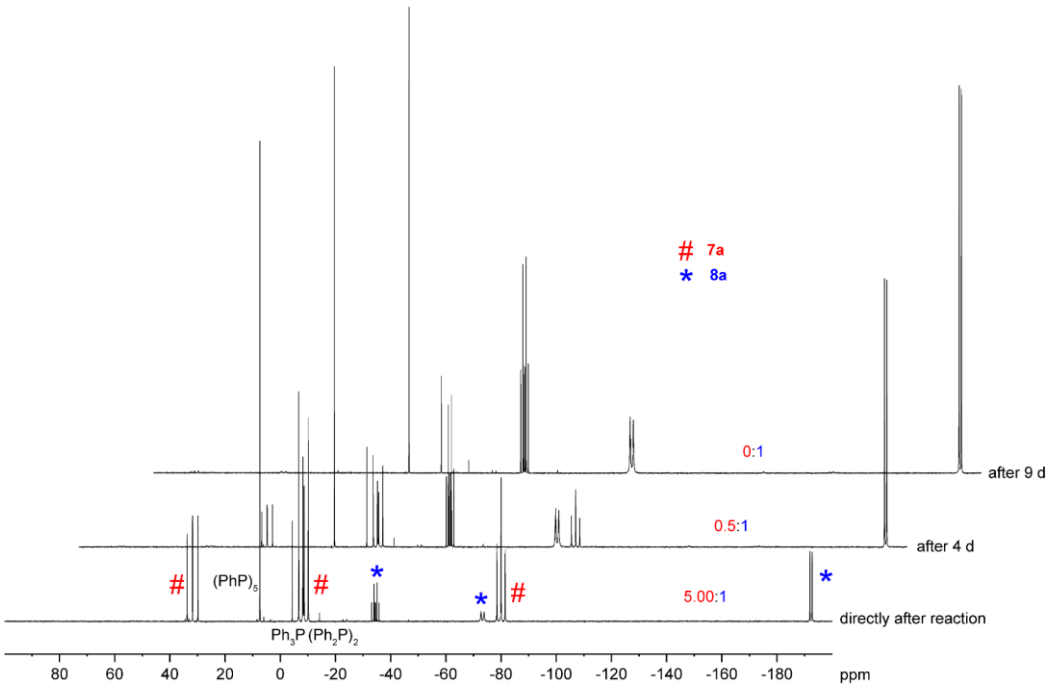


Figure S8: $^{31}P\{^1H\}$ NMR spectra of the reaction of $[K(thf)_{0.7}][\mathbf{5}]$ with Ph_2PCl in toluene-d_8 at room temperature directly after the reaction and after 4 and 9 days.

2.7 [Cp'''Co(η^3-P_4Cy_2)] (7b)

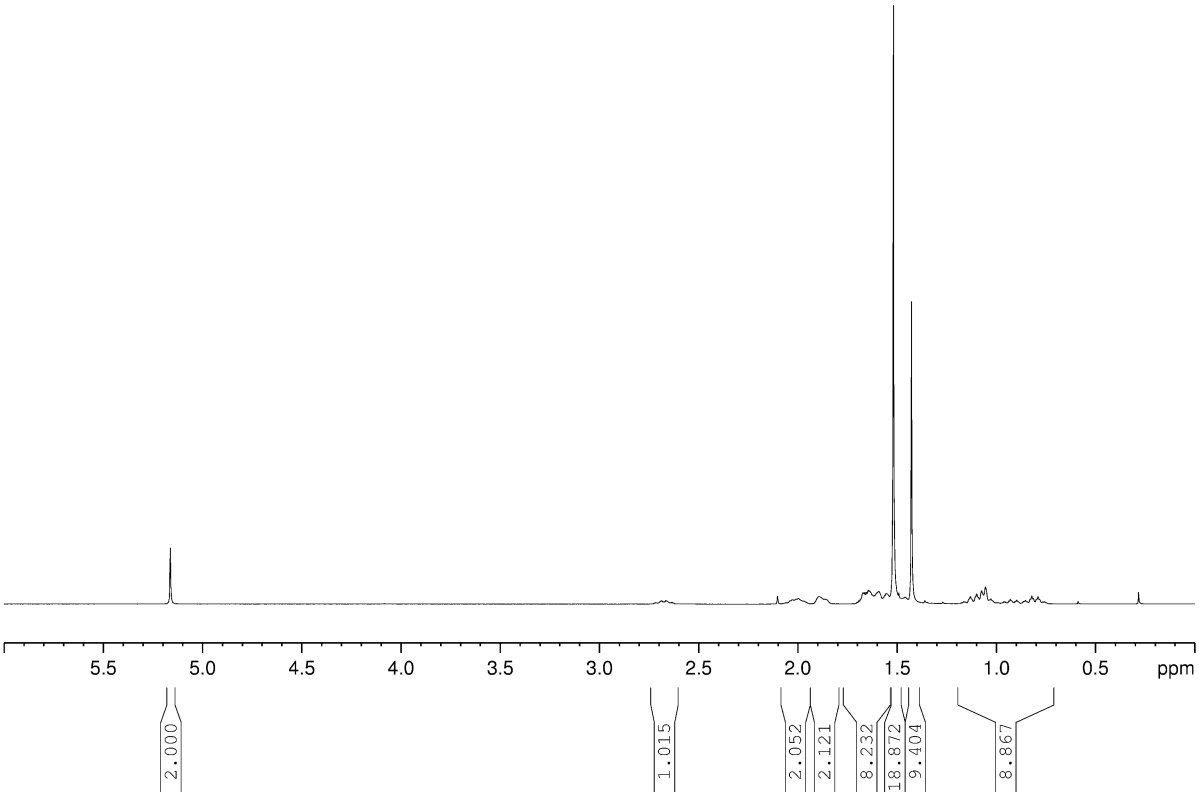


Figure S9: ^{1}H NMR spectrum of **7b** in C_6D_6 at room temperature.

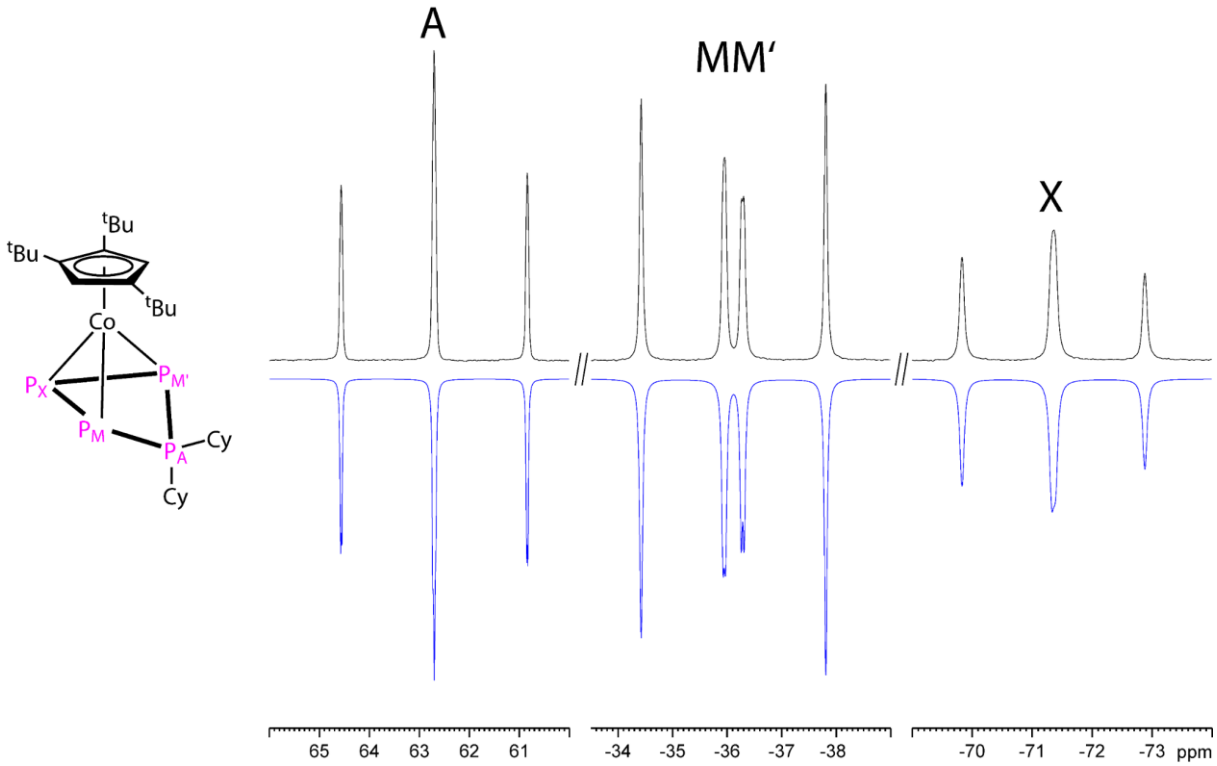


Figure S10: $^{31}P\{^{1}H\}$ NMR spectrum of **7b** in C_6D_6 at room temperature (experimental (black) and simulated (blue)).

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]	
$^{1}J_{P_AP_M}$	300.51	P_A	62.69
$^{1}J_{P_AP_{M'}}$	302.99	P_M	-36.13
$^{1}J_{P_MP_X}$	246.68	P_M	-36.12
$^{1}J_{P_MP_{X'}}$	247.51	P_X	-71.32
$^{2}J_{P_MP_{M'}}$	-6.92		
$^{2}J_{P_AP_X}$	3.80		
R value		1.19 %	

2.8 Reaction of $[K(thf)_{0.7}][Cp'''Co(\eta^3\text{-}P_3)]$ ($[K(thf)_{0.7}][\mathbf{5}]$) with Cy_2PCl

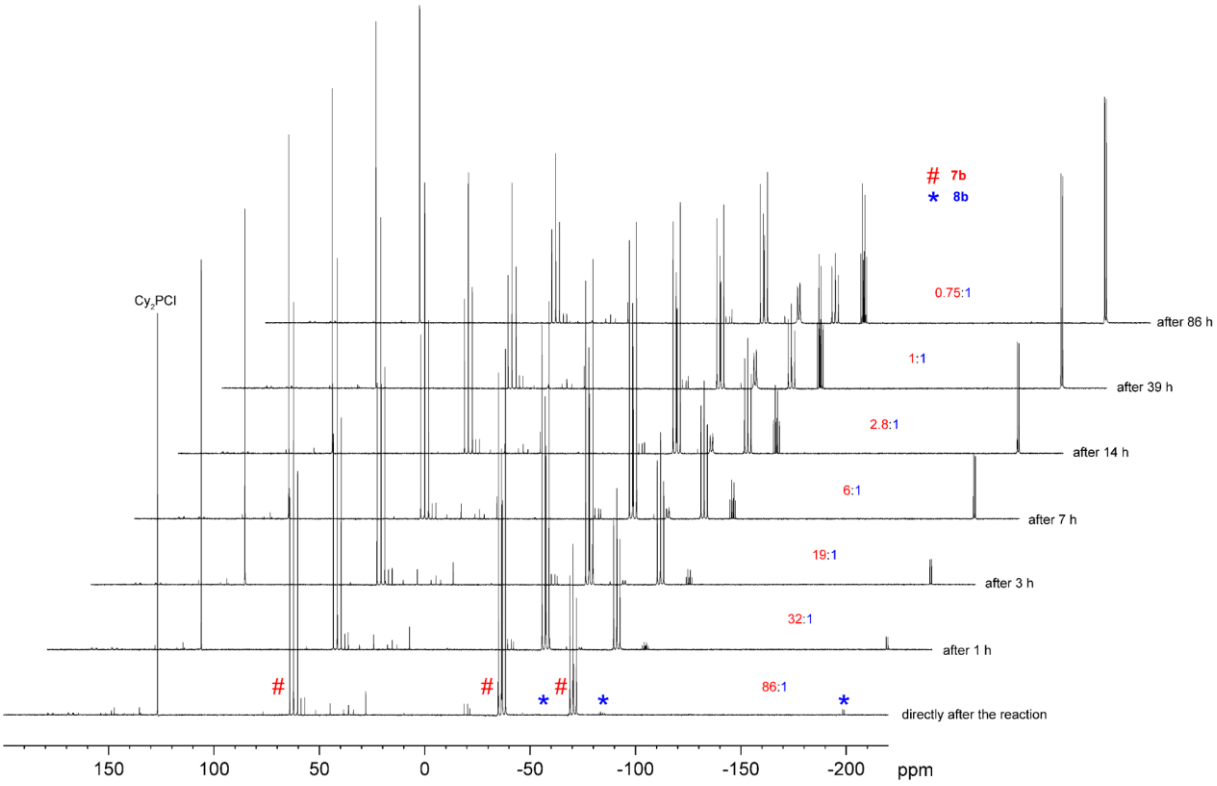


Figure S11: $^{31}P\{^1H\}$ NMR spectra of the reaction of $[K(thf)_{0.7}][\mathbf{5}]$ with Cy_2PCl in toluene-d_8 before thermolysis and after 1, 3, 7,14, 39 and 86 h at 60 °C.

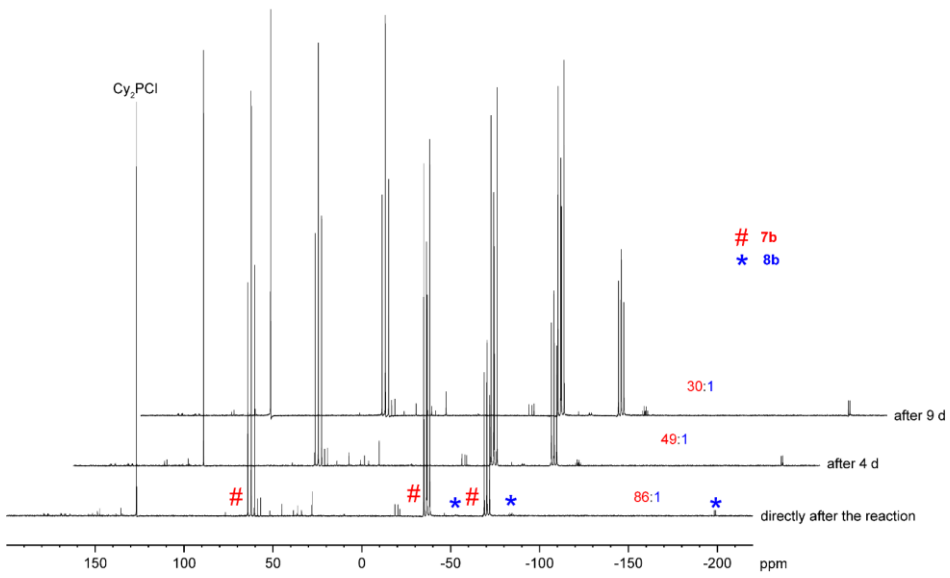


Figure S12: $^{31}P\{^1H\}$ NMR spectra of the reaction of $[K(thf)_{0.7}][\mathbf{5}]$ with Cy_2PCl in toluene-d_8 at room temperature directly after the reaction and after 4 and 9 days.

2.9 [Cp’’’Co(η^3-P_4tBu_2)] (7c)

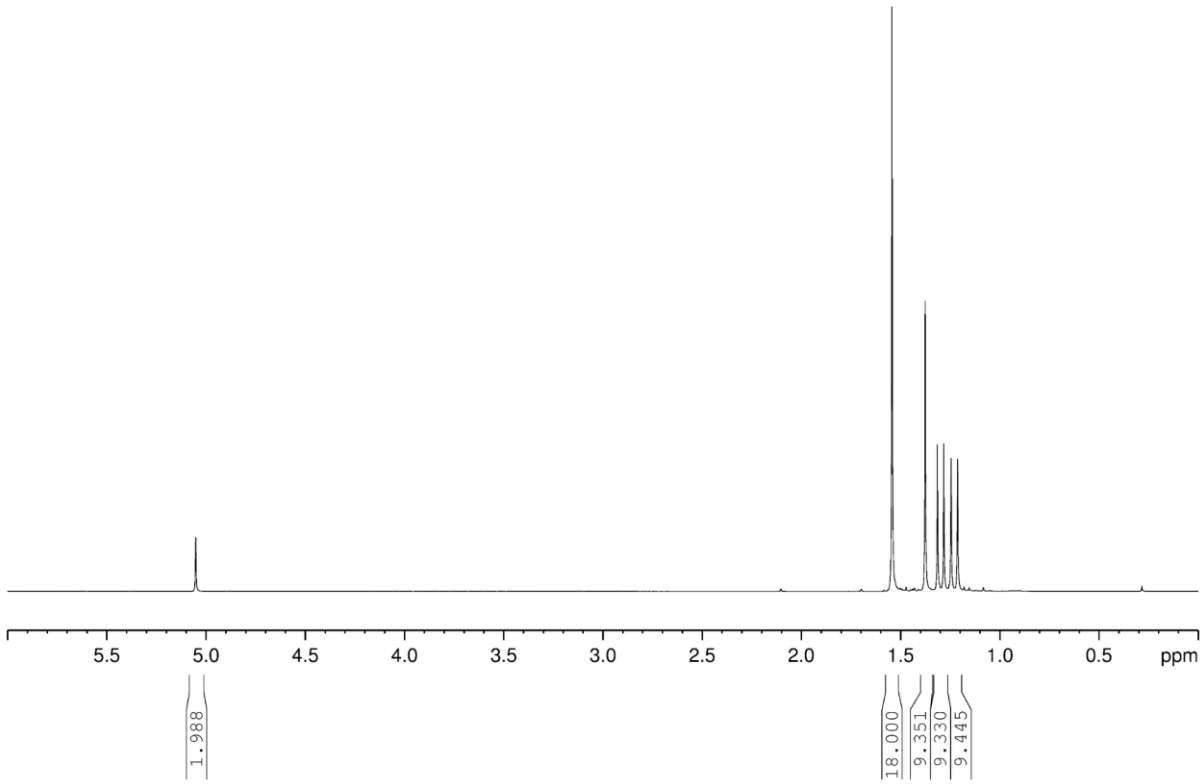


Figure S13: ^{1}H NMR spectrum of **7c** in C_6D_6 at room temperature.

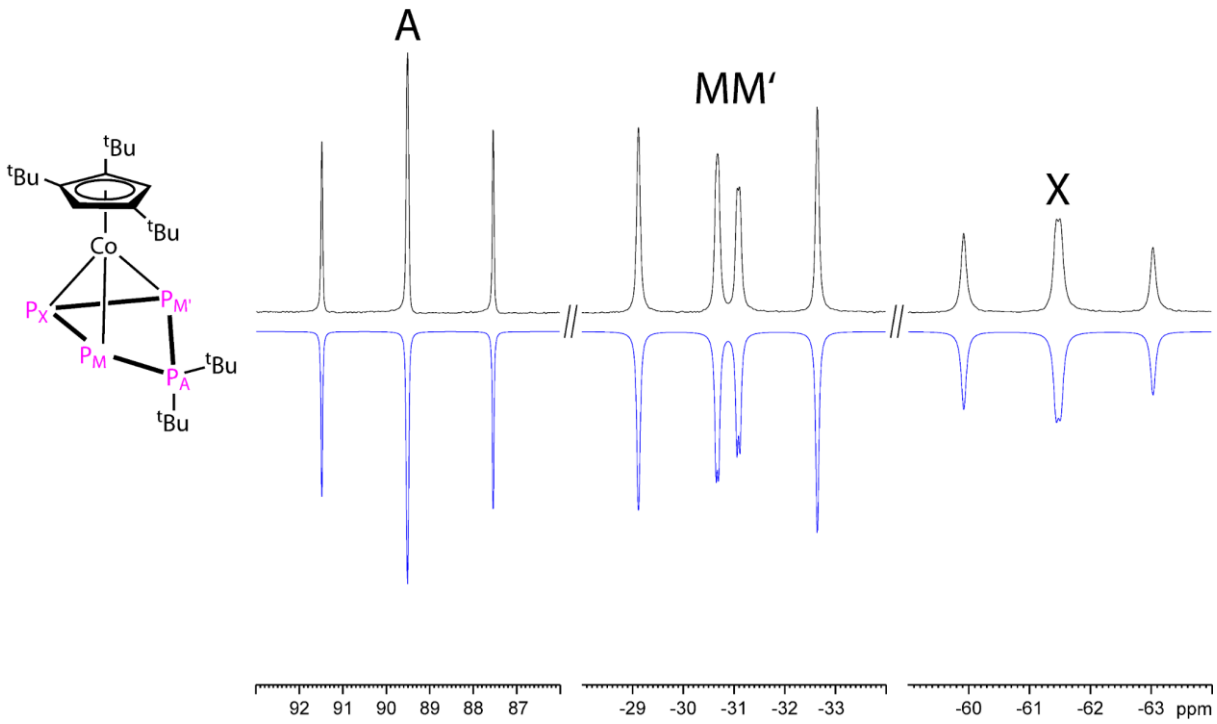


Figure S14: $^{31}P\{^{1}H\}$ NMR spectrum of **7c** in C_6D_6 at room temperature (experimental (black) and simulated (blue)).

Table S3: Coupling constants and chemical shifts obtained from the simulation of the $^{31}P\{^{1}H\}$ NMR spectrum.

coupling constants [Hz]		chemical shifts [ppm]	
$^{1}J_{P_AP_M}$	319.64	P_A	89.50
$^{1}J_{P_AP_{M'}}$	319.71	P_M	-30.89
$^{1}J_{P_MP_X}$	252.52	P_M	-30.90
$^{1}J_{P_MP_{X'}}$	252.01	P_X	-61.43
$^{2}J_{P_MP_{M'}}$	3.16		
$^{2}J_{P_AP_X}$	2.41		
R value		0.28 %	

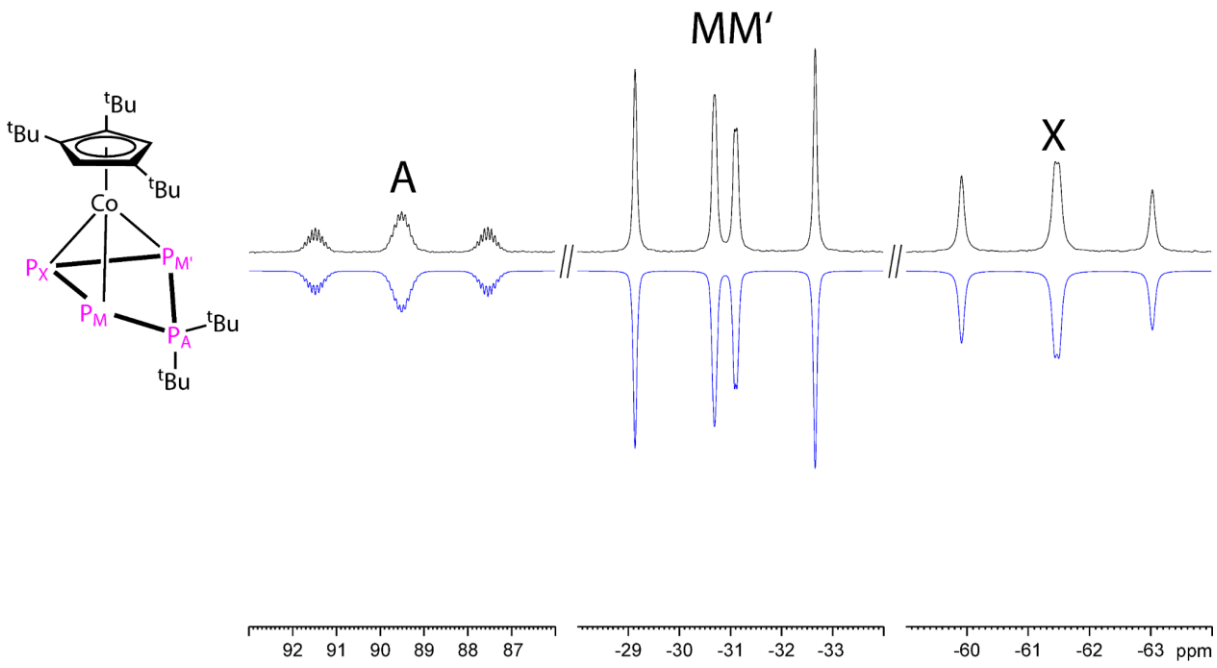


Figure S15: ^{31}P NMR spectrum of **7c** in C_6D_6 at room temperature (experimental (black) and simulated (blue)).

Table S4: Coupling constants and chemical shifts obtained from the simulation of the ^{31}P NMR spectrum.

coupling constants [Hz]		chemical shifts [ppm]	
$^1J_{P_AP_M}$	319.72	P_A	89.50
$^1J_{P_AP_{M'}}$	319.55	P_M	-30.91
$^1J_{P_MP_X}$	252.27	P_M	-30.91
$^1J_{P_MP_{X'}}$	252.33	P_X	-61.43
$^2J_{P_MP_{M'}}$	5.04		
$^2J_{P_AP_X}$	-0.16		
$^3J_{P_AH}$	13.13		
$^4J_{P_MH}$	1.05		
$^4J_{P_{M'}H}$	2.88		
$^5J_{P_XH}$	1.85	$^3J_{P_AH}$	13.13
R value		0.38 %	

2.10 Reaction of $[K(thf)_{0.7}][Cp'''Co(\eta^3\text{-}P_3)]$ ($[K(thf)_{0.7}][\mathbf{5}]$) with $^tBu_2PCl$

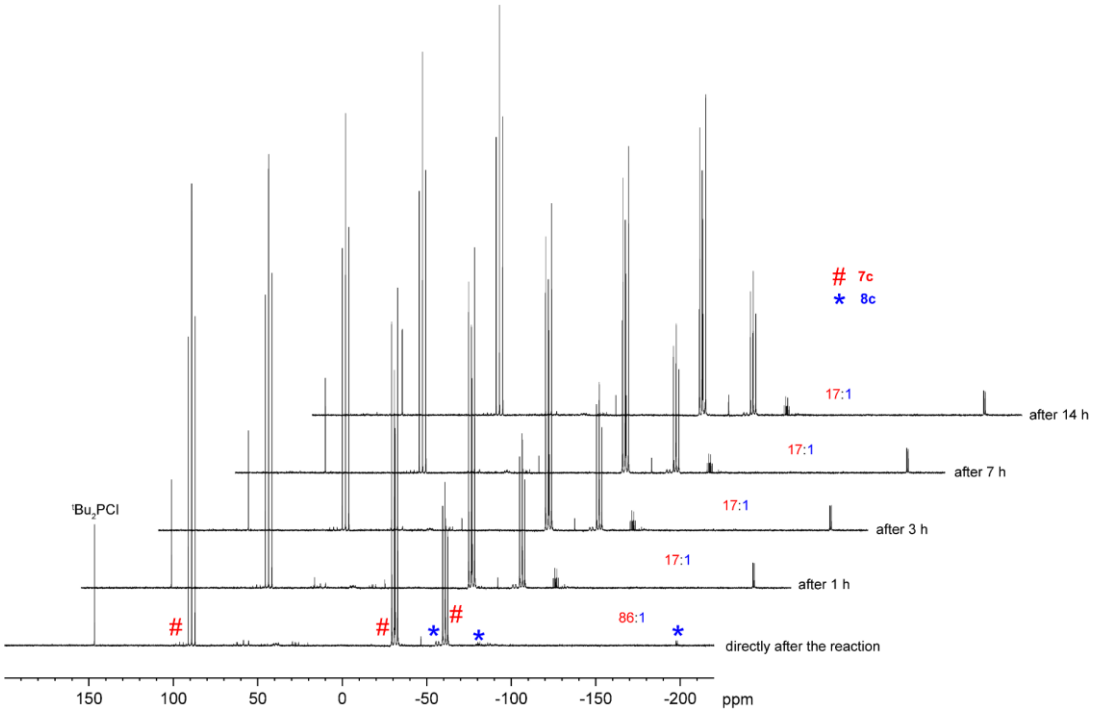


Figure S16: $^{31}P\{^1H\}$ NMR spectra of the reaction of $[K(thf)_{0.7}][\mathbf{5}]$ with $^tBu_2PCl$ in toluene-d_8 before thermolysis and after 1, 3, 7 and 14 h at 60 °C.

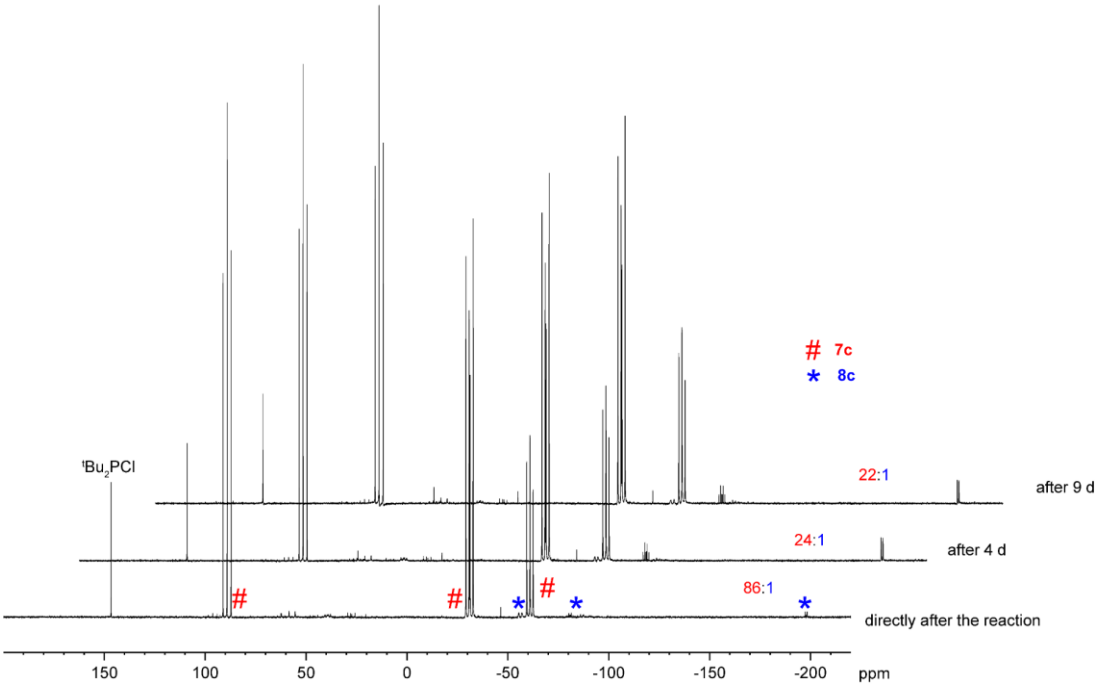


Figure S17: $^{31}P\{^1H\}$ NMR spectra of the reaction of $[K(thf)_{0.7}][\mathbf{5}]$ with $^tBu_2PCl$ in toluene-d_8 at room temperature directly after the reaction and after 4 and 9 days.

2.11 [Cp'''Co(η^2:η^1-P_4Ph_2)] (8a)

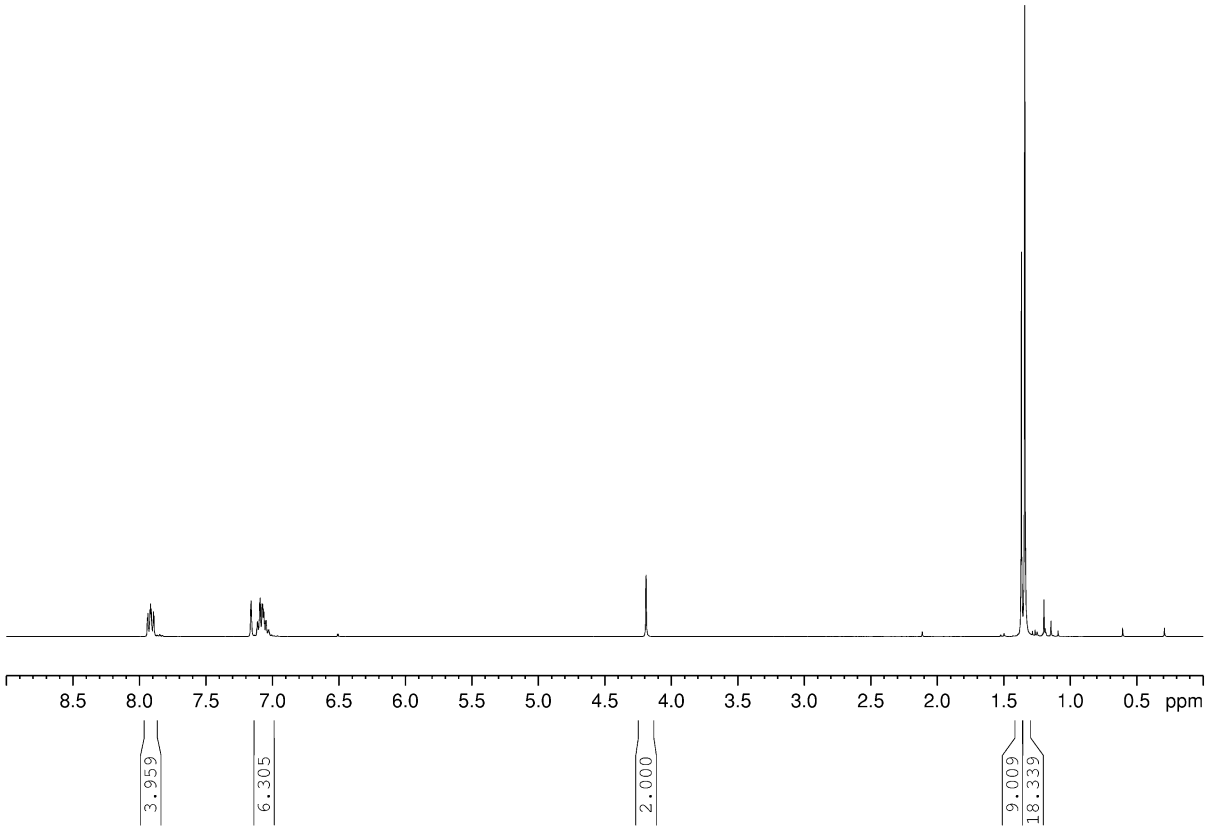


Figure S18: ^{1}H NMR spectrum of **8a** in C_6D_6 at room temperature.

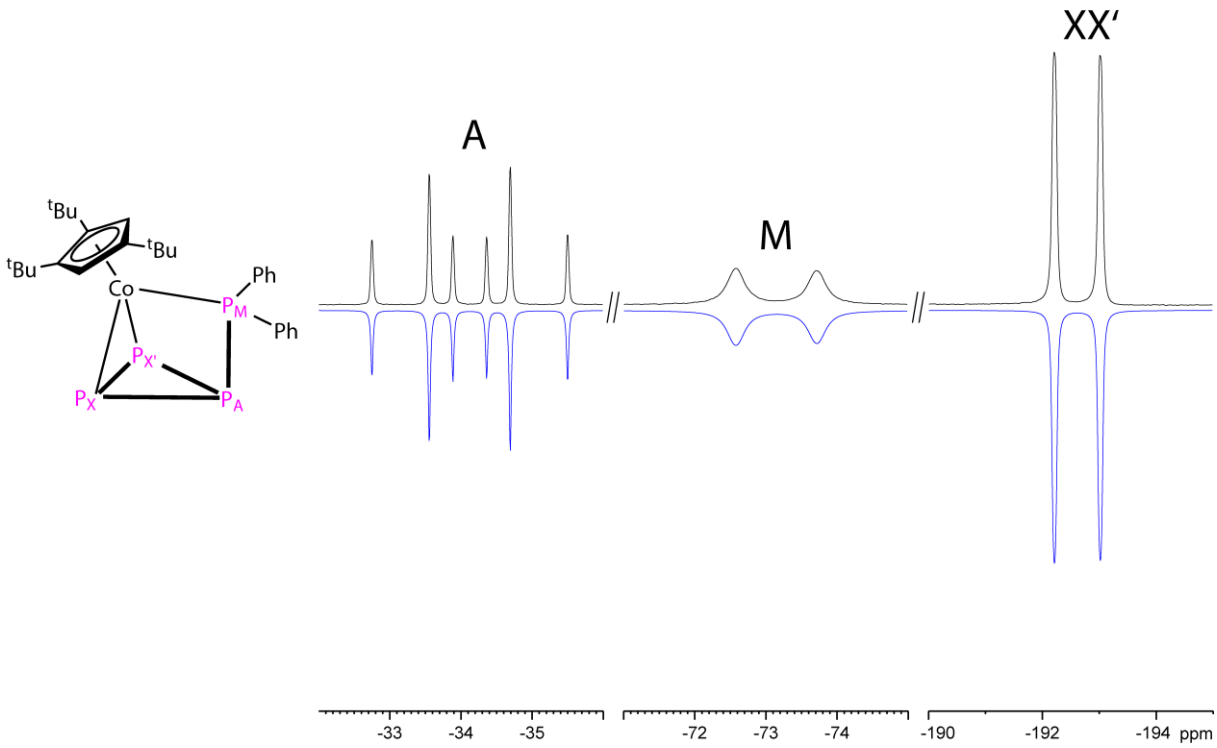


Figure S19: $^{31}P\{^{1}H\}$ NMR spectrum of **8a** in C_6D_6 at room temperature (experimental (black) and simulated (blue)).

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

coupling constants [Hz]		chemical shifts [ppm]	
$^{1}J_{P_AP_M}$	184.31	P_A	-34.13
$^{1}J_{P_AP_X}$	130.58	P_M	-73.14
$^{1}J_{P_AP_{X'}}$	130.54	P_X	-192.62
$^{2}J_{P_MP_X}$	4.00	$P_{X'}$	-192.62
$^{2}J_{P_MP_{X'}}$	-11.07		
$^{1}J_{P_XP_{X'}}$	-2.00		
R value		0.32 %	

2.12 [Cp'''Co(η²:η¹-P₄Cy₂)] (8b)

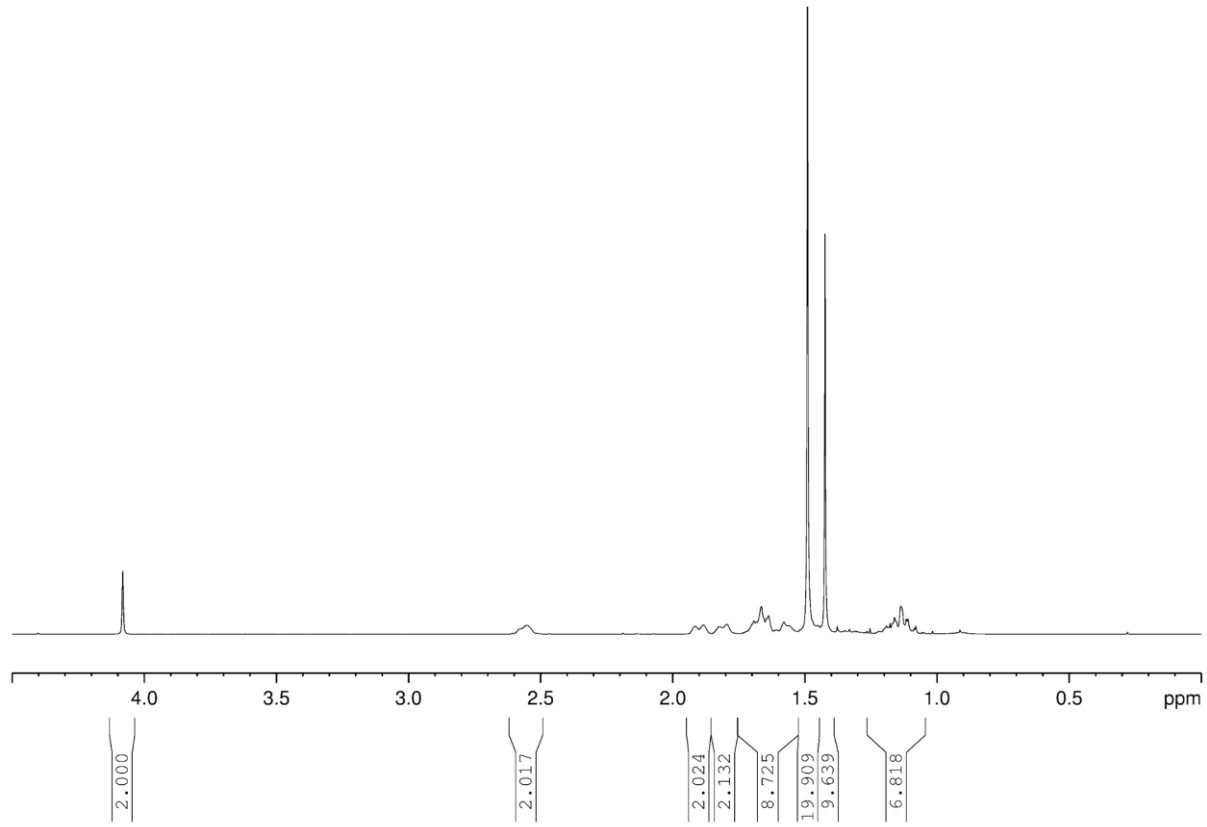


Figure S20: ^{1}H NMR spectrum of **8b** in C_6D_6 at room temperature.

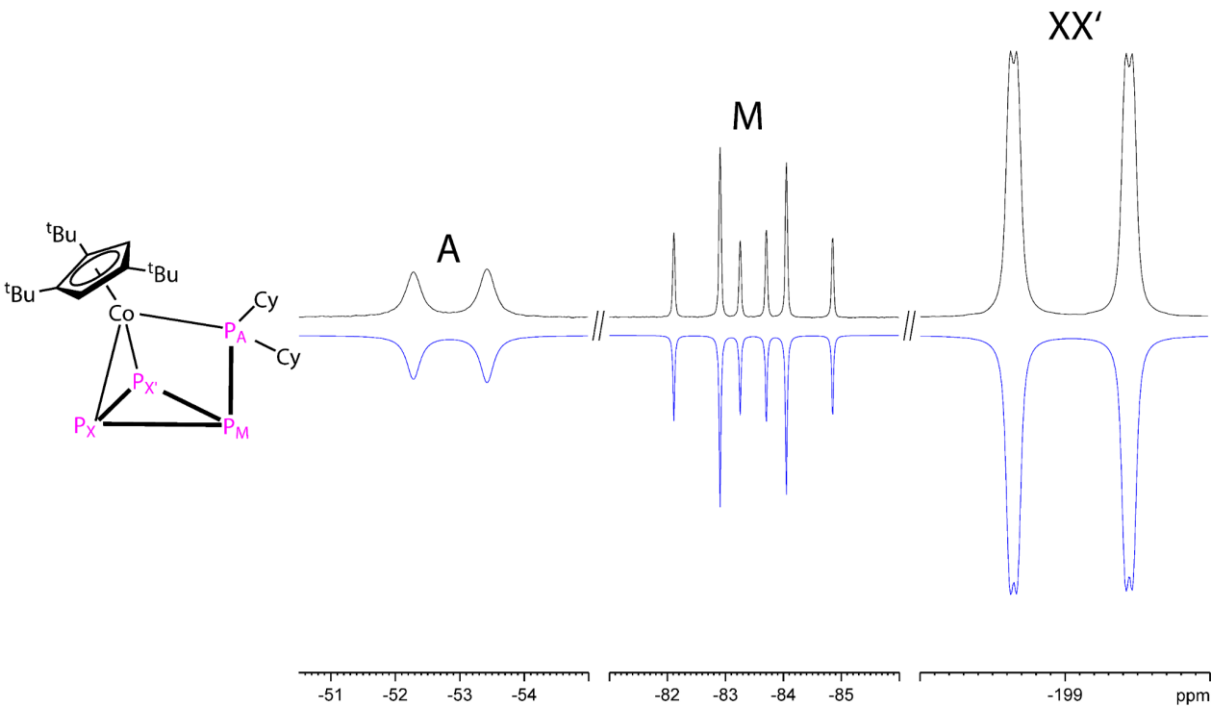


Figure S21: $^{31}P\{^{1}H\}$ NMR spectrum of **8b** in C_6D_6 at room temperature (experimental (black) and simulated (blue)).

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

coupling constants [Hz]		chemical shifts [ppm]	
$^{1}J_{P_A P_M}$	185.20	P_A	-52.86
$^{1}J_{P_M P_X}$	129.18	P_M	-83.47
$^{1}J_{P_M P_{X'}}$	129.23	P_X	-199.02
$^{2}J_{P_A P_X}$	-3.22	$P_{X'}$	-199.07
$^{2}J_{P_A P_{X'}}$	2.92		
$^{1}J_{P_X P_{X'}}$	-.230		
R value		0.34 %	

2.13 [Cp'''Co(η²:η¹-P₄ᵗBu₂)] (8c)

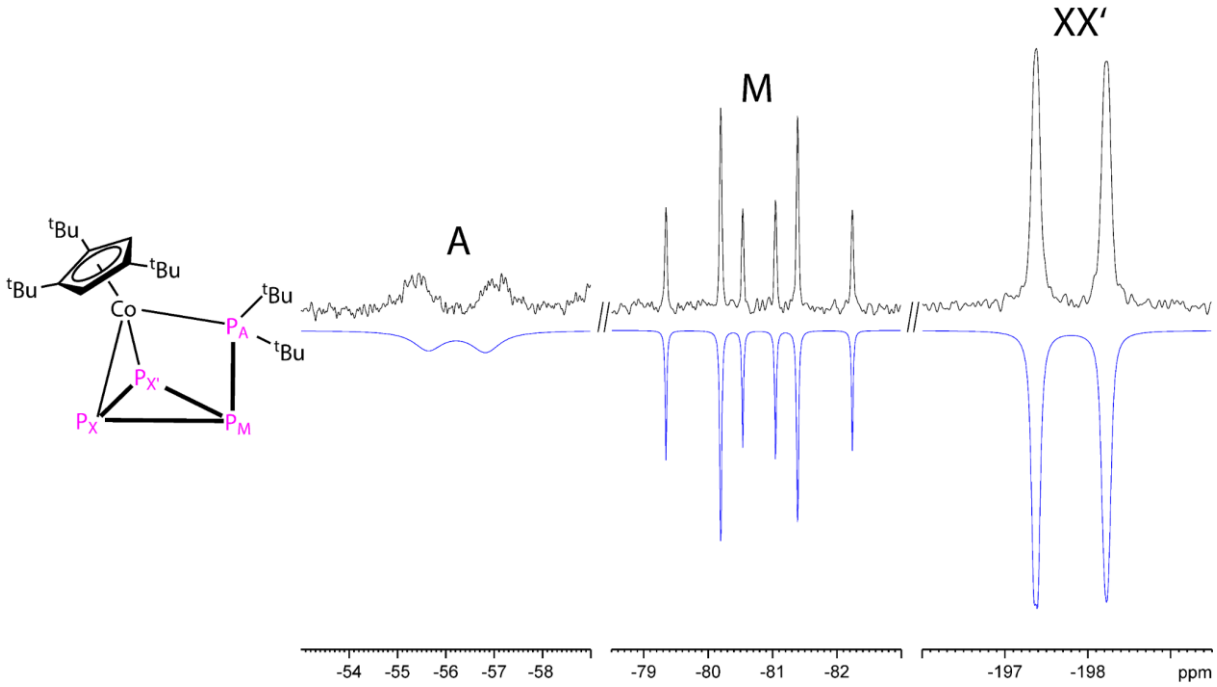


Figure S22: Part of the $^{31}P\{^{1}H\}$ NMR spectrum of the thermolysis of **7c** in toluene-d_8 after 7h at 60 °C at room temperature (experimental (black) and simulated (blue)).

Table S7: Coupling constants and chemical shifts obtained from the partial simulation of the $^{31}P\{^{1}H\}$ NMR spectrum.

coupling constants [Hz]		chemical shifts [ppm]	
$^{1}J_{P_AP_M}$	193.24	P_A	-56.24
$^{1}J_{P_MP_X}$	136.85	P_M	-80.78
$^{1}J_{P_MP_{X'}}$	138.95	P_X	-197.78
$^{2}J_{P_AP_X}$	8.49	$P_{X'}$	-197.81
$^{2}J_{P_AP_{X'}}$	8.18		
$^{1}J_{P_XP_{X'}}$	-3.63		
R value		3.15 %	

2.14 Reaction of $[K(thf)_{0.8}][Cp'''Co(\eta^3\text{-}As_3)]$ ($[K(thf)_{0.8}][6]$) with Ph_2PCl

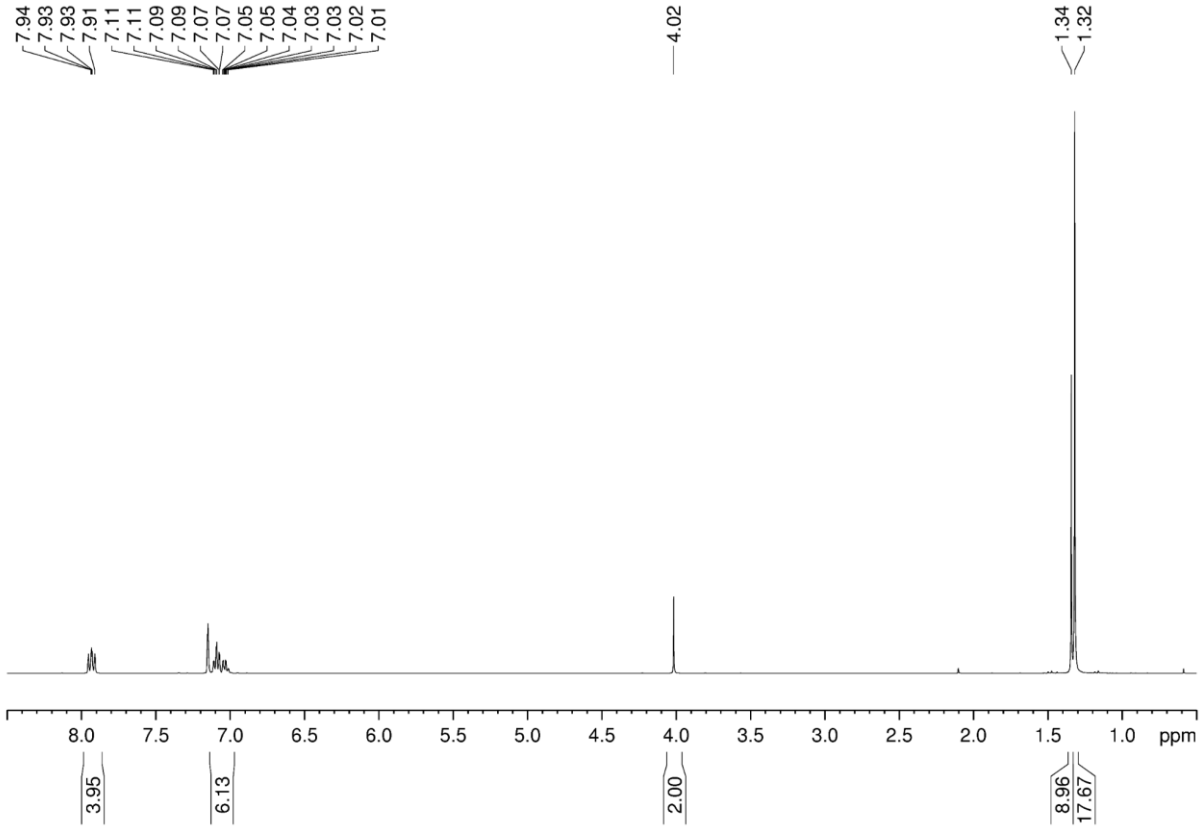


Figure S23: ^{1}H NMR spectrum of **10a** in C_6D_6 at room temperature.

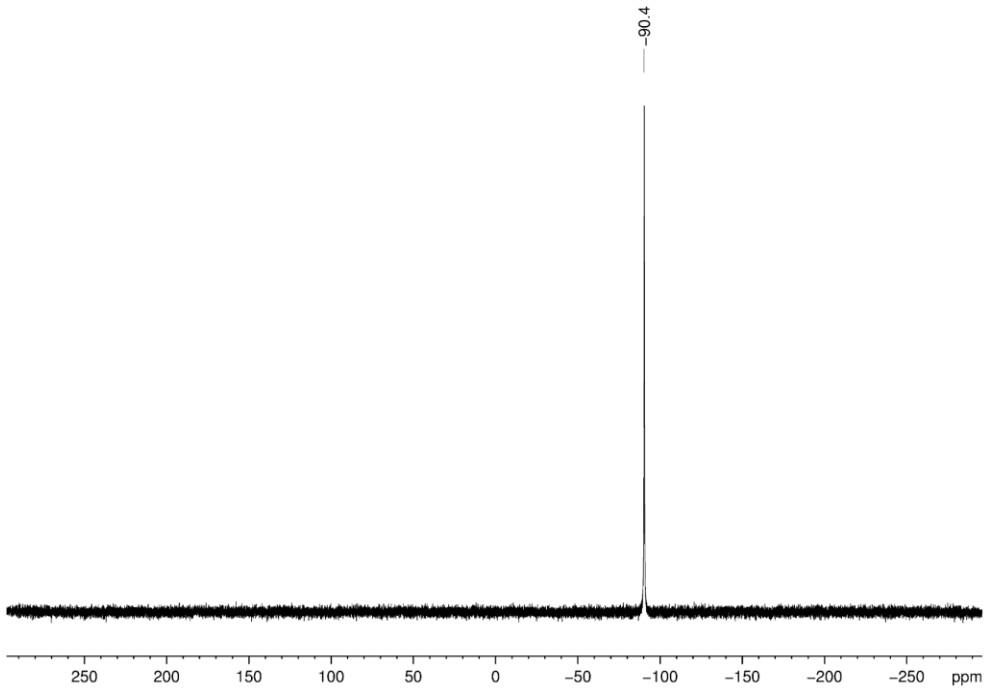


Figure S24: $^{31}P\{^{1}H\}$ NMR spectrum of **10a** in C_6D_6 at room temperature.

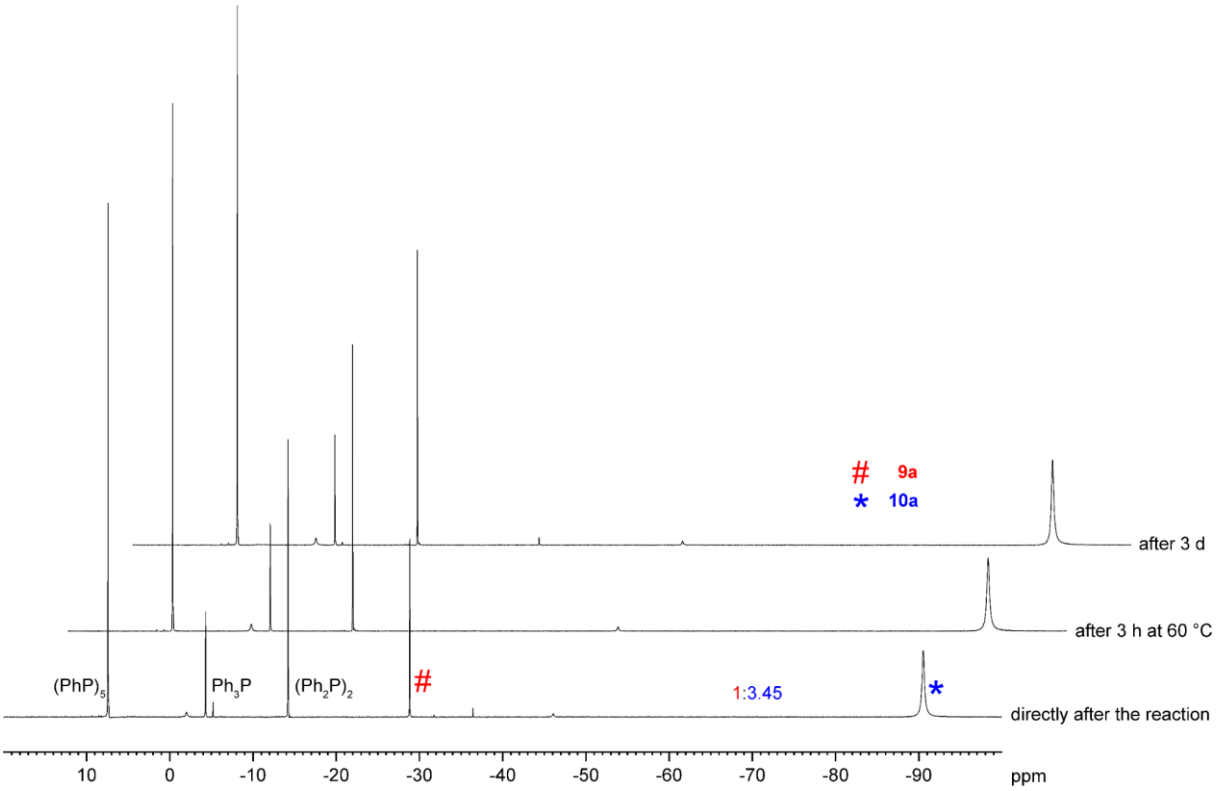


Figure S25: $^{31}P\{^{1}H\}$ NMR spectra of the reaction of $[K(thf)_{0.8}]$[**6**] with Ph_2PCl in toluene-d_8 before thermolysis and after 3 h at 60 °C and the $^{31}P\{^{1}H\}$ NMR spectrum after 3 days at room temperature.

2.15 [Cp'''Co(η^3-As_3PCy_2)] (9b) + [Cp'''Co(η^2:η^1-As_3PCy_2)] (10b)

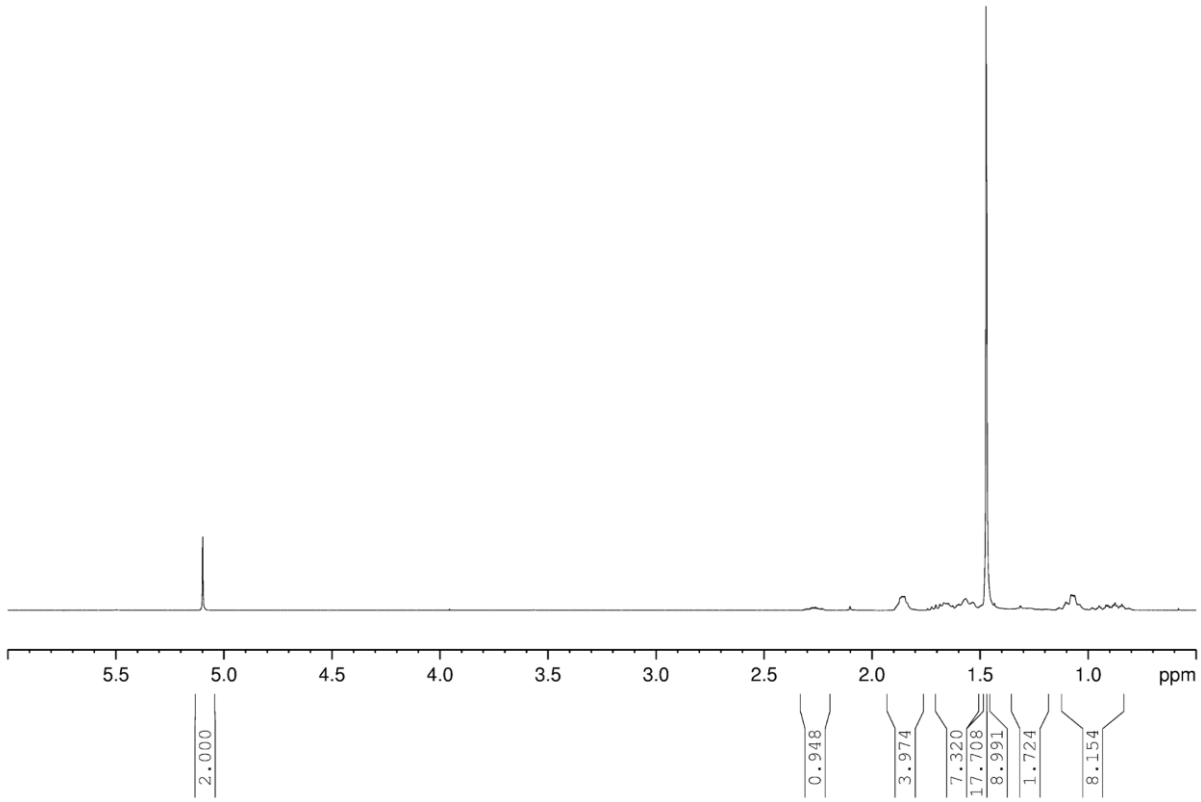


Figure S26: ^{1}H NMR spectrum of **9b** in C_6D_6 at room temperature.

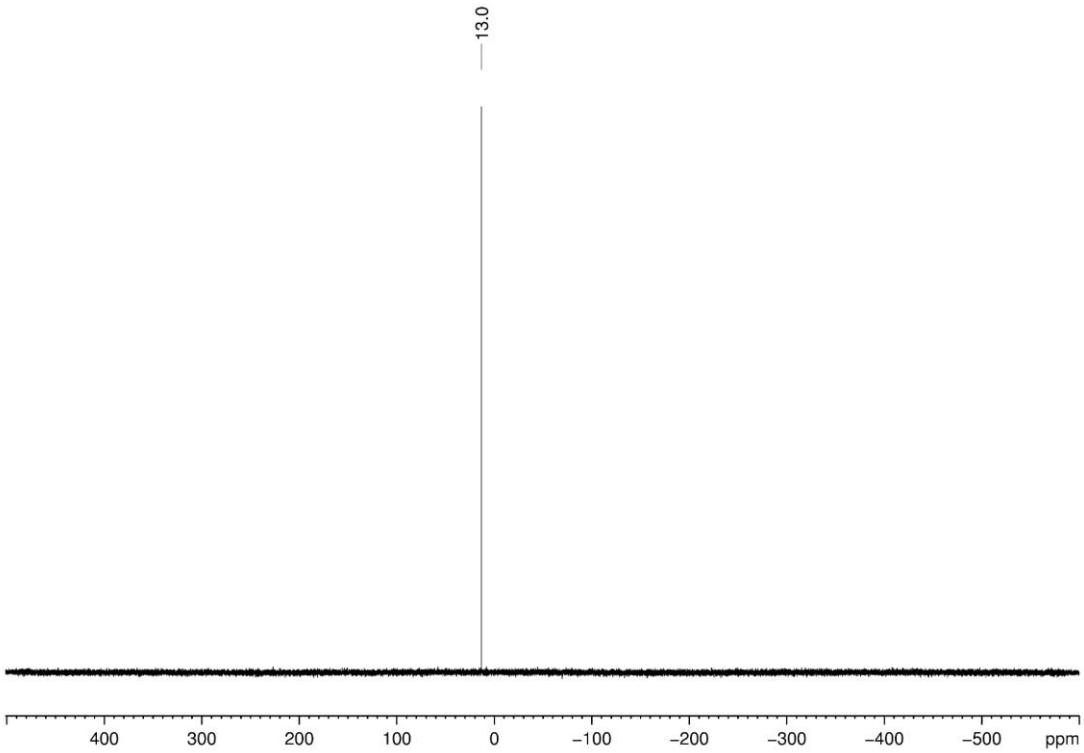


Figure S27: $^{31}P\{^{1}H\}$ NMR spectrum of **9b** in C_6D_6 at room temperature.

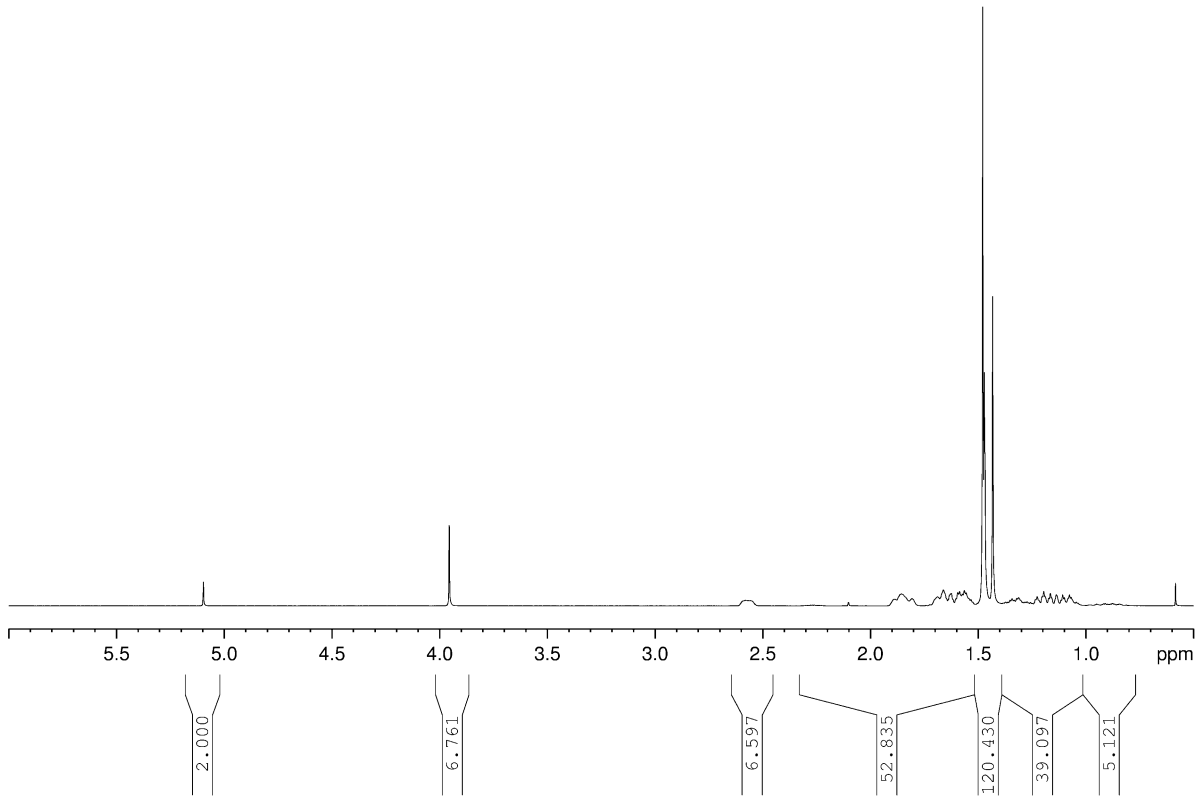


Figure S28: ^{1}H NMR spectrum of a mixture of **9b** and **10b** (1:3) in C_6D_6 at room temperature.

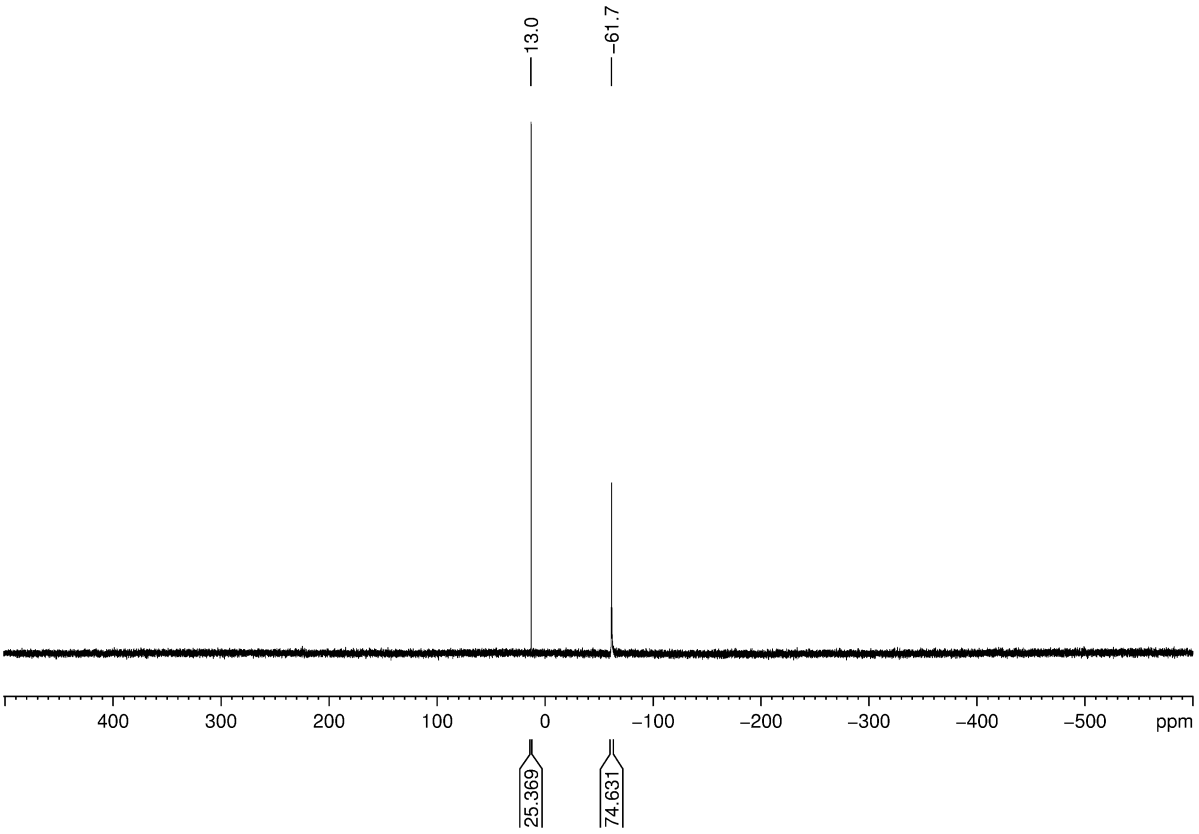


Figure S29: $^{31}P\{^{1}H\}$ NMR spectrum of a mixture of **9b** and **10b** (1:3) in C_6D_6 at room temperature.

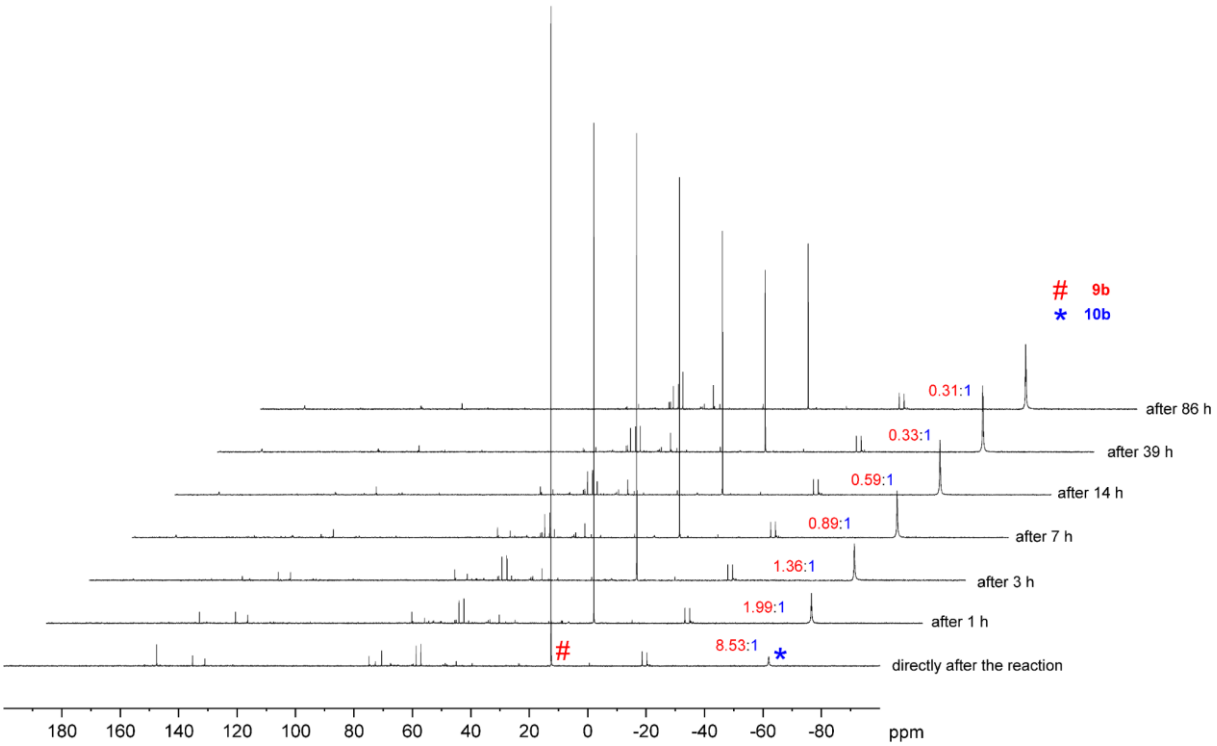


Figure S30: $^{31}P\{^{1}H\}$ NMR spectra of the reaction of $[K(thf)_{0.8}]$[**6**] with Cy_2PCl in toluene-d_8 before thermolysis and after 1, 3, 7, 14, 39 and 86 h at 60 °C.

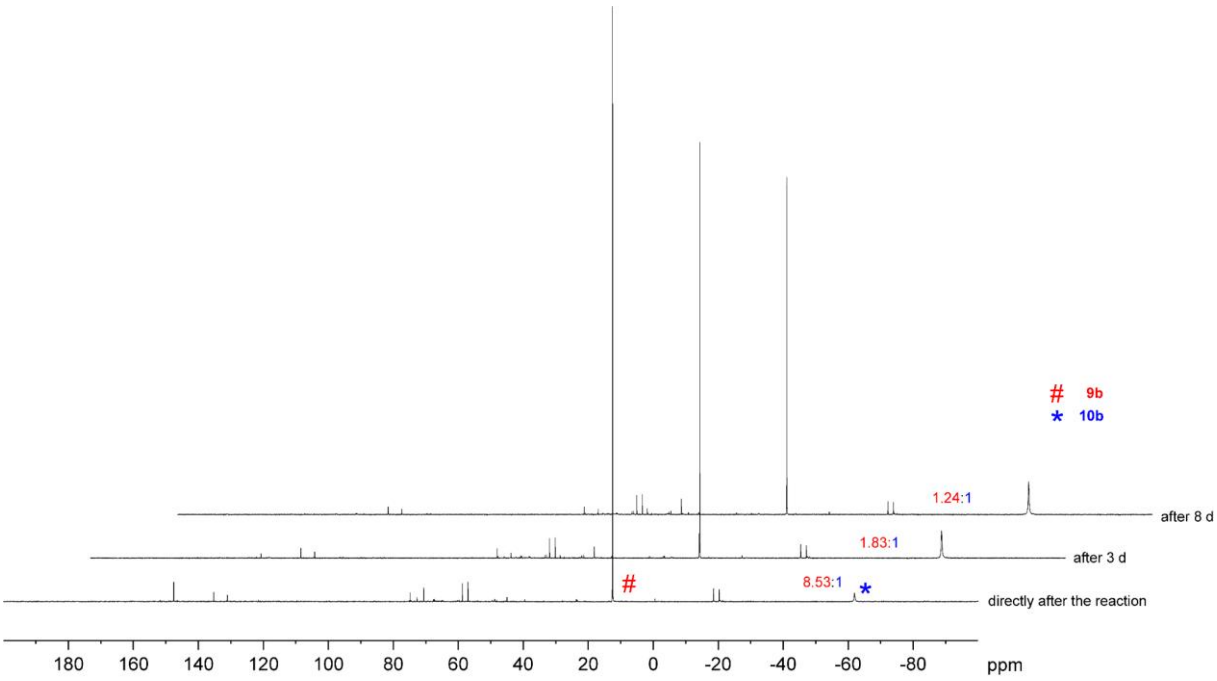


Figure S31: $^{31}P\{^{1}H\}$ NMR spectra of the reaction of $[K(thf)_{0.8}]$[**6**] with Cy_2PCl in toluene-d_8 at room temperature directly after the reaction and after 3 and 8 days.

2.16 [Cp'''Co(η^3-As$_3$P^{t}Bu$_2$)] (9c)

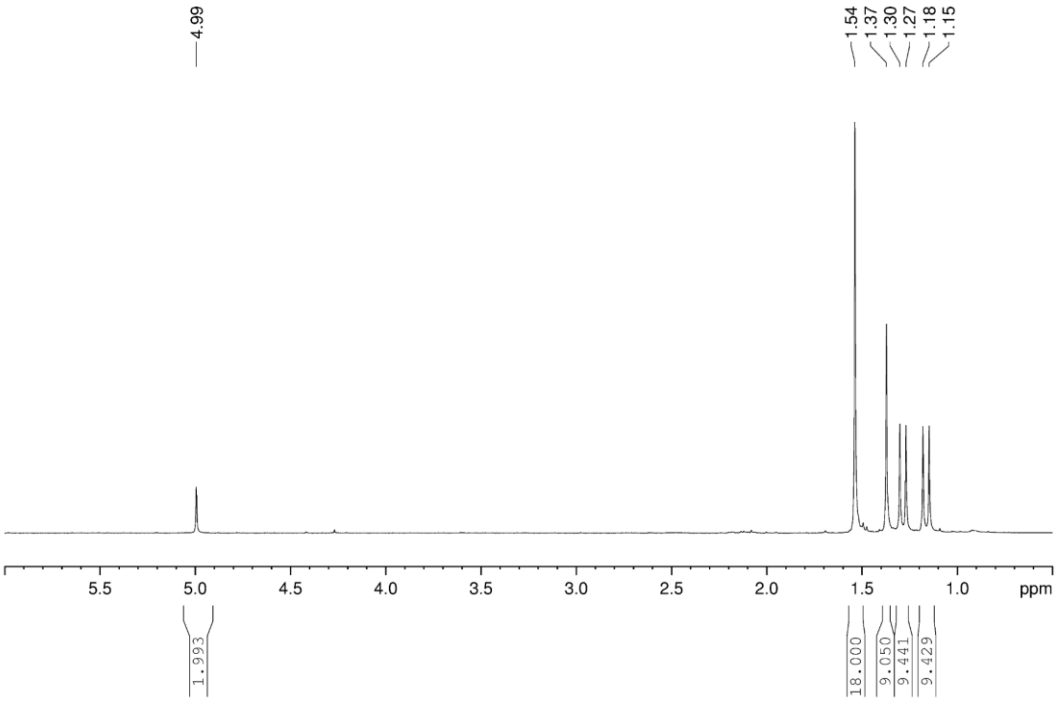


Figure S32: ^{1}H NMR spectrum of **9c** in C_6D_6 at room temperature.

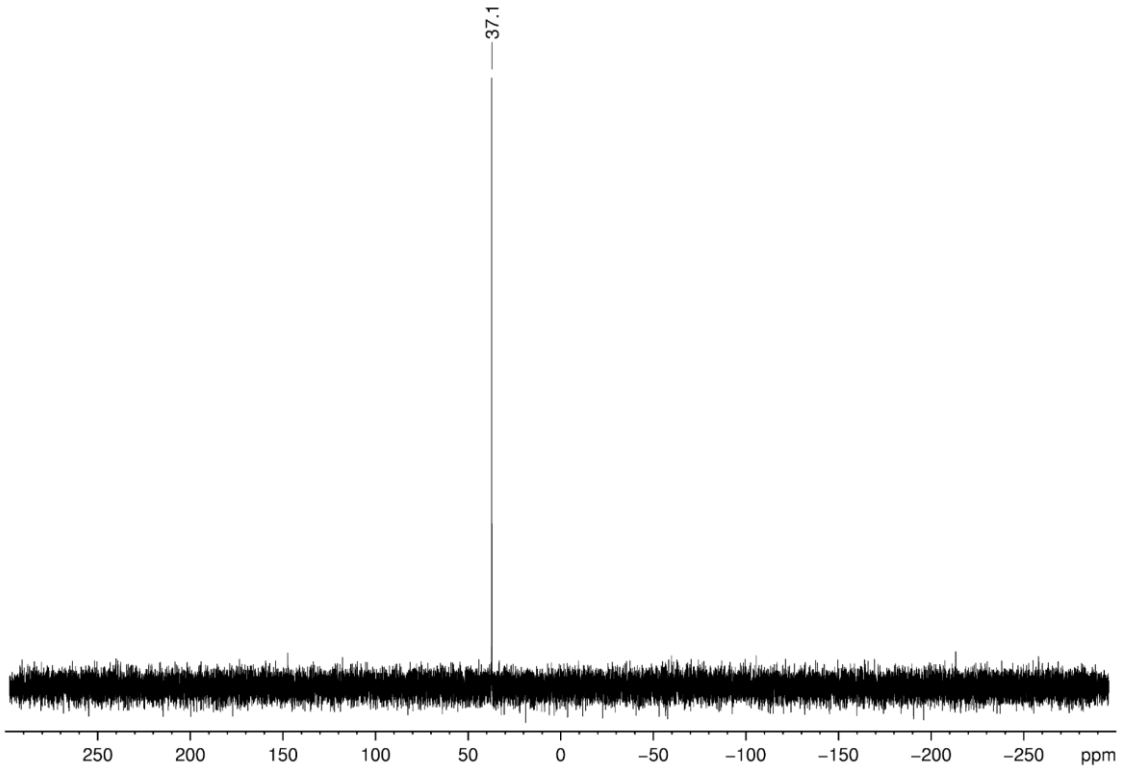


Figure S33: ^{31}P{^{1}H} NMR spectrum of **9c** in C_6D_6 at room temperature.

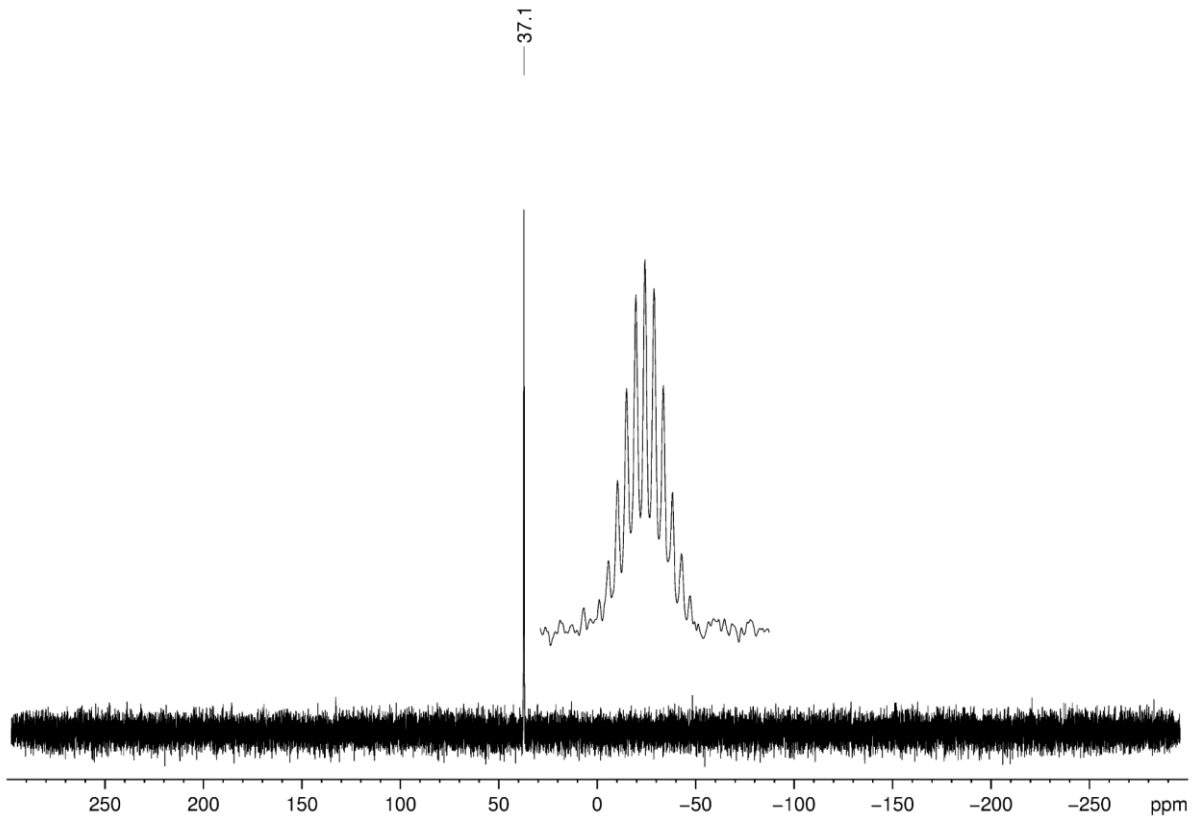


Figure S34: ^{31}P NMR spectrum of **9c** in C_6D_6 at room temperature.

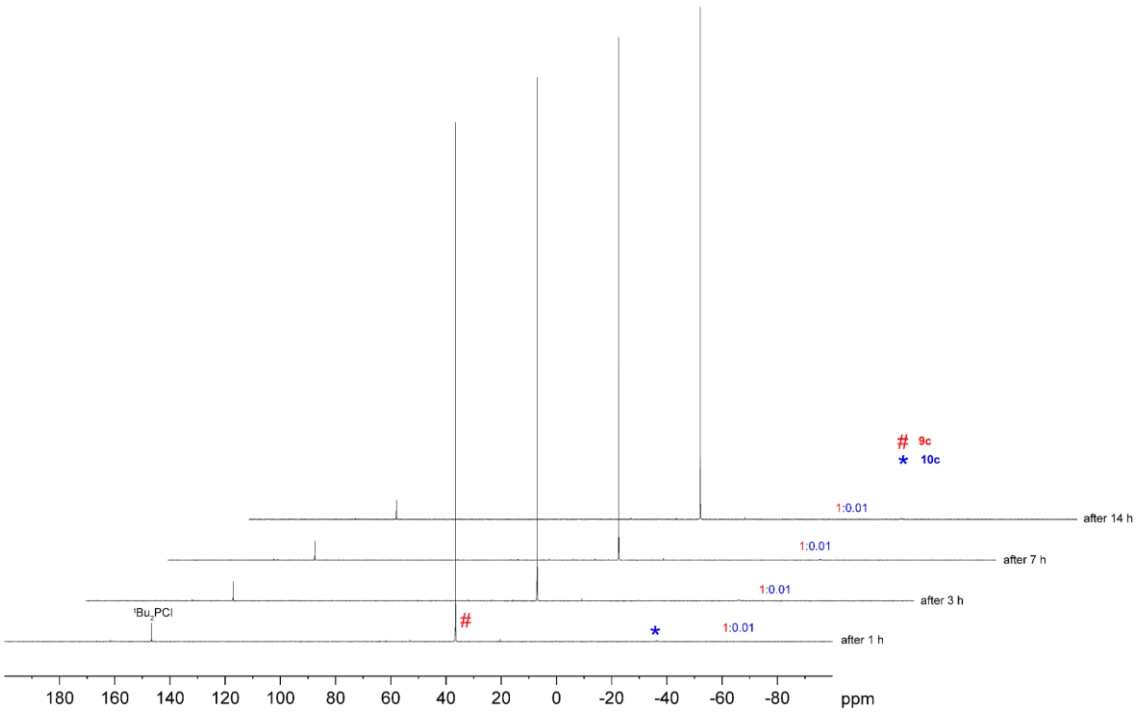


Figure S35: $^{31}P\{^1H\}$ NMR spectra of the reaction of $[K(thf)_{0.8}]$[**6**] with $^tBu_2PCl$ in toluene-d_8 after 1, 3, 7 and 14 h at 60 °C.

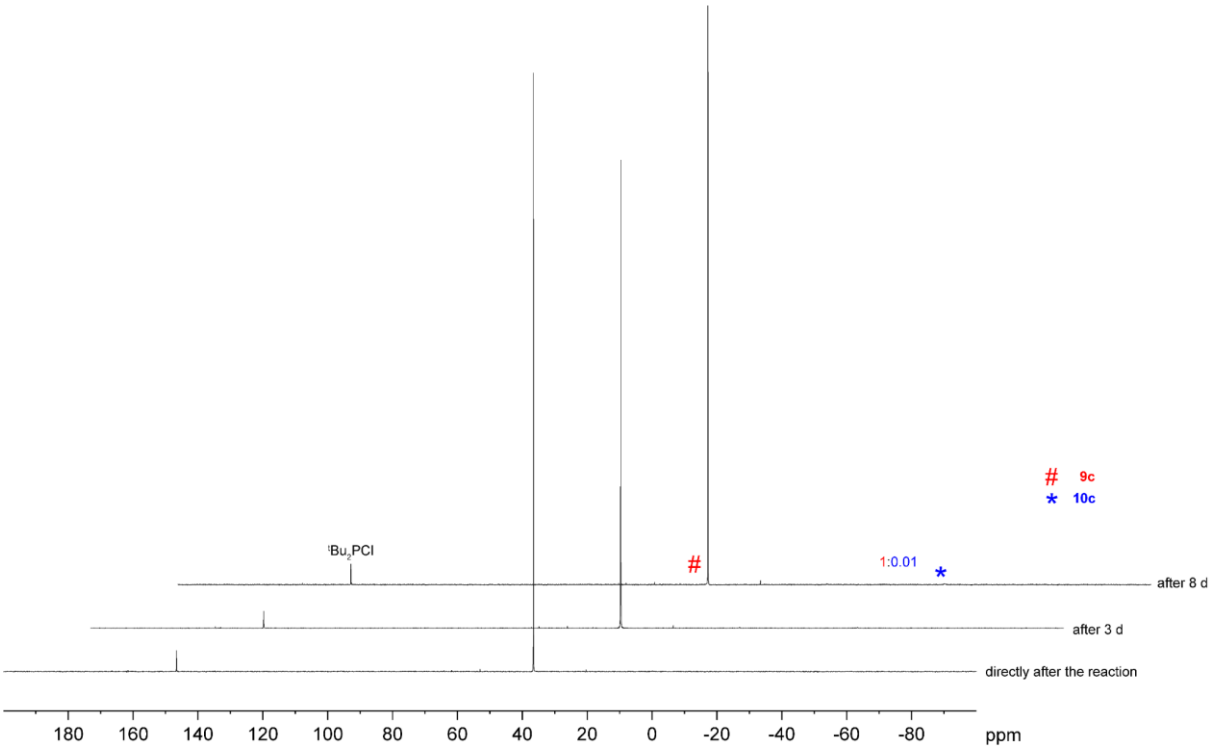


Figure S36: $^{31}P\{^{1}H\}$ NMR spectra of the reaction of $[K(thf)_{0.8}]$[**6**] with $^{t}Bu_2PCl$ in toluene-d_8 at room temperature directly after the reaction and after 3 and 8 days.

2.17 [Cp’’’Co(η^3-P$_3$SiL)] (L = (^{t}BuN)$_2$CPh) (11)

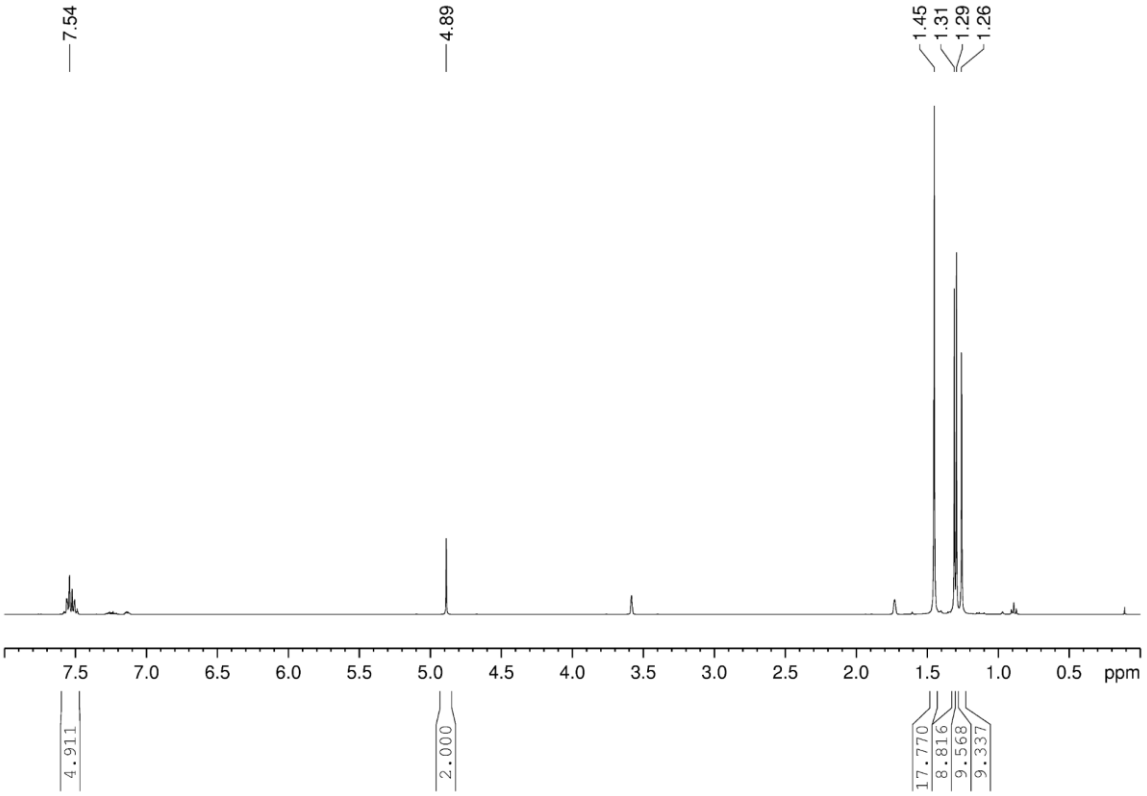


Figure S37: ^{1}H NMR spectrum of **11** in thf-d$_8$ at room temperature.

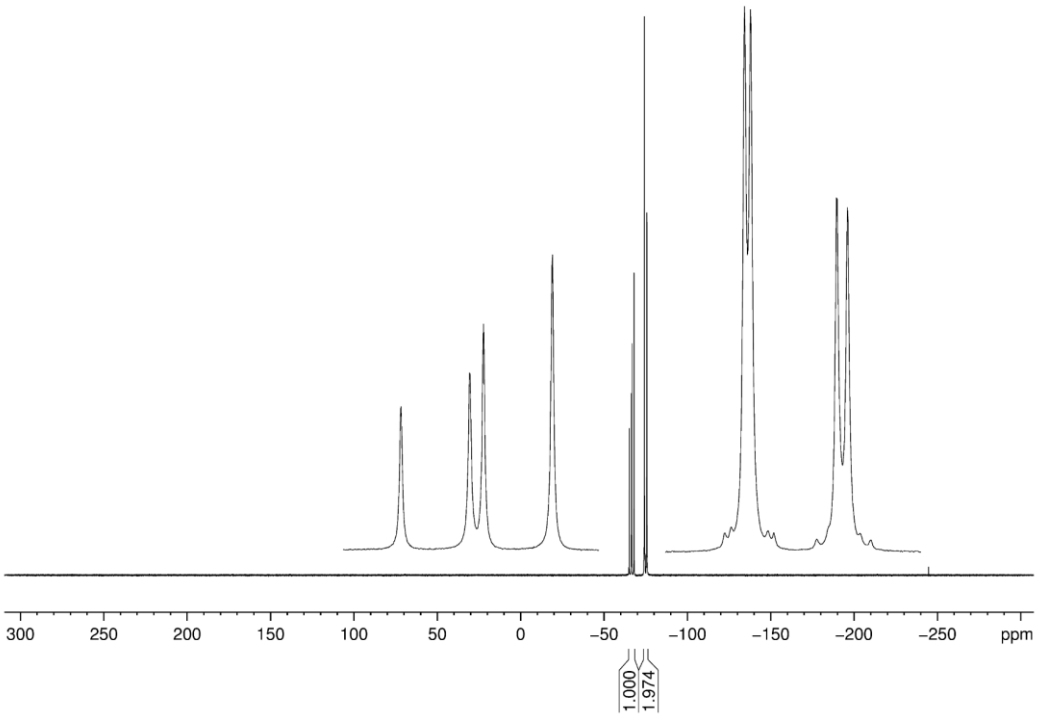


Figure S38: ^{31}P{^{1}H} NMR spectrum of **11** in thf-d$_8$ at room temperature.

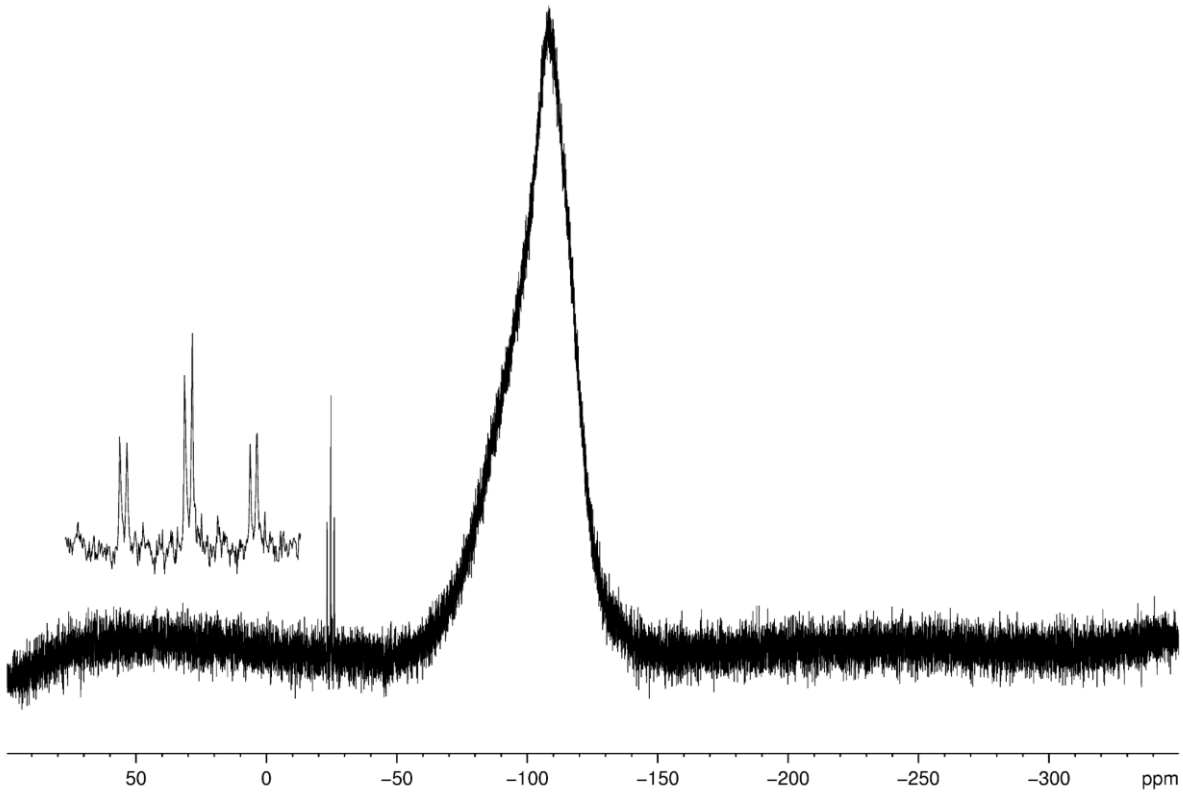


Figure S39: $^{29}Si\{^{1}H\}$ NMR spectrum of **11** in thf-d_8 at room temperature.

2.18 [Cp'''Co(η^3-As_3SiL)] (L = (^{t}BuN)$_2$CPh) (12)

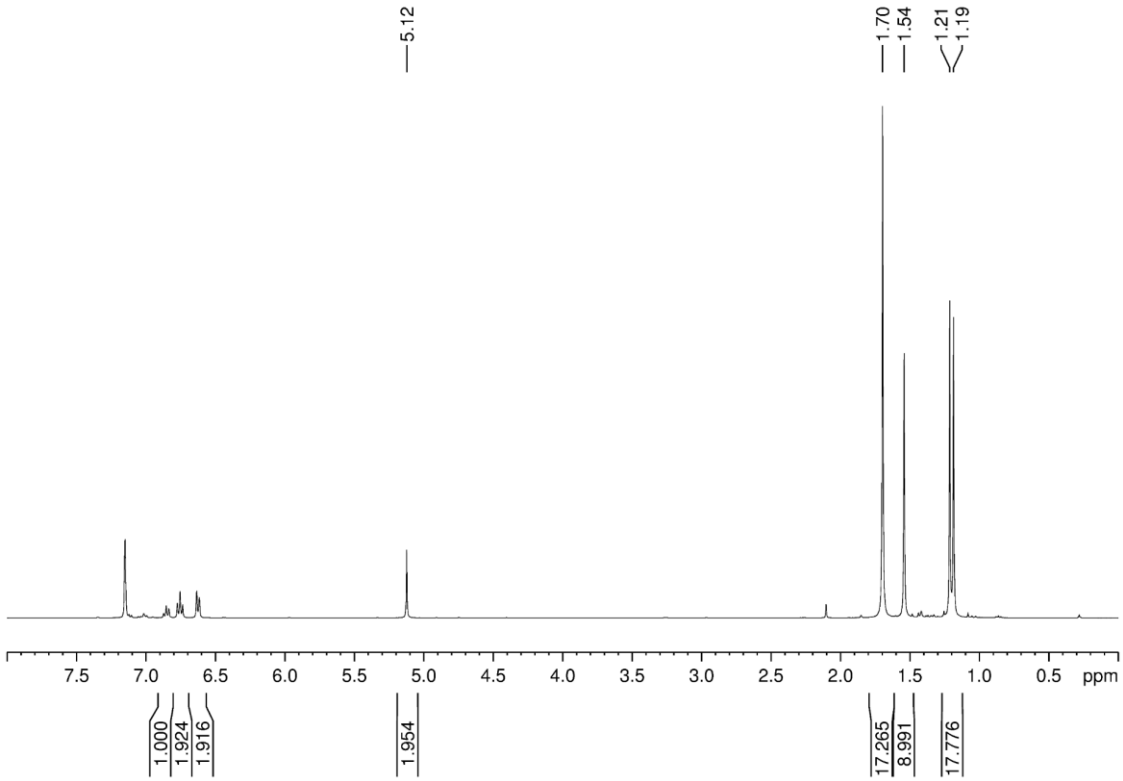


Figure S40: ^{1}H NMR spectrum of **12** in C_6D_6 at room temperature.

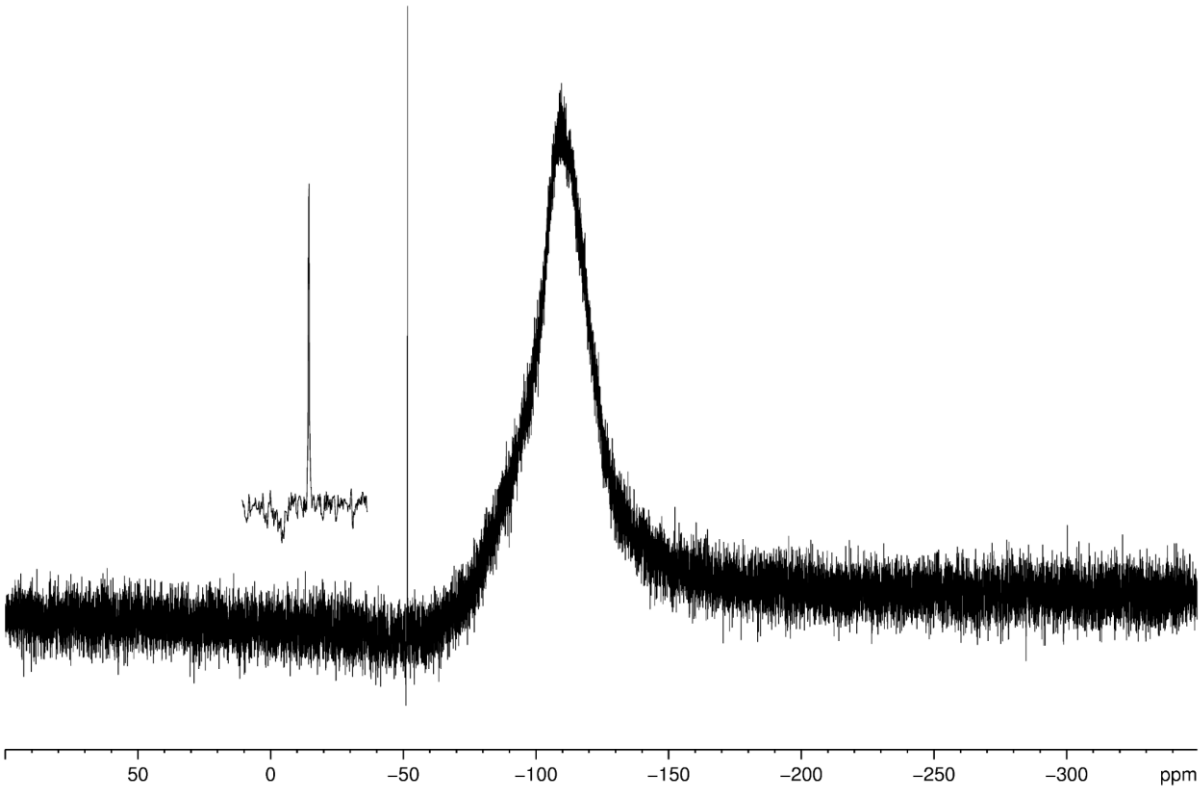


Figure S41: ^{29}Si{^{1}H} NMR spectrum of **12** in C_6D_6 at room temperature.

2.19 [Cp'''Co(η^2:η^1-$As_3P_2Ph_4$)][TEF] (13)

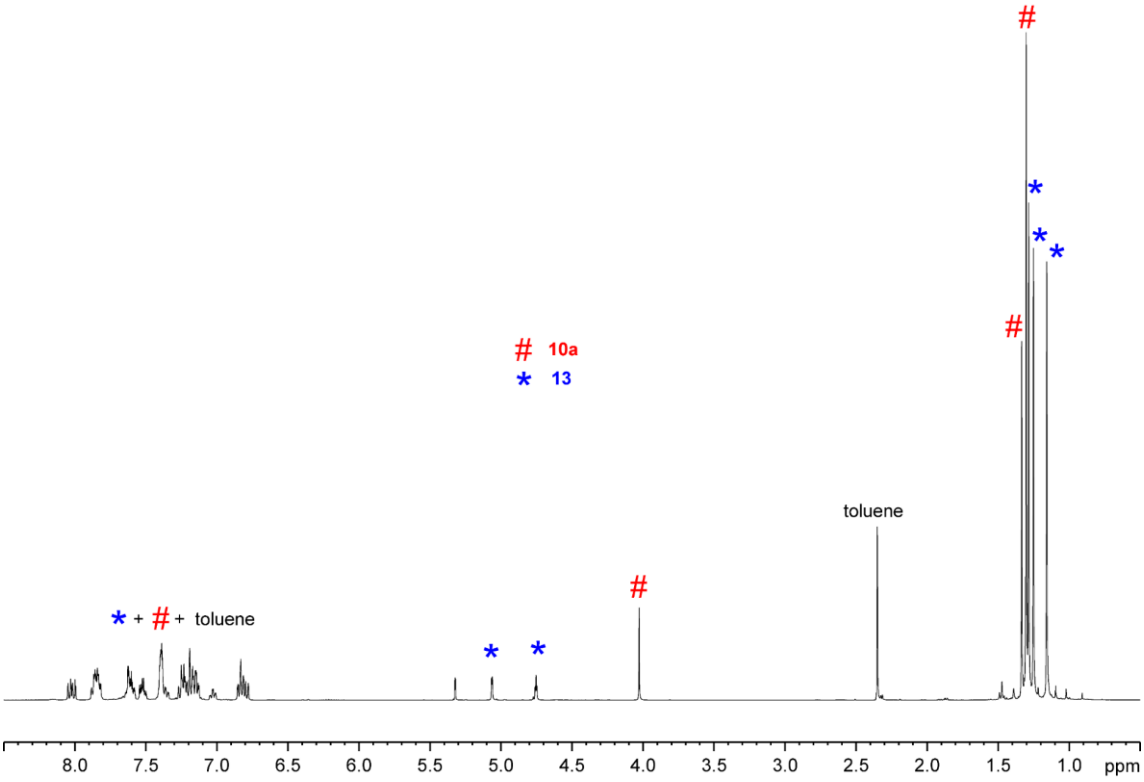


Figure S42: ^{1}H NMR spectrum of the reaction of **10a** with Ph_2PCl/Tl[TEF] in CD_2Cl_2 at room temperature.

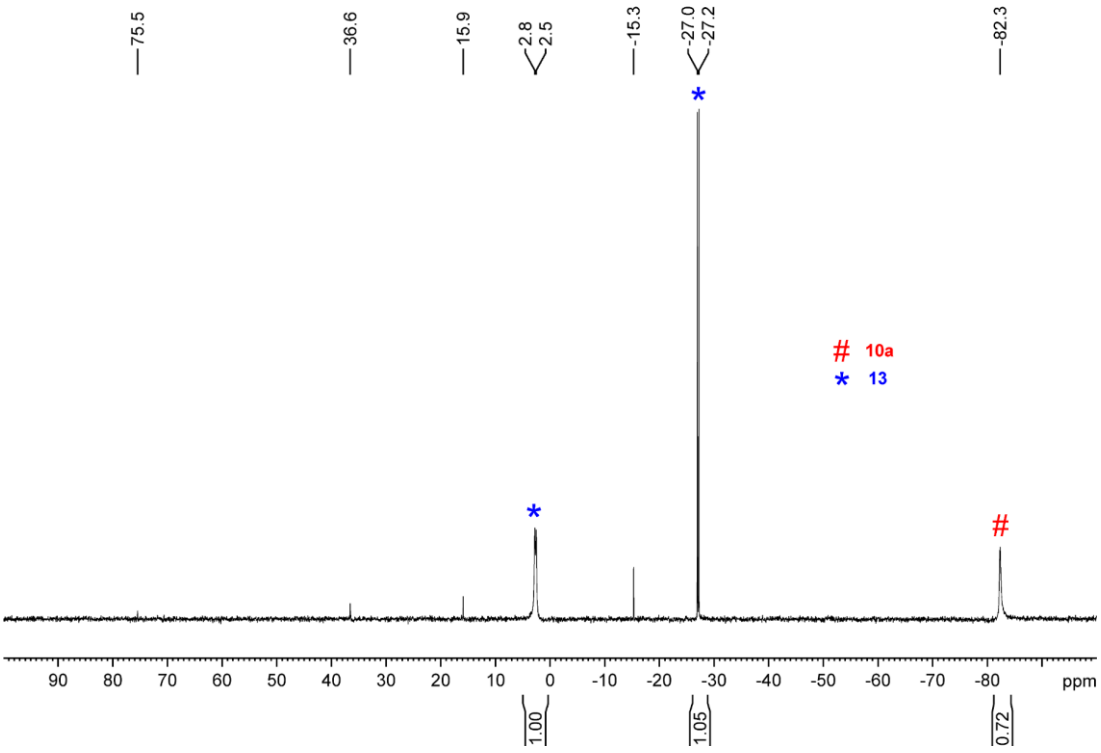


Figure S43: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **10a** with Ph_2PCl/Tl[TEF] in CD_2Cl_2 at room temperature.

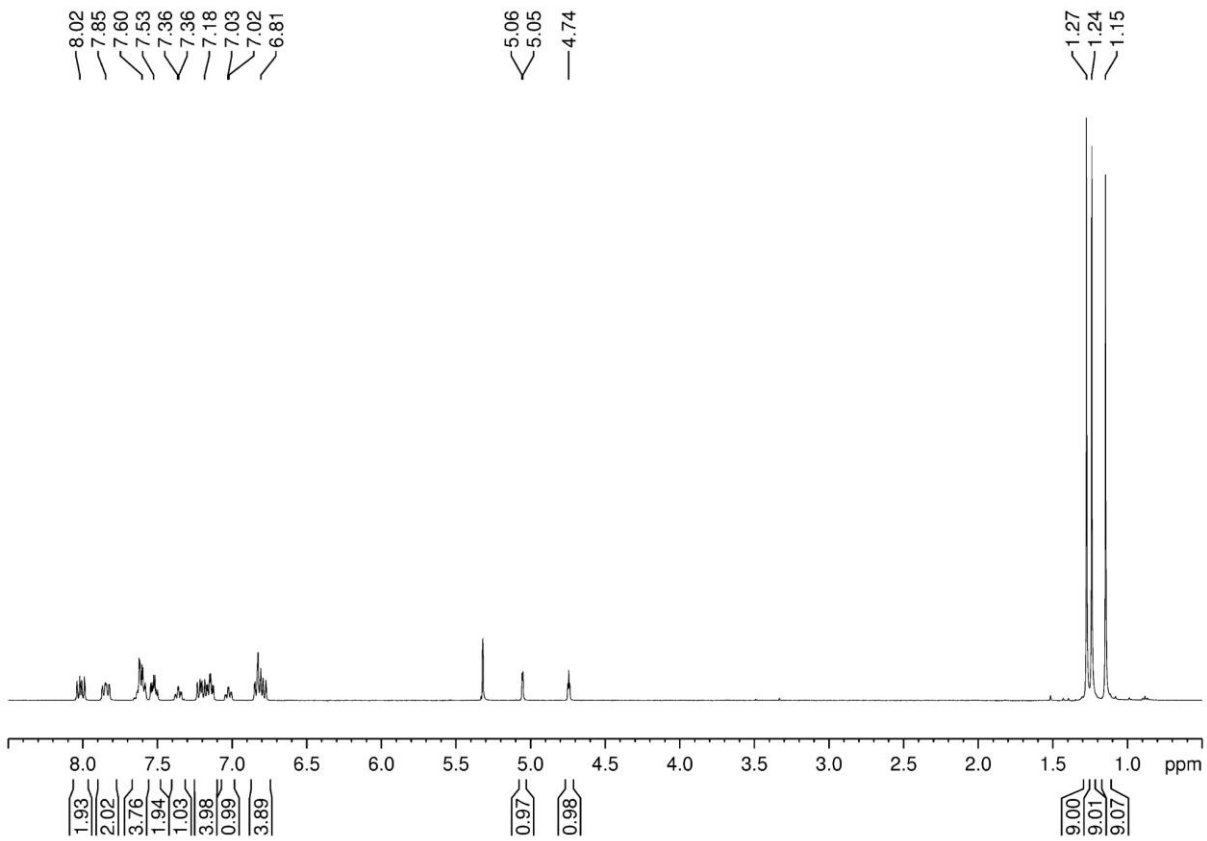


Figure S44: ^{1}H NMR spectrum **14** in CD_2Cl_2 at room temperature.

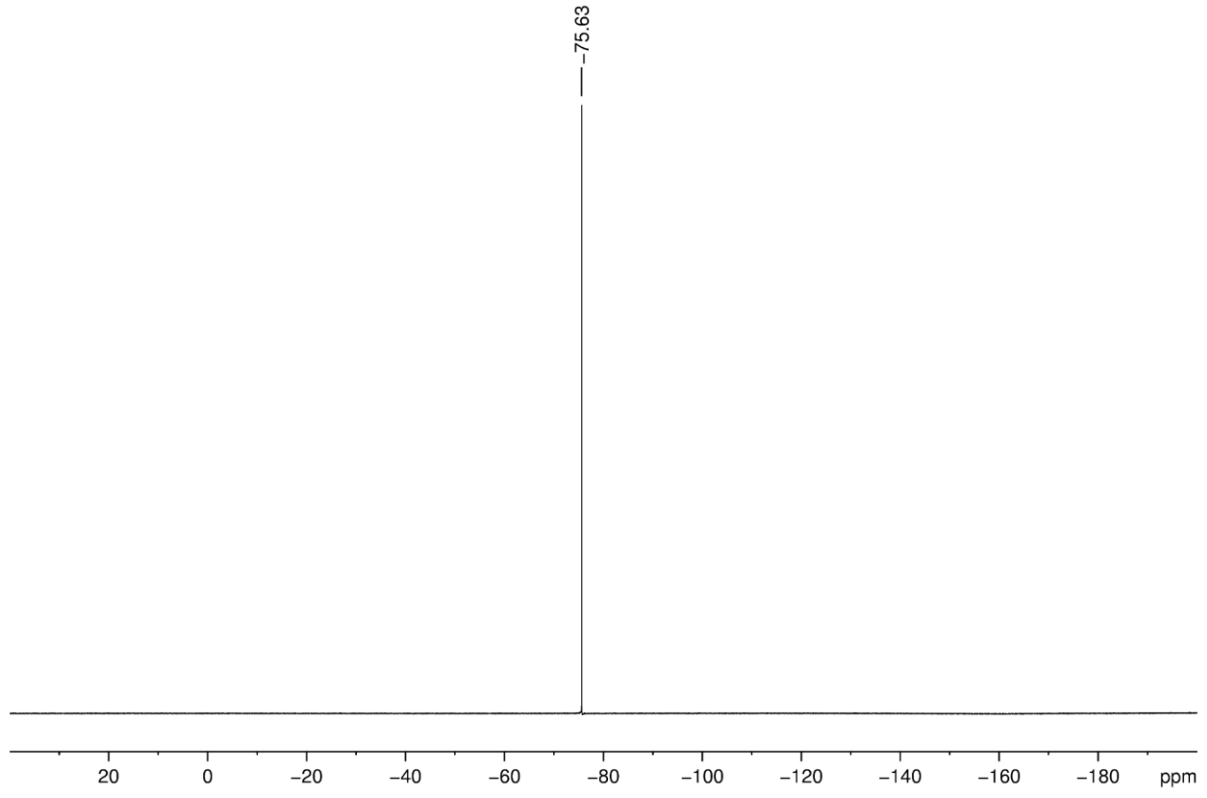


Figure S45: $^{19}F\{^{1}H\}$ NMR spectrum **14** in CD_2Cl_2 at room temperature.

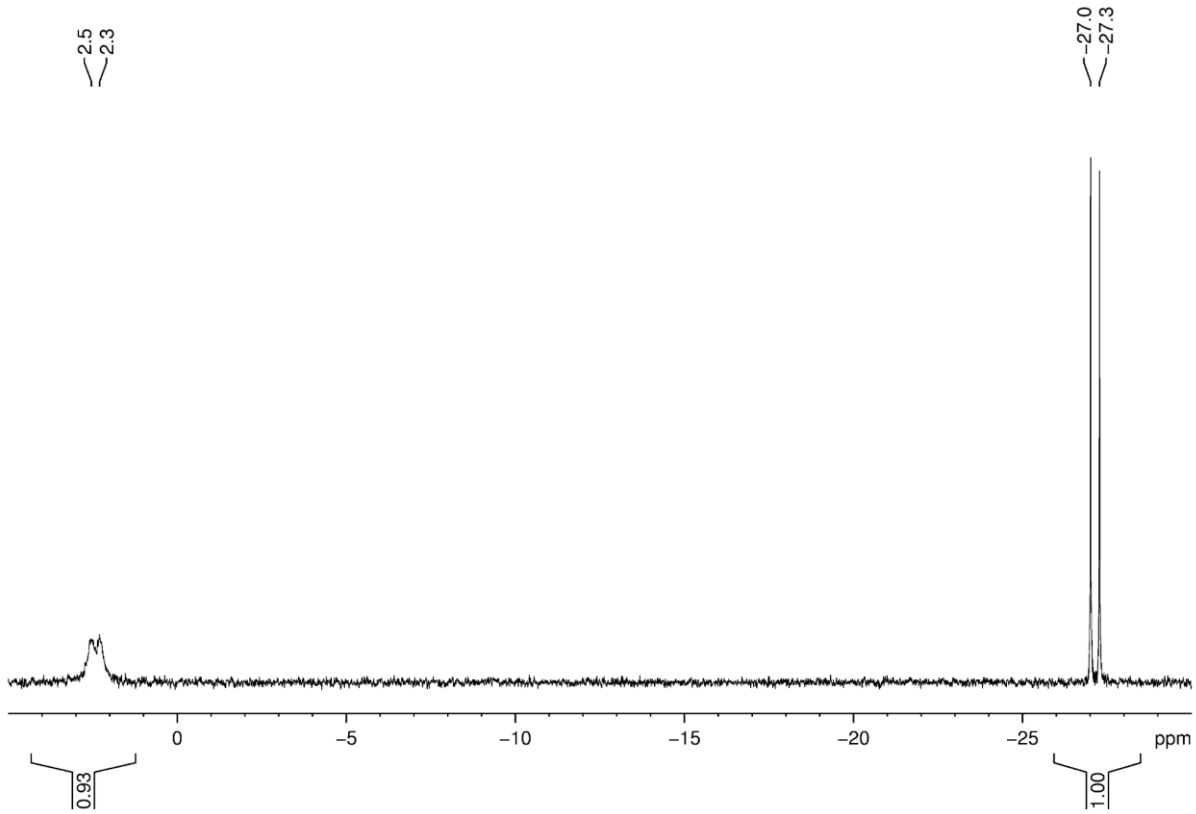


Figure S46: $^{31}P\{^{1}H\}$ NMR spectrum **14** in CD_2Cl_2 at room temperature.

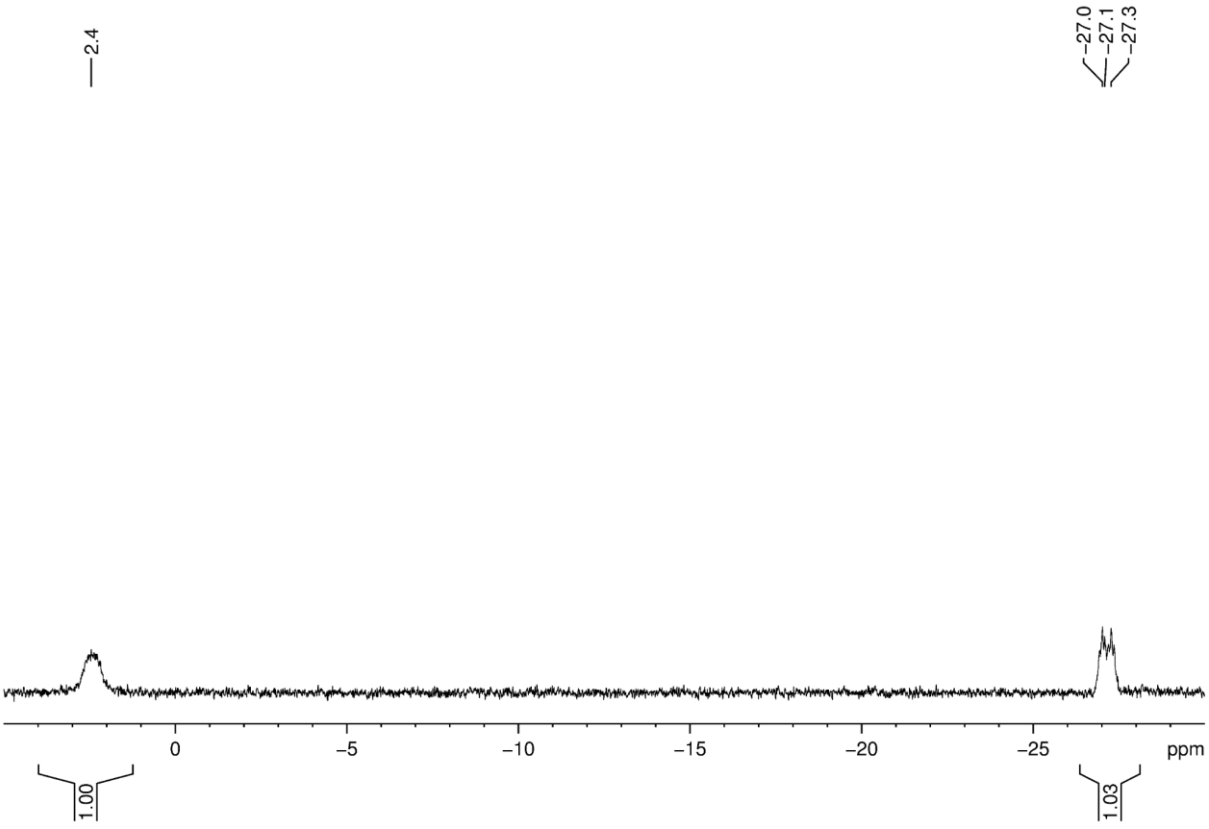


Figure S47: $^{31}P\{^{1}H\}$ NMR spectrum **14** in CD_2Cl_2 at room temperature.

3. Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on either a Gemini Ultra diffractometer (Oxford diffraction) with an AtlasS2 detector applying Cu-K*α* radiation (λ = 1.54178 Å) ([K(18-c-6)]Cp‴, [K(18-c-6)][**5**], [K(18-c-6)][**6**]), on a SuperNova, Dualflex diffractometer (Rigaku, formerly Agilent Technologies) with TitanS2 detector from applying Cu-K*α* radiation (λ = 1.54178 Å) (**10a**) or on a XtaLAB Synergy R, DW system with HyPix-Arc 150 detector applying Cu-K*α* radiation (λ = 1.54178 Å) (**7b**, **7c**, **8a**, **9b**, **9c**, **10b**, **11**, **12**, **13**). All measurements were performed at 123 K except **10b** and **11** (measured at 100 K). Data collection and reduction were performed with CrysAlispro (Version 171.38.46, 2015 (**5**), Version 171.40.14a, 2018 ([K(18-c-6]Cp‴, **6**), Version 171.41.81a, 2020 (**11**), Version 171.41.83a, 2020 (**7b**, **7c**, **8a**, **9b**, **9c**, **10a**, **10b**, **12**, **13**). For the compounds (**5**, **11**) an analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid was applied.[5] For the compounds ([K(18-c-6)]Cp‴, **6**, **7b**, **7c**, **8a**, **9b**, **9c**, **10a**, **10b**, **12**, **13**) a gaussian absorption correction based on gaussian integration over a multifaceted crystal model was applied. 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[6]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined in calculated positions using riding on pivot atom model.

CCDC-2068519 ([K(18-c-6)]Cp‴), CCDC-2068508 (**5**), CCDC-2068509 (**6**), CCDC-2068510 (**7b**), CCDC-2068511 (**7c**), CCDC-2068512 (**8a**), CCDC-2068513 (**9b**), CCDC-2068514 (**9c**), CCDC-2068515 (**10a**), CCDC-2068516 (**10b**), CCDC-2068517 (**11**), CCDC-2068518 (**12**) and CCDC-2069835 (**13**) 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).

3.1 [K(18-c-6)]Cp’’’

[K(18-c-6)]Cp’’’ crystallizes from a concentrated solution in thf layered with *n*-hexane at room temperature in the monoclinic space group $P2_1/n$ as colorless blocks. The asymmetric units contains one molecule [K(18-c-6)]Cp’’’. The structure in the solid state is depicted in Figure S48.

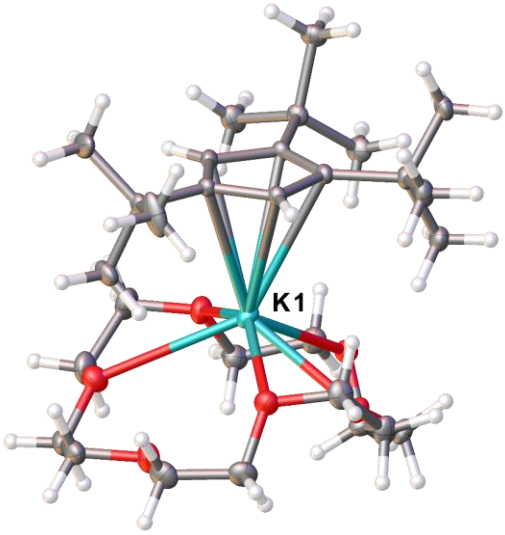


Figure S48: Molecular structure of [K(18-c-6)]Cp’’’ in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

3.2 [K(18-c-6)][Cp'''Co(η^3-P_3)] ([K(18-c-6)][5])

Compound [K(18-c-6)][**5**] crystallizes from a concentrated solution in thf layered with *n*-hexane at room temperature in the monoclinic space group *C2/c* as light red plates. The asymmetric unit contains one anion [**5**], one [K(18-c-6] counterion and one molecule thf. The thf molecule is disordered over two positions with side occupancies of 23 and 77 %. The restrains SADI, SIMU and RIGU were applied to describe the disorder properly. The structure in solid state is depicted in Figure S49 and S50.

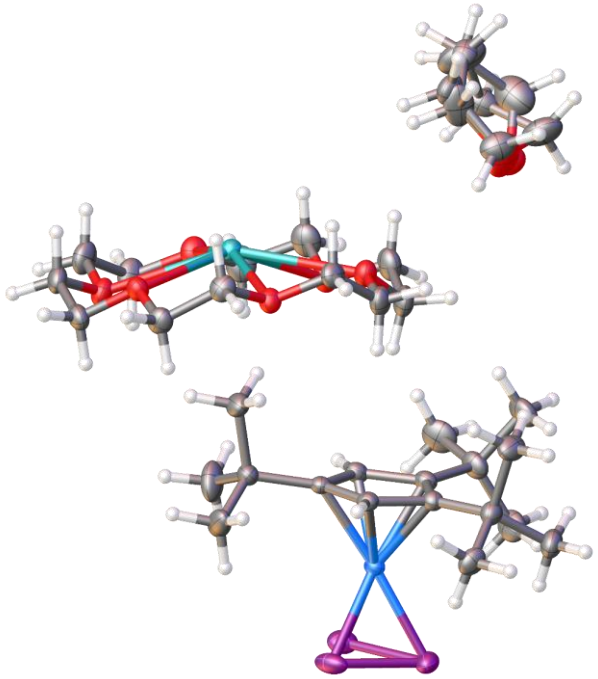


Figure S49: Molecular structure of [K(18-c-6)][**5**] in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

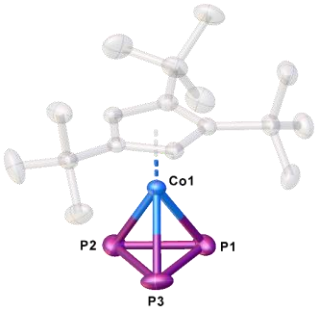


Figure S50: Molecular structure of the anion [**5**] in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]:P1-P2 2.1587(7), P2-P3 2.1640(7), P1-P3 2.1561(7), P1-P2-P3 59.84(2), P1-P3-P2 59.96(2), P2-P1-P3 60.20(2).

3.3 [K(18-c-6)][Cp'''Co(η^3-As$_3$)] ([K(18-c-6)][6])

Compound [K(18-c-6)][**6**] crystallizes from a concentrated solution in thf layered with *n*-hexane at room temperature in the monoclinic space group *C2/c* as dark brown plates. The asymmetric unit contains one anion [**6**], one [K(18-c-6] counterion and one molecule thf. The structure in solid state is depicted in Figure S51 and S52.

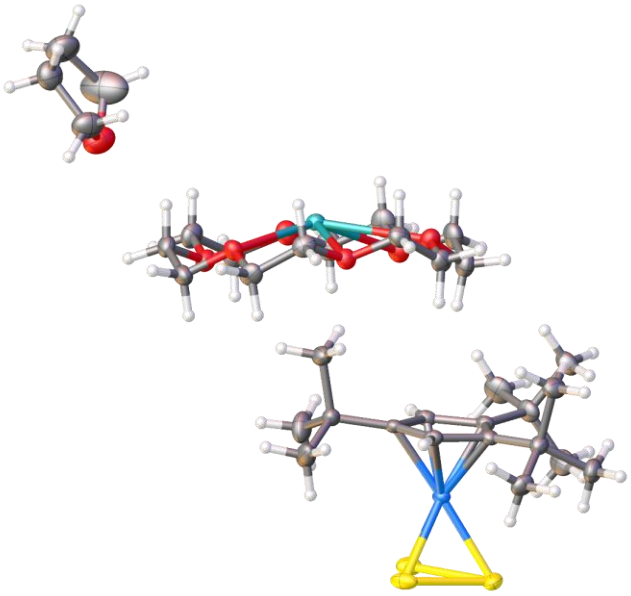


Figure S51: Molecular structure of [K(18-c-6)][**6**] in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

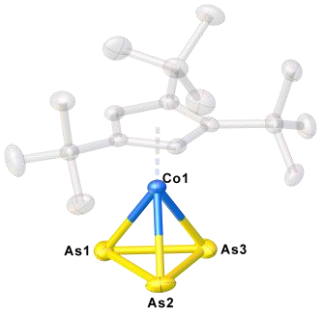


Figure S52: Molecular structure of the anion [**6**] in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: As1-As2 2.3969(4), As2-As3 2.3876(4), As1-As3 2.3892(4), As1-As2-As3 59.914(13), As1-As3-As2 60.235(13), As2-As1-As3 59.851(13).

3.4 [Cp'''Co(η^3-P_4Cy_2)] (7b)

Compound **7b** crystallizes from a concentrated solution in toluene layered with MeCN at -30 °C in the triclinic space group $P\bar{1}$ as dark red blocks. The asymmetric unit contains one molecule **7b**. The structure in solid state is depicted in Figure S53 and S54.

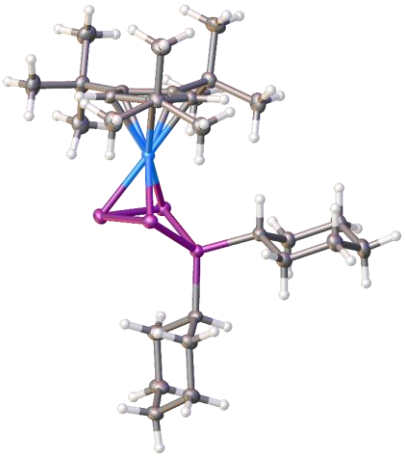


Figure S53: Molecular structure of **7b** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

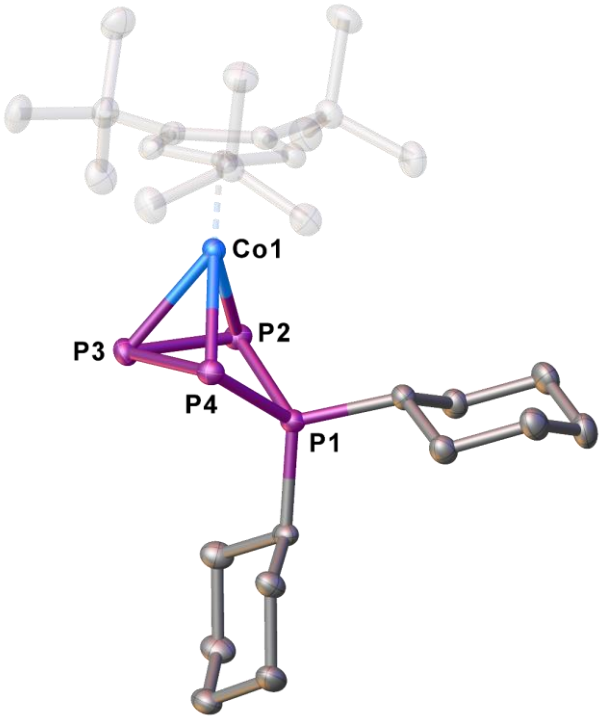


Figure S54: Molecular structure of **7b** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.1583(5), P2-P3 2.2021(6), P3-P4 2.2029(6), P1-P4 2.1544(5), P2-P3-P4-P1 -29.432.

3.5 [Cp'''Co(η^3-$P_4{}^tBu_2$)] (7c)

Compound **7c** crystallizes from a concentrated solution in CH_2Cl_2 layered with MeCN at room temperature in the monoclinic space group *P2₁/c* as dark red blocks. The asymmetric unit contains two molecules of **7c**. The structure in solid state is depicted in Figure S55 and S56.

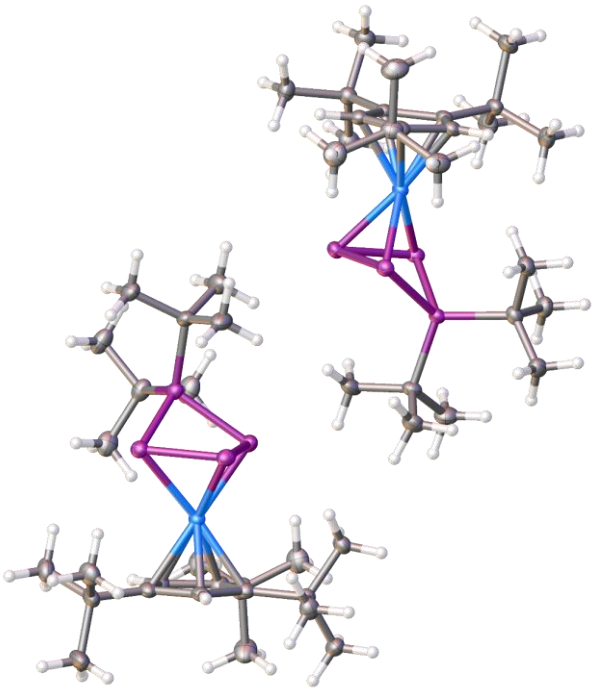


Figure S55: Molecular structure of **7c** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

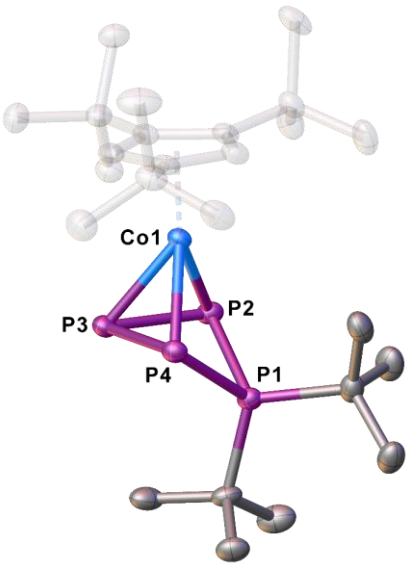


Figure S56: Molecular structure of one molecule **7c** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. P5-P8 represent the second molecule. Selected bond lengths [Å] and angles [°]: P1-P2 2.1810(8), P2-P3 2.2023(8), P3-P4 2.2017(8), P1-P4 2.1756(8), P2-P3-P4-P1 -31.908. P5-P6 2.1790(8), P6-P7 2.2037(8), P7-P8 2.1991(9), P5-P8 2.1815(8), P6-P7-P8-P5 -32.519.

3.6 [Cp'''Co(η^2:η^1-P_4Ph_2)] (8a)

Compound **8a** crystallizes from a concentrated solution in toluene layered with MeCN at -30 °C in the orthorhombic space group *Pna2₁* as light red plates. The asymmetric unit contains one molecule **8a**. The structure in solid state is depicted in Figure S57 and S58.

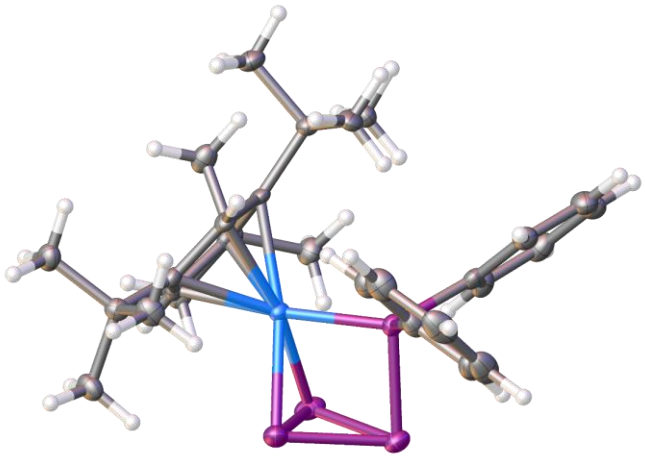


Figure S57: Molecular structure of **8a** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

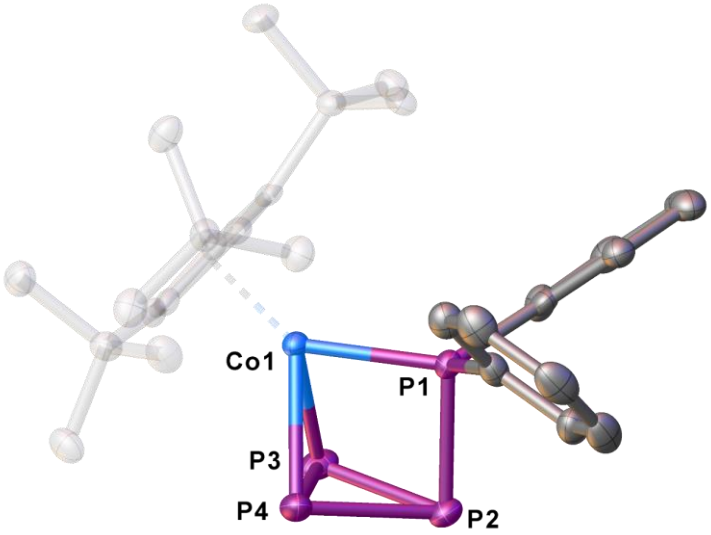


Figure S58: Molecular structure of one molecule **8a** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.1774(15), P2-P3 2.2309(15), P3-P4 2.1316(17), P2-P4 2.2372(15), P2-P3-P4-P1 52.103.

3.7 [Cp'''Co(η^3-As_3PCy_2)] (9b)

Compound **9b** crystallizes from a concentrated solution in *o*-difluorobenzene layered with MeCN at room temperature in the monoclinic space group $P2_1/n$ as dark brown blocks. The asymmetric unit contains one molecule **9b**. The structure in solid state is depicted in Figure S59 and S60.

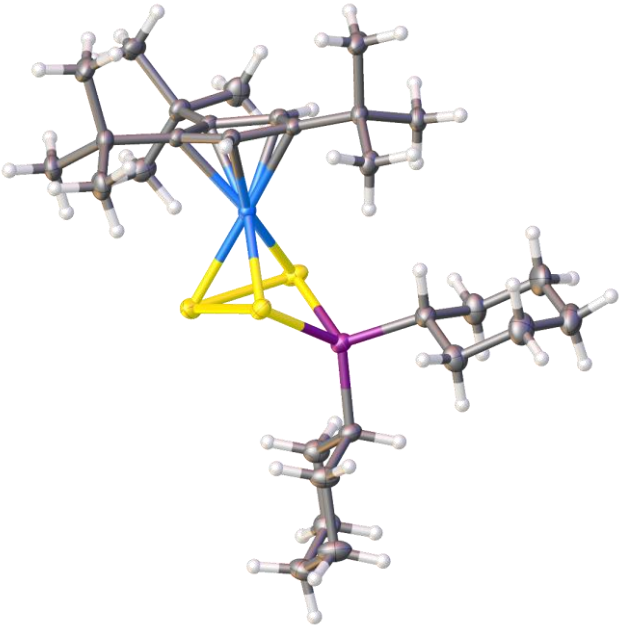


Figure S59: Molecular structure of **9b** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

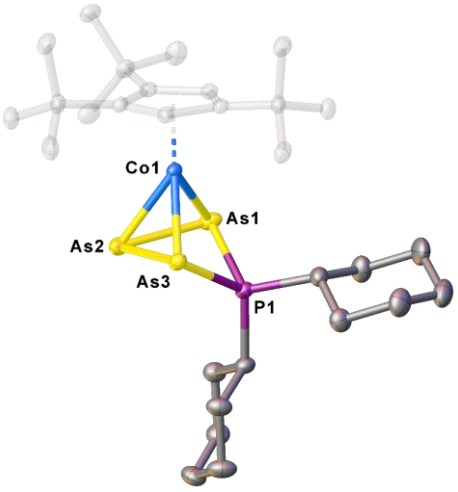


Figure S60: Molecular structure of **9b** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-As1 2.2967(5), As1-As2 2.4381(3), As2-As3 2.4264(3), P1-As3 2.3002(5), As1-As2-As3-P1 -33.407.

3.8 [Cp'''Co(η^3-$As_3P^tBu_2$)] (9c)

Compound **9c** crystallizes from a concentrated solution in CH_2Cl_2 layered with MeCN at room temperature in the monoclinic space group *P2₁/n* as dark red blocks. The asymmetric unit contains one molecule **9c**. The structure in solid state is depicted in Figure S61 and S62.

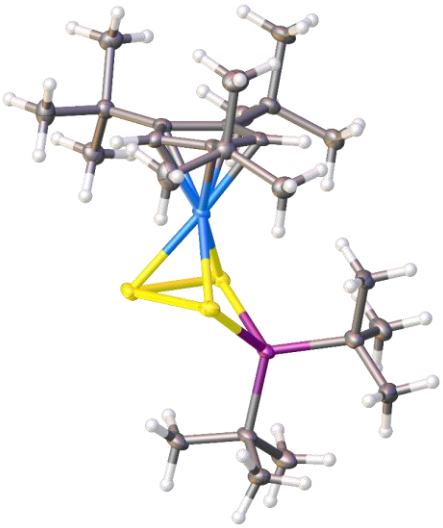


Figure S61: Molecular structure of **9c** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

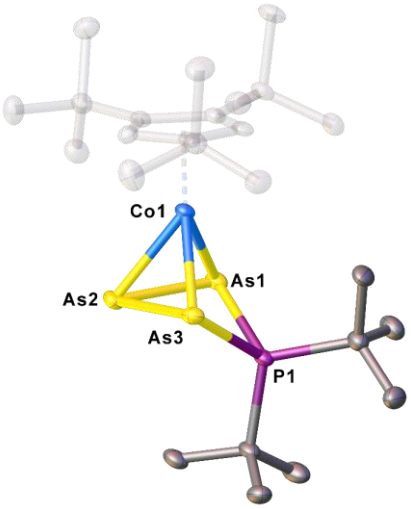


Figure S62: Molecular structure of **9c** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-As1 2.3052(8), As1-As2 2.4404(4), As2-As3 2.4196(5), P1-As3 2.3113(7), As1-As2-As3-P1 -31.994.

3.9 [Cp'''Co(η^2:η^1-As_3PPh_2)] (10a)

Compound **10a** crystallizes from a concentrated solution in toluene layered with MeCN at -30 °C in the triclinic space group $P\bar{1}$ as dark brown blocks. The asymmetric unit contains one molecule **10a**. The structure in solid state is depicted in Figure S63 and S64.

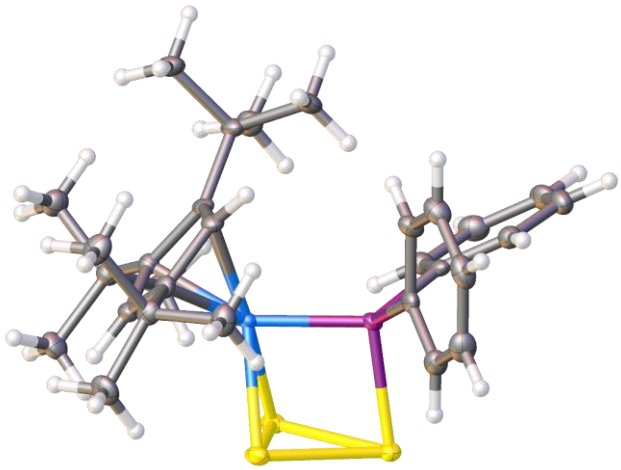


Figure S63: Molecular structure of **10a** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

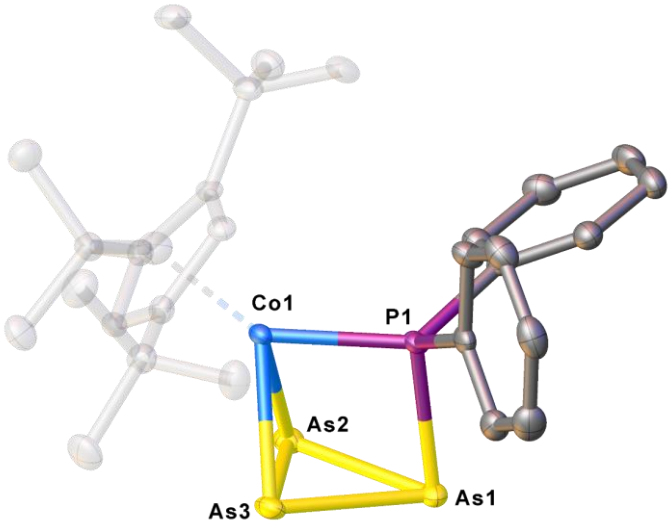


Figure S64: Molecular structure of **10a** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-As1 2.3111(8), As1-As2 2.4699(5), As2-As3 2.3531(5), As1-As3 2.4644(5), As1-As2-As3-P1 53.056.

3.10 [Cp'''Co(η^2:η^1-As_3PCy_2)] (10b)

Compound **10b** crystallizes from a concentrated solution in toluene layered with MeCN at -30 °C in the monoclinic space group *P2₁/n* as light red needles. The asymmetric unit contains one molecule **10b**. The structure in solid state is depicted in Figure S65 and S66.

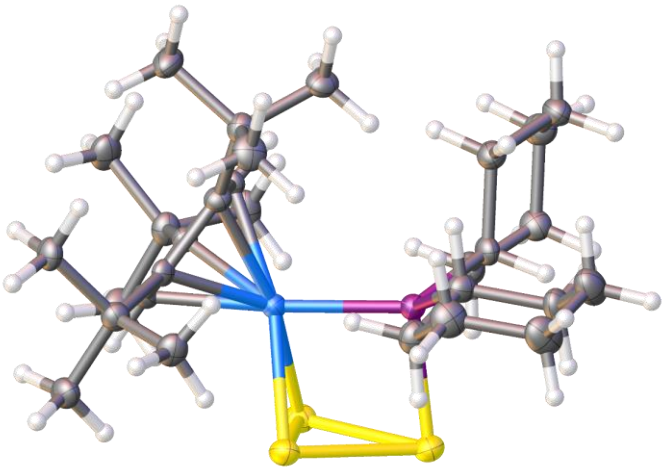


Figure S65: Molecular structure of **10b** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

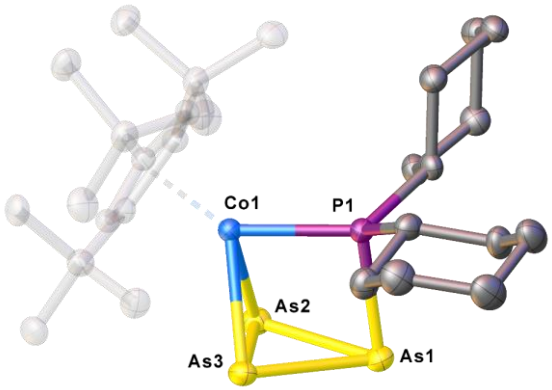


Figure S66: Molecular structure of **10b** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-As1 2.2991(11), As1-As2 2.4731(6), As2-As3 2.3496(6), As1-As3 2.4717(7), As1-As2-As3-P1 52.204.

3.11 [Cp'''Co(η^3-P$_3$SiL)] (L = (^{t}BuN)$_2$CPh) (11)

Compound **11** crystallizes from a concentrated solution in *o*-difluorobenzene layered with *n*-pentane at -30 °C in the triclinic space group $P\bar{1}$ as light green blocks. The asymmetric unit contains one molecule **11**, 0.3 toluene and 0.15 *o*-difluorobenzene molecules. The solvent molecules are located on the same position. The restraints SADI, SIMU, FLAT, DFIX were applied to describe the solvent molecules properly. Since the measured crystal was twinned, a HKLF5 refinement was applied. The structure in solid state is depicted in Figure S67 and S68.

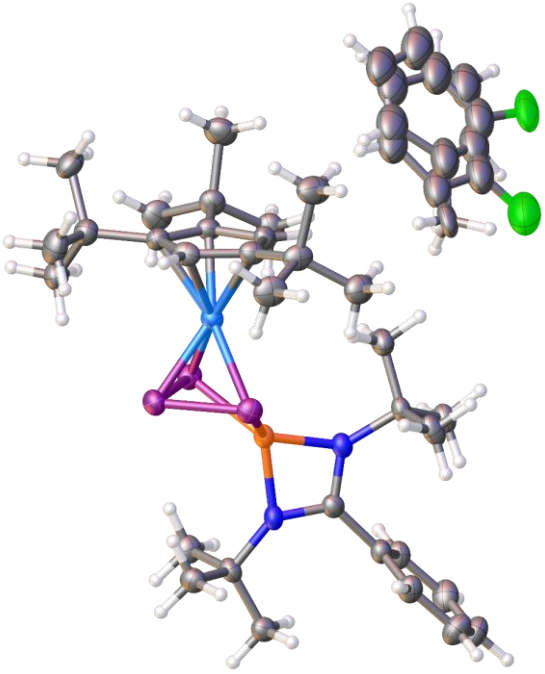


Figure S67: Molecular structure of **11** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

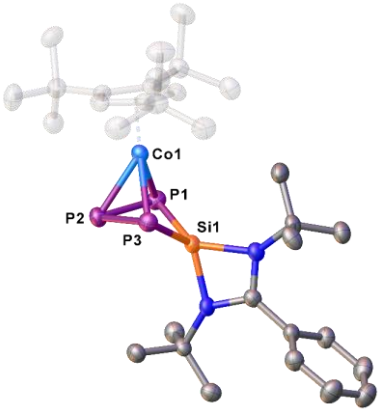


Figure S68: Molecular structure of **11** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Si1-P1 2.1682(17), P1-P2 2.2283(19), P2-P3 2.2032(18), Si1-P3 2.1696(18), P1-P2-P3-Si1 -30.168.

3.12 [Cp'''Co(η^3-As_3SiL)] (L = (^{t}BuN)$_2$CPh) (12)

Compound **12** crystallizes from a concentrated solution in a mixture of toluene and *n*-pentane at -30 °C in the orthorhombic space group *Iba2* as dark brown needles. The asymmetric unit contains one molecule **12** and 0.5 molecules toluene. One ^{t}Bu group of the amidinato ligand is disordered over two positions with side occupancies of 50 and 50 %. The restraints SADI and SIMU were applied to describe the disorder and the solvent molecule. The structure in solid state is depicted in Figure S69 and S70.

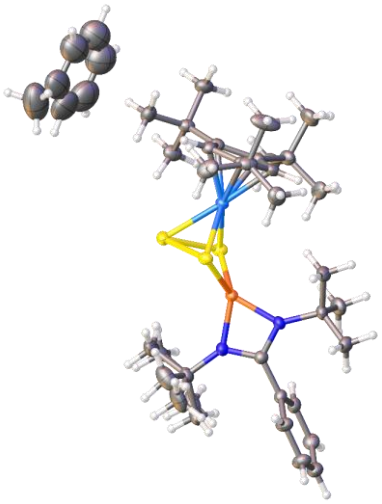


Figure S69: Molecular structure of **12** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

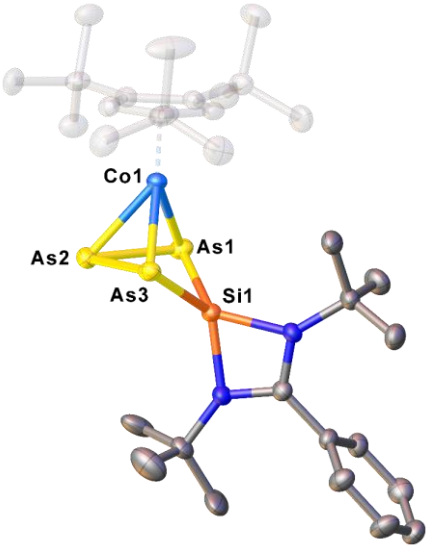


Figure S70: Molecular structure of **12** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Si1-As1 2.2853(14), As1-As2 2.4417(8), As2-As3 2.4342(8), Si1-As3 2.2775(14), As1-As2-As3-Si1 -30.438.

3.13 [Cp'''Co(η^2:η^1-As$_3$P$_2$Ph$_4$)][TEF] (13)

Compound **13** crystallizes from a concentrated solution in CH_2Cl_2 layered with *n*-pentane at room temperature in the monoclinic space group *P2$_1$/n* as dark red blocks. The asymmetric unit contains one cation of **13** and one [TEF] counterion. Two ^{t}Bu groups of the Cp''' are disordered over two positions with side occupancies of 70/30 % and 72/28 %, respectively. Several side groups of [TEF] are disordered over two and three positions, respectively. The restraints SADI, SIMU and DFIX were applied to describe the disorder properly. The structure in solid state is depicted in Figure S71 and S72.

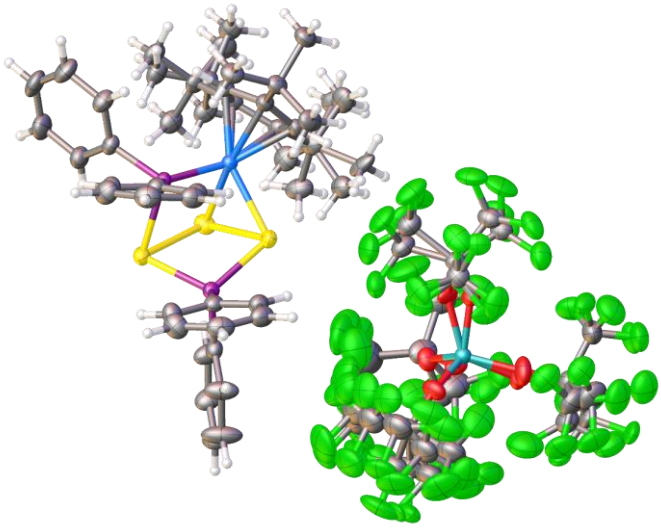


Figure S71: Molecular structure of **13** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

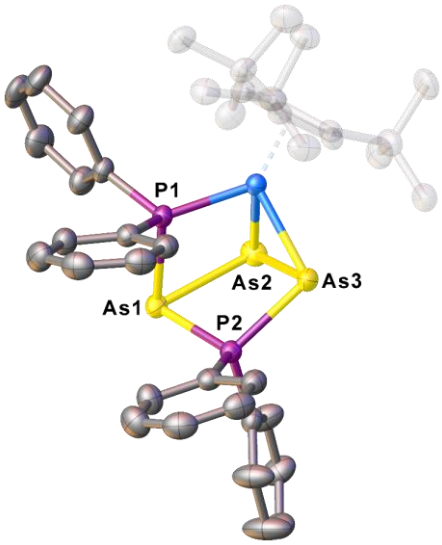


Figure S72: Molecular structure of the cation in **13** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-As1 2.3277(8), As1-P2 2.877(8), As1-As2 2.5758(5), As2-As3 2.4360(5), As3-P2 2.2999(8), As1-As2-As3-P2 21.255.

3.14 Crystallographic information

Table S8: Crystallographic data for all compounds

	[K(18-c-6)]Cp‴	[K(18-c-6)][**5**]	[K(18-c-6)][**6**]	**7b**
CCDC	2068519	2068508	2068509	2068510
Formula	$C_{29}H_{53}KO_6$	$C_{33}H_{61}CoKO_7P_3$	$C_{33}H_{61}As_3CoKO_7$	$C_{29}H_{51}CoP_4$
$D_{calc.}$/ g cm^{-3}	1.175	1.280	1.487	1.242
μ/mm^{-1}	1.827	5.833	7.404	6.363
Formula Weight	536.81	760.75	892.60	582.50
Colour	clear colourless	clear light red	clear dark brown	clear dark red
Shape	block	plate	plate	block
Size/mm^3	1.35×0.81×0.48	0.14×0.10×0.03	0.30×0.22×0.10	0.13×0.09×0.07
T/K	123	123	123	123.00(10)
Crystal System	monoclinic	monoclinic	monoclinic	triclinic
Space Group	$P2_1/n$	$C2/c$	$C2/c$	P-1
a/Å	12.5984(4)	30.2249(6)	30.1599(3)	10.1837(3)
b/Å	16.4532(5)	11.1053(2)	11.17800(10)	10.4065(3)
c/Å	14.7366(4)	23.5687(4)	23.6964(2)	16.2817(4)
α/°	90	90	90	77.135(2)
β/°	96.374(3)	93.551(2)	93.3930(10)	88.821(2)
γ/°	90	90	90	68.166(2)
V/Å^3	3035.78(16)	7895.8(3)	7974.70(13)	1557.80(8)
Z	4	8	8	2
Z'	1	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184	1.54184
Radiation type	Cu K_α	CuK_α	Cu K_α	Cu K_α
θ_{min}/°	4.041	3.758	3.737	2.790
θ_{max}/°	71.877	72.979	72.134	73.334
Measured Refl.	10964	13394	14506	18014
Independent Refl.	5746	7514	7559	5956
Reflections with I > 2(I)	4933	6972	6388	5551
R_{int}	0.0413	0.0233	0.0248	0.0248
Parameters	334	460	415	316
Restraints	0	66	0	0
Largest Peak	0.594	0.307	0.581	0.306
Deepest Hole	-0.603	-0.334	-0.559	-0.222
GooF	1.033	1.037	0.993	1.057
wR_2 (all data)	0.1309	0.0804	0.0812	0.0667
wR_2	0.1273	0.0780	0.0797	0.0658
R_1 (all data)	0.0556	0.0342	0.0369	0.0292
R_1	0.0498	0.0311	0.0310	0.0267

	7c	**8a**	**9b**	**9c**
CCDC	2068511	2068512	2068513	2068514
Formula	$C_{25}H_{47}CoP_4$	$C_{29}H_{39}CoP_4$	$C_{29}H_{51}As_3CoP$	$C_{25}H_{47}As_3CoP$
$D_{calc.}$/ g cm^{-3}	1.247	1.334	1.509	1.526
μ/mm^{-1}	6.963	6.980	8.371	9.077
Formula Weight	530.43	570.41	714.35	662.28
Colour	clear dark red	clear light red	clear dark brown	clear dark red
Shape	block	plate	block	block
Size/mm^3	0.40×0.22×0.13	0.30×0.09×0.06	0.16×0.13×0.10	0.29×0.23×0.15
T/K	123.00(10)	122.8(2)	123.00(10)	123.01(10)
Crystal System	monoclinic	orthorhombic	monoclinic	monoclinic
Flack Parameter		-0.021(4)		
Hooft Parameter		-0.0408(15)		
Space Group	$P2_1/c$	$Pna2_1$	$P2_1/n$	$P2_1/n$
a/Å	11.36840(10)	19.9527(2)	9.76050(10)	11.95260(10)
b/Å	32.1117(3)	17.0952(2)	26.8846(2)	19.9509(2)
c/Å	15.49090(10)	8.32470(10)	12.35050(10)	12.79890(10)
α/°	90	90	90	90
β/°	91.7220(10)	90	104.0680(10)	109.1460(10)
γ/°	90	90	90	90
V/Å^3	5652.53(8)	2839.52(6)	3143.66(5)	2883.27(5)
Z	8	4	4	4
Z'	2	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184	1.54184
Radiation type	Cu K_α	Cu K_α	Cu K_α	Cu K_α
θ_{min}/°	2.752	3.404	3.288	4.276
θ_{max}/°	75.150	73.276	73.421	73.030
Measured Refl.	47338	12825	18649	15821
Independent Refl.	11121	4884	6065	5565
Reflections with I > 2(I)	9838	4670	5762	5362
R_{int}	0.0556	0.0278	0.0233	0.0382
Parameters	571	316	316	286
Restraints	0	1	0	0
Largest Peak	0.723	0.324	0.403	0.928
Deepest Hole	-0.450	-0.436	-0.385	-1.450
GooF	1.073	1.044	1.041	1.053
wR_2 (all data)	0.1292	0.1010	0.0611	0.1142
wR_2	0.1265	0.1001	0.0604	0.1134
R_1 (all data)	0.0507	0.0385	0.0249	0.0423
R_1	0.0458	0.0368	0.0234	0.0413

	10a	**10b**	**11**	**12**
CCDC	2068515	2068516	2068517	2068518
Formula	$C_{29}H_{39}As_3CoP$	$C_{29}H_{51}As_3CoP$	$C_{35}H_{55}CoF_{0.3}N_2P_3Si$	$C_{35.5}H_{56}As_3CoN_2Si$
$D_{calc.}$/ g cm^{-3}	1.636	1.535	1.237	1.430
μ/mm^{-1}	9.227	8.513	5.368	6.890
Formula Weight	702.26	714.35	689.44	822.60
Colour	clear dark brown	clear light red	clear yellow	clear dark brown
Shape	block	needle	block	needle
Size/mm^3	0.23×0.20×0.12	0.06×0.03×0.02	0.12×0.03×0.03	0.17×0.03×0.02
T/K	123.00(10)	100.00(10)	100.01(11)	123.00(10)
Crystal System	triclinic	monoclinic	triclinic	orthorhombic
Flack Parameter				-0.025(3)
Hooft Parameter				-0.0489(12)
Space Group	*P*-1	*P*2$_1$/*n*	*P*-1	*Iba*2
a/Å	9.8743(3)	11.4067(2)	9.1256(2)	38.4780(3)
b/Å	9.8999(2)	18.5988(4)	11.1103(2)	22.6217(2)
c/Å	15.0948(4)	14.9530(4)	18.6766(7)	8.77920(10)
α/°	83.199(2)	90	101.919(3)	90
β/°	77.824(2)	102.974(2)	92.285(2)	90
γ/°	83.313(2)	90	90.166(2)	90
V/Å^3	1425.87(7)	3091.31(12)	1851.17(9)	7641.75(13)
Z	2	4	2	8
Z'	1	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184	1.54184
Radiation type	Cu K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$
θ_{min}/°	4.518	3.854	2.420	2.266
θ_{max}/°	66.638	73.109	74.132	73.263
Measured Refl.	17769	15969	11064	41068
Independent Refl.	5021	5841	11064	7355
Reflections with I > 2(I)	4547	4436	8937	6961
R_{int}	0.0589	0.0520	.	0.0322
Parameters	316	316	504	461
Restraints	0	0	283	113
Largest Peak	0.694	0.926	0.641	0.447
Deepest Hole	-1.130	-0.759	-0.754	-0.600
GooF	1.013	0.980	1.074	1.044
wR_2 (all data)	0.1001	0.1151	0.1769	0.0776
wR_2	0.0991	0.1092	0.1653	0.0765
R_1 (all data)	0.0428	0.0631	0.0803	0.0340
R_1	0.0402	0.0432	0.0645	0.0314

	13			
CCDC	2069835			
Formula	$C_{57}H_{49}AlAs_3CoF_{36}O_4P_2$			
$D_{calc.}$/ g cm^{-3}	1.790			
μ/mm^{-1}	5.436			
Formula Weight	1854.57			
Colour	clear dark red			
Shape	block			
Size/mm^3	0.18×0.09×0.06			
T/K	123.01(10)			
Crystal System	monoclinic			
Space Group	$P2_1/n$			
a/Å	10.85358(6)			
b/Å	26.67722(14)			
c/Å	24.07410(14)			
α/°	90			
β/°	99.0545(5)			
γ/°	90			
V/Å^3	6883.64(6)			
Z	4			
Z'	1			
Wavelength/Å	1.54184			
Radiation type	Cu K_α			
θ_{min}/°	2.489			
θ_{max}/°	73.195			
Measured Refl.	95862			
Independent Refl.	13601			
Reflections with I > 2(I)	12862			
R_{int}	0.0382			
Parameters	1520			
Restraints	1439			
Largest Peak	0.994			
Deepest Hole	-0.633			
GooF	1.051			
wR_2 (all data)	0.1191			
wR_2	0.1180			
R_1 (all data)	0.0466			
R_1	0.0450			

4. Computational Details

Gaussian 09 program package was used throughout.[8] Density functional theory (DFT) in form of BP86[9] (Becke's exchange and Perdew 86 correlation functional) or Becke's three-parameter hybrid functioncal B3LYP[10] with def2-SVP and 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 supporting information concerning the DFT calculations were created with Chemcraft.[15] Stationary points were verified by analytical frequency analysis. The transition states were verified by slightly changing its molecular geometry along its imaginary frequency and then performing geometry optimizations on the obtained structures. For the calculations of the reactions mechanism all geometries have been optimized at the BP86/def2-SVP level of theory. The nature of the stationary points and transition states has been determined by frequency analysis at the BP86/def2-SVP level of theory. The energies used in all diagrams has been calculated as single point calculations on the B3LYP/def2-TZVP level of theory with included dispersion GD3BJ and CPM model. For the energy diagrams the SCF energies without zero point correction have been used. To check if stationary point nature of $[Cp^{H}Co(\eta^2{:}\eta^1\text{-}P_4Me_2)]$ (**P-2**) is still valid at B3LYP-GD3BJ/def2-TZVP, CPM level of theory frequency analysis of **P-1**, **P-2** and **TS-5** was conducted.

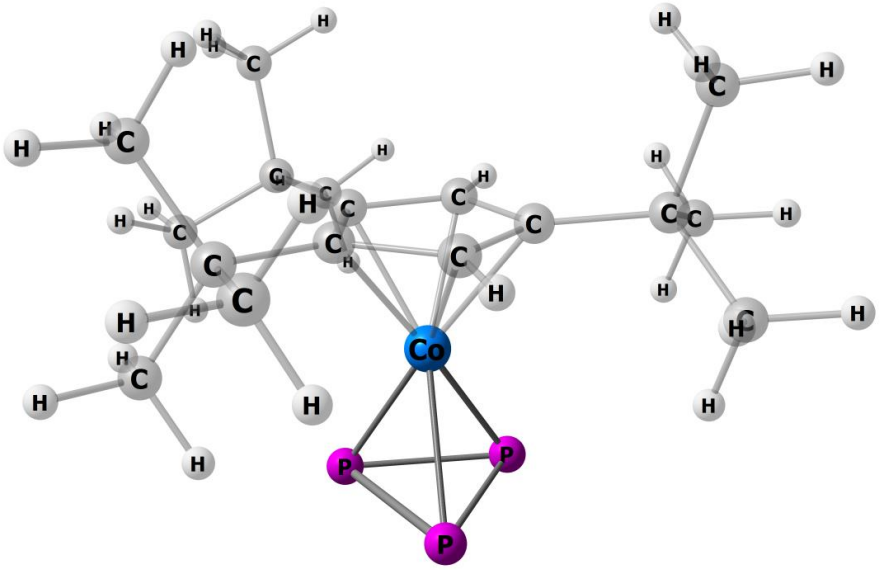
4.1 Details for Cp''' compounds

Table S9: Total energies for optimized geometries, optimization at the BP86/def2-SVP level and single point energies at the B3LYP/def2-TZVP level of theory including solvent effects and dispersion correction GD3BJ.

	BP86/def2-SVP total energy [Ha]	B3LYP/def2-TZVP total energy [Ha]
[**5**] $[Cp'''Co(\eta^3\text{-}P_3)]^-$	-3071.62228121	-3072.79099698
[**6**] $[Cp'''Co(\eta^3\text{-}As_3)]^-$	-8755.43569604	-8756.44208718
7a $[Cp'''Co(\eta^3\text{-}P_4Ph_2)]$	-3875.81137692	-3877.60687225
7b $[Cp'''Co(\eta^3\text{-}P_4Cy_2)]$	-3883.04688736	-3884.87586579
7c $[Cp'''Co(\eta^3\text{-}P_4{}^t\!Bu_2)]$	-3728.29701936	-3729.94988002
8a $[Cp'''Co(\eta^2{:}\eta^1\text{-}P_4Ph_2)]$	-3875.81961643	-3877.61957558
8b $[Cp'''Co(\eta^2{:}\eta^1\text{-}P_4Cy_2)]$	-3883.04458724	-3884.87662585
8c $[Cp'''Co(\eta^2{:}\eta^1\text{-}P_4{}^t\!Bu_2)]$	-3728.29294074	-3729.94885268
9a $[Cp'''Co(\eta^3\text{-}As_3PPh_2)]$	-9559.62630722	-9561.25952305
9b $[Cp'''Co(\eta^3\text{-}As_3PCy_2)]$	-9566.86443620	-9568.53146555

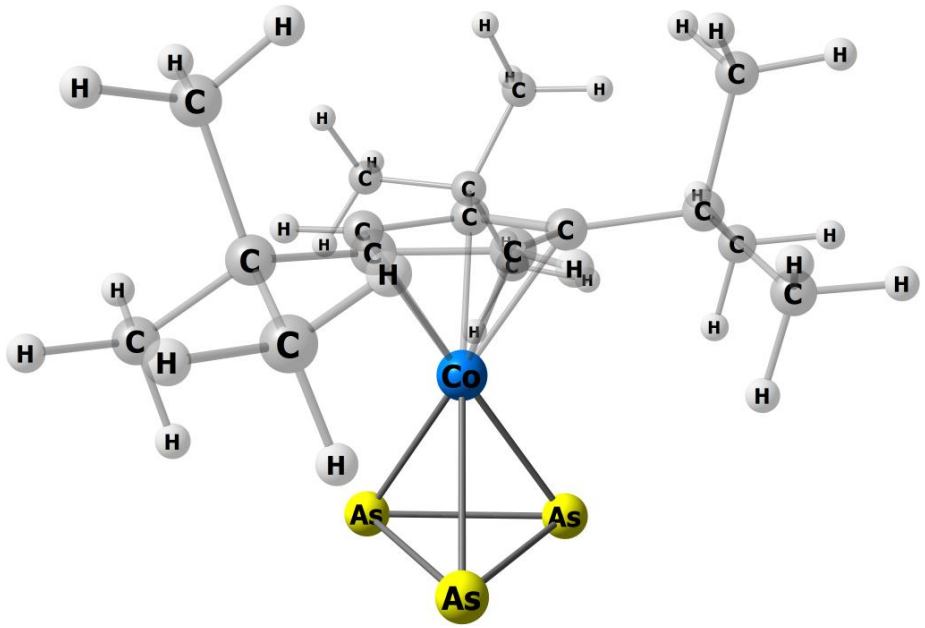
9c [Cp'''Co(η^3-$As_3P^tBu_2$)]	-9412.11179292	-9413.60412441
10a [Cp'''Co(η^2:η^1-As_3PPh_2)]	-9559.63464297	-9561.27507649
10b [Cp'''Co(η^2:η^1-As_3PCy_2)]	-9566.85790484	-9568.52983577
10c [Cp'''Co(η^2:η^1-$As_3P^tBu_2$)]	-9412.10436931	-9413.60119064
11 [Cp'''Co(η^3-$P_3Si(^tBuN)_2CPh$)]	-4055.47786624	-4057.56542088
12 [Cp'''Co(η^3-$As_3Si(^tBuN)_2CPh$)]	-9739.28936049	-9741.21726378

Table S10: Optimized geometry of [**5**]. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



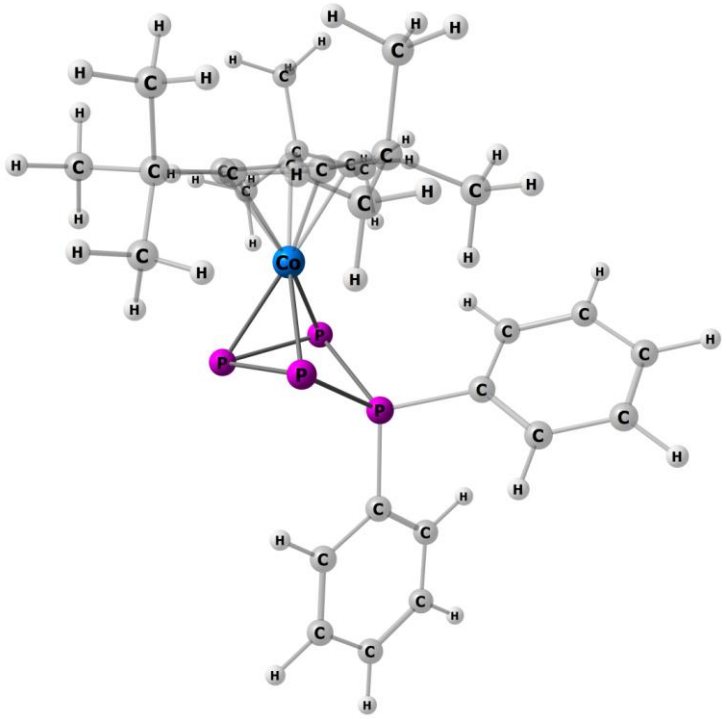
Co	10.602550000	3.977659000	9.795649000	C	9.986792000	0.178998000	10.350621000
P	10.648072000	2.988791000	7.711719000	H	10.232075000	0.520331000	9.323453000
P	9.758149000	4.989182000	7.914074000	H	9.332464000	-0.717844000	10.278269000
P	11.941830000	4.733615000	8.083632000	H	10.924123000	-0.142804000	10.843146000
C	11.440785000	3.010384000	11.409444000	C	8.946758000	0.805918000	12.567713000
C	10.017072000	2.642477000	11.204527000	H	9.874624000	0.601808000	13.139488000
C	9.248669000	3.874601000	11.300006000	H	8.343377000	-0.129940000	12.549476000
H	8.158826000	3.941048000	11.204887000	H	8.373980000	1.575265000	13.127052000
C	10.123906000	5.002625000	11.501864000	C	7.902390000	1.500996000	10.393325000
C	11.454494000	4.458712000	11.560920000	H	7.203181000	2.141233000	10.968639000
H	12.358218000	5.063117000	11.698171000	H	7.399666000	0.520660000	10.243008000
C	12.744846000	2.184897000	11.551138000	H	8.067981000	1.974396000	9.404050000
C	13.921070000	3.115953000	11.946096000	C	9.724035000	6.454533000	11.764695000
H	14.109443000	3.879915000	11.164826000	C	10.741511000	7.424722000	11.122209000
H	14.850247000	2.516665000	12.062868000	H	11.761434000	7.279014000	11.535587000
H	13.730858000	3.638659000	12.906787000	H	10.450882000	8.482214000	11.311998000
C	13.171185000	1.496666000	10.229291000	H	10.797424000	7.256173000	10.027445000
H	12.417265000	0.779056000	9.860986000	C	9.693753000	6.688354000	13.299574000
H	14.130366000	0.946563000	10.368451000	C	8.323684000	6.752790000	11.185085000
H	13.305598000	2.258789000	9.435187000	H	8.303690000	6.545212000	10.095097000
C	12.620872000	1.136931000	12.687625000	H	8.049982000	7.818075000	11.353025000
H	12.341826000	1.625011000	13.645880000	H	7.541974000	6.128109000	11.666836000
H	13.588687000	0.608818000	12.840980000	H	9.395632000	7.733112000	13.544396000
H	11.855671000	0.366990000	12.469075000	H	8.972275000	6.000466000	13.789737000
C	9.256259000	1.296308000	11.126392000	H	10.691848000	6.500976000	13.749201000

Table S11: Optimized geometry of [**6**]. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



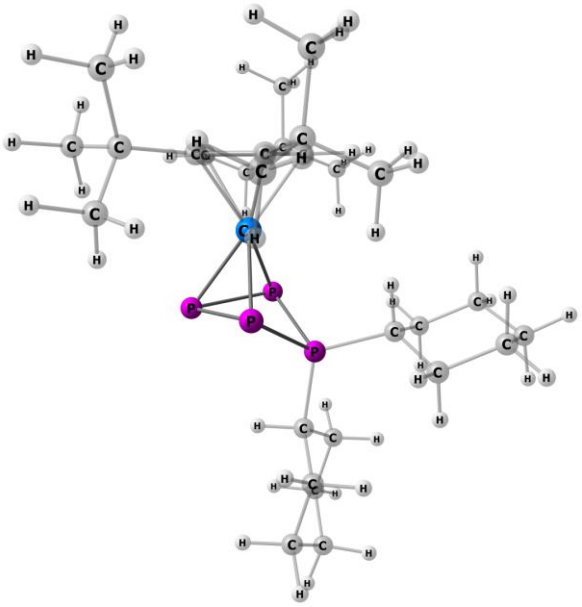
As	16.712210000	4.876835000	15.521252000	H	19.369673000	7.741226000	10.017955000
As	17.991899000	2.847573000	15.909438000	C	16.137308000	1.257984000	10.745331000
As	19.133670000	4.979323000	15.737458000	H	16.417067000	1.808321000	9.821636000
Co	18.132887000	3.988339000	13.776603000	H	15.177093000	0.728876000	10.552073000
C	18.634314000	5.030143000	12.080106000	H	16.911600000	0.486096000	10.920628000
C	17.299415000	4.497588000	12.007697000	C	18.709631000	0.154180000	13.074258000
H	16.401156000	5.109963000	11.871313000	H	18.405508000	0.436784000	14.103572000
C	19.496243000	3.892262000	12.282287000	H	19.364343000	-0.743188000	13.136273000
H	20.585704000	3.947546000	12.388307000	H	17.804480000	-0.143574000	12.511386000
C	17.300248000	3.047975000	12.138016000	C	14.822194000	3.185795000	11.587902000
C	18.718964000	2.663879000	12.349230000	H	14.634406000	3.915244000	12.402056000
C	19.048133000	6.477096000	11.809642000	H	13.892634000	2.593114000	11.443978000
C	19.476313000	1.312890000	12.401492000	H	15.012345000	3.749657000	10.650829000
C	20.792085000	1.476333000	13.209502000	C	15.551136000	1.472003000	13.215397000
H	21.511092000	2.158996000	12.712827000	H	16.306138000	0.745829000	13.561961000
H	21.296617000	0.491034000	13.315475000	H	14.602506000	0.919134000	13.025574000
H	20.578676000	1.880466000	14.220290000	H	15.387332000	2.189228000	14.044845000
C	15.995431000	2.234779000	11.942180000	C	18.045601000	7.462032000	12.452446000
C	19.853478000	0.899869000	10.951442000	H	18.345708000	8.514985000	12.252552000
H	18.951875000	0.742017000	10.325013000	H	17.994778000	7.302030000	13.548834000
H	20.444893000	-0.043679000	10.944987000	H	17.021512000	7.323015000	12.046983000
H	20.461677000	1.692056000	10.466399000	C	20.457651000	6.763858000	12.371316000
C	19.066768000	6.700133000	10.272398000	H	21.226830000	6.126693000	11.885635000
H	18.063429000	6.516357000	9.833258000	H	20.489806000	6.565224000	13.462822000
H	19.779315000	6.004401000	9.780224000	H	20.741229000	7.824681000	12.192822000

Table S12: Optimized geometry of **7a**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



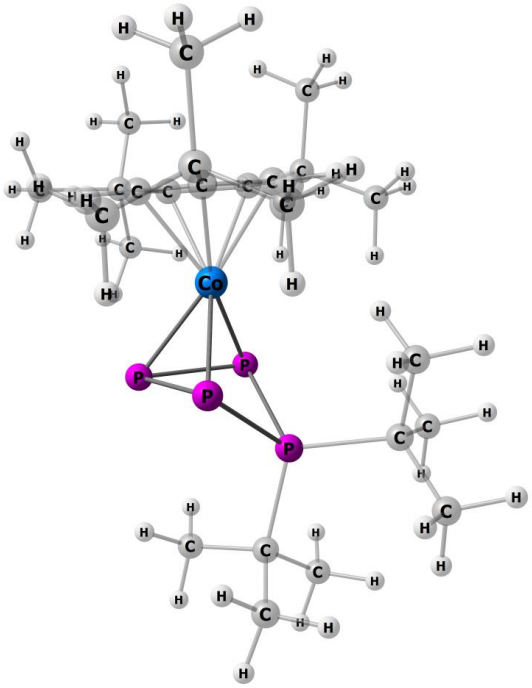
Co	0.971229000	-0.478808000	0.309657000	H	4.115124000	1.269372000	4.430569000
P	-0.158113000	-2.400286000	0.531798000	C	4.106564000	-2.815159000	-0.720726000
P	-0.782510000	-0.623548000	1.770560000	H	4.920274000	-2.468224000	-0.050881000
P	-0.583647000	-1.089440000	-1.255410000	H	4.546342000	-3.555790000	-1.420872000
C	2.915976000	-0.798949000	0.863761000	H	3.349406000	-3.346452000	-0.108830000
H	3.294586000	-1.701069000	1.354416000	C	1.542937000	1.700428000	3.531681000
C	0.939566000	2.679116000	-1.756033000	H	1.656677000	1.878984000	4.621721000
H	-0.014245000	2.166324000	-1.520042000	H	0.489403000	1.409182000	3.341005000
H	0.787338000	3.297379000	-2.665036000	H	1.738407000	2.664019000	3.016838000
H	1.166951000	3.377802000	-0.926517000	C	2.238678000	-0.696313000	3.869309000
C	2.413887000	0.348908000	1.561870000	H	2.941065000	-1.511008000	3.598232000
C	2.000416000	1.280665000	0.545911000	H	1.205645000	-1.062959000	3.694157000
H	1.578192000	2.272158000	0.738744000	H	2.353845000	-0.507667000	4.957612000
C	2.855105000	-0.606077000	-0.570453000	P	-2.145714000	-0.221885000	0.061116000
C	2.248202000	0.732583000	-0.773610000	C	-2.365735000	3.883058000	0.540789000
C	2.447095000	-2.301679000	-2.485731000	H	-1.996235000	4.630258000	1.260986000
H	1.714913000	-2.902913000	-1.907220000	C	-2.074416000	2.521763000	0.737242000
H	2.960502000	-2.987320000	-3.194209000	C	-3.123763000	4.288837000	-0.571277000
H	1.878977000	-1.564909000	-3.079889000	H	-1.473398000	2.202361000	1.604027000
C	2.080139000	1.657636000	-2.004641000	C	-2.553905000	1.557026000	-0.174361000
C	3.478351000	-1.651242000	-1.531730000	C	-3.597796000	3.330628000	-1.486964000
C	1.744919000	0.950829000	-3.335175000	H	-4.191472000	3.646510000	-2.359578000
H	2.552248000	0.281100000	-3.684256000	C	-3.318132000	1.968808000	-1.290655000
H	1.591614000	1.713015000	-4.128084000	H	-3.696308000	1.221657000	-2.007202000
H	0.811303000	0.357372000	-3.249572000	C	-3.913694000	-2.302021000	-0.648554000
C	2.516756000	0.595572000	3.068071000	H	-3.041472000	-2.734011000	-1.165861000
C	4.636612000	-1.007511000	-2.338471000	C	-5.145469000	-2.978907000	-0.646117000
H	4.286329000	-0.231833000	-3.045730000	C	-3.788516000	-1.058762000	0.009363000
H	5.165119000	-1.782673000	-2.933348000	H	-5.238044000	-3.944357000	-1.168521000
H	5.377614000	-0.535656000	-1.659623000	C	-6.253481000	-2.427060000	0.020201000
C	3.403986000	2.457564000	-2.167906000	C	-4.904241000	-0.508546000	0.681904000
H	3.634737000	3.033976000	-1.248121000	H	-4.815195000	0.459730000	1.200401000
H	3.319789000	3.176662000	-3.011064000	C	-6.130258000	-1.192819000	0.685397000
H	4.266603000	1.793106000	-2.371375000	H	-6.996723000	-0.758597000	1.209411000
C	3.972509000	1.062501000	3.348024000	H	-7.217755000	-2.959851000	0.022290000
H	4.210525000	1.990073000	2.786589000	H	-3.347727000	5.356295000	-0.726158000
H	4.707890000	0.287891000	3.046557000				

Table S13: Optimized geometry of **7b**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



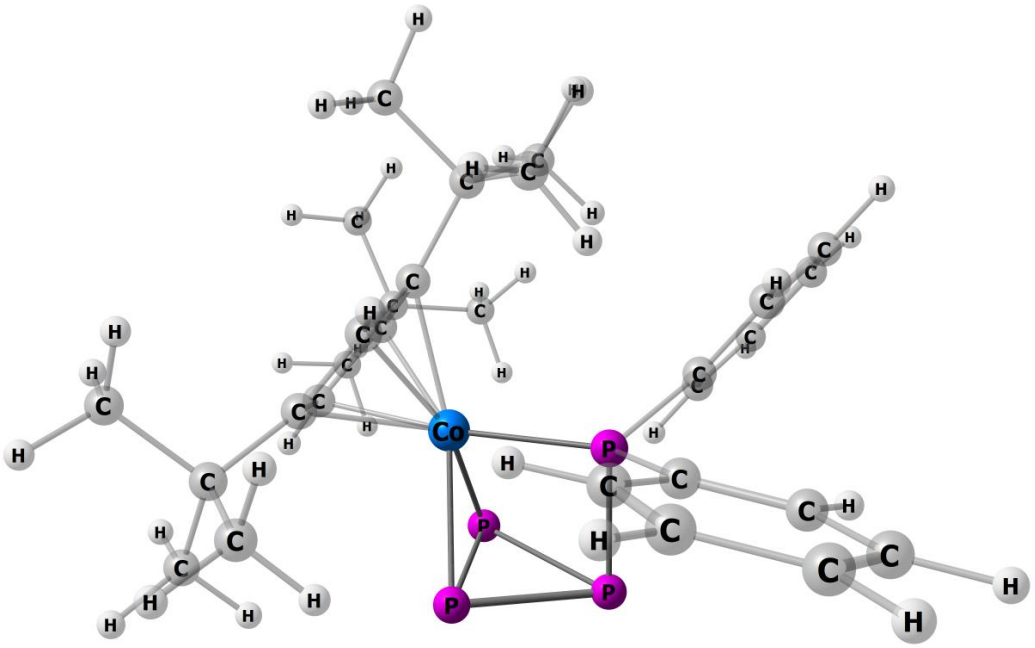
Co	-1.175790000	-0.343431000	-0.417526000
P	-0.141113000	-2.203538000	-1.121102000
P	0.606534000	-0.215051000	-1.873743000
P	0.331392000	-1.420313000	0.939640000
C	-3.064230000	-0.287355000	-1.210128000
H	-3.410937000	-0.879412000	-2.062915000
C	-1.317764000	1.679060000	2.801555000
H	-0.344966000	1.217212000	2.535850000
H	-1.306744000	1.901185000	3.889113000
H	-1.398023000	2.650640000	2.274709000
C	-2.477931000	1.017530000	-1.316828000
C	-2.148096000	1.421915000	0.022411000
H	-1.711756000	2.388645000	0.295492000
C	-3.125230000	-0.715217000	0.174089000
C	-2.528675000	0.386165000	0.965187000
C	-2.900710000	-3.045849000	1.281497000
H	-2.128244000	-3.423186000	0.579250000
H	-3.486035000	-3.920939000	1.638261000
H	-2.377490000	-2.611158000	2.150131000
C	-2.492433000	0.718504000	2.479052000
C	-3.832388000	-2.038841000	0.562137000
C	-2.332103000	-0.481532000	3.436097000
H	-3.178038000	-1.191446000	3.387210000
H	-2.279846000	-0.111572000	4.482014000
H	-1.394968000	-1.036996000	3.227070000
C	-2.437915000	1.886251000	-2.575021000
C	-5.084544000	-1.736550000	1.427923000
H	-4.829195000	-1.306964000	2.415481000
H	-5.658838000	-2.669833000	1.610806000
H	-5.757404000	-1.020192000	0.911534000
C	-3.816693000	1.464283000	2.809728000
H	-3.922916000	2.376688000	2.187310000
H	-3.832869000	1.771110000	3.877770000
H	-4.703882000	0.827439000	2.623570000
C	-3.809543000	2.612176000	-2.659292000
H	-3.984661000	3.243583000	-1.763284000
H	-4.644084000	1.883657000	-2.726981000
H	-3.850011000	3.267580000	-3.555894000
C	-4.343604000	-2.763345000	-0.710031000
H	-5.096275000	-2.162680000	-1.261181000
H	-4.828841000	-3.718267000	-0.419248000
H	-3.511671000	-3.008899000	-1.401427000
C	-1.316590000	2.944789000	-2.498180000
H	-1.316434000	3.572851000	-3.414018000
H	-0.322691000	2.460991000	-2.408919000
H	-1.450860000	3.625128000	-1.631565000
C	-2.244505000	1.029631000	-3.846076000
H	-3.066875000	0.296837000	-3.979367000
H	-1.286231000	0.470932000	-3.812384000
H	-2.230930000	1.677631000	-4.747813000
C	3.505195000	-1.326380000	-0.391321000
P	1.940531000	-0.317347000	-0.114804000
C	2.276178000	1.387227000	0.592899000
H	3.903893000	2.084782000	-0.695229000
C	2.868826000	2.388148000	-0.424077000
H	2.277827000	2.373793000	-1.365463000
C	2.898664000	3.808670000	0.173089000
H	3.065493000	-2.188170000	-0.948502000
C	4.144760000	-1.887504000	0.896775000
C	4.551755000	-0.659232000	-1.306517000
H	4.561609000	-1.054303000	1.505246000
H	3.372929000	-2.384862000	1.523040000
C	5.277387000	-2.874359000	0.547579000
H	1.225611000	1.704496000	0.794292000
C	3.051349000	1.405711000	1.926477000
H	4.070589000	-0.280197000	-2.233968000
H	4.992466000	0.222188000	-0.788053000
C	5.679566000	-1.652840000	-1.650336000
C	3.084819000	2.830128000	2.515519000
H	2.049356000	3.129306000	2.796701000
H	3.676734000	2.835673000	3.456358000
C	3.656335000	3.847227000	1.512167000
H	2.596826000	0.696233000	2.651416000
H	4.095581000	1.060310000	1.753657000
H	3.356215000	4.514028000	-0.553895000
H	1.852541000	4.158017000	0.330346000
H	5.756690000	-3.244058000	1.479843000
H	4.837050000	-3.767561000	0.048256000
C	6.325723000	-2.236081000	-0.381450000
H	4.731865000	3.616982000	1.330283000
H	3.628459000	4.871371000	1.942948000
H	6.853957000	-1.421457000	0.166737000
H	7.104750000	-2.980957000	-0.652499000
H	5.257198000	-2.480497000	-2.264893000
H	6.444617000	-1.153286000	-2.283399000

Table S14: Optimized geometry of **7c**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



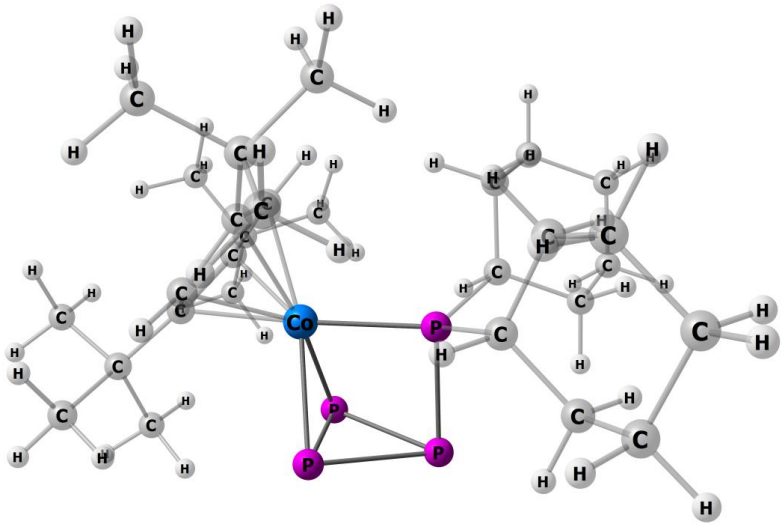
Co	0.587850000	0.146583000	-0.338212000	H	4.275638000	-0.261701000	-2.712604000
P	-0.908603000	-1.599684000	-0.173090000	H	2.639579000	-0.758902000	-3.280841000
P	-2.622346000	-0.164650000	-0.033751000	H	4.002327000	-1.916274000	-3.334288000
P	-0.505729000	-0.546285000	-2.129459000	C	2.108656000	-2.863543000	1.866401000
P	-1.285991000	1.285200000	-1.081277000	H	1.113347000	-3.074815000	1.424517000
C	2.384891000	0.834538000	-1.023092000	H	2.184392000	-3.432380000	2.817155000
H	2.592952000	1.114414000	-2.060208000	H	2.885151000	-3.262722000	1.189184000
C	2.133590000	-0.408362000	0.942593000	C	-1.885322000	1.140713000	2.328015000
C	2.553986000	-0.498241000	-0.474302000	H	-0.917734000	0.624800000	2.186224000
C	1.902047000	1.741968000	-0.021889000	H	-2.040567000	1.331114000	3.412957000
C	-3.064096000	0.303918000	1.791586000	H	-1.815329000	2.121088000	1.814616000
C	1.746911000	0.970122000	1.178466000	C	-4.979632000	0.640886000	-1.399555000
H	1.429166000	1.376459000	2.144874000	H	-5.408790000	1.158873000	-0.521263000
C	2.277675000	-1.357650000	2.159403000	H	-5.821560000	0.385870000	-2.080547000
C	-4.218837000	-0.649664000	-1.028521000	H	-4.320883000	1.355140000	-1.937008000
C	4.554448000	-2.052535000	-0.681603000	C	-5.103291000	-1.625260000	-0.225588000
H	4.425018000	-2.550806000	0.297778000	H	-4.547114000	-2.541045000	0.064242000
H	5.217036000	-1.174668000	-0.530777000	H	-5.955063000	-1.946927000	-0.864799000
H	5.082845000	-2.766511000	-1.348833000	H	-5.535694000	-1.173427000	0.687973000
C	3.206241000	-1.623315000	-1.320092000	C	-3.777754000	-1.356887000	-2.326871000
C	1.227337000	-1.019257000	3.247954000	H	-3.172597000	-0.696383000	-2.978493000
H	1.329283000	0.010600000	3.643653000	H	-4.688693000	-1.656109000	-2.891245000
H	1.348419000	-1.709800000	4.108499000	H	-3.181900000	-2.269150000	-2.123267000
H	0.198543000	-1.139493000	2.853820000	C	3.686107000	-1.106057000	2.769465000
C	2.286756000	-2.852330000	-1.526911000	H	4.494440000	-1.343131000	2.050420000
H	2.842532000	-3.663255000	-2.045723000	H	3.834754000	-1.736196000	3.672759000
H	1.418810000	-2.579783000	-2.163026000	H	3.804285000	-0.043732000	3.067503000
H	1.891159000	-3.263106000	-0.582551000	C	1.481116000	3.683789000	-1.606364000
C	1.806353000	3.263114000	-0.155736000	H	0.500464000	3.279899000	-1.935006000
C	-3.177536000	-1.003273000	2.606587000	H	2.255561000	3.335727000	-2.320510000
H	-4.046567000	-1.622312000	2.310359000	H	1.436045000	4.790702000	-1.683343000
H	-3.294803000	-0.754638000	3.684378000	C	0.741716000	3.853828000	0.793624000
H	-2.264016000	-1.625852000	2.503917000	H	0.728190000	4.961422000	0.714031000
C	-4.348196000	1.148013000	1.916007000	H	0.947876000	3.601544000	1.854546000
H	-4.287018000	2.083962000	1.323236000	H	-0.269012000	3.476174000	0.536760000
H	-4.473976000	1.444142000	2.980990000	C	3.199257000	3.832137000	0.233886000
H	-5.265726000	0.602711000	1.621089000	H	3.993586000	3.437143000	-0.433019000
C	3.546398000	-1.097448000	-2.739364000	H	3.466836000	3.558876000	1.275935000
				H	3.203983000	4.940756000	0.156733000

Table S15: Optimized geometry of **8a**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



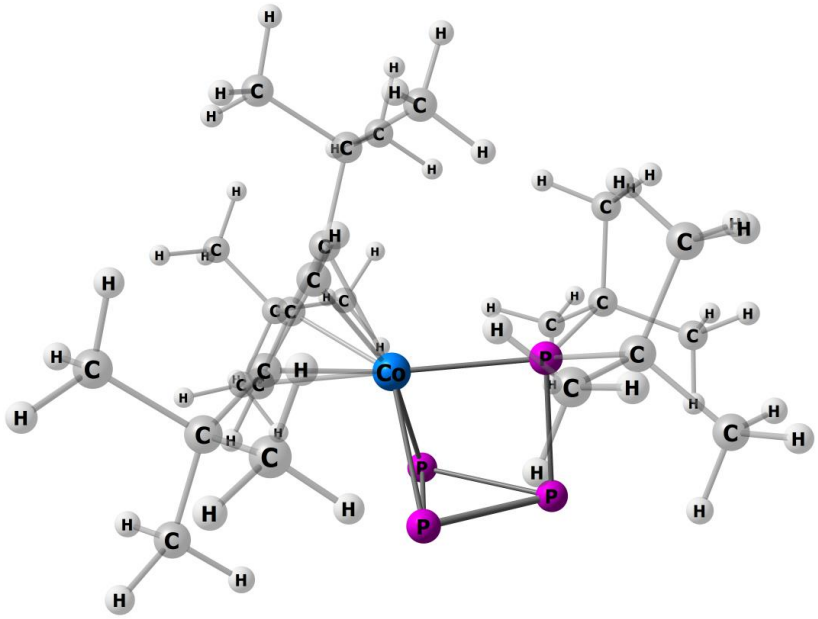
Co	-0.757059000	-0.227132000	-0.456261000	H	-3.927466000	3.070962000	1.122053000
P	1.440753000	-0.330013000	-0.536351000	H	-3.337172000	4.552740000	0.300204000
P	-0.566189000	-1.846089000	-2.119749000	H	-2.353930000	3.792735000	1.583397000
P	1.414499000	-0.870168000	-2.699528000	C	3.324961000	3.305479000	-1.214424000
P	-0.581326000	0.238126000	-2.726176000	H	3.288468000	4.081350000	-1.995738000
C	-1.276208000	0.789334000	1.323466000	C	-1.556617000	-0.639901000	1.426230000
C	-0.523977000	1.464616000	2.497348000	H	-1.147482000	-1.295999000	2.201886000
C	3.416127000	1.309934000	0.760064000	C	-3.907727000	-2.580683000	-1.015854000
H	3.468379000	0.531861000	1.537284000	H	-4.435499000	-3.556953000	-1.043522000
C	4.209921000	2.463670000	0.886069000	H	-3.157987000	-2.577807000	-1.835034000
H	4.868966000	2.576872000	1.761857000	H	-4.659140000	-1.793738000	-1.233818000
C	3.783770000	-1.864604000	0.053606000	C	4.459049000	-2.973597000	0.588494000
H	4.341576000	-1.120959000	-0.537798000	H	5.541061000	-3.088736000	0.414841000
C	2.530343000	2.154551000	-1.343341000	C	-2.501568000	-1.039251000	0.436394000
H	1.877443000	2.038187000	-2.223622000	C	-2.310267000	-3.565596000	0.668521000
C	2.565670000	1.140704000	-0.357339000	H	-1.830532000	-3.467840000	1.664783000
C	-3.245485000	-2.374551000	0.364656000	H	-1.509562000	-3.650789000	-0.094486000
C	-2.770762000	0.141364000	-0.339101000	H	-2.885729000	-4.515248000	0.672832000
H	-3.433672000	0.165986000	-1.209818000	C	-1.068164000	3.426942000	-0.901266000
C	0.514650000	0.489709000	3.110574000	H	-0.248338000	3.468925000	-0.165166000
H	0.043136000	-0.390936000	3.590026000	H	-1.317045000	4.467989000	-1.199807000
H	1.097015000	1.011057000	3.898042000	H	-0.684429000	2.895704000	-1.795632000
H	1.227536000	0.120135000	2.347499000	C	-3.326482000	2.642407000	-1.554751000
C	-4.358689000	-2.316480000	1.448189000	H	-2.926426000	2.030456000	-2.389664000
H	-5.045378000	-1.462620000	1.271891000	H	-3.499809000	3.665413000	-1.948659000
H	-3.927514000	-2.199936000	2.464135000	H	-4.312570000	2.230693000	-1.256095000
H	-4.961113000	-3.249943000	1.435086000	C	4.166155000	3.465556000	-0.098616000
C	-2.059033000	1.293110000	0.190411000	H	4.790060000	4.368007000	0.000626000
C	-2.333666000	2.715209000	-0.364573000	C	2.375536000	-3.791187000	1.541288000
C	1.696584000	-2.682330000	1.005930000	H	1.818508000	-4.546798000	2.118097000
H	0.609762000	-2.572403000	1.143557000	C	0.227320000	2.771748000	2.168920000
C	2.394059000	-1.703700000	0.266695000	H	0.993433000	2.622251000	1.383587000
C	3.757873000	-3.937803000	1.336641000	H	0.750203000	3.129560000	3.080545000
H	4.290686000	-4.806970000	1.754287000	H	-2.120923000	0.832914000	3.894578000
C	-1.588661000	1.759299000	3.594641000	C	-3.021672000	3.577336000	0.727685000
H	-2.348324000	2.486615000	3.247304000	H	-0.450491000	3.583627000	1.848313000
H	-1.099405000	2.180672000	4.498935000				

Table S16: Optimized geometry of **8b**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



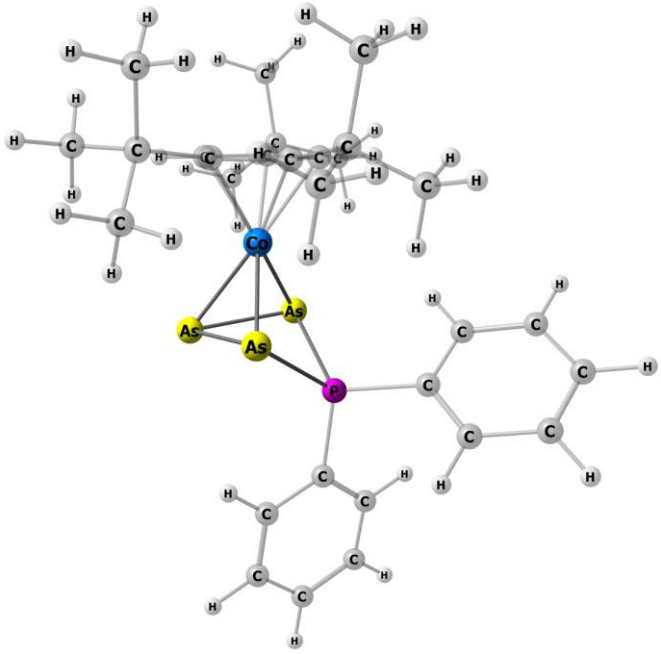
P	0.593828000	1.042595000	-2.513641000
P	0.973996000	-1.085130000	-2.243531000
P	-1.130320000	-0.436869000	-2.788957000
Co	0.824742000	0.238552000	-0.354009000
C	1.195288000	1.300159000	1.475361000
C	2.090831000	1.683190000	0.437112000
H	2.204624000	2.706619000	0.065525000
C	1.363752000	-0.124301000	1.624769000
H	0.821434000	-0.739034000	2.351612000
C	2.880244000	0.551531000	-0.016464000
C	2.396119000	-0.620891000	0.749192000
C	0.484868000	2.258315000	2.432233000
C	2.900654000	-2.071788000	0.955250000
C	1.707102000	-3.019356000	1.241013000
H	1.154841000	-2.750540000	2.163627000
H	2.077343000	-4.056807000	1.377906000
H	0.990280000	-3.015000000	0.394711000
C	4.128770000	0.796142000	-0.912107000
C	3.823514000	-2.063911000	2.207449000
H	4.704160000	-1.406830000	2.061083000
H	4.193831000	-3.089246000	2.422417000
H	3.279687000	-1.700641000	3.103871000
C	1.592780000	2.936725000	3.288188000
H	2.274339000	3.542404000	2.656290000
H	2.207007000	2.181449000	3.821178000
H	1.139412000	3.609026000	4.048009000
C	5.392707000	0.522326000	-0.052199000
H	5.368589000	1.107112000	0.891227000
H	6.305837000	0.815496000	-0.613055000
H	5.495905000	-0.546880000	0.215708000
C	3.672401000	-2.697104000	-0.224899000
H	3.060821000	-2.705351000	-1.149882000
H	3.925601000	-3.749861000	0.021061000
H	4.625325000	-2.177870000	-0.437366000
C	4.197440000	2.286708000	-1.339362000
H	3.300683000	2.590911000	-1.917700000
H	5.080784000	2.438007000	-1.993714000
H	4.308059000	2.970447000	-0.472982000
C	4.191696000	-0.020447000	-2.224967000
H	4.095305000	-1.108098000	-2.072656000
H	5.166676000	0.163571000	-2.725531000
H	3.391424000	0.289958000	-2.925915000
C	-0.287489000	3.354525000	1.668767000
H	-0.727075000	4.088809000	2.376755000
H	-1.106889000	2.919052000	1.066278000
H	0.375452000	3.911600000	0.975481000
C	-0.458881000	1.499825000	3.389117000
H	0.104801000	0.815428000	4.056520000
H	-1.204167000	0.890278000	2.839902000
H	-1.011311000	2.213114000	4.035940000
C	-2.717247000	1.190522000	-0.454353000
P	-1.369302000	-0.160594000	-0.593780000
C	-2.069183000	-1.810657000	0.023769000
H	-4.216226000	-1.582945000	-0.309683000
C	-3.392699000	-2.260231000	-0.629853000
H	-3.324343000	-2.177832000	-1.736482000
C	-3.747085000	-3.705075000	-0.223509000
H	-2.091056000	2.110535000	-0.518209000
C	-3.484904000	1.227078000	0.884058000
C	-3.711395000	1.237326000	-1.637837000
H	-4.113452000	0.312849000	0.972663000
H	-2.783926000	1.210766000	1.743224000
C	-4.397299000	2.466621000	0.976510000
H	-1.265130000	-2.494274000	-0.339280000
C	-2.127027000	-1.958913000	1.559402000
H	-3.162642000	1.241816000	-2.604284000
H	-4.339956000	0.318998000	-1.639957000
C	-4.622109000	2.478045000	-1.549287000
C	-2.481711000	-3.404539000	1.960094000
H	-1.653871000	-4.081307000	1.646819000
H	-2.548924000	-3.485952000	3.066948000
C	-3.793650000	-3.870563000	1.305246000
H	-1.154392000	-1.664339000	2.004866000
H	-2.891510000	-1.269641000	1.980024000
H	-4.718431000	-3.998512000	-0.677644000
H	-2.983630000	-4.397895000	-0.646167000
H	-4.952219000	2.454639000	1.939948000
H	-3.763518000	3.382837000	0.993492000
C	-5.372856000	2.544096000	-0.209040000
H	-4.639322000	-3.269203000	1.712857000
H	-4.007175000	-4.927636000	1.574715000
H	-6.091050000	1.693701000	-0.148444000
H	-5.983769000	3.470925000	-0.149811000
H	-3.998410000	3.393903000	-1.667846000
H	-5.338681000	2.478387000	-2.399094000

Table S16: Optimized geometry of **8c**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



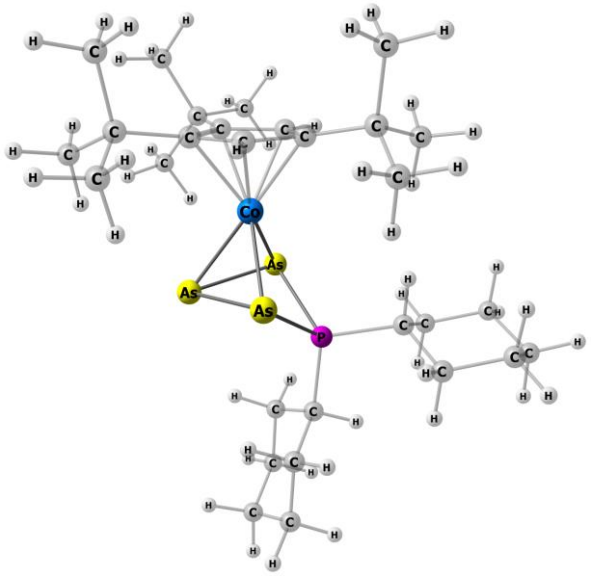
Co	0.274398000	0.320457000	-0.352421000	H	1.080806000	-3.449849000	-0.884517000
P	-1.981430000	-0.016058000	-0.032667000	H	2.074317000	-3.756033000	-2.339882000
P	-0.473731000	2.100224000	-1.650685000	H	0.812917000	-2.479458000	-2.361019000
P	-2.361954000	0.899981000	-2.039718000	C	3.188031000	-1.280670000	-2.594457000
P	-0.286092000	0.161332000	-2.597395000	H	2.402539000	-0.722804000	-3.145350000
C	1.497521000	-0.841963000	0.992389000	H	3.556521000	-2.084515000	-3.265192000
C	1.348798000	-1.933323000	2.080230000	H	4.038962000	-0.595906000	-2.401689000
C	2.319648000	2.894784000	0.626745000	C	1.051103000	-3.365155000	1.588599000
C	2.277011000	0.584736000	-0.667442000	H	0.126563000	-3.411351000	0.980773000
H	2.687643000	0.954993000	-1.612293000	H	0.910854000	-4.032723000	2.464558000
C	0.226863000	-1.547262000	3.078904000	H	1.875476000	-3.790937000	0.987661000
H	0.481577000	-0.650096000	3.677339000	C	-2.907755000	-1.742826000	-0.199291000
H	0.054443000	-2.375415000	3.797249000	H	-1.149310000	-2.588565000	-1.228007000
H	-0.723018000	-1.345493000	2.547746000	H	-2.401290000	-1.962743000	-2.342327000
C	3.591180000	2.871910000	1.522141000	H	-2.681141000	-3.501318000	-1.461144000
H	4.396428000	2.263338000	1.060461000	H	-4.552327000	-0.863565000	-1.391671000
H	3.372366000	2.442420000	2.521691000	H	-4.972507000	-1.140041000	0.337033000
H	3.979599000	3.902725000	1.667513000	H	-4.851821000	-2.522095000	-0.787561000
C	2.076507000	-0.818179000	-0.348964000	C	-2.241254000	-2.482931000	-1.376621000
C	2.638322000	-1.916926000	-1.290236000	C	-4.400788000	-1.539536000	-0.523732000
C	2.689959000	-1.957502000	2.871703000	C	-2.767043000	-2.622226000	1.058921000
H	3.541270000	-2.257112000	2.229192000	H	-3.243020000	-2.186144000	1.956155000
H	2.625222000	-2.679425000	3.713990000	H	-3.259913000	-3.601591000	0.868115000
H	2.921752000	-0.957969000	3.293351000	H	-1.708390000	-2.833241000	1.299793000
C	3.844848000	-2.611358000	-0.602683000	C	-3.000784000	1.117577000	1.211818000
H	4.606441000	-1.865320000	-0.293337000	H	-2.491367000	-0.100190000	2.991606000
H	4.329711000	-3.319134000	-1.308209000	H	-4.143619000	-0.409911000	2.349170000
H	3.552134000	-3.187251000	0.295714000	H	-3.794750000	1.098453000	3.235075000
C	1.371320000	0.550920000	1.419224000	H	-5.022104000	0.916813000	0.299952000
H	1.001108000	0.863903000	2.402218000	H	-4.046412000	2.266486000	-0.363436000
C	2.680651000	3.561841000	-0.719401000	H	-4.761921000	2.394425000	1.272166000
H	2.963738000	4.622468000	-0.554044000	C	-3.372413000	0.369373000	2.508092000
H	1.824865000	3.545831000	-1.426039000	C	-4.276215000	1.691954000	0.558389000
H	3.542349000	3.063131000	-1.209597000	C	-2.081237000	2.295898000	1.582484000
C	1.910667000	1.430327000	0.437683000	H	-1.808455000	2.899120000	0.693907000
C	1.228447000	3.726375000	1.329680000	H	-2.613233000	2.962931000	2.296747000
H	0.930768000	3.281795000	2.301696000	C	1.588538000	-2.962198000	-1.733060000
H	0.323679000	3.808184000	0.696137000	H	-1.142869000	1.954609000	2.059380000
H	1.601224000	4.752199000	1.534553000				

Table S17: Optimized geometry of **9a**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



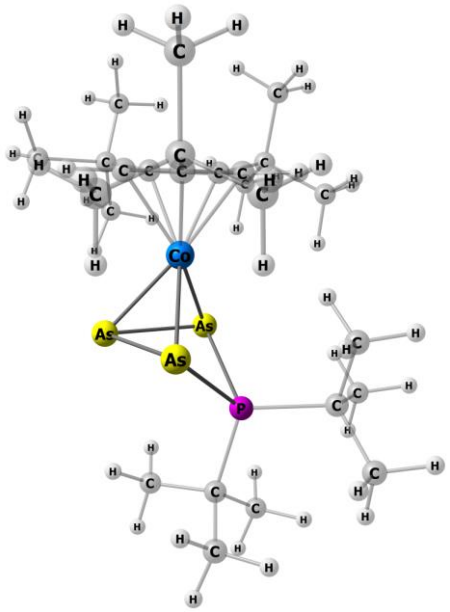
Co	1.110367000	-0.340810000	0.180337000	H	4.469336000	-0.022337000	4.501280000
As	-0.080701000	-2.375905000	-0.062378000	C	4.150035000	-2.306970000	-1.613186000
As	-0.704692000	-0.734159000	1.666751000	H	4.978249000	-2.224387000	-0.879694000
As	-0.508471000	-0.463988000	-1.563389000	H	4.557390000	-2.803612000	-2.518461000
C	3.061397000	-0.842270000	0.548831000	H	3.370781000	-2.973997000	-1.190612000
H	3.434778000	-1.855264000	0.729967000	C	1.920846000	0.813702000	3.903324000
C	1.104031000	3.298314000	-0.841748000	H	2.068529000	0.643508000	4.990616000
H	0.140736000	2.751812000	-0.797228000	H	0.841145000	0.686030000	3.680974000
H	0.972912000	4.181219000	-1.501301000	H	2.194024000	1.868690000	3.693084000
H	1.324844000	3.685480000	0.172933000	C	2.431865000	-1.621012000	3.490145000
C	2.612785000	0.046571000	1.581065000	H	3.044364000	-2.364124000	2.939328000
C	2.187167000	1.244672000	0.907887000	H	1.363736000	-1.849455000	3.291158000
H	1.792803000	2.135272000	1.408550000	H	2.615522000	-1.775605000	4.574460000
C	2.973055000	-0.218496000	-0.756839000	P	-2.202406000	0.045854000	0.006016000
C	2.392292000	1.125954000	-0.524479000	C	-2.414816000	3.965597000	1.326688000
C	2.533065000	-1.192484000	-3.119519000	H	-1.985850000	4.560068000	2.148987000
H	1.782532000	-1.934435000	-2.775245000	C	-2.105054000	2.598453000	1.219338000
H	3.034867000	-1.616023000	-4.016214000	C	-3.268362000	4.571209000	0.388231000
H	1.990719000	-0.284370000	-3.434257000	H	-1.430770000	2.122085000	1.950194000
C	2.236422000	2.396643000	-1.398049000	C	-2.657777000	1.824184000	0.176128000
C	3.569949000	-0.922127000	-2.003614000	C	-3.816764000	3.805874000	-0.658252000
C	1.906975000	2.162588000	-2.888052000	H	-4.485204000	4.277747000	-1.396101000
H	2.702254000	1.613996000	-3.425400000	C	-3.516350000	2.438757000	-0.765883000
H	1.791052000	3.143514000	-3.395475000	H	-3.953060000	1.843828000	-1.584301000
H	0.953728000	1.607234000	-3.011354000	C	-3.942277000	-1.849015000	-1.162339000
C	2.783892000	-0.171615000	3.085950000	H	-3.076437000	-2.115409000	-1.790237000
C	4.756880000	-0.088711000	-2.556275000	C	-5.158992000	-2.539580000	-1.298638000
H	4.437016000	0.887883000	-2.967300000	C	-3.823287000	-0.804286000	-0.219613000
H	5.267197000	-0.641443000	-3.373922000	H	-5.246205000	-3.348408000	-2.041490000
H	5.505171000	0.108940000	-1.760464000	C	-6.258807000	-2.200569000	-0.491529000
C	3.570599000	3.190108000	-1.294233000	C	-4.931263000	-0.468436000	0.593437000
H	3.803832000	3.436142000	-0.237721000	H	-4.846994000	0.342966000	1.334345000
H	3.500544000	4.143368000	-1.861391000	C	-6.142156000	-1.165361000	0.455083000
H	4.425571000	2.613817000	-1.700023000	H	-7.001563000	-0.897862000	1.090559000
C	4.280605000	0.092760000	3.412245000	H	-7.210923000	-2.744280000	-0.598927000
H	4.577559000	1.121265000	3.118704000	H	-3.508307000	5.643175000	0.471350000
H	4.942086000	-0.616021000	2.872217000				

Table S18: Optimized geometry of **9b**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



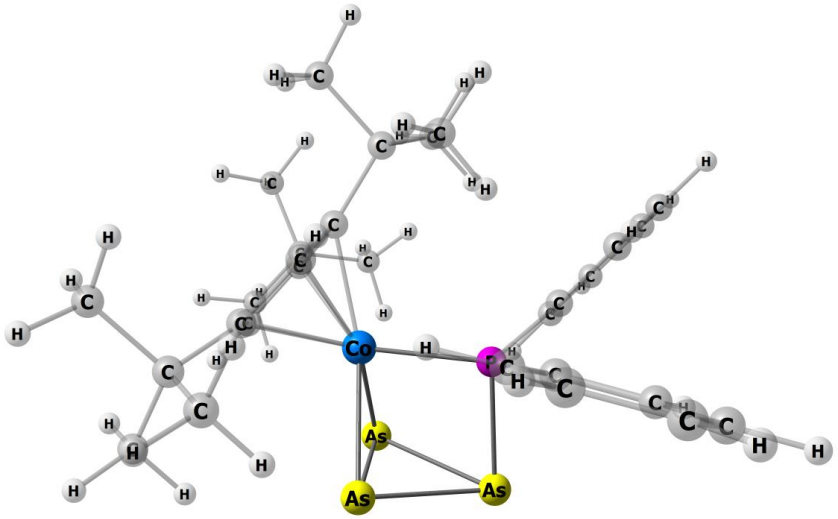
As	-0.512186000	-0.347103000	-1.661983000				
As	-0.337826000	-0.567806000	1.598091000	H	3.436582000	4.299375000	-0.151465000
As	0.346866000	-2.131342000	-0.187954000	H	2.423818000	5.300370000	-1.249464000
Co	1.234458000	0.058171000	-0.086130000	H	3.310144000	3.873465000	-1.887710000
P	-2.079170000	-0.087764000	0.081348000	C	4.235454000	-2.498441000	-0.800612000
C	2.582286000	1.009470000	-1.300865000	H	4.806421000	-2.473206000	0.145877000
H	2.519278000	1.096371000	-2.391928000	H	4.798994000	-3.149638000	-1.501687000
C	2.041295000	1.969183000	-0.374972000	H	3.254549000	-2.978521000	-0.604842000
C	3.091061000	0.201801000	0.839317000	C	3.153454000	-1.891343000	2.376411000
C	3.231748000	-0.085470000	-0.604869000	H	2.063155000	-1.876796000	2.585802000
C	0.586074000	3.342116000	-1.941931000	H	3.658653000	-2.325310000	3.266510000
H	1.098189000	2.925510000	-2.833628000	H	3.319254000	-2.572131000	1.524826000
H	0.255597000	4.371304000	-2.198561000	C	5.453334000	-0.475112000	-1.688476000
H	-0.311587000	2.717683000	-1.754887000	H	5.363387000	0.503276000	-2.204148000
C	2.340813000	1.444765000	0.926323000	H	6.069562000	-1.144685000	-2.326292000
H	2.050112000	1.927685000	1.864537000	H	6.003896000	-0.304187000	-0.741916000
C	4.053440000	-1.103248000	-1.434021000	C	-3.614436000	-1.206190000	0.063094000
C	1.511923000	3.363854000	-0.706178000	H	-4.447971000	-0.544074000	0.396793000
C	0.750040000	3.966816000	0.493522000	C	3.295623000	0.374152000	3.368642000
H	-0.088827000	3.311354000	0.807295000	H	3.697422000	1.407309000	3.324533000
H	0.333273000	4.961455000	0.228849000	H	3.717994000	-0.109406000	4.273986000
H	1.412345000	4.109282000	1.372253000	H	2.195838000	0.430284000	3.506448000
C	-2.754900000	1.659442000	0.257202000	C	-3.928809000	-1.705846000	-1.364109000
H	-1.829222000	2.277002000	0.205923000	H	-4.034846000	-0.849204000	-2.064059000
C	-5.110428000	-3.742037000	-0.388080000	H	-3.061231000	-2.298353000	-1.733009000
H	-4.309588000	-4.442159000	-0.719435000	C	-5.201895000	-2.573035000	-1.384269000
H	-6.056078000	-4.326296000	-0.388713000	H	-6.081812000	-1.938843000	-1.126407000
C	5.226666000	-0.452360000	2.039173000	H	-5.382587000	-2.950555000	-2.414073000
H	5.614817000	-1.096624000	1.227096000	C	-3.678780000	2.079279000	-0.906101000
H	5.660636000	-0.821958000	2.992799000	H	-4.575841000	1.418828000	-0.929308000
H	5.610331000	0.575008000	1.866661000	H	-3.158012000	1.939724000	-1.878392000
C	-3.509412000	-2.384384000	1.055237000	C	-3.415657000	1.901587000	1.632053000
H	-2.631471000	-3.011114000	0.780959000	H	-4.294553000	1.226262000	1.749361000
H	-3.309414000	-2.009757000	2.082063000	H	-2.706294000	1.639791000	2.447172000
C	3.380211000	-1.342559000	-2.811586000	C	-4.141385000	3.541523000	-0.747960000
H	2.339126000	-1.707199000	-2.689430000	H	-3.260291000	4.215315000	-0.850491000
H	3.948315000	-2.110633000	-3.376744000	H	-4.835606000	3.808680000	-1.573924000
H	3.354401000	-0.432342000	-3.443202000	C	-3.885314000	3.363037000	1.775110000
C	3.676481000	-0.457126000	2.115369000	H	-4.397358000	3.500105000	2.752132000
C	-4.787631000	-3.243569000	1.031041000	H	-2.994144000	4.031223000	1.794250000
H	-4.675590000	-4.101169000	1.729214000	C	-4.809009000	3.779854000	0.617562000
H	-5.644469000	-2.641448000	1.413996000	H	-5.753203000	3.189586000	0.670997000
C	2.742548000	4.261388000	-1.016616000	H	-5.103888000	4.846215000	0.723106000

Table S19: Optimized geometry of **9c**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



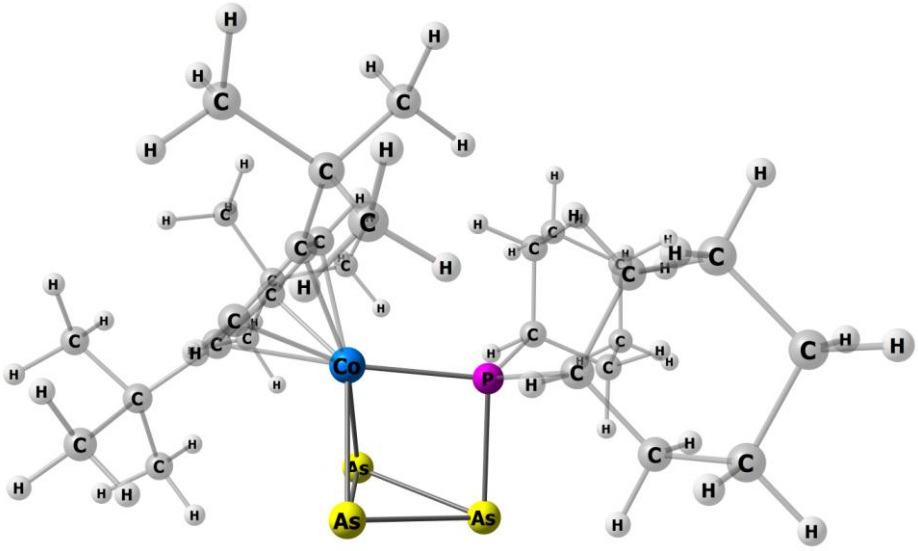
As	-1.175650000	1.469985000	-0.820110000	H	4.208085000	-1.781318000	-3.240456000
As	-0.768838000	-1.633143000	-0.009151000	H	4.462498000	-0.139677000	-2.578976000
As	-0.364976000	-0.443857000	-2.138572000	C	4.774374000	-1.958786000	-0.586842000
Co	0.773726000	0.193316000	-0.196290000	H	5.417255000	-1.068543000	-0.424093000
P	-2.594523000	-0.123726000	0.213487000	H	5.317725000	-2.651494000	-1.264512000
C	2.743293000	-0.456834000	-0.343101000	H	4.656957000	-2.472423000	0.386062000
C	2.580445000	0.895075000	-0.848948000	C	1.376408000	-1.121022000	3.337839000
H	2.804608000	1.209320000	-1.872904000	H	1.421876000	-0.093793000	3.749860000
C	2.100977000	1.772511000	0.180117000	H	1.512225000	-1.819108000	4.190191000
C	1.927346000	0.957900000	1.349671000	H	0.362672000	-1.282992000	2.918750000
H	1.601648000	1.331390000	2.326854000	C	2.348008000	-2.897371000	1.931675000
C	2.040579000	3.300097000	0.107351000	H	1.366185000	-3.134684000	1.472655000
C	2.314318000	-0.413663000	1.072123000	H	2.429257000	-3.486143000	2.869772000
C	-3.815861000	-1.216075000	-2.093314000	H	3.146999000	-3.253904000	1.256793000
H	-3.222297000	-0.527850000	-2.726850000	C	3.849170000	-1.118629000	2.909494000
H	-4.741346000	-1.485682000	-2.649046000	H	4.677176000	-1.306881000	2.197905000
H	-3.218502000	-2.138013000	-1.945604000	H	4.002259000	-1.772302000	3.795108000
C	2.528727000	-2.796193000	-1.453317000	H	3.928631000	-0.063317000	3.242702000
H	2.161509000	-3.254995000	-0.519612000	C	-5.079161000	-1.576098000	0.034587000
H	3.100610000	-3.570715000	-2.008876000	H	-4.511285000	-2.499289000	0.273893000
H	1.643127000	-2.528465000	-2.066926000	H	-5.947881000	-1.877566000	-0.591744000
C	3.415695000	-1.548704000	-1.216685000	H	-5.486716000	-1.161040000	0.976895000
C	-1.785461000	1.101063000	2.600103000	C	-3.079488000	-1.047161000	2.853016000
H	-0.816820000	0.610517000	2.387791000	H	-3.949716000	-1.660888000	2.549044000
H	-1.891788000	1.231201000	3.699798000	H	-3.185114000	-0.830082000	3.939056000
H	-1.751242000	2.109658000	2.139598000	H	-2.165392000	-1.663644000	2.723053000
C	-2.981619000	0.281402000	2.072408000	C	-4.258583000	1.124900000	2.260070000
C	1.025256000	3.880209000	1.115458000	H	-4.213522000	2.074302000	1.687612000
H	-0.002198000	3.524132000	0.895375000	H	-4.350440000	1.395538000	3.335453000
H	1.024901000	4.989541000	1.065857000	H	-5.185923000	0.587806000	1.980537000
H	1.272752000	3.596416000	2.159350000	C	3.459682000	3.819147000	0.472672000
C	-4.221004000	-0.566143000	-0.754500000	H	3.753931000	3.494922000	1.492621000
C	2.460683000	-1.394718000	2.264623000	H	3.489772000	4.929657000	0.442370000
C	-4.998662000	0.733509000	-1.052291000	H	4.221532000	3.434588000	-0.236786000
H	-5.398181000	1.219333000	-0.142356000	C	1.683553000	3.788533000	-1.314183000
H	-5.863725000	0.498845000	-1.711635000	H	2.417611000	3.438640000	-2.068829000
H	-4.361801000	1.468298000	-1.588374000	H	1.677706000	4.898455000	-1.349099000
C	3.743907000	-0.983630000	-2.623710000	H	0.677397000	3.436358000	-1.624814000
H	2.831013000	-0.642156000	-3.153354000				

Table S20: Optimized geometry of **10a**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



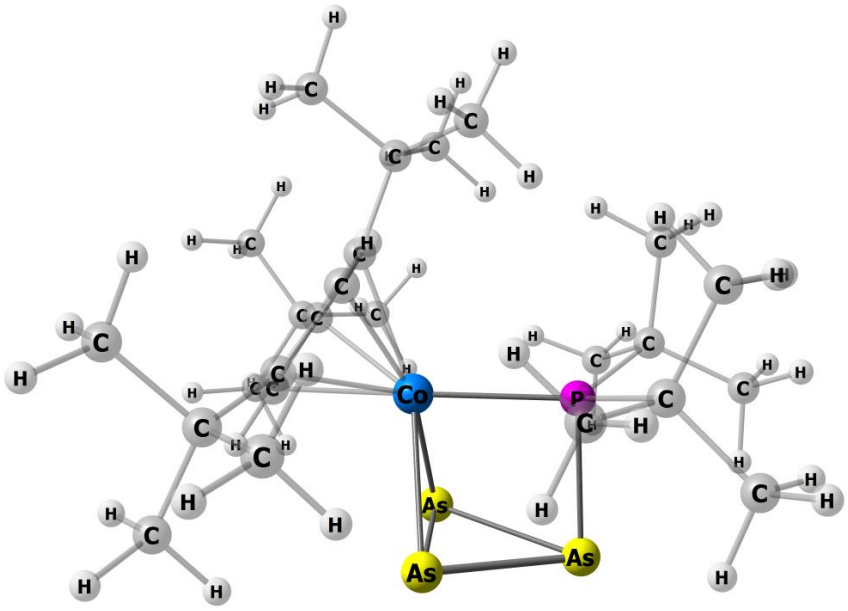
Co	-0.764964000	-0.153051000	-0.076703000	H	-2.215566000	1.774737000	3.951807000
P	1.445122000	-0.158670000	-0.097415000	C	-3.271775000	3.684305000	0.307992000
As	-0.473759000	-2.219038000	-1.361211000	H	-4.127204000	3.212233000	0.835079000
As	1.647751000	-1.172507000	-2.201402000	H	-3.671563000	4.517705000	-0.307948000
As	-0.611960000	-0.123767000	-2.509686000	H	-2.606567000	4.130190000	1.071608000
C	-1.356186000	1.208892000	1.441232000	C	3.118662000	3.437632000	-1.327003000
C	-0.654357000	2.169291000	2.434319000	H	3.031665000	4.084392000	-2.214711000
C	3.336301000	1.768487000	0.921214000	C	-1.555481000	-0.174478000	1.858594000
H	3.437107000	1.121909000	1.806320000	H	-1.116312000	-0.616250000	2.759423000
C	4.067693000	2.968081000	0.859209000	C	-3.830552000	-2.731705000	-0.028172000
H	4.727327000	3.245676000	1.697150000	H	-4.315532000	-3.707262000	0.184944000
C	3.814764000	-1.452409000	0.848663000	H	-3.092253000	-2.892635000	-0.841598000
H	4.355504000	-0.861133000	0.091766000	H	-4.616826000	-2.048534000	-0.410764000
C	2.386865000	2.240718000	-1.267162000	C	4.517179000	-2.378390000	1.636293000
H	1.732620000	1.956858000	-2.107258000	H	5.602470000	-2.504160000	1.493133000
C	2.485765000	1.387995000	-0.142483000	C	-2.472241000	-0.837542000	0.990755000
C	-3.163985000	-2.178160000	1.249987000	C	-2.185310000	-3.227076000	1.820437000
C	-2.802306000	0.123586000	-0.026143000	H	-1.708050000	-2.875140000	2.758668000
H	-3.467744000	-0.081196000	-0.871017000	H	-1.380746000	-3.462656000	1.093796000
C	0.429113000	1.416211000	3.250673000	H	-2.724235000	-4.168324000	2.057934000
H	0.001331000	0.629199000	3.902996000	C	-1.333929000	3.330069000	-1.301388000
H	0.957518000	2.131338000	3.914324000	H	-0.505769000	3.559777000	-0.610441000
H	1.184546000	0.941067000	2.594941000	H	-1.654458000	4.278396000	-1.784039000
C	-4.273342000	-1.900386000	2.304413000	H	-0.930591000	2.664426000	-2.091671000
H	-4.993318000	-1.139687000	1.937357000	C	-3.543563000	2.278819000	-1.718958000
H	-3.840793000	-1.526354000	3.255451000	H	-3.120627000	1.530566000	-2.420895000
H	-4.839514000	-2.830452000	2.525492000	H	-3.789287000	3.183847000	-2.312249000
C	-2.161534000	1.403931000	0.231354000	H	-4.495540000	1.879831000	-1.312193000
C	-2.539484000	2.658519000	-0.599555000	C	3.961278000	3.807392000	-0.262694000
C	1.745971000	-2.066683000	1.974915000	H	4.536417000	4.745730000	-0.310448000
H	0.656528000	-1.953314000	2.083065000	C	2.451512000	-2.992845000	2.764109000
C	2.419949000	-1.279979000	1.018005000	H	1.912080000	-3.599338000	3.509247000
C	3.837859000	-3.148842000	2.598940000	C	0.027945000	3.406360000	1.814273000
H	4.390794000	-3.876091000	3.214683000	H	0.791494000	3.120283000	1.064962000
C	-1.740237000	2.640033000	3.445398000	H	0.540960000	3.981499000	2.613211000
H	-2.542157000	3.222184000	2.951545000	H	-0.692385000	4.094070000	1.334830000
H	-1.280610000	3.283376000	4.226277000				

Table S21: Optimized geometry of **10b**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



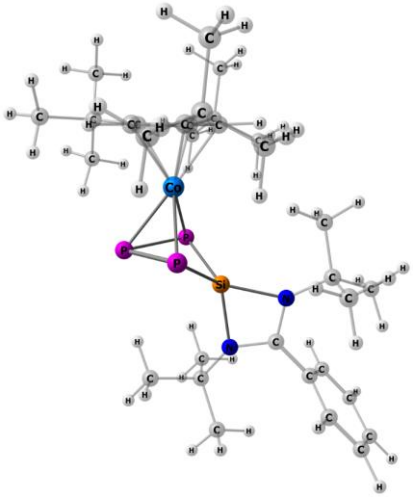
As	-0.618304000	-0.397928000	-2.496224000
As	-1.010226000	1.734662000	-1.452294000
As	1.283306000	1.234348000	-2.292258000
Co	-0.803116000	-0.252106000	-0.082250000
C	-1.178702000	-1.889272000	1.267437000
C	-2.098593000	-1.858677000	0.179704000
H	-2.245318000	-2.682167000	-0.526532000
C	-1.306713000	-0.607781000	1.913119000
H	-0.745623000	-0.302823000	2.803115000
C	-2.872202000	-0.629991000	0.180956000
C	-2.342777000	0.186267000	1.296985000
C	-0.498268000	-3.144578000	1.816722000
C	-2.820139000	1.466207000	2.032026000
C	-1.606756000	2.240003000	2.609575000
H	-1.031827000	1.646680000	3.347868000
H	-1.960107000	3.152371000	3.133862000
H	-0.913787000	2.551050000	1.801386000
C	-4.158070000	-0.535309000	-0.690151000
C	-3.708047000	1.007832000	3.224454000
H	-4.601223000	0.450931000	2.877351000
H	-4.057863000	1.886830000	3.807388000
H	-3.143947000	0.343155000	3.910747000
C	-1.631276000	-4.073072000	2.341482000
H	-2.299935000	-4.399053000	1.518555000
H	-2.254105000	-3.553485000	3.099059000
H	-1.201363000	-4.981910000	2.815121000
C	-5.381580000	-0.592146000	0.265981000
H	-5.323452000	-1.473459000	0.938567000
H	-6.320711000	-0.672035000	-0.322280000
H	-5.463022000	0.311839000	0.899954000
C	-3.614571000	2.483351000	1.187585000
H	-3.029427000	2.828962000	0.310653000
H	-3.842835000	3.374672000	1.809187000
H	-4.581539000	2.083793000	0.830214000
C	-4.269277000	-1.770383000	-1.623862000
H	-3.403696000	-1.845438000	-2.314667000
H	-5.181811000	-1.674507000	-2.248076000
H	-4.353716000	-2.721625000	-1.059857000
C	-4.268822000	0.700971000	-1.614037000
H	-4.145044000	1.658586000	-1.081878000
H	-5.270368000	0.711894000	-2.095229000
H	-3.508805000	0.665667000	-2.419844000
C	0.287668000	-3.897562000	0.722241000
H	0.677436000	-4.860899000	1.114575000
H	1.145524000	-3.299819000	0.359876000
H	-0.351999000	-4.124930000	-0.155100000
C	0.422371000	-2.801061000	3.005971000
H	-0.159165000	-2.414788000	3.868549000
H	1.169075000	-2.028765000	2.734601000
H	0.970112000	-3.703108000	3.350134000
C	2.755716000	-1.141972000	-0.419364000
P	1.403313000	0.205084000	-0.190719000
C	2.090217000	1.566319000	0.944127000
H	4.245348000	1.449894000	0.596893000
C	3.425353000	2.195938000	0.493500000
H	3.378966000	2.468589000	-0.583760000
C	3.765848000	3.437506000	1.341389000
H	2.139915000	-1.992795000	-0.791854000
C	3.466337000	-1.595061000	0.872905000
C	3.800880000	-0.826971000	-1.513736000
H	4.078926000	-0.754400000	1.268033000
H	2.730133000	-1.846065000	1.663217000
C	4.389278000	-2.804301000	0.618755000
H	1.294093000	2.336044000	0.802693000
C	2.123129000	1.220240000	2.448623000
H	3.294405000	-0.534061000	-2.458906000
H	4.419240000	0.046143000	-1.205792000
C	4.721620000	-2.036074000	-1.773564000
C	2.462222000	2.463607000	3.294061000
H	1.636418000	3.205424000	3.197485000
H	2.510139000	2.189238000	4.370533000
C	3.783241000	3.112531000	2.845000000
H	1.145980000	0.798635000	2.761508000
H	2.885650000	0.434906000	2.642069000
H	4.744230000	3.857869000	1.021772000
H	3.007105000	4.229192000	1.143999000
H	4.902025000	-3.090945000	1.562830000
H	3.767278000	-3.680589000	0.324116000
C	5.415598000	-2.513484000	-0.487693000
H	4.624873000	2.412901000	3.058008000
H	3.986432000	4.030784000	3.437686000
H	6.118691000	-1.723293000	-0.135826000
H	6.035489000	-3.413824000	-0.689919000
H	4.114640000	-2.869707000	-2.196248000
H	5.473303000	-1.775111000	-2.549828000

Table S22: Optimized geometry of **10c**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



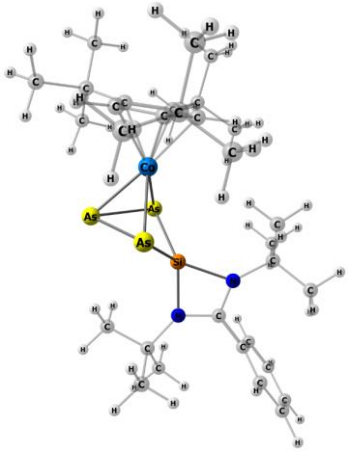
Co	-0.408540000	-0.217705000	-0.023831000	H	-2.320506000	-0.438754000	-3.179689000
P	1.722670000	0.559528000	0.420885000	H	-3.601708000	0.631472000	-3.818054000
As	0.737437000	-2.304957000	-0.592309000	H	-4.004642000	-0.572071000	-2.559308000
As	2.677827000	-0.856661000	-1.203551000	C	-1.877322000	3.702966000	0.554636000
As	0.425936000	-0.635542000	-2.269626000	H	-0.894964000	3.674934000	0.044921000
C	-1.952625000	1.089051000	0.763342000	H	-1.912000000	4.623941000	1.173530000
C	-2.095115000	2.467530000	1.452239000	H	-2.658439000	3.806887000	-0.220905000
C	-2.281019000	-2.650160000	1.556906000	C	2.416299000	2.319303000	-0.138220000
C	-2.310509000	-0.879488000	-0.416517000	H	0.737015000	2.528996000	-1.555366000
H	-2.547747000	-1.579508000	-1.224144000	H	2.219942000	1.857039000	-2.293958000
C	-1.111488000	2.571146000	2.647899000	H	2.145052000	3.601422000	-1.878241000
H	-1.392834000	1.898280000	3.482420000	H	4.337439000	1.470065000	-0.845893000
H	-1.110148000	3.603928000	3.053332000	H	4.436786000	2.249028000	0.772529000
H	-0.079595000	2.315709000	2.340577000	H	4.301160000	3.253084000	-0.698182000
C	-3.657158000	-2.519725000	2.270711000	C	1.843284000	2.583236000	-1.546205000
H	-4.451770000	-2.215822000	1.557901000	C	3.955688000	2.307441000	-0.223774000
H	-3.620823000	-1.762623000	3.081012000	C	1.969201000	3.476889000	0.777192000
H	-3.953107000	-3.491820000	2.720296000	H	2.401490000	3.427081000	1.792606000
C	-2.331599000	0.567396000	-0.547961000	H	2.303409000	4.437836000	0.325938000
C	-2.912302000	1.223677000	-1.831072000	H	0.869782000	3.529674000	0.875289000
C	-3.535736000	2.534479000	2.040577000	C	2.637084000	0.052041000	2.099960000
H	-4.308134000	2.501545000	1.247891000	H	1.702146000	1.668745000	3.294620000
H	-3.671482000	3.477219000	2.613184000	H	3.397394000	2.014429000	2.801174000
H	-3.723838000	1.685659000	2.729590000	H	3.063323000	0.823757000	4.086725000
C	-4.271123000	1.896278000	-1.492525000	H	4.731411000	0.288473000	1.386037000
H	-4.954887000	1.179620000	-0.991499000	H	4.063878000	-1.363297000	1.176886000
H	-4.766452000	2.243121000	-2.424443000	H	4.521918000	-0.780119000	2.804740000
H	-4.159690000	2.776945000	-0.831860000	C	2.696898000	1.214410000	3.111121000
C	-1.709869000	-0.067176000	1.621164000	C	4.065014000	-0.471284000	1.837539000
H	-1.445804000	-0.001521000	2.683021000	C	1.811619000	-1.087320000	2.721924000
C	-2.395275000	-3.755890000	0.484647000	H	1.762849000	-1.969632000	2.053030000
H	-2.601410000	-4.734161000	0.967254000	H	2.287132000	-1.407080000	3.675982000
H	-1.458852000	-3.859262000	-0.102349000	C	-1.968093000	2.241332000	-2.513753000
H	-3.223912000	-3.555669000	-0.225412000	H	-1.611094000	3.026983000	-1.827192000
C	-1.999169000	-1.279084000	0.930730000	H	-2.494569000	2.740236000	-3.355553000
C	-1.218406000	-3.055362000	2.598091000	H	-1.078018000	1.726820000	-2.929855000
H	-1.102920000	-2.290033000	3.393056000	C	-3.224381000	0.140162000	-2.897384000
H	-0.230105000	-3.203358000	2.120056000	H	0.773525000	-0.771526000	2.939202000
H	-1.508649000	-4.006363000	3.092731000				

Table S23: Optimized geometry of **11**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Co	1.826028000	-0.133924000	-0.377069000
P	0.154536000	0.138916000	-2.041453000
P	0.334147000	-1.601998000	0.707957000
Si	-1.175681000	-0.415830000	-0.375133000
P	0.989036000	-1.876123000	-1.449274000
N	-2.948852000	-1.102262000	-0.631860000
N	-2.452165000	0.754237000	0.407364000
C	-4.932890000	-2.384857000	-1.508772000
H	-5.673675000	-2.066988000	-0.750759000
H	-5.225152000	-3.396319000	-1.858444000
H	-4.996718000	-1.695615000	-2.375555000
C	-4.924247000	0.182542000	0.306707000
C	-3.494728000	-2.447231000	-0.951673000
C	-3.473793000	-0.052603000	0.026705000
C	-2.442657000	2.195080000	0.775185000
C	-5.476709000	-0.203826000	1.547709000
H	-4.832988000	-0.669841000	2.309945000
C	-5.750626000	0.788524000	-0.664817000
H	-5.325001000	1.082197000	-1.636927000
C	3.687052000	0.298843000	-1.097883000
H	4.061866000	0.018864000	-2.087024000
C	-3.449660000	-3.324661000	0.321775000
H	-2.416977000	-3.376949000	0.724105000
H	-3.787247000	-4.356794000	0.092004000
H	-4.114872000	-2.916970000	1.111181000
C	3.800869000	-0.518048000	0.094729000
C	2.900820000	2.741557000	-1.736123000
C	-6.839590000	0.012005000	1.809847000
H	-7.263726000	-0.294353000	2.779045000
C	-2.571778000	-3.047913000	-2.032821000
H	-2.570258000	-2.418515000	-2.945920000
H	-2.921356000	-4.064068000	-2.306284000
H	-1.525074000	-3.128290000	-1.674296000
C	3.007047000	1.531029000	-0.806319000
C	3.139075000	0.246597000	1.175576000
C	2.676713000	1.492657000	0.589773000
H	2.191211000	2.302919000	1.144414000
C	-1.049476000	2.479255000	1.368344000
H	-0.898716000	1.911314000	2.308193000
H	-0.945462000	3.559941000	1.593642000
H	-0.244545000	2.189008000	0.662562000
C	4.629214000	-1.828485000	0.079370000
C	-3.509628000	2.541899000	1.836251000
H	-4.541595000	2.491663000	1.440522000
H	-3.338326000	3.578637000	2.192603000
C	1.620031000	3.558258000	-1.463816000
H	0.715920000	2.948215000	-1.665068000
H	1.586895000	4.456385000	-2.116589000
H	1.572261000	3.910074000	-0.412485000
C	-7.658487000	0.620182000	0.841643000
H	-8.726215000	0.791416000	1.050636000
C	3.088902000	0.099275000	2.718373000
C	5.869371000	-1.670340000	1.000108000
H	6.458889000	-0.772368000	0.718959000
H	6.533613000	-2.556265000	0.907205000
H	5.596579000	-1.572102000	2.068174000
C	4.336832000	0.835050000	3.285079000
H	5.281119000	0.369348000	2.939760000
H	4.329527000	0.809874000	4.396301000
H	4.350752000	1.897640000	2.965245000
C	1.826984000	0.799035000	3.286878000
H	1.818248000	1.890337000	3.093999000
H	1.789005000	0.664077000	4.388138000
H	0.908229000	0.359953000	2.847786000
C	3.059245000	-1.342118000	3.270401000
H	2.178357000	-1.899933000	2.890950000
H	2.985531000	-1.305670000	4.378069000
H	3.971372000	-1.916899000	3.026970000
C	4.138930000	3.634878000	-1.444005000
H	4.143922000	3.983354000	-0.390146000
H	4.140074000	4.529780000	-2.103255000
H	5.082557000	3.077632000	-1.619276000
C	2.929376000	2.317241000	-3.221005000
H	3.882742000	1.815401000	-3.486860000
H	2.832370000	3.208452000	-3.876605000
H	2.095647000	1.623508000	-3.454848000
C	5.175172000	-2.098205000	-1.347150000
H	4.353996000	-2.200749000	-2.085652000
H	5.746875000	-3.049779000	-1.348575000
H	-3.434041000	1.864598000	2.711215000
C	-7.111122000	1.009144000	-0.393964000
H	-7.748531000	1.485086000	-1.155695000
C	3.816233000	-3.086975000	0.470794000
H	3.283384000	-2.981964000	1.430656000
H	4.491090000	-3.966981000	0.548091000
H	3.057495000	-3.309819000	-0.308272000
C	-2.656456000	3.047691000	-0.497778000
H	-1.889523000	2.811293000	-1.263756000
H	-2.584972000	4.129061000	-0.258238000
H	-3.658367000	2.863668000	-0.937482000
H	5.861840000	-1.297542000	-1.691339000

Table S24: Optimized geometry of **12**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



As	-0.266905000	0.629750000	1.642350000	H	7.830977000	-1.074653000	-1.817828000
As	-0.068351000	0.894715000	-1.801434000	C	5.867582000	-0.637106000	-0.998431000
As	-1.011127000	2.327425000	-0.010647000	H	5.408452000	-0.470117000	-1.985209000
Co	-1.805378000	0.139937000	-0.218306000	C	-5.870596000	0.374048000	1.821119000
Si	1.336100000	0.411181000	-0.023515000	H	-6.547179000	1.099608000	2.321663000
C	-3.678425000	0.252560000	-1.028597000	H	-5.600085000	-0.395808000	2.568811000
H	-4.074668000	1.096331000	-1.602137000	H	-6.444642000	-0.125907000	1.013031000
N	2.602841000	-1.010926000	-0.060907000	C	-1.685701000	-2.048779000	-3.453152000
N	3.121070000	1.097461000	0.136653000	H	-0.758221000	-1.459880000	-3.297937000
C	-2.646672000	-1.734782000	-0.513585000	H	-1.721979000	-2.359123000	-4.519219000
H	-2.156903000	-2.709221000	-0.618600000	H	-1.614694000	-2.971624000	-2.841115000
C	-3.780270000	0.108887000	0.412610000	C	-3.056927000	-1.335049000	3.366843000
C	-3.001117000	-0.874472000	-1.606549000	H	-2.183729000	-0.656273000	3.454709000
C	3.749526000	2.434971000	-0.004285000	H	-2.983874000	-2.084965000	4.182912000
C	5.083073000	-0.515070000	0.169364000	H	-3.977336000	-0.750461000	3.547907000
C	-2.939884000	-1.220962000	-3.097040000	C	-2.982748000	0.048206000	-3.975990000
C	3.634715000	-0.147887000	0.079128000	H	-3.919676000	0.622214000	-3.821829000
C	5.675183000	-0.742633000	1.431318000	H	-2.936745000	-0.227219000	-5.050832000
H	5.068977000	-0.638037000	2.344513000	H	-2.126360000	0.718977000	-3.756245000
C	-3.108656000	-1.168146000	0.741235000	C	-4.304029000	-3.001767000	1.943188000
C	2.509161000	-2.481464000	0.107730000	H	-5.252974000	-2.430363000	1.972219000
C	3.682459000	-3.232563000	-0.557809000	H	-4.301556000	-3.705610000	2.803383000
H	4.646966000	-3.067215000	-0.041271000	H	-4.302943000	-3.600633000	1.009070000
H	3.795412000	-2.932934000	-1.619761000	C	-1.795443000	-2.955007000	1.995302000
H	3.471531000	-4.321566000	-0.532495000	H	-1.765251000	-3.649495000	1.132566000
C	-4.627642000	1.105405000	1.246040000	H	-1.765732000	-3.576658000	2.914616000
C	7.811124000	-1.209514000	0.356167000	H	-0.881385000	-2.327592000	1.967795000
H	8.875999000	-1.481168000	0.428649000	C	-4.202288000	-2.078778000	-3.396584000
C	2.447893000	-2.816829000	1.616862000	H	-4.198316000	-3.019302000	-2.807158000
H	2.287071000	-3.904353000	1.769347000	H	-4.244952000	-2.347510000	-4.474234000
H	1.615694000	-2.270306000	2.105754000	H	-5.130186000	-1.525525000	-3.142338000
H	3.393590000	-2.537209000	2.125218000	C	4.078310000	2.689493000	-1.494587000
C	7.033064000	-1.090048000	1.521625000	H	4.843278000	1.974965000	-1.862305000
H	7.486631000	-1.265622000	2.509811000	H	4.477604000	3.715722000	-1.634203000
C	1.197406000	-2.907707000	-0.583157000	H	3.167901000	2.583327000	-2.119341000
H	1.250292000	-2.720861000	-1.675077000	C	5.022825000	2.577373000	0.857978000
H	0.329492000	-2.341130000	-0.187189000	H	4.816985000	2.317665000	1.916581000
H	1.015261000	-3.989653000	-0.421836000	H	5.364320000	3.632640000	0.827248000
C	-3.063970000	-2.063993000	2.006897000	H	5.856810000	1.946433000	0.496044000
C	-5.167488000	2.239564000	0.336018000	C	2.707515000	3.464729000	0.479757000
H	-5.747369000	2.959828000	0.950216000	H	1.772016000	3.403868000	-0.113488000
H	-5.844719000	1.856916000	-0.455038000	H	3.115248000	4.490937000	0.378585000
H	-4.341659000	2.800819000	-0.147715000	H	-4.531457000	2.440570000	2.981827000
C	-3.842976000	1.807871000	2.380846000	C	7.226197000	-0.981216000	-0.902091000
H	-3.060458000	2.470094000	1.955328000	H	2.444636000	3.293474000	1.543371000
H	-3.344222000	1.104663000	3.068540000				

4.2 Model system $[Cp^{H}CoP_3]^-$ + PMe_2^+

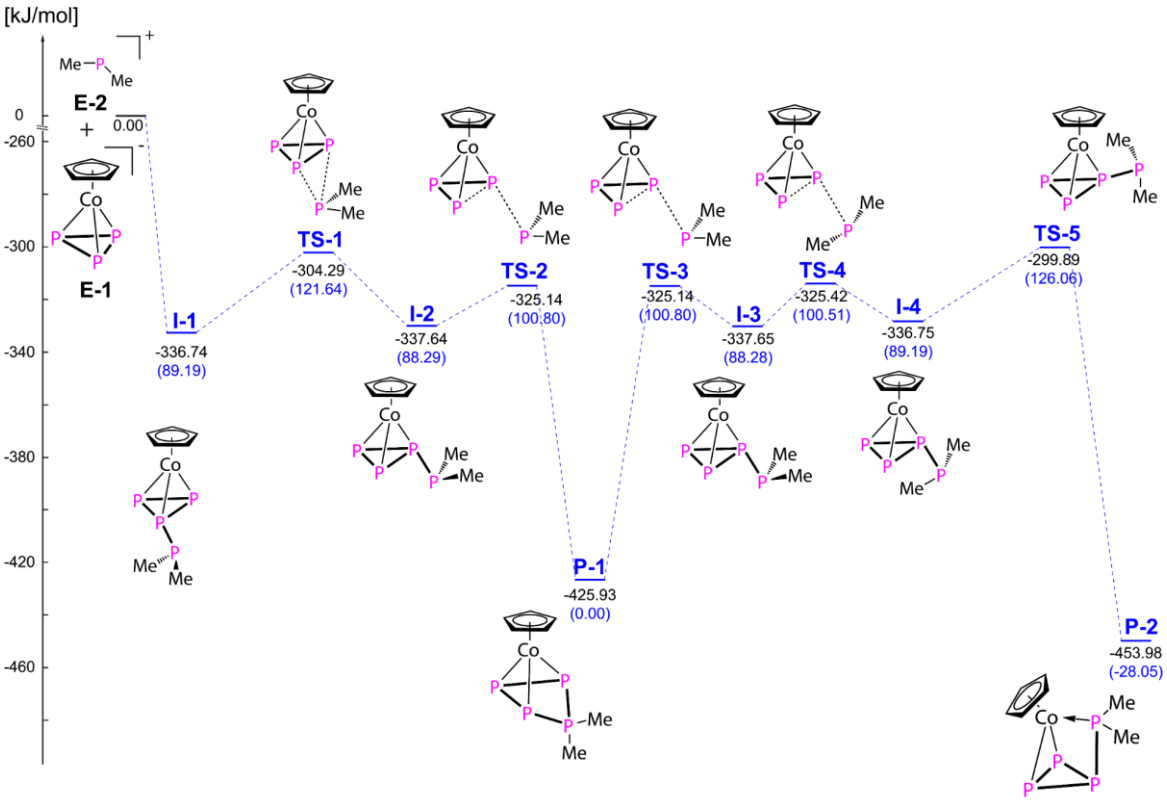
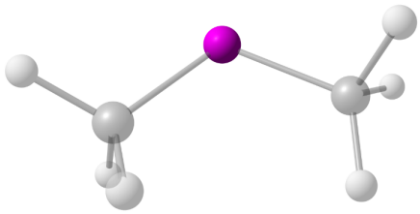


Figure S73. Pathway of the reaction of $[Cp^{H}CoP_3]^-$ with PMe_2^+. Optimization conducted at the BP86/def2-SVP level of theory. Energy values obtained from single point calculation at the B3LYP/def2-SVP level of theory including solvent effects and dispersion correction (GD3BJ).

Table S25: Total energies for optimized geometries, optimization at the BP86/def2-SVP level and single point energies at the B3LYP/def2-TZVP level of theory including solvent effects and dispersion correction GD3BJ.

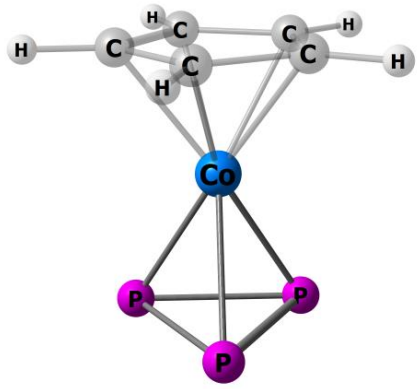
	BP86/def2-SVP total energy [Ha]	B3LYP/def2-TZVP total energy [Ha]
E-1 PMe_2^+	-420.715050551	-421.005180115
E-2 $[Cp^HCoP_3]^-$	-2600.23091948	-2600.79338366
I-1	-3021.21140299	-3021.92682249
I-2	-3021.21191669	-3021.92716445
I-3	-3021.21191696	-3021.92716657
I-4	-3021.21140289	-3021.92682580
TS-1	-3021.20283745	-3021.91446067
TS-2	-3021.21036332	-3021.92240128
TS-3	-3021.21036332	-3021.92240128
TS-4	-3021.20976802	-3021.92250837
TS-5	-3021.19664403	-3021.91277719
P-1	-3021.23818703	-3021.96079231
P-2	-3021.25000834	-3021.97147658

Table S26: Optimized geometry of E-1. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



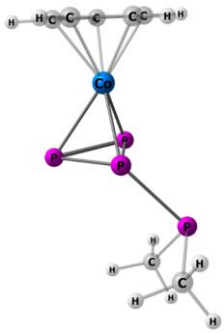
P	1.618447000	-0.014501000	0.484690000	C	2.656163000	1.080504000	-0.484410000
C	2.639334000	-1.463838000	0.753196000	H	3.042674000	1.767027000	0.330530000
H	2.375612000	-1.985642000	1.699019000	H	3.539469000	0.642516000	-0.992861000
H	2.237274000	-2.147228000	-0.056873000	H	2.054242000	1.750885000	-1.136111000
H	3.732183000	-1.366078000	0.589760000				

Table S27: Optimized geometry of **E-2**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



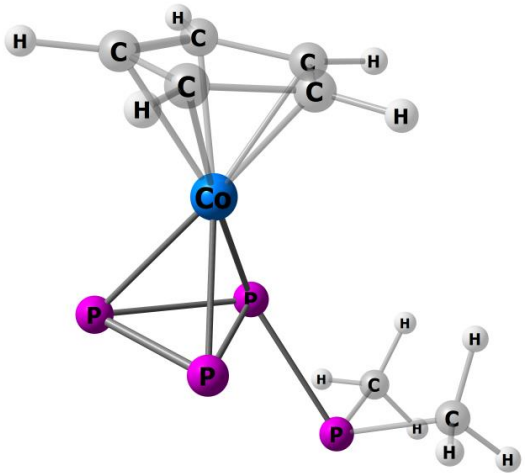
Co	-1.638534000	-0.698380000	-0.995253000	C	-2.308685000	1.162720000	-0.471721000
P	-0.778352000	-2.709100000	-1.669924000	C	-1.841529000	-0.580310000	1.027145000
P	0.247160000	-0.859952000	-2.288733000	H	-1.341470000	-1.199557000	1.785233000
P	-1.696120000	-1.393365000	-3.180317000	C	-3.117383000	-0.861526000	0.400201000
C	-1.342185000	0.658708000	0.480417000	H	-3.760992000	-1.730332000	0.597811000
C	-3.390672000	0.204841000	-0.534328000	H	-0.393074000	1.143130000	0.751178000
H	-4.281116000	0.283344000	-1.174535000	H	-2.229683000	2.094160000	-1.049546000

Table S28: Optimized geometry of **I-1**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



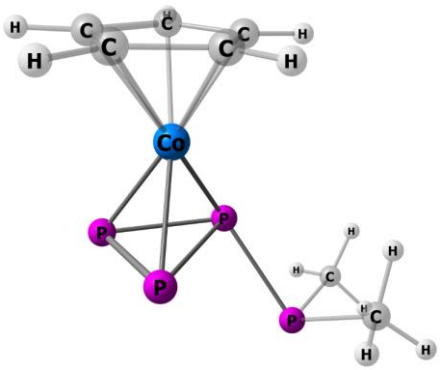
Co	1.716230000	0.042743000	0.016911000	H	3.608357000	1.583328000	1.405895000
P	1.395801000	-1.357577000	1.743021000	C	1.108255000	-4.625049000	1.827779000
P	2.350503000	-3.359419000	2.422636000	H	1.237034000	-5.542597000	2.441009000
P	1.635389000	-2.075544000	-0.475424000	H	0.058288000	-4.275323000	1.921307000
P	-0.249416000	-1.302124000	0.290239000	H	1.310576000	-4.874936000	0.767534000
C	2.171089000	1.151591000	-1.626515000	C	1.770540000	-3.217199000	4.204326000
H	2.099994000	0.828966000	-2.673453000	H	2.274082000	-2.354679000	4.686614000
C	2.959901000	1.561433000	0.519710000	H	0.671508000	-3.099637000	4.306800000
C	3.322131000	1.023332000	-0.770674000	H	0.102225000	1.992889000	-1.229903000
C	1.114000000	1.778510000	-0.861278000	H	4.293411000	0.591810000	-1.043572000
C	1.607694000	2.060386000	0.457780000	H	2.085929000	-4.137965000	4.741337000
H	1.050954000	2.534264000	1.275703000				

Table S29: Optimized geometry of **I-2**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



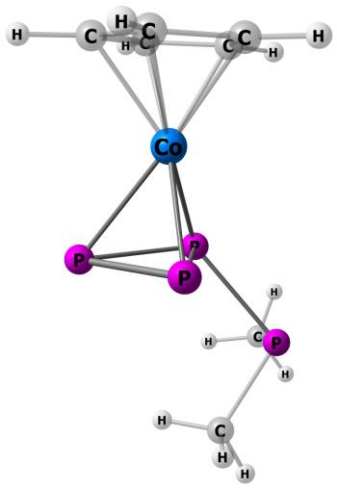
Co	-1.169277000	-0.012963000	-0.112270000	H	-3.236323000	-0.603562000	-1.954974000
P	0.902528000	0.527074000	0.588708000	H	-2.632267000	0.325439000	2.330754000
P	3.030653000	-0.019664000	-0.167264000	H	-1.423079000	-2.062977000	1.795172000
P	-0.171253000	2.134397000	-0.443484000	C	3.752068000	-0.235639000	1.555074000
P	0.267244000	0.424977000	-1.691461000	H	4.786963000	-0.626137000	1.445629000
C	-3.168771000	0.298198000	0.127971000	H	3.813013000	0.753844000	2.052046000
H	-3.690527000	1.253996000	-0.012329000	H	3.174020000	-0.930591000	2.199956000
C	-1.975580000	-1.448014000	1.072068000	C	2.784785000	-1.829670000	-0.586771000
C	-2.610132000	-0.184893000	1.359895000	H	2.113047000	-2.355595000	0.123842000
C	-2.920234000	-0.683517000	-0.906591000	H	2.365971000	-1.917038000	-1.609128000
C	-2.187261000	-1.774165000	-0.319353000	H	3.778551000	-2.326449000	-0.568755000
H	-1.848590000	-2.683211000	-0.832101000				

Table S30: Optimized geometry of **I-3**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



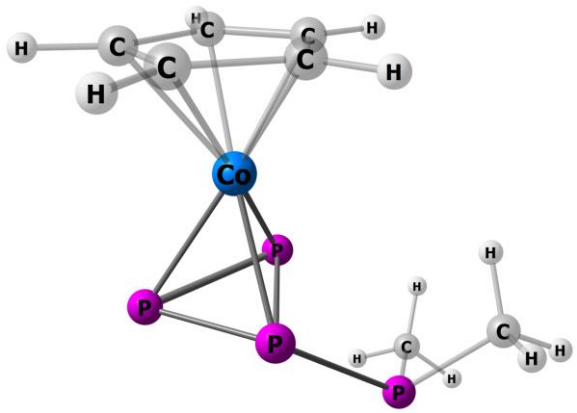
Co	-1.156375000	-0.037481000	0.029906000	H	-2.417632000	0.173133000	-2.537199000
P	3.027268000	-0.015458000	0.402875000	C	3.865625000	0.573429000	-1.173178000
P	0.171036000	-0.797589000	1.582270000	H	4.880585000	0.938427000	-0.904670000
P	0.972355000	-0.400564000	-0.611437000	H	3.985152000	-0.284502000	-1.865590000
P	-0.137051000	-2.199703000	-0.033679000	H	3.319401000	1.387351000	-1.694860000
C	-1.905384000	1.621593000	-0.863606000	C	2.709849000	1.659046000	1.182543000
C	-3.123302000	-0.301430000	-0.435540000	H	3.690572000	2.154983000	1.346619000
H	-3.629971000	-1.267988000	-0.555963000	H	2.078904000	2.321477000	0.553351000
C	-2.483551000	0.451140000	-1.478017000	H	-3.373687000	0.105756000	1.784313000
C	-2.231678000	1.623527000	0.543514000	H	-1.314468000	2.387834000	-1.383214000
H	-1.957107000	2.395889000	1.272926000	H	2.216770000	1.520091000	2.165297000
C	-2.979928000	0.422857000	0.809725000				

Table S31: Optimized geometry of **I-4**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



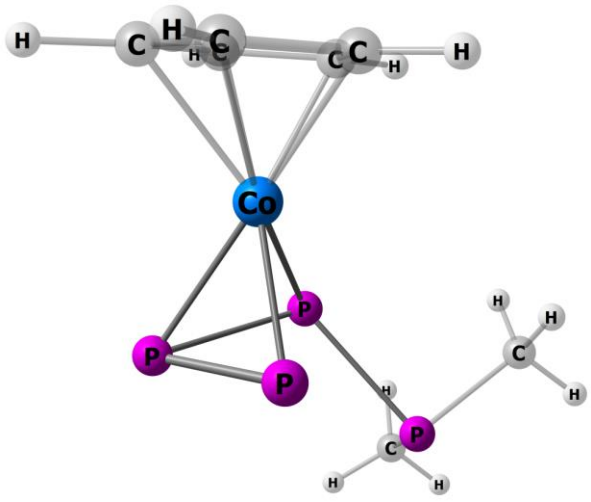
Co	-1.418408000	-0.796567000	-0.991375000	C	-2.377460000	-0.916875000	0.798559000
P	1.520242000	-2.198655000	-3.667452000	H	-2.937023000	-1.779207000	1.183911000
P	-1.100649000	-2.776902000	-1.835787000	H	0.327012000	1.034276000	0.227078000
P	-0.219316000	-0.876712000	-2.888327000	H	-1.969305000	2.017385000	-0.878472000
P	-2.316274000	-1.490847000	-3.102939000	C	0.638247000	-3.420281000	-4.775860000
C	-0.667744000	0.574202000	0.298468000	H	1.378427000	-3.814346000	-5.504812000
C	-2.924733000	0.155481000	-0.005471000	H	0.254111000	-4.263470000	-4.168431000
H	-3.966485000	0.229276000	-0.344349000	H	-0.206822000	-2.963937000	-5.333620000
C	-1.876695000	1.094997000	-0.291840000	C	2.072573000	-0.977336000	-4.984368000
C	-0.975413000	-0.653138000	0.994727000	H	2.910003000	-1.439978000	-5.550353000
H	-0.268197000	-1.271340000	1.561942000	H	1.268765000	-0.696705000	-5.696641000
				H	2.460197000	-0.060431000	-4.495357000

Table S32: Optimized geometry of **TS-1**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



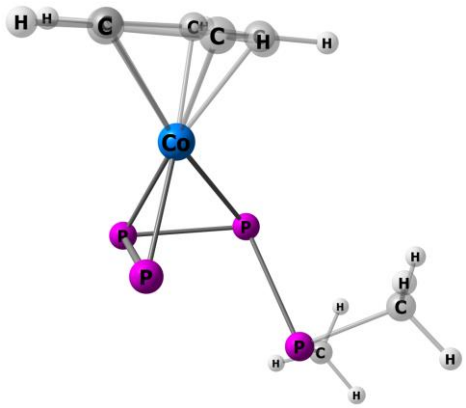
Co	1.421073000	0.105408000	-0.002976000	H	1.761217000	2.267193000	1.784797000
P	1.603469000	-2.026113000	0.424275000	H	0.212815000	2.653195000	-0.438415000
P	0.245413000	-2.589382000	2.879194000	H	3.759689000	0.295542000	-1.633003000
P	-0.083503000	-1.517904000	-0.851604000	H	3.958841000	0.820134000	1.046424000
P	-0.232389000	-0.746825000	1.179325000	C	1.502523000	-3.995692000	2.869896000
C	1.812694000	1.448160000	-1.501720000	H	1.384742000	-4.518087000	3.846451000
H	1.432613000	1.395667000	-2.530347000	H	1.251061000	-4.713523000	2.064169000
C	3.138924000	1.130870000	0.385961000	H	2.555594000	-3.668188000	2.752748000
C	3.038476000	0.859228000	-1.027357000	C	1.158220000	-1.404406000	4.000102000
C	1.162355000	2.104584000	-0.397070000	H	2.113810000	-1.049593000	3.557986000
C	1.979673000	1.897155000	0.774493000	H	0.518812000	-0.524389000	4.215484000
				H	1.380709000	-1.919847000	4.958886000

Table S33: Optimized geometry of **TS-2**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



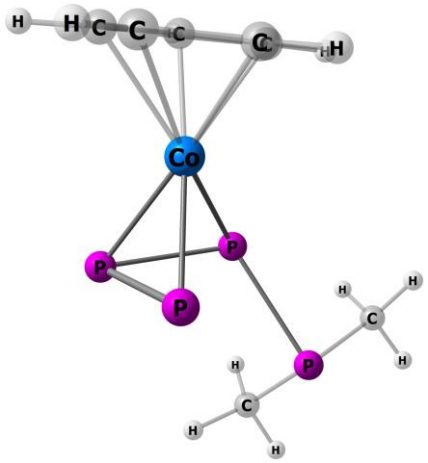
Co	-1.145561000	-0.081904000	0.036411000	H	-3.368610000	-0.413335000	1.780064000
P	2.774964000	0.269412000	0.538717000	H	-1.444735000	2.590907000	-0.816161000
P	0.222997000	-1.018427000	1.353250000	H	-2.454377000	0.627655000	-2.420817000
P	0.926049000	-0.004100000	-0.886775000	C	4.024700000	0.160540000	-0.856651000
P	0.083197000	-2.014838000	-0.563757000	H	5.008548000	0.516800000	-0.483103000
C	-1.989292000	1.700740000	-0.474615000	H	4.136309000	-0.900469000	-1.159042000
C	-3.116996000	-0.322056000	-0.474818000	H	3.727194000	0.759175000	-1.745168000
H	-3.583400000	-1.260082000	-0.803235000	C	2.596406000	2.128807000	0.678321000
C	-2.526043000	0.669149000	-1.326930000	H	3.534355000	2.547060000	1.101483000
C	-2.303943000	1.381916000	0.899251000	H	2.390976000	2.621572000	-0.296586000
H	-2.057618000	1.989010000	1.779562000	H	1.769238000	2.360427000	1.379319000
C	-2.996975000	0.123861000	0.897670000				

Table S34: Optimized geometry of **TS-3**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



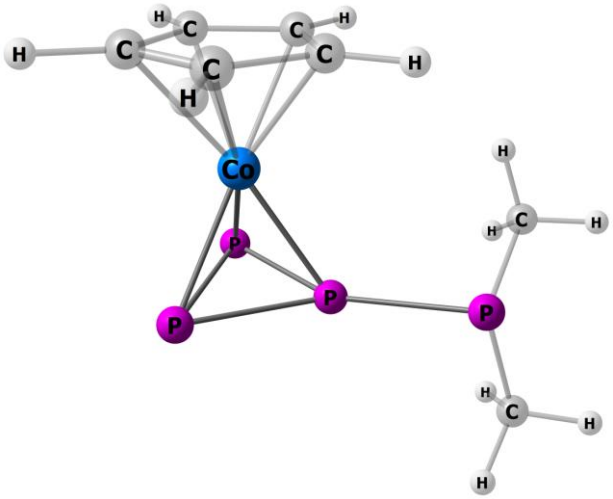
Co	-1.145561000	-0.081904000	0.036411000	C	-2.996975000	0.123861000	0.897670000
P	2.774964000	0.269412000	0.538717000	H	-3.368610000	-0.413335000	1.780064000
P	0.222997000	-1.018427000	1.353250000	H	-1.444735000	2.590907000	-0.816161000
P	0.926049000	-0.004100000	-0.886775000	H	-2.454377000	0.627655000	-2.420817000
P	0.083197000	-2.014838000	-0.563757000	C	4.024700000	0.160540000	-0.856651000
C	-1.989292000	1.700740000	-0.474615000	H	5.008548000	0.516800000	-0.483103000
C	-3.116996000	-0.322056000	-0.474818000	H	4.136309000	-0.900469000	-1.159042000
H	-3.583400000	-1.260082000	-0.803235000	H	3.727194000	0.759175000	-1.745168000
C	-2.526043000	0.669149000	-1.326930000	C	2.596406000	2.128807000	0.678321000
C	-2.303943000	1.381916000	0.899251000	H	3.534355000	2.547060000	1.101483000
H	-2.057618000	1.989010000	1.779562000	H	2.390976000	2.621572000	-0.296586000
				H	1.769238000	2.360427000	1.379319000

Table S35: Optimized geometry of **TS-4**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



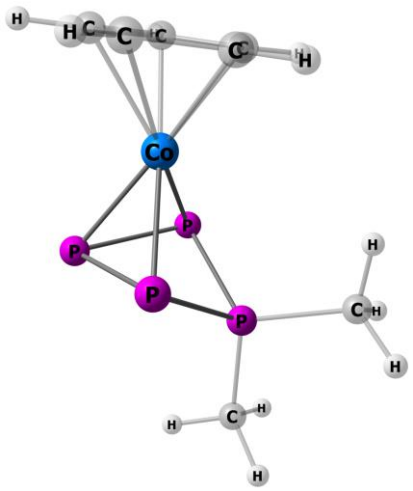
Co	-1.086649000	0.239853000	0.130536000	C	-3.029077000	-0.094537000	0.693024000
P	2.883600000	-0.286131000	0.927855000	H	-3.512365000	-1.070964000	0.828352000
P	0.143056000	-1.477544000	0.409496000	H	-1.254996000	2.647558000	1.576260000
P	1.088526000	0.708664000	-0.270978000	H	-2.062978000	2.672265000	-1.032635000
P	0.161615000	-0.753481000	-1.631743000	C	3.927041000	-0.597818000	-0.595458000
C	-1.845276000	1.865943000	1.079863000	H	4.956370000	-0.851916000	-0.262629000
C	-2.975197000	0.656960000	-0.541935000	H	3.518130000	-1.471203000	-1.142771000
H	-3.398925000	0.337112000	-1.502959000	H	3.971066000	0.271624000	-1.285161000
C	-2.271680000	1.884635000	-0.298065000	C	3.572033000	1.381864000	1.448495000
C	-2.332440000	0.656499000	1.702231000	H	4.599306000	1.228846000	1.843523000
H	-2.193347000	0.365709000	2.751205000	H	3.604691000	2.117725000	0.615913000
				H	2.951370000	1.793491000	2.270465000

Table S36: Optimized geometry of **TS-5**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



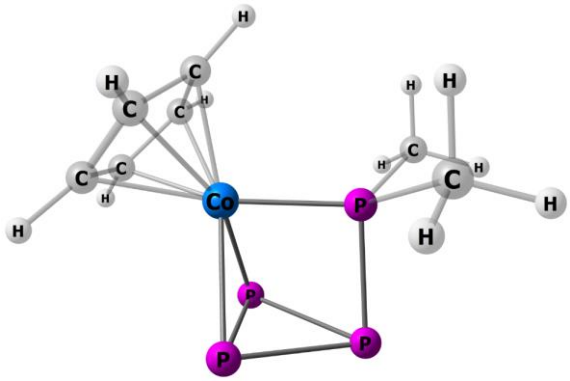
Co	-1.490821000	-0.648751000	-0.580141000	C	-3.420816000	-0.464346000	0.044773000
P	2.095229000	-0.641425000	0.810765000	H	-4.230306000	-1.185596000	-0.126321000
P	-0.968935000	-2.789148000	-0.990314000	H	-0.831978000	0.949978000	1.699767000
P	0.641971000	-1.355588000	-0.755551000	H	-1.460717000	2.227600000	-0.641997000
P	-0.603242000	-1.159348000	-2.555002000	C	3.675587000	-1.418565000	0.176940000
C	-1.630598000	0.666146000	1.001285000	H	4.511676000	-1.046812000	0.808094000
C	-3.055594000	0.624276000	-0.831933000	H	3.615489000	-2.518332000	0.301092000
H	-3.542782000	0.874041000	-1.783374000	H	3.888025000	-1.180299000	-0.885060000
C	-1.954884000	1.337136000	-0.232744000	C	2.333669000	1.109713000	0.192766000
C	-2.538962000	-0.433969000	1.185866000	H	3.153651000	1.566267000	0.787659000
H	-2.553122000	-1.126098000	2.037265000	H	2.600177000	1.160170000	-0.882668000
				H	1.407765000	1.691628000	0.367322000

Table S37: Optimized geometry of **P-1**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Co	0.609182000	0.311313000	-0.559425000	H	0.952611000	1.879457000	1.796238000
P	-0.692893000	-1.531183000	-0.876921000	H	1.960298000	2.825149000	-0.563458000
P	-2.382428000	-0.253377000	-0.251377000	H	2.801096000	-1.506150000	-0.366298000
P	-0.458087000	0.015699000	-2.504208000	H	1.473488000	-0.802242000	1.918429000
P	-1.279585000	1.500996000	-1.016009000	C	-2.690521000	-0.229124000	1.568398000
C	2.608350000	0.683367000	-0.912176000	H	-3.424307000	0.563419000	1.823932000
H	3.099723000	0.734073000	-1.892516000	H	-3.080342000	-1.211925000	1.906044000
C	1.737227000	-0.126942000	1.094063000	H	-1.728330000	-0.019349000	2.073739000
C	2.450055000	-0.498439000	-0.109508000	C	-4.047252000	-0.608973000	-0.980100000
C	2.006681000	1.785930000	-0.213414000	H	-3.943682000	-0.640733000	-2.082236000
C	1.463800000	1.282274000	1.029933000	H	-4.423224000	-1.588424000	-0.617928000
				H	-4.766302000	0.189263000	-0.701450000

Table S38: Optimized geometry of **P-2**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Co	-0.826655000	-0.345412000	-0.495418000	C	-2.702052000	-0.869622000	0.247419000
P	1.325315000	-0.369194000	-0.493066000	H	-3.287598000	-1.749943000	-0.048653000
P	-0.579610000	-2.137874000	-1.931870000	H	-0.437142000	0.894312000	2.026270000
P	1.444464000	-1.228840000	-2.531136000	H	-1.648395000	2.352106000	0.059989000
P	-0.561220000	-0.134905000	-2.778771000	C	2.257027000	-1.453793000	0.689809000
C	-1.192561000	0.519732000	1.322103000	H	2.167449000	-1.049953000	1.720095000
C	-2.756991000	0.423283000	-0.382359000	H	1.812778000	-2.467976000	0.667523000
H	-3.391848000	0.691483000	-1.237049000	H	3.331014000	-1.515172000	0.416401000
C	-1.830509000	1.294597000	0.288290000	C	2.293017000	1.213319000	-0.434106000
C	-1.741281000	-0.815862000	1.312482000	H	2.216849000	1.664560000	0.577482000
H	-1.478882000	-1.633270000	1.995511000	H	3.362663000	1.036359000	-0.671826000
				H	1.864650000	1.920741000	-1.170628000

4.3 Model system $[Cp^{H}CoAs_3]^-$ + PMe_2^+

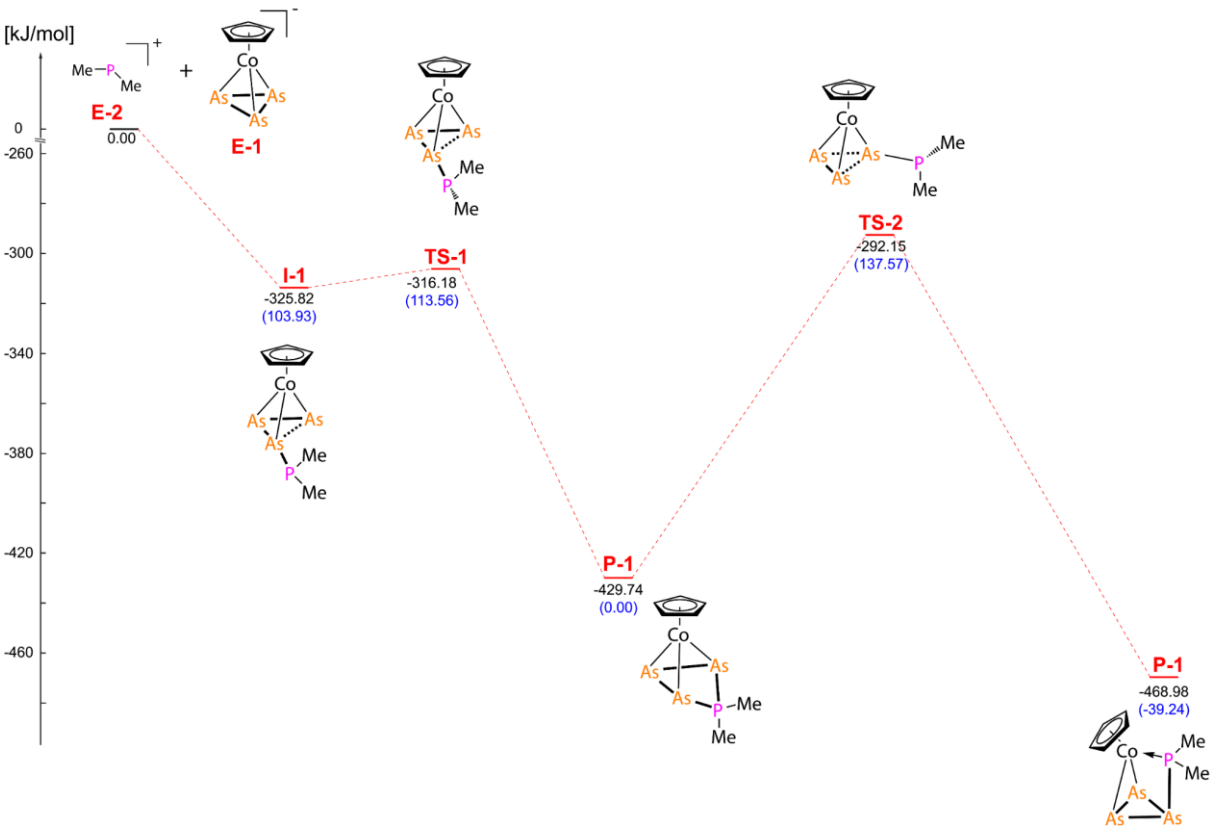
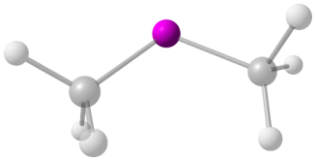


Figure S74. Pathway of the reaction of $[Cp^{H}CoAs_3]^-$ with PMe_2^+. Optimization conducted at the BP86/def2-SVP level of theory. Energy values obtained from single point calculation at the B3LYP/def2-SVP level of theory including solvent effects and dispersion correction (GD3BJ).

Table S39: Total energies for optimized geometries, optimization at the BP86/def2-SVP level and single point energies at the B3LYP/def2-TZVP level of theory including solvent effects and dispersion correction GD3BJ.

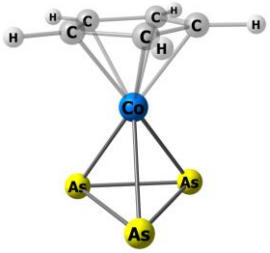
	BP86/def2-SVP total energy [Ha]	B3LYP/def2-TZVP total energy [Ha]
E-1 PMe_2^+	-420.715050551	-421.005180115
E-2 $[Cp^{H}CoAs_3]^-$	-8284.04643115	-8284.44318169
I-1	-8705.02196608	-8705.57245879
TS-1	-8705.02064556	-8705.56878951
TS-2	-8705.01278625	-8705.55963690
P-1	-8705.05420539	-8705.61204268
P-2	-8705.06844349	-8705.62698683

Table S40: Optimized geometry of **E-1**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



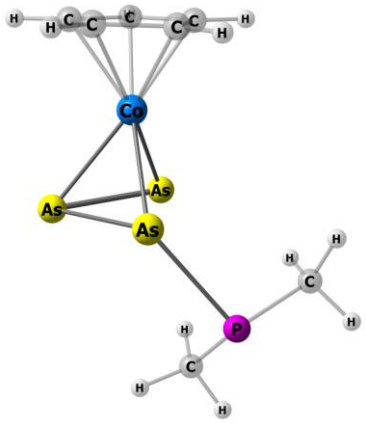
P	1.618447000	-0.014501000	0.484690000	C	2.656163000	1.080504000	-0.484410000
C	2.639334000	-1.463838000	0.753196000	H	3.042674000	1.767027000	0.330530000
H	2.375612000	-1.985642000	1.699019000	H	3.539469000	0.642516000	-0.992861000
H	2.237274000	-2.147228000	-0.056873000	H	2.054242000	1.750885000	-1.136111000
H	3.732183000	-1.366078000	0.589760000				

Table S41: Optimized geometry of **E-2**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



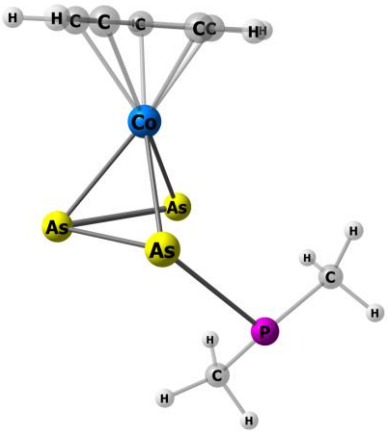
Co	-1.645542000	-0.693242000	-0.993062000	C	-2.314522000	1.168321000	-0.464572000
As	-0.763754000	-2.837721000	-1.619913000	C	-1.844746000	-0.576388000	1.031133000
As	0.369938000	-0.799062000	-2.302376000	H	-1.344948000	-1.196414000	1.788655000
As	-1.768665000	-1.390094000	-3.293535000	C	-3.122222000	-0.856277000	0.406853000
C	-1.346614000	0.663640000	0.486137000	H	-3.765163000	-1.725413000	0.603638000
C	-3.398902000	0.212797000	-0.523444000	H	-0.398591000	1.149324000	0.757713000
H	-4.292633000	0.294518000	-1.158518000	H	-2.236270000	2.100393000	-1.041081000

Table S42: Optimized geometry of **I-1**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



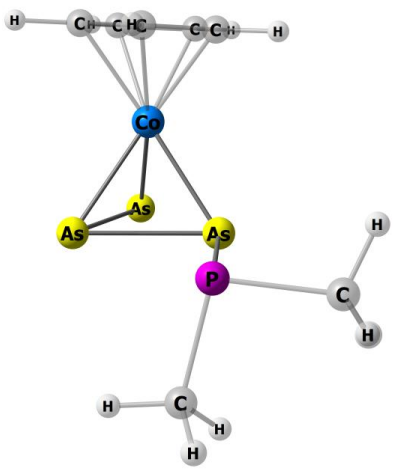
Co	1.403133000	0.255792000	0.026705000	H	3.193412000	-0.225361000	-2.166604000
As	-0.413337000	0.068028000	1.324176000	H	3.222002000	0.690874000	2.161668000
P	-2.886835000	0.692202000	-1.056554000	H	2.209614000	2.871757000	0.849147000
As	0.177576000	-1.905079000	0.121163000	C	-3.731149000	-0.518357000	0.090604000
As	-0.554035000	-0.100383000	-1.343093000	H	-4.812345000	-0.259647000	0.111872000
C	3.391639000	-0.224074000	0.091283000	H	-3.635081000	-1.540850000	-0.327492000
H	3.809541000	-1.216715000	0.304144000	H	-3.334556000	-0.514606000	1.126222000
C	2.534728000	1.929359000	0.390503000	C	-2.866063000	2.243520000	-0.005172000
C	3.074329000	0.786128000	1.077914000	H	-2.626865000	2.063744000	1.062679000
C	3.066847000	0.293527000	-1.208233000	H	-2.129631000	2.958979000	-0.424288000
C	2.509691000	1.610881000	-1.017209000	H	-3.871321000	2.713671000	-0.079027000
H	2.133776000	2.265775000	-1.814706000				

Table S43: Optimized geometry of **TS-1**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



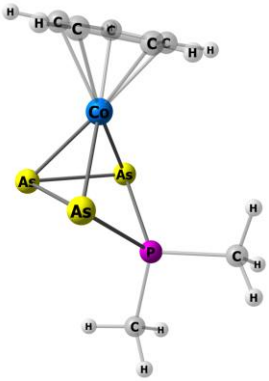
Co	1.556597000	0.205330000	0.006826000	H	-0.154134000	2.206516000	-1.116198000
As	2.260637000	-1.751096000	0.914345000	H	4.047704000	0.829736000	-1.235031000
P	0.457432000	-2.247329000	3.286474000	H	3.547541000	1.794347000	1.279591000
As	0.615596000	-1.921281000	-0.820032000	C	0.734426000	-4.046669000	2.857039000
As	-0.184136000	-0.833842000	1.196816000	H	0.514646000	-4.645836000	3.767531000
C	1.884287000	1.368240000	-1.648326000	H	0.009327000	-4.343194000	2.072160000
H	1.756391000	1.060320000	-2.694315000	H	1.759772000	-4.277993000	2.503418000
C	2.829645000	1.742441000	0.450886000	C	2.039579000	-1.791233000	4.188009000
C	3.095069000	1.239162000	-0.874653000	H	2.958325000	-2.243548000	3.761023000
C	0.873723000	1.966300000	-0.816016000	H	2.147760000	-0.687442000	4.192197000
C	1.456833000	2.182733000	0.487126000	H	1.925289000	-2.121355000	5.243897000
H	0.944523000	2.618880000	1.354932000				

Table S44: Optimized geometry of **TS-2**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



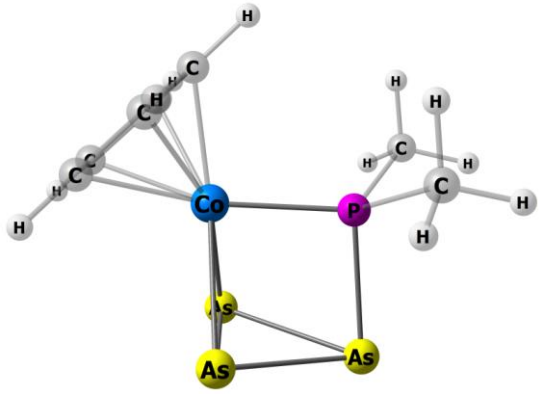
Co	-1.587961000	-0.663706000	-0.487829000	H	-4.426861000	-1.149284000	-0.665216000
P	2.199702000	-0.183659000	0.617345000	H	-1.402672000	0.444732000	2.131701000
As	-0.165253000	-2.554468000	-0.263836000	H	-1.543485000	2.129582000	-0.021819000
As	0.631617000	-0.382202000	-1.265781000	C	3.525086000	-1.419707000	0.144452000
As	-1.185110000	-1.982607000	-2.315699000	H	4.429018000	-1.216755000	0.759267000
C	-2.059804000	0.329046000	1.260654000	H	3.170988000	-2.445371000	0.370298000
C	-3.117910000	0.696987000	-0.794859000	H	3.805606000	-1.363782000	-0.928258000
H	-3.418235000	1.148716000	-1.748982000	C	3.051939000	1.371299000	0.002015000
C	-2.126944000	1.209972000	0.116367000	H	3.935185000	1.566194000	0.648975000
C	-2.998232000	-0.737997000	1.042642000	H	3.398273000	1.295171000	-1.050732000
H	-3.187678000	-1.578441000	1.723081000	H	2.364629000	2.236530000	0.095308000
C	-3.651417000	-0.511573000	-0.220607000				

Table S45: Optimized geometry of **P-1**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Co	0.687011000	0.327103000	-0.555674000	H	1.082888000	1.903304000	1.790755000
As	-0.655710000	-1.618397000	-0.785711000	H	2.052415000	2.842410000	-0.590038000
P	-2.482007000	-0.269947000	-0.194876000	H	2.891773000	-1.490736000	-0.392044000
As	-0.419646000	0.018064000	-2.620394000	H	1.601699000	-0.775204000	1.913122000
As	-1.279642000	1.603919000	-0.933600000	C	-2.867503000	-0.261456000	1.616680000
C	2.678007000	0.694833000	-0.948291000	H	-3.612314000	0.527602000	1.851198000
H	3.153392000	0.741759000	-1.936704000	H	-3.268671000	-1.247148000	1.932640000
C	1.849724000	-0.106097000	1.078833000	H	-1.929315000	-0.054517000	2.167560000
C	2.538014000	-0.483730000	-0.135704000	C	-4.118250000	-0.623332000	-0.991564000
C	2.095092000	1.802846000	-0.240180000	H	-3.971882000	-0.645353000	-2.089029000
C	1.576536000	1.304270000	1.014401000	H	-4.505941000	-1.606798000	-0.653030000
				H	-4.850111000	0.170685000	-0.734598000

Table S46: Optimized geometry of **P-2**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Co	-0.826990000	-0.356883000	-0.520498000	C	-2.693732000	-0.855500000	0.270993000
P	1.328435000	-0.383937000	-0.529437000	H	-3.307979000	-1.722013000	-0.007231000
As	-0.644726000	-2.280446000	-1.971648000	H	-0.356681000	0.864636000	2.000800000
As	1.577051000	-1.291459000	-2.661196000	H	-1.598864000	2.351336000	0.076424000
As	-0.623261000	-0.071333000	-2.909828000	C	2.224628000	-1.434872000	0.714313000
C	-1.134627000	0.504423000	1.313718000	H	2.062259000	-1.027279000	1.734516000
C	-2.746765000	0.441177000	-0.348894000	H	1.814481000	-2.462863000	0.675879000
H	-3.407552000	0.726604000	-1.178014000	H	3.314434000	-1.464577000	0.505852000
C	-1.787235000	1.293991000	0.300577000	C	2.260064000	1.220693000	-0.419094000
C	-1.700885000	-0.823019000	1.308900000	H	2.102043000	1.679486000	0.579820000
H	-1.433784000	-1.648054000	1.980780000	H	3.347618000	1.064875000	-0.577158000
				H	1.872551000	1.913691000	-1.191081000

4.4 Model system $[Cp^{H}CoP_3]^- + PR_2^+$

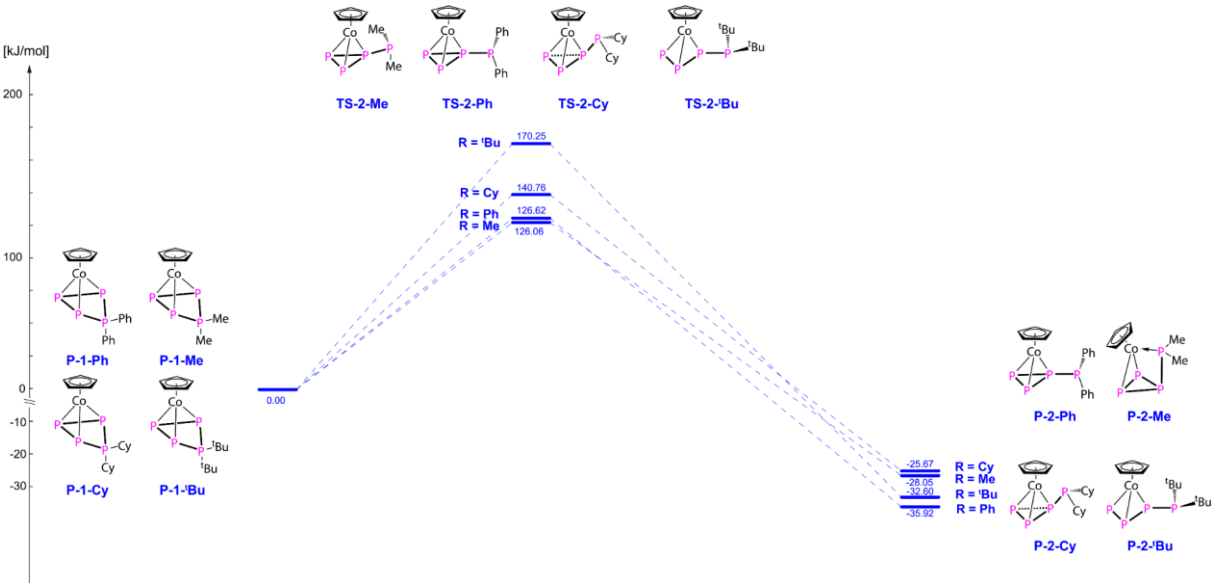
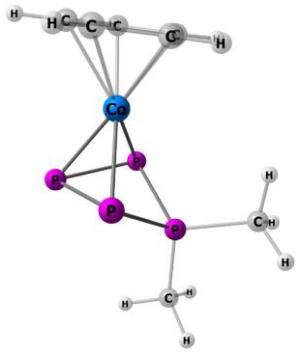


Figure S75. Pathway of the reaction of $[Cp^{H}CoP_3]^-$ with PR_2^+. Optimization conducted at the BP86/def2-SVP level of theory. Energy values obtained from single point calculation at the B3LYP/def2-SVP level of theory including solvent effects and dispersion correction (GD3BJ).

Table S47: Total energies for optimized geometries, optimization at the BP86/def2-SVP level and single point energies at the B3LYP/def2-TZVP level of theory including solvent effects and dispersion correction GD3BJ.

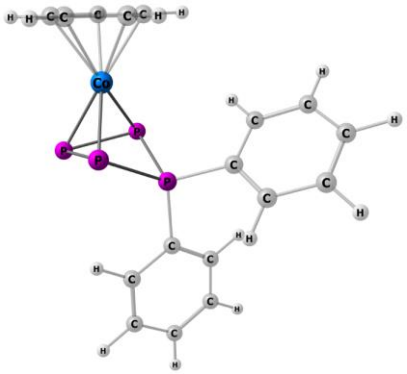
	BP86/def2-SVP total energy [Ha]	B3LYP/def2-TZVP total energy [Ha]
P-1-Me	-3021.23818703	-3021.96079231
P-1-Ph	-3404.42944279	-3405.60389269
P-1-Cy	-3411.66581443	-3412.87356008
P-1-^{t}Bu	-3256.91778493	-3257.94941136
TS-2-Me	-3021.19664403	-3021.91277719
TS-2-Ph	-3404.39101384	-3405.55566462
TS-2-Cy	-3411.62620844	-3412.81994664
TS-2-^{t}Bu	-3256.86547658	-3257.88456659
P-2-Me	-3021.25000834	-3021.97147658
P-2-Ph	-3404.44236317	-3405.61757257
P-2-Cy	-3411.67462868	-3412.88334421
P-2-^{t}Bu	-3256.92767614	-3257.96182853

Table S48: Optimized geometry of **P-1-Me**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



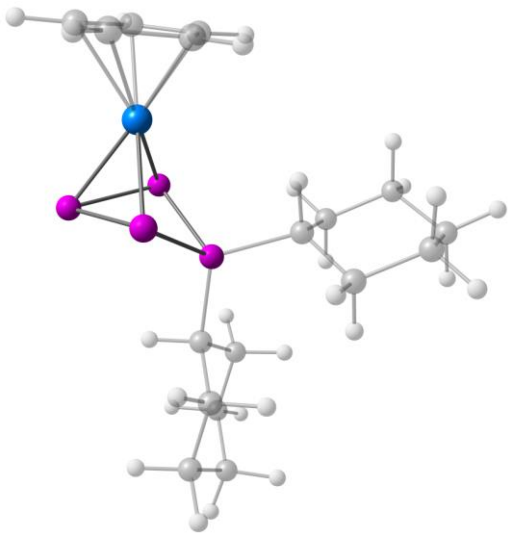
Co	0.609182000	0.311313000	-0.559425000	H	0.952611000	1.879457000	1.796238000
P	-0.692893000	-1.531183000	-0.876921000	H	1.960298000	2.825149000	-0.563458000
P	-2.382428000	-0.253377000	-0.251377000	H	2.801096000	-1.506150000	-0.366298000
P	-0.458087000	0.015699000	-2.504208000	H	1.473488000	-0.802242000	1.918429000
P	-1.279585000	1.500996000	-1.016009000	C	-2.690521000	-0.229124000	1.568398000
C	2.608350000	0.683367000	-0.912176000	H	-3.424307000	0.563419000	1.823932000
H	3.099723000	0.734073000	-1.892516000	H	-3.080342000	-1.211925000	1.906044000
C	1.737227000	-0.126942000	1.094063000	H	-1.728330000	-0.019349000	2.073739000
C	2.450055000	-0.498439000	-0.109508000	C	-4.047252000	-0.608973000	-0.980100000
C	2.006681000	1.785930000	-0.213414000	H	-3.943682000	-0.640733000	-2.082236000
C	1.463800000	1.282274000	1.029933000	H	-4.423224000	-1.588424000	-0.617928000
				H	-4.766302000	0.189263000	-0.701450000

Table S49: Optimized geometry of **P-1-Ph**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



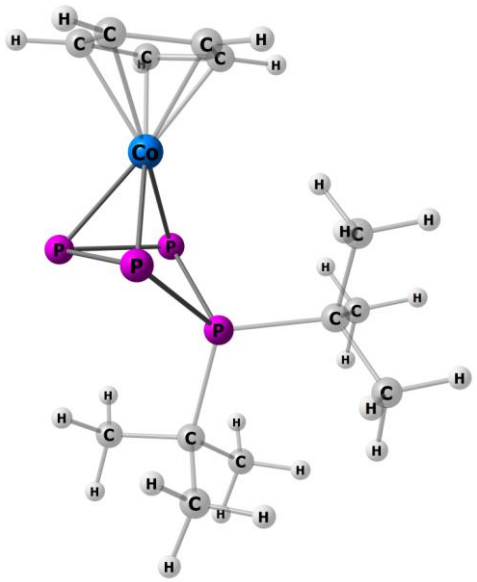
Co	0.915374000	-0.488904000	0.417658000	H	-4.107507000	3.551044000	-2.461165000
P	-0.149765000	-2.438957000	0.659933000	C	-3.280554000	1.889509000	-1.332076000
P	-0.838506000	-0.656247000	1.851541000	H	-3.727666000	1.126282000	-1.989439000
P	-0.555265000	-1.183698000	-1.169791000	C	-3.923712000	-2.369666000	-0.555625000
C	2.951969000	-0.768813000	0.601506000	H	-3.040539000	-2.844969000	-1.012863000
H	3.464635000	-1.723608000	0.776425000	C	-5.162538000	-3.033121000	-0.546591000
C	2.472627000	0.129491000	1.617146000	C	-3.804618000	-1.086115000	0.021593000
C	1.848902000	1.254634000	0.955192000	H	-5.250079000	-4.030941000	-1.005033000
H	1.398256000	2.123895000	1.451045000	C	-6.284162000	-2.426935000	0.045831000
C	2.638235000	-0.203977000	-0.682157000	C	-4.934174000	-0.480953000	0.619871000
C	1.949170000	1.049198000	-0.462818000	H	-4.849986000	0.518667000	1.075794000
P	-2.147604000	-0.280519000	0.087585000	C	-6.167728000	-1.151618000	0.629669000
C	-2.151937000	3.846966000	0.347687000	H	-7.044877000	-0.674973000	1.095771000
H	-1.714121000	4.611512000	1.009016000	H	-7.253861000	-2.949684000	0.053779000
C	-1.925226000	2.484769000	0.610384000	H	-3.106376000	5.299784000	-0.963396000
C	-2.933264000	4.231811000	-0.755907000	H	2.870168000	-0.650310000	-1.657747000
H	-1.307149000	2.178066000	1.469983000	H	1.579057000	1.726900000	-1.242818000
C	-2.493830000	1.498515000	-0.223917000	H	2.560131000	-0.014998000	2.701610000
C	-3.495326000	3.251939000	-1.595470000				

Table S50: Optimized geometry of **P-1-Cy**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



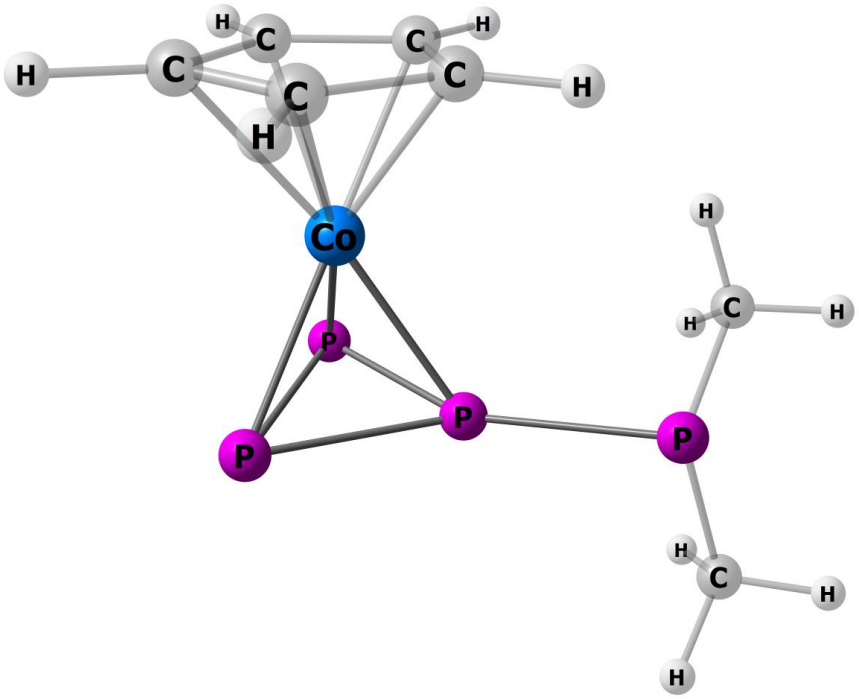
Co	-1.137144000	-0.324261000	-0.534615000	H	1.173275000	1.594805000	0.822790000
P	-0.154707000	-2.167855000	-1.338614000	C	3.036577000	1.293692000	1.889945000
P	0.601127000	-0.146816000	-1.998666000	H	4.264206000	-0.117509000	-2.181881000
P	0.330439000	-1.498766000	0.758344000	H	5.026153000	0.265529000	-0.612889000
C	-3.177303000	-0.442536000	-0.837369000	C	5.817413000	-1.530633000	-1.551086000
H	-3.715210000	-1.257448000	-1.338937000	C	3.047445000	2.682276000	2.559520000
C	-2.641093000	0.729442000	-1.473459000	H	2.011858000	2.938203000	2.881274000
C	-1.998903000	1.534769000	-0.457369000	H	3.661856000	2.650159000	3.485206000
H	-1.509409000	2.503959000	-0.618686000	C	3.568667000	3.769329000	1.603270000
C	-2.879913000	-0.368723000	0.566966000	H	2.617956000	0.532436000	2.583078000
C	-2.144488000	0.855244000	0.800816000	H	4.085823000	0.988894000	1.675967000
C	3.521089000	-1.313538000	-0.498246000	H	3.192509000	4.551170000	-0.409524000
P	1.935315000	-0.334872000	-0.235711000	H	1.724583000	4.105319000	0.493779000
C	2.228998000	1.330545000	0.575867000	H	5.586429000	-3.400395000	1.411886000
H	3.792148000	2.151878000	-0.720353000	H	4.828126000	-3.790477000	-0.150900000
C	2.759713000	2.409737000	-0.395074000	C	6.335826000	-2.223004000	-0.278530000
H	2.135571000	2.436452000	-1.314948000	H	4.642854000	3.573330000	1.378178000
C	2.773501000	3.792206000	0.285987000	H	3.532385000	4.765651000	2.094338000
H	3.133962000	-2.115240000	-1.171723000	H	6.790724000	-1.458847000	0.393890000
C	4.032920000	-1.996562000	0.789214000	H	7.149951000	-2.935790000	-0.532123000
C	4.649683000	-0.571377000	-1.243586000	H	5.470794000	-2.301949000	-2.276350000
H	4.374124000	-1.224878000	1.514428000	H	6.638147000	-0.976032000	-2.055528000
H	3.204174000	-2.549833000	1.281709000	H	-1.779618000	1.209218000	1.773929000
C	5.203697000	-2.946747000	0.472134000	H	-3.154598000	-1.112264000	1.326177000
				H	-2.701832000	0.967923000	-2.543132000

Table S51: Optimized geometry of **P-1-^{t}Bu**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



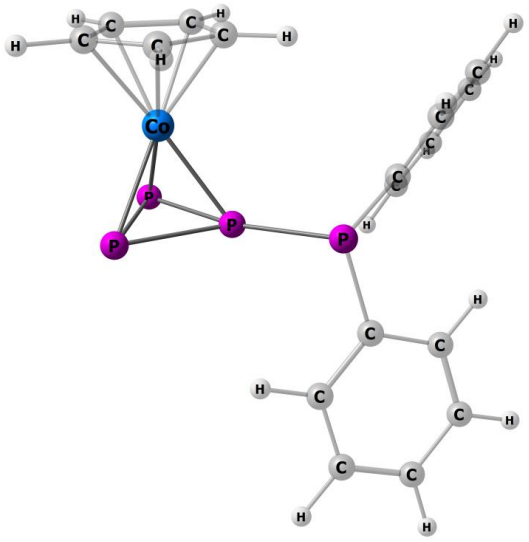
Co	0.561484000	0.018295000	-0.341864000
P	-0.938516000	-1.672334000	-0.029599000
P	-2.608535000	-0.181002000	-0.078270000
P	-0.465643000	-0.874736000	-2.085794000
P	-1.222828000	1.093047000	-1.294539000
C	2.143049000	1.319454000	-0.608290000
H	2.205671000	2.122732000	-1.353600000
C	2.312039000	-0.762148000	0.425317000
C	2.572348000	-0.040966000	-0.790694000
C	1.605251000	1.438423000	0.727358000
C	-3.014900000	0.502454000	1.688157000
C	1.710088000	0.155693000	1.366108000
H	1.414019000	-0.081346000	2.396533000
C	-4.222233000	-0.739634000	-1.000234000
C	-3.135983000	-0.703132000	2.645529000
H	-4.003851000	-1.350745000	2.414052000
H	-3.261253000	-0.333043000	3.686999000
H	-2.221396000	-1.332611000	2.621558000
C	-4.285898000	1.373645000	1.726856000
H	-4.220546000	2.232355000	1.027421000
H	-4.397357000	1.793072000	2.751172000
H	-5.212002000	0.808262000	1.505443000
C	-1.815835000	1.372608000	2.117720000
H	-0.861797000	0.819446000	2.034221000
H	-1.962212000	1.695036000	3.172319000
H	-1.726586000	2.283183000	1.489797000
C	-4.963992000	0.514747000	-1.508466000
H	-5.383619000	1.131266000	-0.691340000
H	-5.811015000	0.200351000	-2.157602000
H	-4.295657000	1.156563000	-2.120233000
C	-5.115936000	-1.605453000	-0.089567000
H	-4.571161000	-2.491904000	0.296886000
H	-5.977403000	-1.982941000	-0.683706000
H	-5.534351000	-1.047207000	0.770735000
C	-3.794881000	-1.591096000	-2.213945000
H	-3.173654000	-1.016987000	-2.929375000
H	-4.710146000	-1.929894000	-2.747906000
H	-3.219058000	-2.488450000	-1.910842000
H	1.204655000	2.355383000	1.178669000
H	3.018060000	-0.458089000	-1.703018000
H	2.524565000	-1.823974000	0.604516000

Table S52: Optimized geometry of **TS-2-Me**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



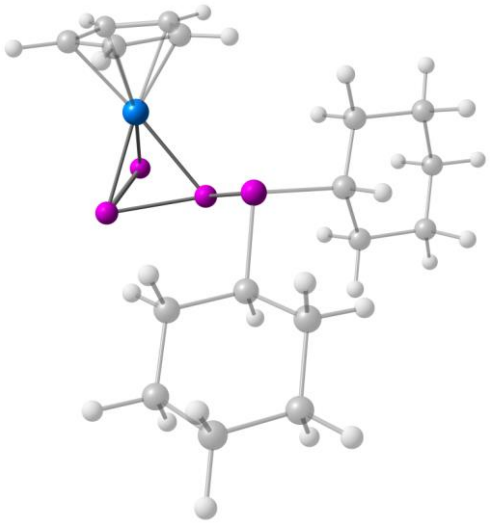
Co	-1.490821000	-0.648751000	-0.580141000	C	-3.420816000	-0.464346000	0.044773000
P	2.095229000	-0.641425000	0.810765000	H	-4.230306000	-1.185596000	-0.126321000
P	-0.968935000	-2.789148000	-0.990314000	H	-0.831978000	0.949978000	1.699767000
P	0.641971000	-1.355588000	-0.755551000	H	-1.460717000	2.227600000	-0.641997000
P	-0.603242000	-1.159348000	-2.555002000	C	3.675587000	-1.418565000	0.176940000
C	-1.630598000	0.666146000	1.001285000	H	4.511676000	-1.046812000	0.808094000
C	-3.055594000	0.624276000	-0.831933000	H	3.615489000	-2.518332000	0.301092000
H	-3.542782000	0.874041000	-1.783374000	H	3.888025000	-1.180299000	-0.885060000
C	-1.954884000	1.337136000	-0.232744000	C	2.333669000	1.109713000	0.192766000
C	-2.538962000	-0.433969000	1.185866000	H	3.153651000	1.566267000	0.787659000
H	-2.553122000	-1.126098000	2.037265000	H	2.600177000	1.160170000	-0.882668000
				H	1.407765000	1.691628000	0.367322000

Table S53: Optimized geometry of **TS-2-Ph**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



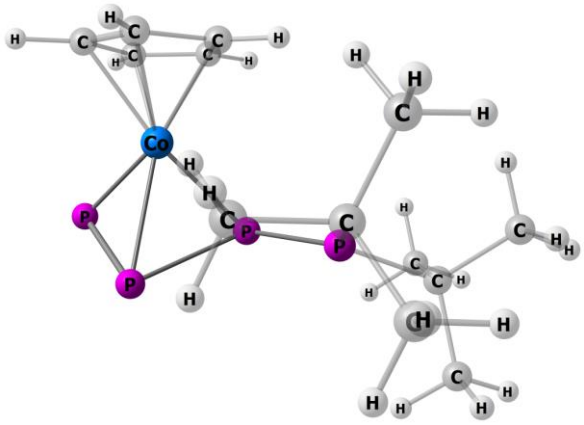
Co	1.697155000	1.788747000	-4.338593000	H	7.943038000	0.566852000	1.426155000
P	3.800625000	0.289302000	-1.417930000	C	8.405439000	0.057718000	-0.640405000
P	3.561114000	0.995306000	-5.345226000	C	6.502930000	-0.033905000	-2.160727000
P	3.658586000	1.624288000	-3.272213000	H	6.101365000	-0.197100000	-3.174758000
P	3.321524000	3.191723000	-4.821481000	C	7.881400000	-0.156518000	-1.928848000
C	0.204326000	1.348311000	-2.977208000	H	8.551957000	-0.420267000	-2.762227000
C	-0.106787000	2.540590000	-4.943679000	H	9.487606000	-0.040393000	-0.459625000
H	-0.259032000	3.363365000	-5.654229000	C	2.040502000	1.026461000	0.627311000
C	0.007914000	2.668537000	-3.512006000	H	1.634937000	0.012583000	0.473471000
C	0.189519000	0.399128000	-4.061004000	C	1.470938000	1.870460000	1.597526000
H	0.301905000	-0.688833000	-3.973261000	C	3.139299000	1.464128000	-0.148570000
C	0.005385000	1.141417000	-5.283117000	H	0.619591000	1.515875000	2.200089000
H	-0.050008000	0.715958000	-6.293404000	C	1.987634000	3.162330000	1.795413000
H	0.340615000	1.106082000	-1.915355000	C	3.652636000	2.767394000	0.058517000
H	-0.038809000	3.600743000	-2.935172000	H	4.502278000	3.123080000	-0.546068000
C	6.160207000	0.531732000	0.185955000	C	3.077438000	3.608779000	1.023660000
H	5.494867000	0.800510000	1.021208000	H	3.480357000	4.623314000	1.173019000
C	7.541124000	0.398188000	0.414143000	H	1.539676000	3.825894000	2.552151000
C	5.626328000	0.320679000	-1.106826000				

Table S54: Optimized geometry of **TS-2-Cy**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



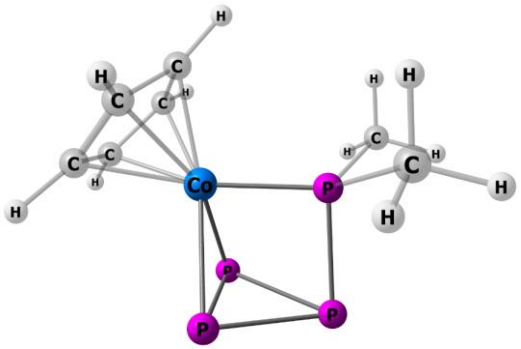
Co	-1.110302000	0.387824000	-0.221436000	H	2.814739000	-1.102094000	2.635444000
P	-0.253268000	-1.721597000	-0.026484000	H	2.060268000	-2.091235000	1.360719000
P	0.992997000	-0.284853000	-1.102301000	C	3.955188000	-2.883395000	2.109627000
P	-1.279820000	-0.943001000	-1.831971000	H	4.380337000	2.054955000	-0.427818000
C	-1.077873000	1.480053000	1.565125000	C	4.050313000	0.852787000	-2.205776000
C	-1.776560000	2.355772000	-0.491729000	H	5.568905000	0.306799000	0.362869000
H	-1.791859000	2.919938000	-1.432881000	H	4.930946000	0.367803000	2.025951000
C	-0.696914000	2.315800000	0.460233000	C	5.985287000	-1.479564000	1.540529000
C	-2.383328000	0.954615000	1.277747000	C	4.830403000	1.747564000	-3.189100000
H	-2.958120000	0.268757000	1.913662000	H	5.754667000	2.122447000	-2.690552000
C	-2.816012000	1.500780000	0.004731000	H	5.170648000	1.144123000	-4.058663000
H	-3.776454000	1.298517000	-0.486974000	C	3.989295000	2.945757000	-3.659598000
H	-0.463762000	1.256508000	2.445892000	H	4.698056000	0.019499000	-1.859908000
H	0.262876000	2.838663000	0.365809000	H	3.191141000	0.379713000	-2.733826000
C	3.681710000	-0.791518000	0.661877000	H	2.820719000	4.594931000	-2.811903000
P	2.542909000	0.697971000	0.329144000	H	4.321946000	4.222627000	-1.929163000
C	3.509386000	1.656266000	-1.004235000	H	3.465928000	-3.503246000	2.891922000
H	1.750777000	2.497826000	-1.974854000	H	4.088448000	-3.547894000	1.224958000
C	2.677737000	2.869653000	-1.478268000	C	5.330619000	-2.392821000	2.589443000
H	2.348508000	3.470459000	-0.601971000	H	3.126721000	2.575143000	-4.260179000
C	3.462128000	3.756209000	-2.463862000	H	4.583972000	3.596320000	-4.336980000
H	3.813886000	-1.373306000	-0.279674000	H	5.207156000	-1.827525000	3.542210000
C	3.037324000	-1.708152000	1.726333000	H	5.994596000	-3.253537000	2.821998000
C	5.069476000	-0.302951000	1.145438000	H	6.219370000	-2.076920000	0.629377000
				H	6.956732000	-1.087285000	1.913195000

Table S55: Optimized geometry of **TS-2-^{t}Bu**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



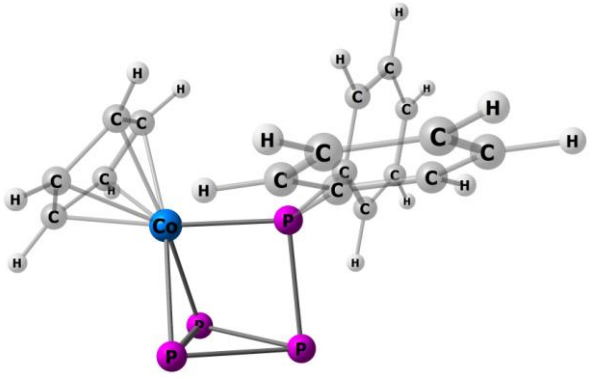
Co	1.973693000	0.138414000	-0.529087000	H	-2.627022000	-2.531628000	1.967572000
P	-1.708533000	-0.345456000	0.067335000	H	-4.187615000	-3.042596000	1.237515000
P	0.504884000	1.280237000	-2.209153000	C	-4.201124000	-1.314628000	-0.928400000
P	0.008909000	-0.667518000	-1.199976000	C	-3.473932000	-2.194036000	1.336465000
P	2.492865000	0.677190000	-2.535420000	C	-2.311801000	-2.965272000	-0.750948000
C	2.522624000	0.971991000	1.360430000	H	-1.441977000	-3.331696000	-0.169036000
C	2.728882000	-1.266810000	0.749236000	H	-3.047480000	-3.796192000	-0.834134000
H	2.552200000	-2.346829000	0.669381000	H	-1.960383000	-2.718873000	-1.772837000
C	1.951154000	-0.332537000	1.520964000	C	-2.082549000	1.087952000	1.300516000
C	3.662418000	0.858986000	0.495429000	H	-4.272320000	0.763847000	1.449818000
H	4.316721000	1.679905000	0.175684000	H	-3.773847000	1.846635000	0.102735000
C	3.787162000	-0.525240000	0.106445000	H	-3.724291000	2.427074000	1.802715000
H	4.564786000	-0.943662000	-0.545455000	H	-1.372540000	2.629083000	-0.111326000
H	2.147031000	1.901515000	1.807807000	H	-0.081760000	1.928873000	0.904817000
H	1.050312000	-0.579352000	2.096725000	H	-1.262281000	3.079182000	1.628244000
C	-2.998006000	-1.763062000	-0.066851000	C	-3.547858000	1.546053000	1.145441000
H	-3.875734000	-1.010159000	-1.943476000	C	-1.144352000	2.243810000	0.902895000
H	-4.746487000	-0.463631000	-0.475519000	C	-1.809203000	0.668777000	2.760953000
H	-4.923051000	-2.156181000	-1.035078000	H	-0.748963000	0.383597000	2.911547000
H	-4.007270000	-1.383536000	1.873070000	H	-2.029392000	1.520930000	3.443800000
				H	-2.440326000	-0.184389000	3.077112000

Table S56: Optimized geometry of **P-2-Me**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



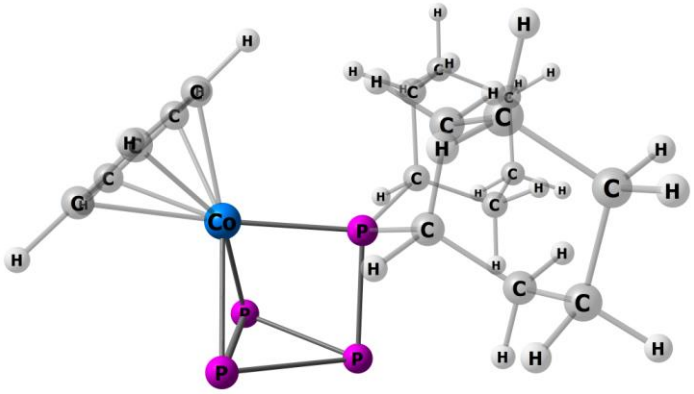
Co	-0.826655000	-0.345412000	-0.495418000	C	-2.702052000	-0.869622000	0.247419000
P	1.325315000	-0.369194000	-0.493066000	H	-3.287598000	-1.749943000	-0.048653000
P	-0.579610000	-2.137874000	-1.931870000	H	-0.437142000	0.894312000	2.026270000
P	1.444464000	-1.228840000	-2.531136000	H	-1.648395000	2.352106000	0.059989000
P	-0.561220000	-0.134905000	-2.778771000	C	2.257027000	-1.453793000	0.689809000
C	-1.192561000	0.519732000	1.322103000	H	2.167449000	-1.049953000	1.720095000
C	-2.756991000	0.423283000	-0.382359000	H	1.812778000	-2.467976000	0.667523000
H	-3.391848000	0.691483000	-1.237049000	H	3.331014000	-1.515172000	0.416401000
C	-1.830509000	1.294597000	0.288290000	C	2.293017000	1.213319000	-0.434106000
C	-1.741281000	-0.815862000	1.312482000	H	2.216849000	1.664560000	0.577482000
H	-1.478882000	-1.633270000	1.995511000	H	3.362663000	1.036359000	-0.671826000
				H	1.864650000	1.920741000	-1.170628000

Table S57: Optimized geometry of **P-2-Ph**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



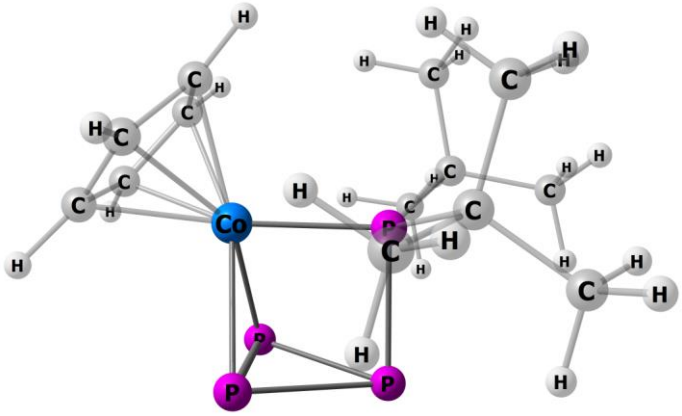
Co	-0.721794000	-0.211442000	-0.490674000	H	0.517582000	-2.760868000	0.731083000
P	1.426114000	-0.397882000	-0.693097000	C	2.351086000	-1.773688000	0.124259000
P	-0.753587000	-1.736865000	-2.227178000	C	3.687428000	-3.989589000	1.254724000
P	1.271719000	-0.869232000	-2.864991000	H	4.210213000	-4.852695000	1.696802000
P	-0.647083000	0.374197000	-2.727869000	C	3.540236000	3.132846000	-1.266861000
C	-1.012421000	1.025169000	1.153544000	H	3.761327000	3.811058000	-2.106454000
C	2.974554000	1.390809000	0.864839000	C	-1.097938000	-0.367086000	1.547942000
H	2.763156000	0.709558000	1.705434000	H	-0.462078000	-0.862961000	2.292947000
C	3.720364000	2.559629000	1.090190000	C	4.424473000	-2.949507000	0.658468000
H	4.083255000	2.788253000	2.105196000	H	5.524902000	-2.998242000	0.630207000
C	3.762923000	-1.846986000	0.093263000	C	-2.161326000	-0.975723000	0.807567000
H	4.347721000	-1.038658000	-0.374169000	C	4.004997000	3.433933000	0.025182000
C	2.792846000	1.964598000	-1.496579000	H	4.590732000	4.349736000	0.203283000
H	2.426070000	1.736625000	-2.510950000	C	2.283485000	-3.924734000	1.283105000
C	2.507090000	1.079544000	-0.433945000	H	1.701439000	-4.737302000	1.746664000
C	-2.728417000	0.029265000	-0.056401000	H	-2.216958000	2.222258000	-0.333240000
H	-3.554781000	-0.120341000	-0.763469000	H	-0.291747000	1.760419000	1.534206000
C	-2.021641000	1.267258000	0.170864000	H	-2.485358000	-2.022053000	0.877552000
C	1.617608000	-2.822283000	0.720684000				

Table S58: Optimized geometry of **P-2-Cy**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



P	2.294421000	-1.122241000	1.620123000
P	2.255126000	1.051422000	1.728604000
P	0.431679000	-0.111553000	2.491399000
Co	1.895155000	0.058444000	-0.319755000
C	1.699648000	0.146725000	-2.370226000
C	2.435571000	-1.038521000	-2.007792000
H	2.160736000	-2.074381000	-2.241514000
C	2.421384000	1.306156000	-1.908710000
H	2.138194000	2.355177000	-2.059413000
C	3.607338000	-0.606819000	-1.297674000
C	3.598224000	0.830831000	-1.235976000
C	-1.182249000	-1.568933000	-0.002438000
P	-0.176072000	-0.007807000	0.353360000
C	-1.220211000	1.558307000	0.189902000
H	-3.242458000	0.880502000	0.668882000
C	-2.497767000	1.613003000	1.053977000
H	-2.271116000	1.317701000	2.101531000
C	-3.122953000	3.021876000	1.017484000
H	-0.371764000	-2.332366000	0.066590000
C	-1.761597000	-1.637478000	-1.431563000
C	-2.251939000	-1.940016000	1.047179000
H	-2.565125000	-0.874694000	-1.543232000
H	-0.979207000	-1.386842000	-2.179403000
C	-2.352287000	-3.031754000	-1.720652000
H	-0.496217000	2.296167000	0.611556000
C	-1.512560000	1.991817000	-1.263178000
H	-1.815260000	-1.909105000	2.069229000
H	-3.072812000	-1.190171000	1.030712000
C	-2.837238000	-3.336577000	0.757606000
C	-2.148457000	3.396007000	-1.301043000
H	-1.402086000	4.140398000	-0.939912000
H	-2.385038000	3.676729000	-2.350446000
C	-3.410041000	3.476341000	-0.424045000
H	-0.576209000	1.979121000	-1.859427000
H	-2.206337000	1.264299000	-1.741134000
H	-4.054436000	3.038104000	1.623972000
H	-2.423870000	3.742238000	1.500961000
H	-2.793552000	-3.052782000	-2.740916000
H	-1.527755000	-3.781257000	-1.721492000
C	-3.402975000	-3.432183000	-0.670334000
H	-4.201959000	2.824649000	-0.861365000
H	-3.820798000	4.509131000	-0.430534000
H	-4.285158000	-2.756556000	-0.760399000
H	-3.778184000	-4.459007000	-0.871043000
H	-2.036294000	-4.099958000	0.889169000
H	-3.623386000	-3.579439000	1.504962000
H	4.359604000	1.454078000	-0.748705000
H	4.376232000	-1.259932000	-0.864153000
H	0.760664000	0.165553000	-2.939268000

Table S59: Optimized geometry of **P-2-^{t}Bu**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Co	0.165879000	0.240254000	-0.403520000	C	-2.352316000	-2.422648000	1.138650000
P	-2.016855000	0.093541000	-0.179207000	H	-2.698140000	-1.952065000	2.078375000
P	-0.335634000	2.012354000	-1.792087000	H	-2.752222000	-3.460733000	1.120931000
P	-2.321550000	0.948221000	-2.222536000	H	-1.247081000	-2.494988000	1.172273000
P	-0.271361000	0.032397000	-2.664797000	C	-2.952377000	1.292329000	1.041009000
C	1.290450000	-1.313566000	0.437663000	H	-2.155959000	0.321131000	2.862723000
C	2.152051000	0.781093000	-0.111409000	H	-3.822324000	-0.203852000	2.433181000
H	2.678385000	1.581161000	-0.648519000	H	-3.544301000	1.415239000	3.131334000
C	2.072767000	-0.596012000	-0.524893000	H	-5.044988000	0.879039000	0.406638000
C	0.870684000	-0.362363000	1.440935000	H	-4.221509000	2.154327000	-0.547599000
H	0.265633000	-0.593847000	2.327482000	H	-4.769605000	2.493524000	1.123514000
C	1.419860000	0.926711000	1.117172000	C	-3.123877000	0.656125000	2.435051000
C	-2.826065000	-1.674611000	-0.126240000	C	-4.322329000	1.714220000	0.467212000
H	-1.204979000	-2.483079000	-1.385722000	C	-2.077968000	2.555551000	1.189407000
H	-2.659631000	-1.994627000	-2.311688000	H	-1.940722000	3.082582000	0.223615000
H	-2.695265000	-3.489945000	-1.316885000	H	-2.576702000	3.258924000	1.892526000
H	-4.729822000	-1.047587000	-1.057772000	H	-1.073071000	2.317024000	1.588347000
H	-4.816376000	-1.194727000	0.733807000	H	2.529120000	-1.019287000	-1.429346000
H	-4.759788000	-2.660314000	-0.281840000	H	1.074926000	-2.389234000	0.425800000
C	-2.312396000	-2.446470000	-1.360497000	H	1.317874000	1.846586000	1.706313000
C	-4.365428000	-1.624484000	-0.182494000				

4.5 Model system $[Cp^{H}CoAs_3]^- + PR_2^+$

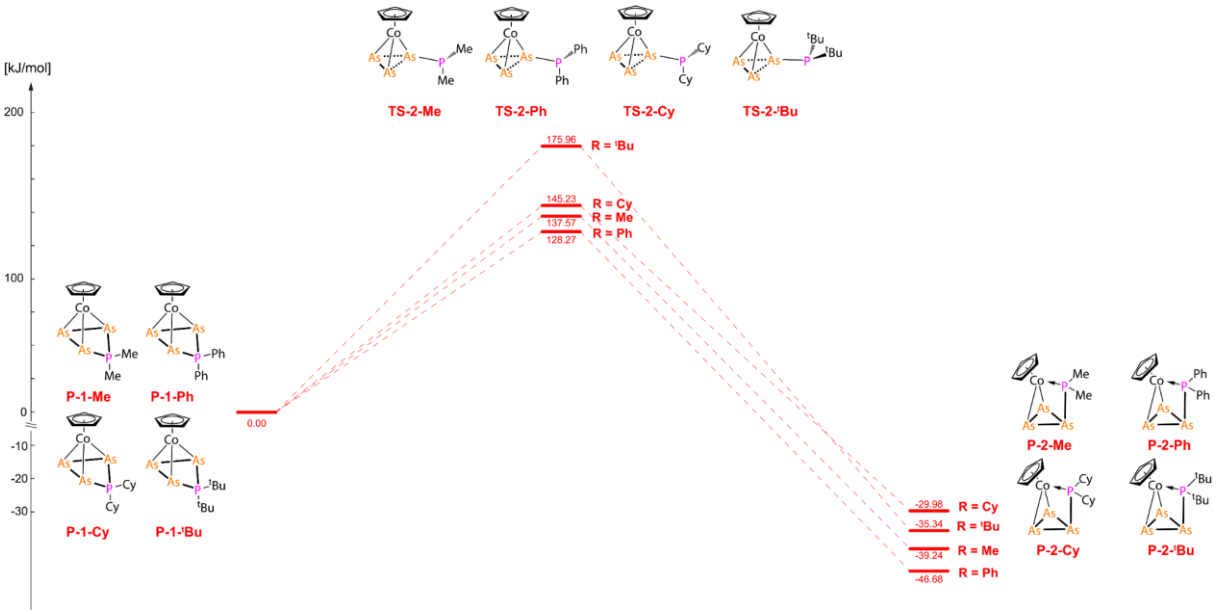
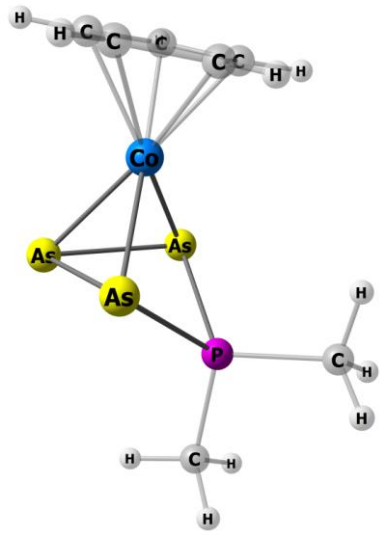


Figure S76. Pathway of the reaction of $[Cp^{H}CoAs_3]^-$ with PR_2^+. Optimization conducted at the BP86/def2-SVP level of theory. Energy values obtained from single point calculation at the B3LYP/def2-SVP level of theory including solvent effects and dispersion correction (GD3BJ).

Table S60: Total energies for optimized geometries, optimization at the BP86/def2-SVP level and single point energies at the B3LYP/def2-TZVP level of theory including solvent effects and dispersion correction GD3BJ.

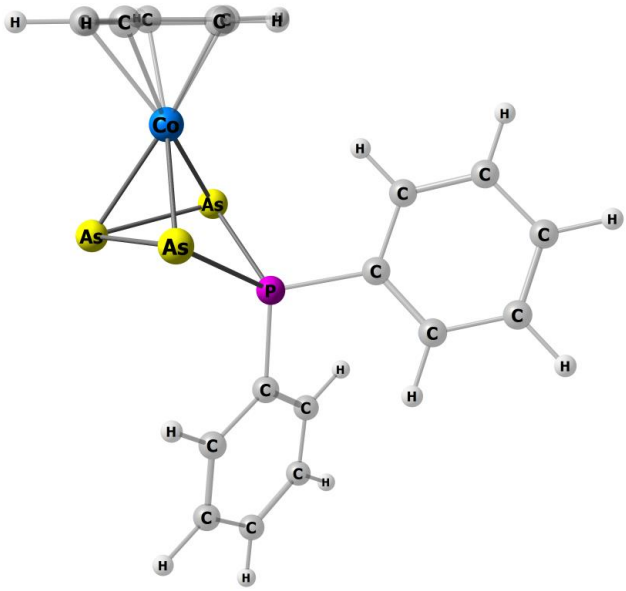
	BP86/def2-SVP total energy [Ha]	B3LYP/def2-TZVP total energy [Ha]
P-1-Me	-8705.05420539	-8705.61204268
P-1-Ph	-9088.24605594	-9089.25634431
P-1-Cy	-9095.48352808	-9096.52764173
P-1-^{t}Bu	-8940.73388329	-8941.60281114
TS-2-Me	-8705.01278625	-8705.55963690
TS-2-Ph	-9088.19906530	-9089.20748899
TS-2-Cy	-9095.42694825	-9096.47232593
TS-2-^{t}Bu	-8940.68016627	-8941.53617343
P-2-Me	-8705.06844349	-8705.62698683
P-2-Ph	-9088.26071554	9089.27412497
P-2-Cy	-9095.49195168	-9096.53906143
P-2-^{t}Bu	-8940.74333781	-8941.61627172

Table S61: Optimized geometry of **P-1-Me**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Co	0.687011000	0.327103000	-0.555674000	H	1.082888000	1.903304000	1.790755000
As	-0.655710000	-1.618397000	-0.785711000	H	2.052415000	2.842410000	-0.590038000
P	-2.482007000	-0.269947000	-0.194876000	H	2.891773000	-1.490736000	-0.392044000
As	-0.419646000	0.018064000	-2.620394000	H	1.601699000	-0.775204000	1.913122000
As	-1.279642000	1.603919000	-0.933600000	C	-2.867503000	-0.261456000	1.616680000
C	2.678007000	0.694833000	-0.948291000	H	-3.612314000	0.527602000	1.851198000
H	3.153392000	0.741759000	-1.936704000	H	-3.268671000	-1.247148000	1.932640000
C	1.849724000	-0.106097000	1.078833000	H	-1.929315000	-0.054517000	2.167560000
C	2.538014000	-0.483730000	-0.135704000	C	-4.118250000	-0.623332000	-0.991564000
C	2.095092000	1.802846000	-0.240180000	H	-3.971882000	-0.645353000	-2.089029000
C	1.576536000	1.304270000	1.014401000	H	-4.505941000	-1.606798000	-0.653030000
				H	-4.850111000	0.170685000	-0.734598000

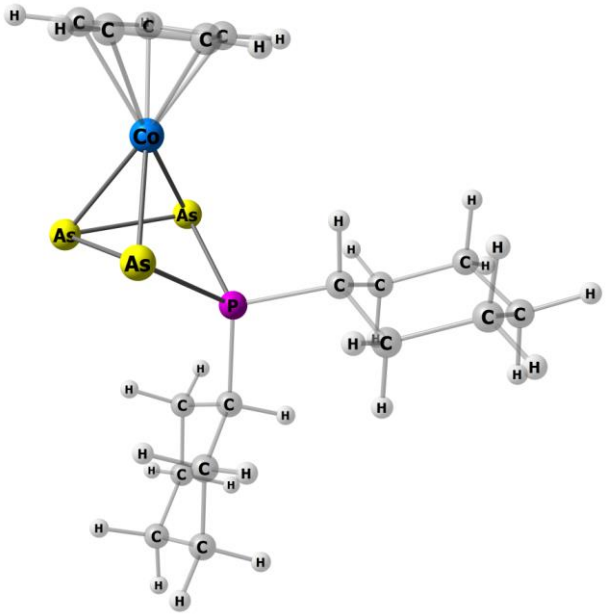
Table S62: Optimized geometry of **P-1-Ph**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Co	1.013238000	-0.485771000	0.535020000	H	-4.839609000	3.596823000	-2.012885000
As	-0.157871000	-2.528469000	0.760075000	C	-3.740851000	1.965808000	-1.091523000
As	-0.869603000	-0.504230000	1.968735000	H	-4.441449000	1.197364000	-1.453754000
As	-0.464172000	-1.084271000	-1.215705000	C	-3.987741000	-2.204253000	-0.800168000
C	3.022892000	-0.908341000	0.731551000	H	-3.138863000	-2.543498000	-1.416483000

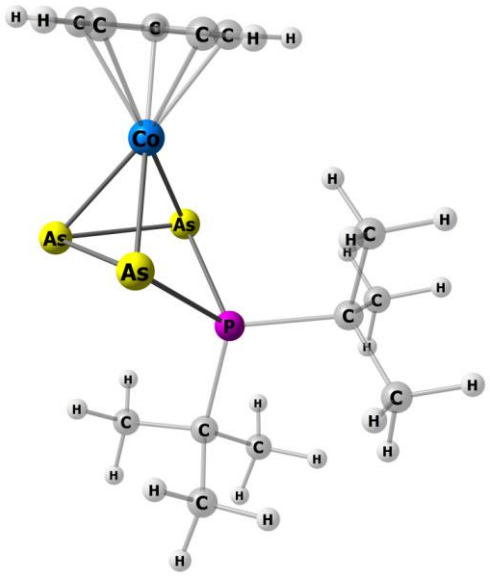
H	3.471258000	-1.901664000	0.863021000	C	-5.196416000	-2.922163000	-0.798887000
C	2.589533000	-0.031779000	1.787885000	C	-3.851573000	-1.045716000	-0.005371000
C	2.054307000	1.163377000	1.176257000	H	-5.296803000	-3.822369000	-1.425845000
H	1.658088000	2.035640000	1.713005000	C	-6.269477000	-2.496661000	0.002872000
C	2.773619000	-0.256334000	-0.525435000	C	-4.931960000	-0.623617000	0.804985000
C	2.166783000	1.026537000	-0.251133000	H	-4.832452000	0.273700000	1.437305000
P	-2.233056000	-0.168333000	0.057917000	C	-6.134736000	-1.347780000	0.805226000
C	-1.956622000	3.942177000	-0.179597000	H	-6.972446000	-1.014488000	1.438500000
H	-1.257221000	4.713878000	0.179633000	H	-7.214229000	-3.063260000	0.007029000
C	-1.726817000	2.593843000	0.137644000	H	-3.254586000	5.365717000	-1.197452000
C	-3.075020000	4.307205000	-0.950803000	H	1.862825000	1.769856000	-0.999450000
H	-0.845628000	2.302079000	0.731401000	H	3.001467000	-0.663789000	-1.518994000
C	-2.621332000	1.593786000	-0.310685000	H	2.658282000	-0.233797000	2.864512000
C	-3.963600000	3.316769000	-1.406195000				

Table S63: Optimized geometry of **P-1-Cy**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



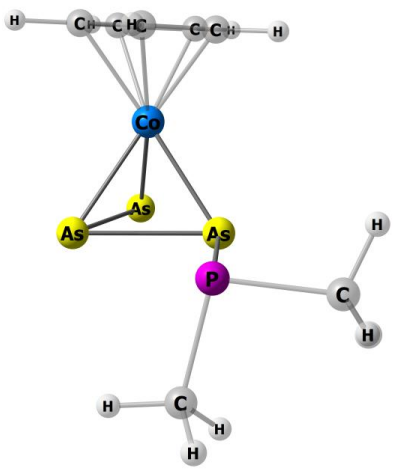
As	-0.545428000	-0.529930000	-1.645614000	C	-4.092949000	-1.629690000	-1.333048000
As	-0.335506000	-0.680791000	1.630635000	H	-4.245482000	-0.701106000	-1.923457000
As	0.487583000	-2.190508000	-0.138824000	H	-3.265622000	-2.181508000	-1.834900000
Co	1.137515000	0.076641000	-0.076473000	C	-5.373587000	-2.486731000	-1.347941000
P	-2.080237000	-0.236239000	0.111857000	H	-6.222829000	-1.884026000	-0.950104000
C	2.579217000	0.876569000	-1.318596000	H	-5.639322000	-2.743487000	-2.396351000
H	2.710916000	0.677748000	-2.390071000	C	-3.579411000	2.018532000	-0.860712000
C	1.758389000	1.917641000	-0.740082000	H	-4.522814000	1.425957000	-0.838620000
C	2.770575000	0.737219000	1.000406000	H	-3.106877000	1.828362000	-1.848824000
C	3.193975000	0.148319000	-0.241819000	C	-3.249542000	1.847659000	1.666691000
C	1.876571000	1.831094000	0.690263000	H	-4.175213000	1.243852000	1.812352000
H	1.394076000	2.494088000	1.420272000	H	-2.541124000	1.536554000	2.465384000
C	-2.648727000	1.546840000	0.275945000	C	-3.923630000	3.513544000	-0.707651000
H	-1.679268000	2.090568000	0.189283000	H	-2.996399000	4.115278000	-0.847645000
C	-5.215005000	-3.761388000	-0.501922000	H	-4.622093000	3.825250000	-1.514139000
H	-4.450560000	-4.420239000	-0.974087000	C	-3.600039000	3.342044000	1.809009000
H	-6.163655000	-4.340542000	-0.493425000	H	-4.069187000	3.526731000	2.799580000
C	-3.490701000	-2.577951000	0.953190000	H	-2.659340000	3.938822000	1.793450000
H	-2.643423000	-3.173261000	0.544373000	C	-4.524697000	3.818701000	0.675404000
H	-3.208437000	-2.320811000	1.996515000	H	-5.510320000	3.305913000	0.767061000
C	-4.775976000	-3.426831000	0.933781000	H	-4.731066000	4.906088000	0.776135000
H	-4.619199000	-4.357532000	1.520689000	H	1.170789000	2.658429000	-1.297752000
H	-5.593053000	-2.868646000	1.447540000	H	3.075779000	0.415638000	2.004563000
C	-3.654428000	-1.294817000	0.110449000	H	3.872476000	-0.707823000	-0.349725000
H	-4.435407000	-0.655136000	0.586378000				

Table S64: Optimized geometry of **P-1-^{t}Bu**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



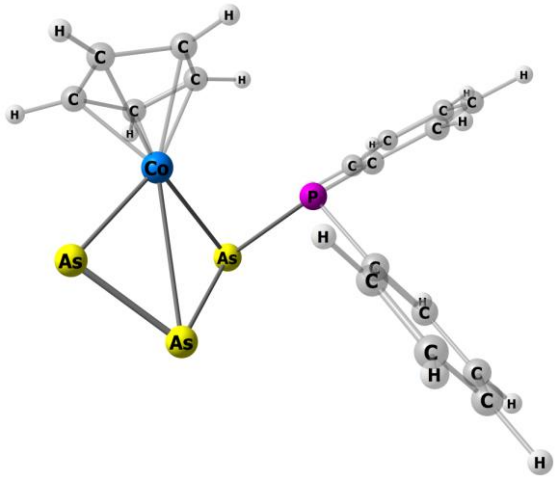
Co	0.670378000	0.029125000	-0.383315000
As	-0.857474000	-1.756688000	-0.000958000
P	-2.649825000	-0.199276000	-0.072135000
As	-0.340231000	-0.925013000	-2.265673000
As	-1.190383000	1.190953000	-1.329473000
C	2.246581000	1.335709000	-0.651366000
H	2.331852000	2.114874000	-1.419708000
C	2.408037000	-0.707360000	0.460943000
C	2.694087000	-0.026719000	-0.773269000
C	1.666611000	1.493012000	0.662494000
C	-3.051949000	0.472482000	1.705596000
C	1.769414000	0.234801000	1.351116000
H	1.449778000	0.031828000	2.381720000
C	-4.274943000	-0.743351000	-0.994330000
C	-3.216743000	-0.734708000	2.654237000
H	-4.101172000	-1.354470000	2.411407000
H	-3.339114000	-0.369140000	3.697800000
H	-2.321374000	-1.391309000	2.632883000
C	-4.298864000	1.377648000	1.739796000
H	-4.207201000	2.236582000	1.043417000
H	-4.409871000	1.796063000	2.764743000
H	-5.235653000	0.834935000	1.507335000
C	-1.832789000	1.303732000	2.157783000
H	-0.890301000	0.729335000	2.077176000
H	-1.979500000	1.611764000	3.216727000
H	-1.712671000	2.222955000	1.547993000
C	-5.000038000	0.518997000	-1.506676000
H	-5.393507000	1.153716000	-0.690256000
H	-5.863377000	0.214019000	-2.138837000
H	-4.329102000	1.140447000	-2.136434000
C	-5.183348000	-1.592161000	-0.082661000
H	-4.651354000	-2.481981000	0.313830000
H	-6.046028000	-1.964029000	-0.678928000
H	-5.600797000	-1.022485000	0.770724000
C	-3.860367000	-1.604872000	-2.205307000
H	-3.216244000	-1.047611000	-2.913958000
H	-4.779897000	-1.917095000	-2.748348000
H	-3.313620000	-2.519581000	-1.899308000
H	1.241813000	2.419601000	1.070251000
H	3.175727000	-0.469220000	-1.654834000
H	2.636440000	-1.757187000	0.686286000

Table S65: Optimized geometry of **TS-2-Me**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Co	-1.587961000	-0.663706000	-0.487829000	H	-4.426861000	-1.149284000	-0.665216000
P	2.199702000	-0.183659000	0.617345000	H	-1.402672000	0.444732000	2.131701000
As	-0.165253000	-2.554468000	-0.263836000	H	-1.543485000	2.129582000	-0.021819000
As	0.631617000	-0.382202000	-1.265781000	C	3.525086000	-1.419707000	0.144452000
As	-1.185110000	-1.982607000	-2.315699000	H	4.429018000	-1.216755000	0.759267000
C	-2.059804000	0.329046000	1.260654000	H	3.170988000	-2.445371000	0.370298000
C	-3.117910000	0.696987000	-0.794859000	H	3.805606000	-1.363782000	-0.928258000
H	-3.418235000	1.148716000	-1.748982000	C	3.051939000	1.371299000	0.002015000
C	-2.126944000	1.209972000	0.116367000	H	3.935185000	1.566194000	0.648975000
C	-2.998232000	-0.737997000	1.042642000	H	3.398273000	1.295171000	-1.050732000
H	-3.187678000	-1.578441000	1.723081000	H	2.364629000	2.236530000	0.095308000
C	-3.651417000	-0.511573000	-0.220607000				

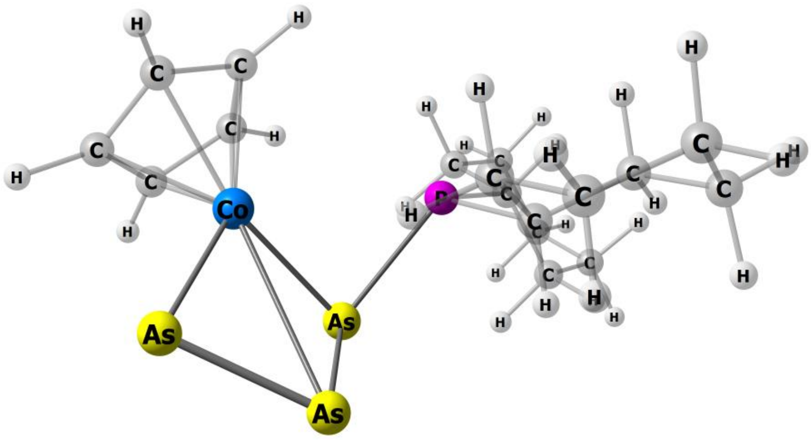
Table S66: Optimized geometry of **TS-2-Ph**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Co	-1.662115000	0.299641000	-0.474541000	H	4.267741000	3.790269000	2.144466000
As	-0.160755000	-2.250409000	-1.613933000	C	3.520140000	4.490260000	0.220445000
As	0.152050000	0.157363000	-1.989479000	C	2.025744000	2.960102000	-0.950200000
As	-2.380894000	-1.687476000	-1.274620000	H	1.413895000	2.723044000	-1.837318000
C	-1.670204000	2.420051000	0.030492000	C	2.713373000	4.185448000	-0.889229000
C	-3.535388000	1.069443000	-0.389012000	H	2.625054000	4.901362000	-1.722304000
H	-4.414519000	0.634901000	-0.882515000	H	4.062137000	5.448155000	0.265781000
C	-2.610394000	2.021541000	-0.982139000	C	2.066657000	-1.933323000	1.281376000
C	-1.952655000	1.655797000	1.198989000	H	1.088024000	-1.942276000	1.787884000
H	-1.368662000	1.676461000	2.128521000	C	2.987033000	-2.972621000	1.506772000

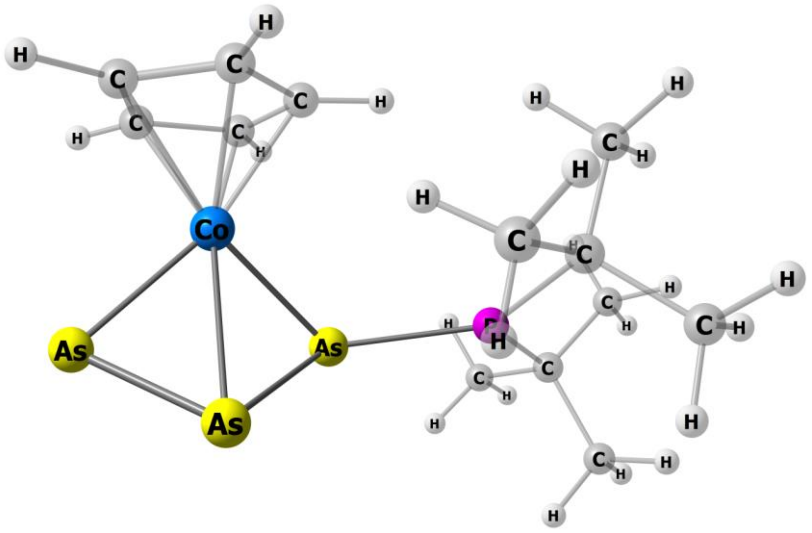
C	-3.114402000	0.834514000	0.961141000	C	2.391739000	-0.865429000	0.413143000
H	-3.596330000	0.167089000	1.686469000	H	2.721348000	-3.800058000	2.183960000
H	-0.842763000	3.129768000	-0.093304000	C	4.241795000	-2.952271000	0.875057000
H	-2.667477000	2.413403000	-2.006097000	C	3.654448000	-0.856496000	-0.224928000
P	1.128469000	0.461281000	0.141074000	H	3.917601000	-0.032791000	-0.907513000
C	2.940368000	2.342609000	1.219026000	C	4.573636000	-1.890941000	0.011324000
H	3.030915000	1.626992000	2.052763000	H	5.556430000	-1.871319000	-0.486827000
C	3.634601000	3.561516000	1.271994000	H	4.964666000	-3.763961000	1.054878000
C	2.129618000	2.021474000	0.102042000				

Table S67: Optimized geometry of **TS-2-Cy**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



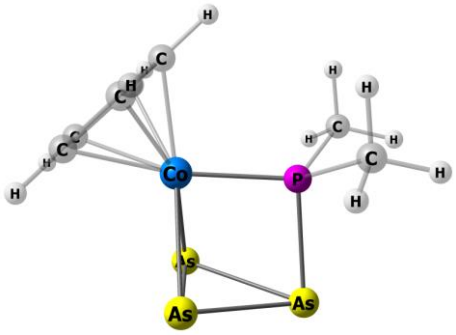
Co	1.756173000	0.006309000	-0.266433000	H	-0.769515000	-2.365811000	-0.283572000
As	0.399253000	-1.558321000	2.246014000	C	-2.705838000	-3.366807000	-0.494795000
As	0.404027000	0.783800000	1.520172000	H	-2.993622000	1.985696000	-0.915605000
As	2.415716000	-1.664145000	1.110671000	C	-2.838419000	2.385203000	1.219285000
C	1.701103000	0.825000000	-2.291689000	H	-4.229457000	0.288432000	-0.067129000
C	3.204532000	1.368823000	-0.622345000	H	-3.688355000	-0.343876000	-1.645226000
H	3.740585000	1.920165000	0.161191000	C	-4.704909000	-1.809809000	-0.389414000
C	2.070038000	1.844366000	-1.373988000	C	-3.703205000	3.660909000	1.231670000
C	2.629429000	-0.276974000	-2.166832000	H	-4.572749000	3.523761000	0.547667000
H	2.621605000	-1.199860000	-2.760554000	H	-4.129031000	3.817974000	2.246638000
C	3.583113000	0.072109000	-1.158459000	C	-2.895291000	4.891672000	0.787884000
H	4.452539000	-0.523746000	-0.850754000	H	-3.443510000	1.505880000	1.526695000
H	0.835860000	0.854574000	-2.965932000	H	-2.026630000	2.478432000	1.976680000
H	1.548639000	2.796719000	-1.219034000	H	-1.617627000	5.538252000	-0.870825000
C	-2.363863000	-0.885664000	0.004510000	H	-3.031586000	4.573989000	-1.360818000
P	-1.134762000	0.558998000	-0.249035000	H	-2.267502000	-4.251023000	-1.006263000
C	-2.188946000	2.145286000	-0.160724000	H	-2.755449000	-3.626788000	0.587545000
H	-0.512583000	3.514644000	0.092546000	C	-4.121976000	-3.083785000	-1.022205000
C	-1.376371000	3.382441000	-0.600600000	H	-2.103156000	5.100186000	1.543603000
H	-0.949831000	3.221279000	-1.614107000	H	-3.543415000	5.794248000	0.759122000
C	-2.237708000	4.661442000	-0.583223000	H	-4.081403000	-2.956731000	-2.128905000
H	-2.454536000	-1.077397000	1.097627000	H	-4.792074000	-3.950488000	-0.833223000
C	-1.784117000	-2.147939000	-0.677426000	H	-4.872398000	-1.983203000	0.698477000
C	-3.771585000	-0.592997000	-0.561239000	H	-5.702126000	-1.578419000	-0.823683000
H	-1.656430000	-1.934290000	-1.763725000				

Table S68: Optimized geometry of **TS-2-^{t}Bu**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



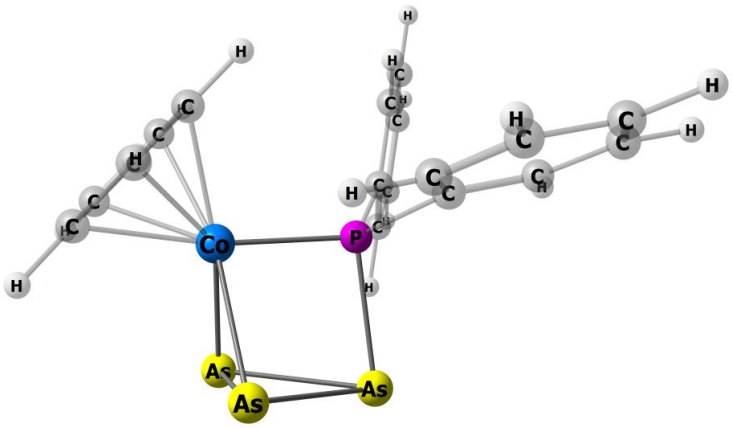
Co	1.626689000	-0.354166000	-0.185457000	H	-5.188044000	-3.042772000	0.459622000
P	-2.293465000	-0.524604000	0.111611000	C	-4.833575000	-0.828849000	-1.161945000
As	0.456981000	1.500198000	-1.633105000	C	-4.371019000	-2.367209000	0.800570000
As	-0.427122000	-0.773104000	-1.207204000	C	-3.194534000	-2.721388000	-1.386975000
As	2.518433000	0.526184000	-2.055424000	H	-2.422192000	-3.352944000	-0.902561000
C	2.070355000	0.003396000	1.873727000	H	-4.026548000	-3.384685000	-1.712943000
C	2.028573000	-2.082888000	0.835252000	H	-2.749703000	-2.269149000	-2.296571000
H	1.715431000	-3.088589000	0.527627000	C	-2.568995000	0.571784000	1.671351000
C	1.304728000	-1.198170000	1.711526000	H	-4.785720000	0.524563000	1.662431000
C	3.275043000	-0.126281000	1.106185000	H	-4.071342000	1.846065000	0.674033000
H	4.075451000	0.620423000	1.026558000	H	-4.060202000	1.944900000	2.468662000
C	3.247832000	-1.413551000	0.452150000	H	-1.599647000	2.323639000	0.749374000
H	4.033723000	-1.823331000	-0.195442000	H	-0.458168000	1.211061000	1.555991000
H	1.780333000	0.878824000	2.469081000	H	-1.522280000	2.273751000	2.545806000
H	0.321540000	-1.404099000	2.152069000	C	-3.952242000	1.253065000	1.603126000
C	-3.755043000	-1.654232000	-0.422086000	C	-1.472129000	1.653340000	1.623383000
H	-4.407761000	-0.321795000	-2.051058000	C	-2.448546000	-0.242511000	2.977759000
H	-5.288222000	-0.053652000	-0.514149000	H	-1.447025000	-0.705504000	3.080301000
H	-5.653287000	-1.500455000	-1.505389000	H	-2.600998000	0.427012000	3.855096000
H	-4.819165000	-1.658938000	1.526574000	H	-3.202925000	-1.051088000	3.039790000
H	-3.620176000	-2.983868000	1.335412000				

Table S69: Optimized geometry of **P-2-Me**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



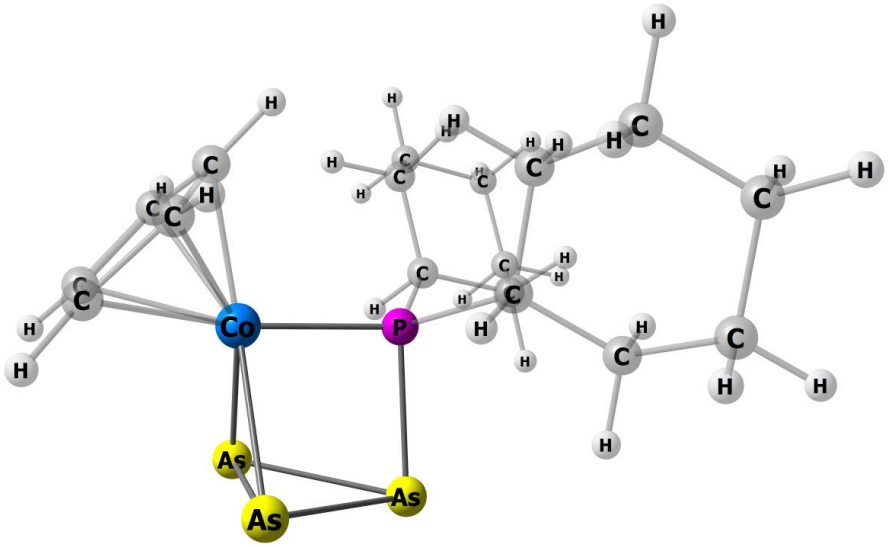
Co	-0.826990000	-0.356883000	-0.520498000	C	-2.693732000	-0.855500000	0.270993000
P	1.328435000	-0.383937000	-0.529437000	H	-3.307979000	-1.722013000	-0.007231000
As	-0.644726000	-2.280446000	-1.971648000	H	-0.356681000	0.864636000	2.000800000
As	1.577051000	-1.291459000	-2.661196000	H	-1.598864000	2.351336000	0.076424000
As	-0.623261000	-0.071333000	-2.909828000	C	2.224628000	-1.434872000	0.714313000
C	-1.134627000	0.504423000	1.313718000	H	2.062259000	-1.027279000	1.734516000
C	-2.746765000	0.441177000	-0.348894000	H	1.814481000	-2.462863000	0.675879000
H	-3.407552000	0.726604000	-1.178014000	H	3.314434000	-1.464577000	0.505852000
C	-1.787235000	1.293991000	0.300577000	C	2.260064000	1.220693000	-0.419094000
C	-1.700885000	-0.823019000	1.308900000	H	2.102043000	1.679486000	0.579820000
H	-1.433784000	-1.648054000	1.980780000	H	3.347618000	1.064875000	-0.577158000
				H	1.872551000	1.913691000	-1.191081000

Table S70: Optimized geometry of **P-2-Ph**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



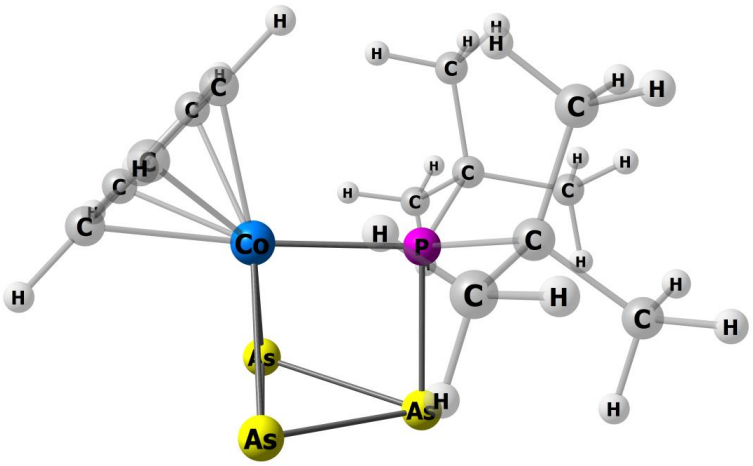
Co	1.128915000	-0.074908000	1.026458000	H	-0.296175000	2.643414000	1.067739000
P	-0.708096000	0.015202000	-0.118464000	C	-1.807272000	1.500820000	0.010021000
As	2.094277000	1.173176000	-0.801790000	C	-3.369018000	3.854208000	0.106853000
As	0.329907000	0.056864000	-2.218732000	H	-3.979446000	4.770518000	0.145663000
As	2.055452000	-1.222691000	-0.897594000	C	-2.647913000	-3.617133000	-0.719011000
C	0.780638000	-1.184226000	2.756608000	H	-2.566748000	-4.466590000	-1.415922000
C	-2.848944000	-1.439397000	1.045240000	C	0.406966000	0.201598000	2.936699000
H	-2.941305000	-0.586716000	1.737555000	H	-0.595088000	0.567532000	3.197320000
C	-3.694603000	-2.550588000	1.199367000	C	-3.873453000	2.696583000	-0.514519000
H	-4.437258000	-2.562070000	2.013355000	H	-4.878785000	2.705474000	-0.965549000
C	-3.098764000	1.526211000	-0.566176000	C	1.571430000	1.019485000	2.741076000
H	-3.501126000	0.625416000	-1.056635000	C	-3.596503000	-3.642840000	0.318070000
C	-1.800357000	-2.506702000	-0.876105000	H	-4.261417000	-4.512750000	0.439216000
H	-1.056265000	-2.494797000	-1.689612000	C	-2.084243000	3.837082000	0.676948000
C	-1.894082000	-1.404013000	0.001235000	H	-1.683307000	4.740573000	1.163808000
C	2.665408000	0.141646000	2.413365000	H	2.769080000	-2.112373000	2.223640000
H	3.695719000	0.447987000	2.189952000	H	0.114965000	-2.051911000	2.845569000
C	2.174693000	-1.212884000	2.430495000	H	1.624834000	2.111030000	2.841388000
C	-1.306850000	2.667006000	0.629582000				

Table S71: Optimized geometry of **P-2-Cy**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



As	-0.605545000	-0.520626000	-2.521096000	H	1.284712000	2.472256000	0.573461000
As	-1.139019000	1.589527000	-1.504263000	C	1.957130000	1.405714000	2.319063000
As	1.180358000	1.253236000	-2.437569000	H	3.601665000	-0.345272000	-2.343362000
Co	-0.652367000	-0.320225000	-0.114396000	H	4.568692000	0.037656000	-0.895746000
C	-1.041271000	-2.184564000	0.734676000	C	4.810131000	-2.010163000	-1.595150000
C	-2.225151000	-1.670246000	0.101559000	C	2.263495000	2.668773000	3.148615000
H	-2.780134000	-2.148903000	-0.716239000	H	1.467567000	3.426120000	2.962551000
C	-0.648983000	-1.229256000	1.739423000	H	2.218688000	2.429860000	4.233540000
H	0.206753000	-1.332541000	2.418996000	C	3.631196000	3.271742000	2.784540000
C	-2.562699000	-0.415867000	0.719243000	H	0.944596000	1.023612000	2.562113000
C	-1.592897000	-0.139839000	1.743062000	H	2.678744000	0.605677000	2.597631000
C	2.732284000	-1.075511000	-0.469154000	H	4.744778000	3.938760000	1.018929000
P	1.433931000	0.301073000	-0.311940000	H	3.011869000	4.348315000	0.995640000
C	2.054829000	1.698522000	0.806561000	H	4.402347000	-3.342373000	1.624843000
H	4.225619000	1.527797000	0.644806000	H	3.433488000	-3.736210000	0.183412000
C	3.435021000	2.285218000	0.443532000	C	5.259906000	-2.638710000	-0.265066000
H	3.485491000	2.518488000	-0.642301000	H	4.436138000	2.560238000	3.082554000
C	3.735752000	3.548793000	1.275211000	H	3.811297000	4.203333000	3.363504000
H	2.123044000	-1.845009000	-0.999143000	H	5.948583000	-1.935017000	0.257640000
C	3.188692000	-1.685893000	0.873725000	H	5.845682000	-3.564881000	-0.451135000
C	3.946042000	-0.753796000	-1.368066000	H	4.219910000	-2.757039000	-2.174335000
H	3.783395000	-0.933697000	1.440371000	H	5.691003000	-1.755323000	-2.223446000
H	2.312162000	-1.939846000	1.506648000	H	-1.589202000	0.726051000	2.416790000
C	4.058726000	-2.938988000	0.647380000	H	-3.417439000	0.219058000	0.450821000
				H	-0.542992000	-3.135391000	0.508778000

Table S72: Optimized geometry of **P-2-^{t}Bu**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Co	-0.306835000	-0.147531000	-0.073557000	C	1.543498000	3.237594000	0.832323000
P	1.789344000	0.421376000	0.319107000	H	1.798455000	3.146128000	1.904575000
As	0.586204000	-2.292019000	-0.757377000	H	1.775517000	4.281638000	0.525420000
As	2.650530000	-0.979851000	-1.365903000	H	0.450498000	3.095989000	0.722703000
As	0.382557000	-0.537703000	-2.363648000	C	2.640518000	-0.160054000	1.988145000
C	-1.695445000	1.406871000	0.150723000	H	1.449722000	1.193097000	3.271088000
C	-2.251674000	-0.855627000	0.164276000	H	3.093951000	1.817875000	2.891912000
H	-2.620913000	-1.838095000	-0.158452000	H	2.889391000	0.477720000	4.053144000
C	-2.261201000	0.345491000	-0.628748000	H	4.737818000	0.364687000	1.466705000
C	-1.320698000	0.846594000	1.428923000	H	4.244559000	-1.288862000	0.977591000
H	-0.872903000	1.402723000	2.262978000	H	4.556891000	-0.917704000	2.700605000
C	-1.681658000	-0.544851000	1.447672000	C	2.506392000	0.901766000	3.098331000
C	2.326300000	2.257801000	-0.068839000	C	4.125821000	-0.509177000	1.759392000
H	0.861794000	2.390560000	-1.713853000	C	1.907514000	-1.435216000	2.454137000
H	2.506666000	1.921953000	-2.251321000	H	1.988639000	-2.255756000	1.713067000
H	2.177006000	3.617038000	-1.759670000	H	2.365667000	-1.788761000	3.404549000
H	4.431139000	1.761197000	-0.527379000	H	0.830588000	-1.250590000	2.632927000
H	4.181396000	2.376289000	1.144142000	H	-1.567923000	-1.238229000	2.290243000
H	4.108133000	3.498291000	-0.242916000	H	-2.641198000	0.431315000	-1.655295000
C	1.943434000	2.552860000	-1.534195000	H	-1.597367000	2.454966000	-0.158447000
C	3.844312000	2.470642000	0.093012000				

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