Supporting Information

Synthesis, Oxidation and Unusual Coordination Chemistry of the Diphosphete Complex $[(Cp'''Co)_2(\mu,\eta^{4:4}\text{-}((CH_3)CP)_2)]$

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Content:

1. Experimental data

All reactions were performed under an atmosphere of dry argon with standard Schlenk techniques. All solvents were freshly collected from a Solvent Purification System by M. Braun and were degassed prior to use. $CH_3C{\equiv}P$,[1] $[\{Cp'''Co\}_2(\mu,\eta^4{:}\eta^4\text{-}C_7H_8)]$,[2] $[\{Cp'''Co\}(\mu\text{-}Cl)]_2$,[3] $[W(CO)_4(nbd)]$,[4] $Tl[Al\{OC(CF_3)_3\}_4]$,[5] and $Ag[Al\{OC(CF_3)_3\}_4]$[6] (will be shortened as Tl[TEF] and Ag[TEF]), have been prepared according to literature procedures. Cu(I) halides were purchased from abcr and used as received after storing in a Glovebox. ^1H, ^{13}C and ^{31}P NMR spectra were recorded at room temperature on a Bruker Avance 400 MHz spectrometer (^1H: 400,130 MHz, ^{31}P: 161,976 MHz, ^{13}C: 100.613 MHz). NMR chemical shifts are reported in parts per million (ppm) relative to external standards Me_4Si or H_3PO_4 (85%). Solid state $^{31}P\{^1H\}$ MAS NMR spectra were recorded at 300 K on a Bruker Avance I 400 spectrometer using a 4.0 mm HX MAS probe at 298 K. For MAS experiments, samples were packed in zirconia rotors. Chemical shifts are referenced to H_3PO_4 (^{31}P, 161.9 MHz) and to adamantane (^{13}C, 100.6 MHz). For both ^{31}P and ^{13}C two-pulse phase-modulation (TPPM) decoupling scheme was used for the ^1H decoupling. ^1H-^{31}P CP/MAS NMR experiments were performed using 3.25 µs proton π/2 pulse length, n_{CP} of 55.0 kHz, contact time of 5.0 ms, n_{dec} of 76.9 kHz and recycle delay of 6.0 s. The ^1H-^{31}P CP/MAS NMR spectrum of complex **1** was acquired collecting two subspectra using a spectral width of 65.0 kHz each. The transmitter offset was set at 43657 Hz and –16197 Hz. ^1H-^{13}C CP/MAS NMR experiments were performed using 3.25 µs proton π/2 pulse length, n_{CP} of 55.0 kHz, contact time of 7.5 ms, n_{dec} of 76.9 kHz and recycle delay of 6.0 s. The simulation of ^1H-^{31}P CP/MAS spectrum was carried out with SIMPSON software.[7] Elemental analyses were performed by the microanalytical laboratory of the University of Regensburg on a Vario EL III apparatus. High-resolution mass spectrometry (HR-MS) analysis was performed in positive mode using a time-of-flight mass spectrometer equipped with an electrospray ion source (Bruker micrOTOF II). For the EI MS, a Finnigan MAT SSQ 710 A, for the ESI MS a Finnigan TSQ 7000 and for the LIFDI MS a MAT 95 mass spectrometer was used.

1.1. Synthesis and characterization of $[Cp'''Co(\eta^4\text{-}P_2C_2Me_2)]$ (1) and $[\{Cp'''Co\}_2(\mu,\eta^4{:}\eta^4\text{-}P_2C_2Me_2)]$ (2):

To a solution of $CH_3C{\equiv}P$ in Et_2O (10 mL, 1.18 mmol) at -80 °C, 5mL Et_2O solution of $[\{Cp'''Co\}_2(\mu,\eta^4{:}\eta^4\text{-}C_7H_8)]$ (400 mg, 0.59 mmol) was added dropwise while stirring. An instant colour change from dark brown to dark green can be observed. The solution is left to warm up to room temperature and stirred additionally for five hours. Meanwhile, crystals of **2** were formed at the solvent border and could be isolated. The residual solution was filtered over silica gel and the solvent removed *in vacuo*. The residue was subjected to column chromatography over dried silica gel (length 15 cm, diameter 3 cm). The solvents were removed *in vacuo* and the residues (mostly oil) were dissolved in small amounts of *n*-hexane from which they were crystallized at room temperature.

Fraction 1 contained dark green **2**, Fraction 2 contained yellow **1**. Overall yield: 20 %. Compound **1** can also be synthesised directly by adding an excess of MeCP to $[\{Cp'''Co\}_2(\mu,\eta^4{:}\eta^4\text{-}C_7H_8)]$.

Clear light orange prisms of **1** and green plates of **2** suitable for single crystal X-ray diffraction were obtained by crystallisation from *n*-hexane at r. t.

^1H-NMR (C_6D_6) δ [ppm] = 1.26 (d, 6H, $^3J_{PH}$ = 9.28 Hz, $C_2P_2(CH_3)_2$), 1.39 (s, 18H, $C_5H_2(C_4H_9)_3$), 1.41 (s, 9H, $C_5H_2(C_4H_9)_3$), 4.36 (s, 2H, $C_5H_2(C_4H_9)_3$); (**1**)

^{31}P-NMR (C_6D_6)	δ [ppm] = 65.5 (s, $\omega_{1/2}$ = 21.3 Hz); (**1**)
^{31}P{^{1}H}-NMR (C_6D_6)	δ [ppm] = 65.5 (s, $\omega_{1/2}$ = 21.3 Hz); (**1**)
^{1}H-^{31}P CP MAS NMR	δ = 71.0 (m, $^{1}J_{P,Co}$ = 160 Hz), 74.1 (m, $^{1}J_{P,Co}$ = 90 Hz) ppm.
^{1}H-^{13}C CP MAS NMR	δ = 18.8 {s, [$(CH_3)CP]_2$}, from 29 to 35 ppm (m, *t*Bu), 80.0 (m, [$(CH_3)CP]_2$}, from 84 to 114 (m, Cp) ppm.
Elemental analysis	calculated for $C_{21}H_{35}CoP_2$ (**1**, 408.15 g·mol^{-1}): C 61.74, H 8.64; found: C 57.25, H 8.25; calculated for $C_{38}H_{64}Co_2P_2$ (**2**, 700.7 g·mol^{-1}): C 65.13, H 9.21; found: C 65.14, H 9.23
EI-MS (toluene, 70eV)	*m/z* [%] = 408.2 (60) [M$^+$] (**1**)
EI-MS (hexane, 70eV)	*m/z* [%] =700.2 (1) [M$^+$] (**2**)

1.2. Synthesis and characterization of [{Cp'''Co}$_2$(μ,η^4:η^4-$P_2C_2Me_2$)][TEF] (3) and [{Cp'''Co}$_2$(μ-CCH_3)(μ-POOH)][TEF] (5):

A solution of 7.13·10^{-2} mmol **2** in 20 mL Et_2O was layered over a solution of 14.20·10^{-2} mmol Ag[TEF] in CH_2Cl_2 and stored at -30 °C until complete diffusion took place. The resulting green solution with dark precipitate was dried *in vacuo*, taken up in 3mL CH_2Cl_2 and filtered over silica gel. The green solution was layered under 15 mL of hexane and stored at -30 °C to yield dark green crystals of **3** suitable for X-ray structure analysis. The residual solution can be subsequently layered with additional hexane to yield microcrystalline powder of **3**. Yield: 92 mg (77%).

Elemental analysis	calculated for $C_{54}H_{64}Co_2P_2AlO_4F_{36}\cdot CH_2Cl_2$ (1752.7 g·mol^{-1}): C 37.68, H 3.79; found: C 37.51, H 3.95
Cation EI-MS (CH_2Cl_2)	*m/z* [%] = 700.4 (100) [M$^+$], 384.2 (15) [Cp'''Co(tol)$^+$]
Anion EI-MS (CH_2Cl_2)	*m/z* [%] = 967.1 (100) [TEF]
EPR (CH_2Cl_2, 77K)	g_{iso} = 2.009823, g_x = 1.858, g_y = 1.995, g_z = 2.079; A_{1x} = 170.58, A_{1y} = 34.56, A_{1z} = 145.29, A_{2x} = 191.95, A_{2y} = 14.18, A_{2z} = 213.82.

After prolonged storage, oxidation of **3** took place to give compound [{Cp'''Co}$_2$(μ-CCH_3)(μ-POOH)][TEF] (**5**). Green rods of **5** were obtained by crystallisation from diffusion of hexane into a solution of **5** in CH_2Cl_2

Cation EI-MS (CH_2Cl_2)	*m/z* [%] = 700.4 (100) [**3**$^+$], 677.4 (27) [$(Cp'''Co)_2MeCP(OH)_2$]
Anion EI-MS (CH_2Cl_2)	*m/z* [%] = 967.1 (100) [TEF]

1.3. Synthesis and characterization of [Cp'''Co(tol)][TEF] (4):

A solution of 0.31 mmol [{Cp'''Co}(μ-Cl)]$_2$ in 10 mL toluene is added to a solution of 0.61 mmol Tl[TEF] in a mixture of 15 mL toluene and 3 mL CH_2Cl_2 and stirred for 24 hours. The resulting red solution with a white precipitate of TlCl is filtered over silica and dried *in vacuo.* The red foaming residue is isolated

and ca. 50 mg are taken up in 3 mL CH_2Cl_2, layered under 10 mL of hexane and stored at -30 °C to yield compound **4** as dark red solid. Yield: 778 mg (94%).

^{1}H-NMR (C_6D_6)	δ [ppm] = -1.9 (s, 3H, $^3J_{PH}$ = 9.28 Hz, $C_6H_5CH_3$), 1.6 (s, 9H, $C_5H_2(C_4H_9)_3$), 2.5 (s, 18H, $C_5H_2(C_4H_9)_3$), 4.9 (s, 5H, $C_6H_5CH_3$) 40.2 (s, 2H, $C_5H_2(C_4H_9)_3$)
^{19}F-NMR (C_6D_6)	δ [ppm] = -75.4 (s)
^{19}F{^{1}H}-NMR (C_6D_6)	δ [ppm] = -75.4 (s)
Elemental analysis	calculated for $C_{40}H_{37}CoAlF_{36}O_4 \cdot CH_2Cl_2$ (1435.1 g·mol^{-1}): C 33.18, H 2.72; found: C 32.36, H 2.70
Cation ESI-MS (CH_2Cl_2)	*m/z* [%] = 384.1 (100) [M^+]
Anion ESI-MS (CH_2Cl_2)	*m/z* [%] = 967.1 (100) [TEF]

1.4. Synthesis and characterization of $[(Cp'''Co)(\mu_5,\eta^{5:1:1}\text{-}\{(CH_3CP)_2CoCp'''\}\{Cu(\mu\text{-}Cl)\}_2)]_n$ (6):

A solution of **2** (83.3 mg, 0.119 mmol) in CH_2Cl_2 (5 mL) was layered with a solution of CuCl (23 mg, 0.238 mmol) in CH_3CN (5 mL). After complete diffusion, the black solution was filtered through a Teflon capillary. The solution was concentrated to 5 mL and stored overnight at -30°C to form orange powder. The dark solution was further decanted from the orange residue and concentrated to approx. 3 mL. Within one day at -30°C brown flat rhombus-shaped crystals of **6** were formed. The crystals were washed with *n*-hexane and dried *in vacuo*. Crystalline yield: 27 mg (47%).

^{31}P-NMR (CD_2Cl_2/CD_3CN):	δ [ppm] = 61.68 (s), -54.61(s)
ESI-MS (hexane, 70 eV)	*m/z* [%] =1761.7 (0.5) $[\{(Cp'''Co)_2(CH_3CP)_2\}_2Cu_4Cl_3]^+$, 1661.6 (0.3) $[\{(Cp'''Co)_2(CH_3CP)_2\}_2Cu_3Cl_2]^+$, 1563.8 (1) $[\{(Cp'''Co)_2(CH_3CP)_2\}_2Cu_2Cl]^+$, 700.4 (19) $[\{(Cp'''Co)_2(CH_3CP)_2\}]^+$

1.5. Synthesis and characterization of $[(Cp'''Co)\{\mu_3,\eta^{4:1:1}\text{-}(CH_3CP)_2\}(CH_3CN)\{Cu(\mu\text{-}X)\}_2]_2$ (X = Br (7a), I (7b)):

A solution of **2** (83.3 mg, 0.119 mmol) in CH_2Cl_2 (5 mL) was layered with a solution of CuX (**7a**: 34 mg, 0.238 mmol; **7b**: 45.2 mg, 0.238 mmol) in CH_3CN (5 mL). After complete diffusion, the black solution was filtered through a Teflon capillary. The solution was concentrated to 5 mL and stored overnight at -30°C to form orange crystals of **7a**/**b** suitable for single crystal x-ray diffraction. Crystals were washed with *n*-hexane and dried *in vacuo.*

Analytical data for 7a:

Crystalline yield: 25 mg, 15%

^{1}H-NMR (CD_2Cl_2/CD_3CN):	δ [ppm] =	1.39 (s, 27 H, $C_5(C_4H_9)_3H_2$), 1.94 (s, 6 H, $C_2(CH_3)_2P_2$), 4.48 (s, 2 H, $C_5(C_4H_9)_3H_2$)
^{31}P{^{1}H}-NMR (CD_2Cl_2/CD_3CN):	δ [ppm] =	31.8 (s)
^{31}P{^{1}H} MAS NMR	δ [ppm] =	15.55 ($^1J_{CuP}$ = 1450 Hz), 19.20 ($^1J_{CuP}$ = 1400 Hz), 26.67 ($^1J_{CuP}$ = 1800 Hz), 29.34 ($^1J_{CuP}$ = 1500 Hz)
ESI-MS (DCM/CH_3CN)	*m/z* [%] =	2127.7 (5) $[(Cp'''Co(CH_3CP)_2)_4Cu_4Br_3]^+$, 1717.1 (0.3) $[(Cp'''Co(CH_3CP)_2)_3Cu_4Br_3]^+$, 1575.2 (26) $[(Cp'''Co(CH_3CP)_2)_3Cu_3Br_2]^+$, 1431.4 (0.7)

	$[(Cp'''Co(CH_3CP)_2)_3Cu_2Br]^+$,	1310.9	(0.3)
	$[(Cp'''Co(CH_3CP)_2)_2Cu_4Br_3]^+$,	1167.1	(3)
	$[(Cp'''Co(CH_3CP)_2)_2Cu_3Br_2]^+$,	1023.2	(100)
	$[(Cp'''Co(CH_3CP)_2)_2Cu_2Br]^+$,	879.3	(10)
	$[(Cp'''Co(CH_3CP)_2)_2Cu]^+$		
Elemental analysis	calc. (%) for $C_{46}H_{76}Br_4Co_2Cu_4N_2P_4$ (1472.63 $gmol^{-1}$): C 37.52, H 5.20, N 1.90; found: C 37.04, H 5.15, N 1.52		

Analytical data for 7b:

Crystalline yield: 45 mg, 24%

^{1}H-NMR (CD_2Cl_2/CD_3CN):	δ [ppm] =	1.22 (s, 3 H, $C_2(CH_3)_2P_2$), 1.39 (s, 9 H, $C_5(C_4H_9)_3H_2$), 1.41 (s, 18 H, $C_5(C_4H_9)_3H_2$), 4.48 (s, 2 H, $C_5(C_4H_9)_3H_2$)	
$^{31}P\{^1H\}$-NMR (CD_2Cl_2/CD_3CN):	δ [ppm] =	57.2 (s)	
EI-MS (hexane, 70eV)	*m/z* [%] =	1832.7 (9) $[(Cp'''Co(CH_3CP)_2)_2Cu_6I_5]^+$,	1640.9 (14)
		$[(Cp'''Co(CH_3CP)_2)_2Cu_5I_4]^+$,	1450.9 (10)
		$[(Cp'''Co(CH_3CP)_2)_2Cu_4I_3]^+$,	1261.1 (28)
		$[(Cp'''Co(CH_3CP)_2)_2Cu_3I_2]^+$,	1071.1 (2)
		$[(Cp'''Co(CH_3CP)_2)_2Cu_2I]^+$,	879.3 (64)
		$[(Cp'''Co(CH_3CP)_2)_2Cu]^+$,	512.1 (2)
		$[(Cp'''Co(CH_3CP)_2)Cu + CH_3CN]^+$	
Elemental analysis	calc. (%) for $C_{46}H_{76}I_4Co_2Cu_4N_2P_4$ (1660.67 $gmol^{-1}$): C 33.27, H 4.61, N 1.69; found: C 32.60, H 4.47, N 1.87		

1.6. Synthesis and characterization of $[(Cp'''Co)\{\mu_3,\eta^{4:1:1}\text{-}(CH_3CP)_2\}(\mu\text{-}W(CO)_4)]_3$ (8):

A solution of $[W(CO)_5(nbd)]$ (184 mg, 0.475 mmol) in *n*-hexane (10 mL) was added to a solution of **2** (166 mg, 0.238 mmol) in *n*-hexane (30 mL) at room temperature. During stirring overnight, the colour changed from dark green to dark brown. The solvent was removed *in vacuo* resulting in an orange brown precipitate. After washing with *n*-pentane and extraction with THF, the solution was concentrated and stored at -30°C. After two weeks, few single crystals suitable for X-ray diffraction studies in the shape of orange rods were obtained. In addition, a bigger amount of orange amorphous solid was obtained. Owing to the impurity of this solid, the yield of **8** could be determined by $^{31}P\{^1H\}$ NMR spectroscopy to be 44%.

^{1}H-NMR	δ [ppm] =	1.09 (s, 9 H, $C_5(C_4H_9)_3H_2$), 1.26 (s, 18 H, $C_5(C_4H_9)_3H_2$), 1.34 (s, 3 H, $C_2(CH_3)_2P_2$), 1.36 (s, 3 H, $C_2(CH_3)_2P_2$), 4.31 (s, 1H, $C_5(C_4H_9)_3H_2$), 4.79 (s, 1H, $C_5(C_4H_9)_3H_2$)
$^{31}P\{^1H\}$-NMR	δ [ppm] =	23.1 (s, $^1J_{PW}$ = 235 Hz)
IR (KBr)	$\tilde{\upsilon}$ [cm^{-1}] =	2021 (m), 1950 (sh, m), 1930 (s), 1913 (s)
FD-MS (toluene)	*m/z* [%] =	2112 (13.5) $[M]^+$

2. NMR Spectra, Cyclovoltammograms and EPR Spectra

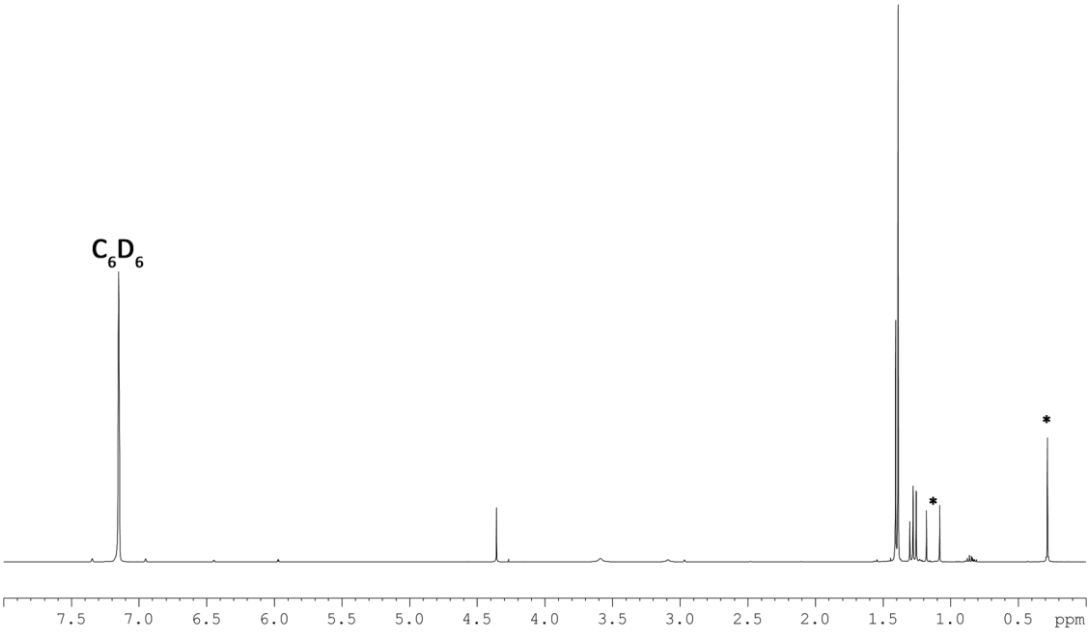


Fig. S1 ^{1}H NMR spectrum of **1** in C_6D_6 at 300 K. Signals marked with an asterisk are silicon grease and minor impurities.

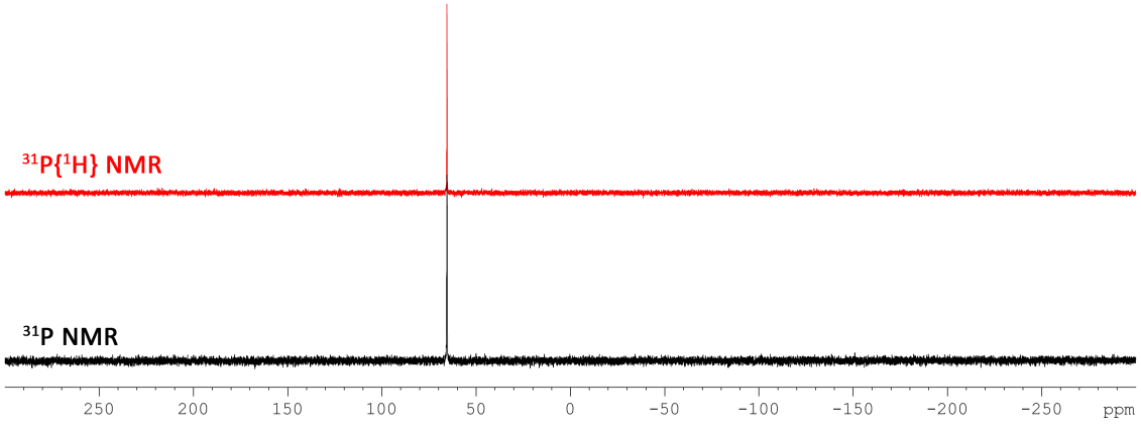


Fig. S2 ^{31}P (black) and ^{31}P{^{1}H} (red) NMR spectra of **1** in C_6D_6 at 300 K.

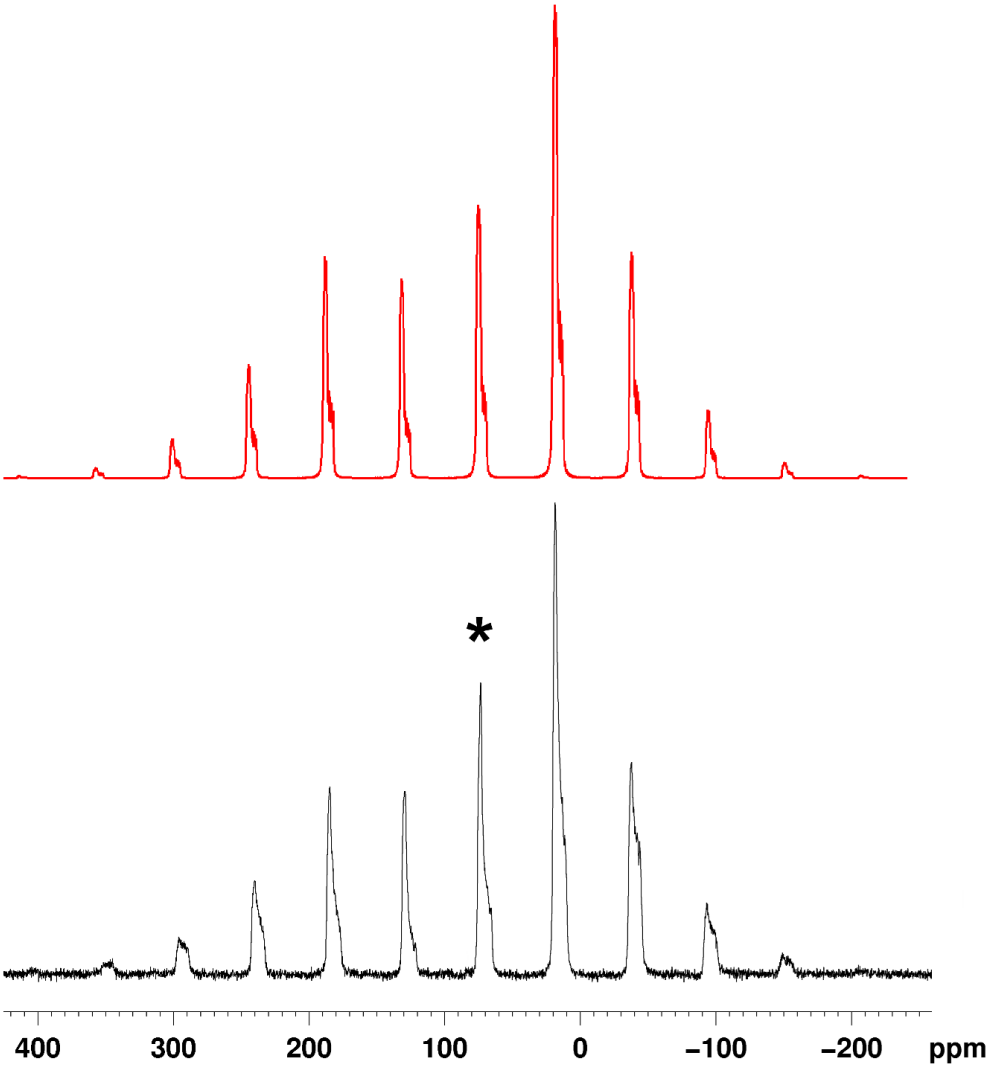


Fig. S3 $^{1}H–^{31}P$ CP/MAS spectrum of **1**, obtained with a MAS rate of 9.0 kHz, a 6.0 s recycle delay (bottom trace), and spectral simulation. The asterisk indicates the isotropic ^{31}P chemical shifts.

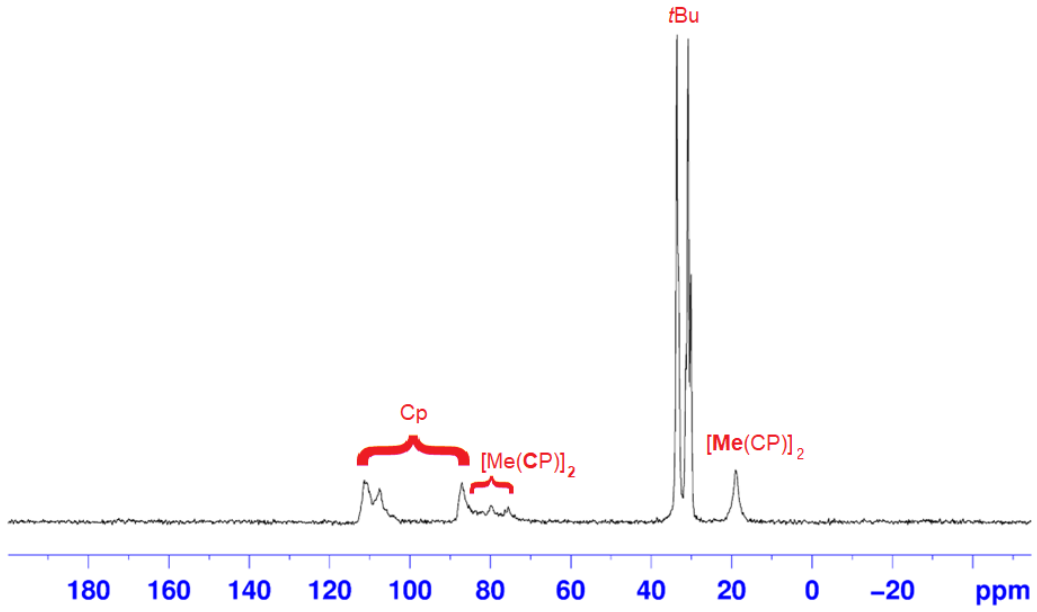


Fig. S4 $^{1}H–^{13}C$ CP/MAS spectrum of **1**, obtained with a MAS rate of 14.0 kHz and a 6.0 s recycle delay.

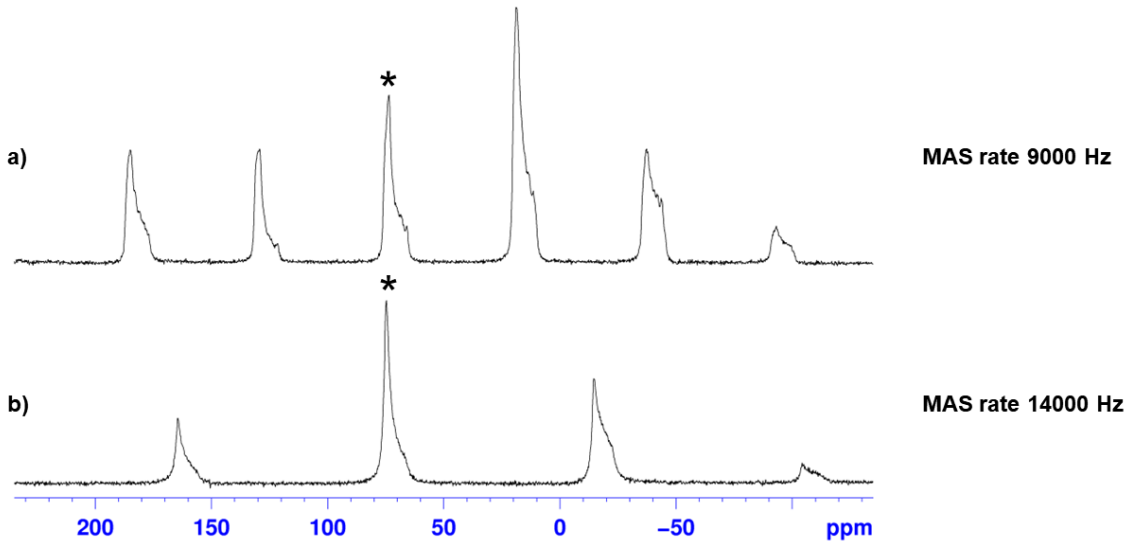


Fig. S5 $^{1}H–^{31}P$ CP/MAS spectrum of **1**, obtained with a MAS rate of: a) 9.0 kHz; b) 14 kHz. The asterisks indicate the isotropic ^{31}P chemical shifts.

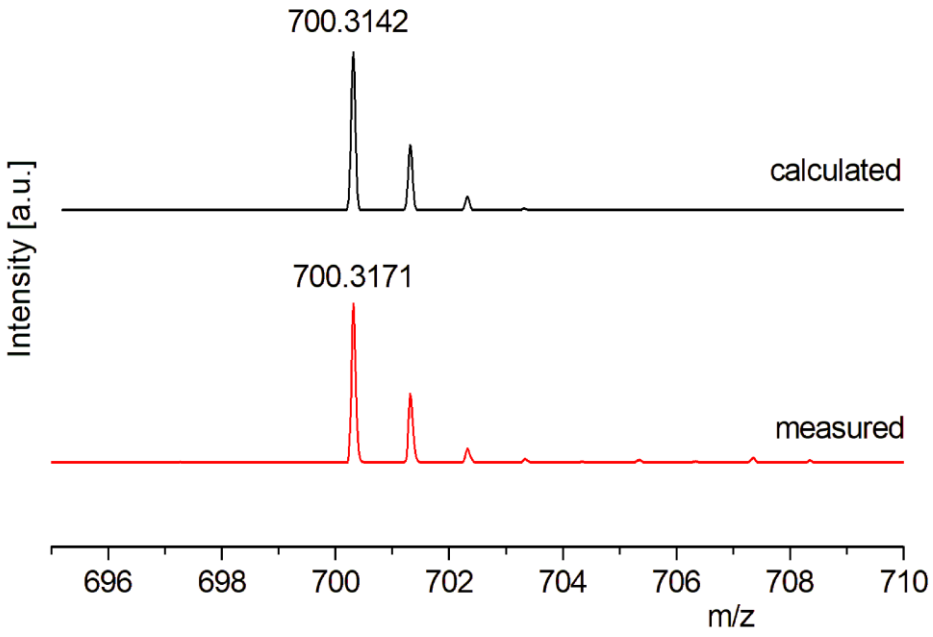


Fig. S6 HRMS(+) spectrogram of **2** in isopropanol showing the peak corresponding to the cation $C_{38}H_{64}Co_2P_2^+$ ($[M]^+$). The error between calculated and observed isotopic patterns is 4.2 ppm.

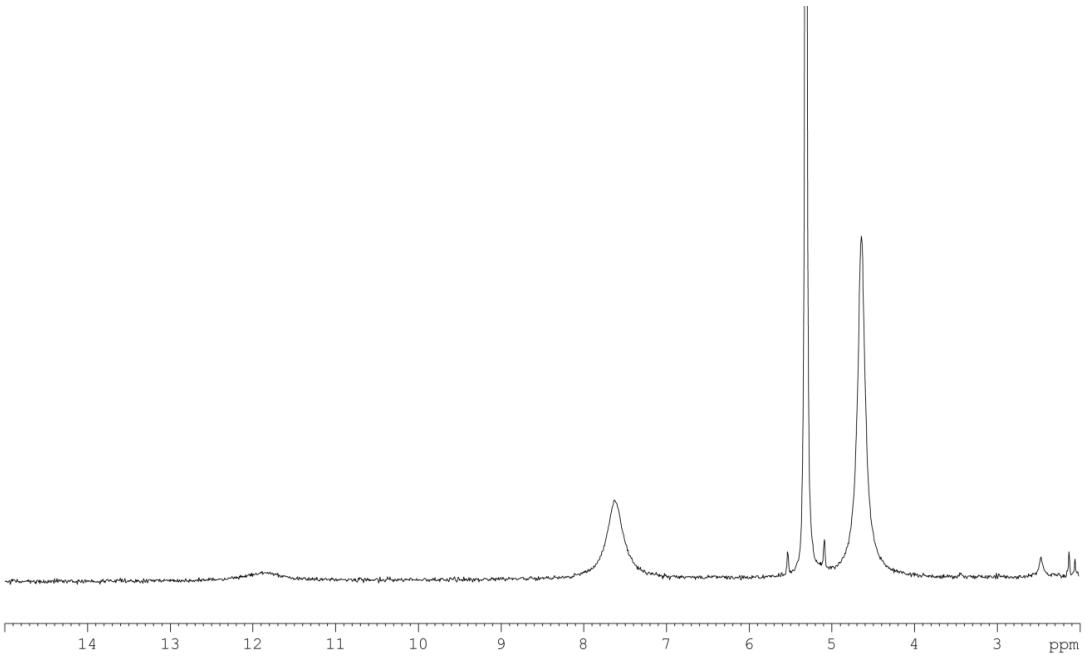


Fig. S7 Paramagnetic ^{1}H NMR spectrum of **3** in CD_2Cl_2 at 300 K.

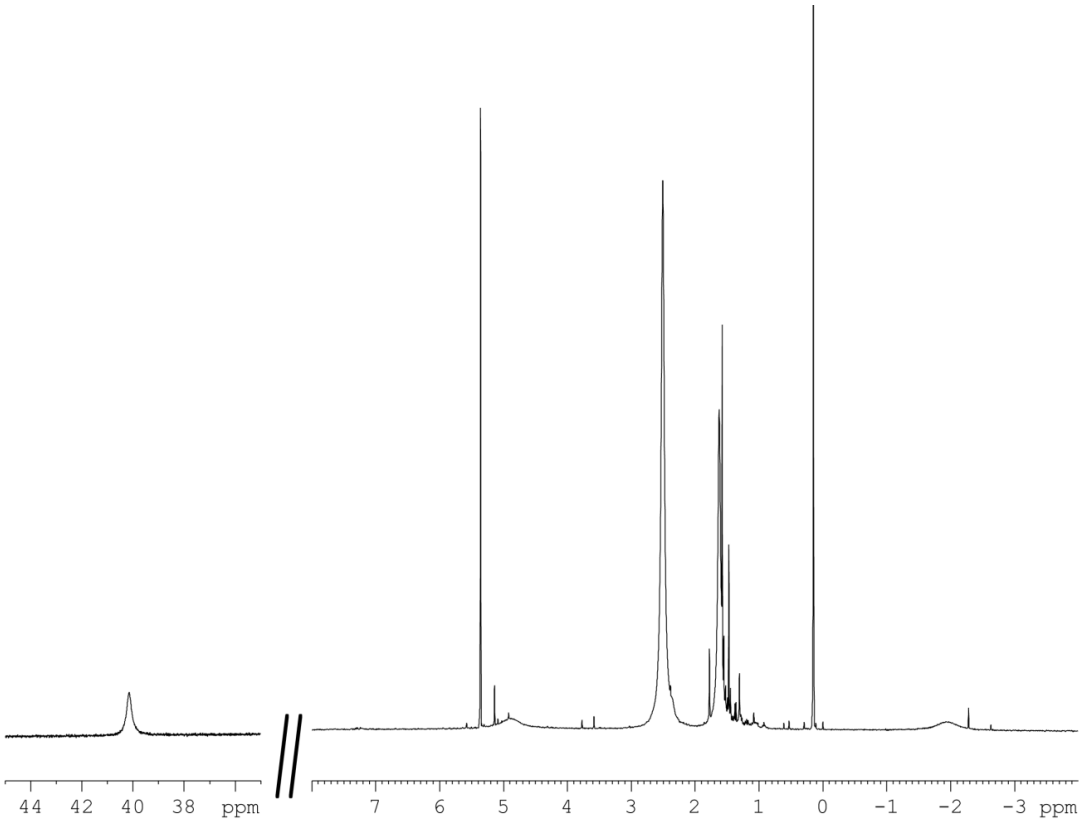


Fig. S8 Paramagnetic ^{1}H NMR spectrum of **4** in CD_2Cl_2 at 300 K.

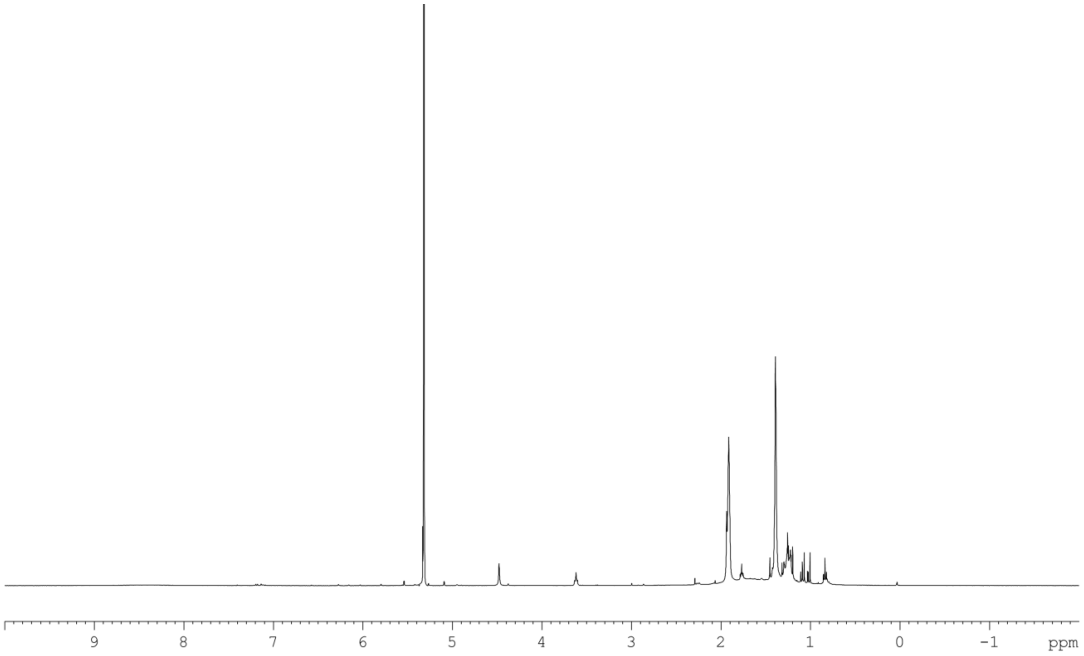


Fig. S9 ^{1}H NMR spectrum of **7a** in a CD_2Cl_2/CD_3CN mixture at 300 K.

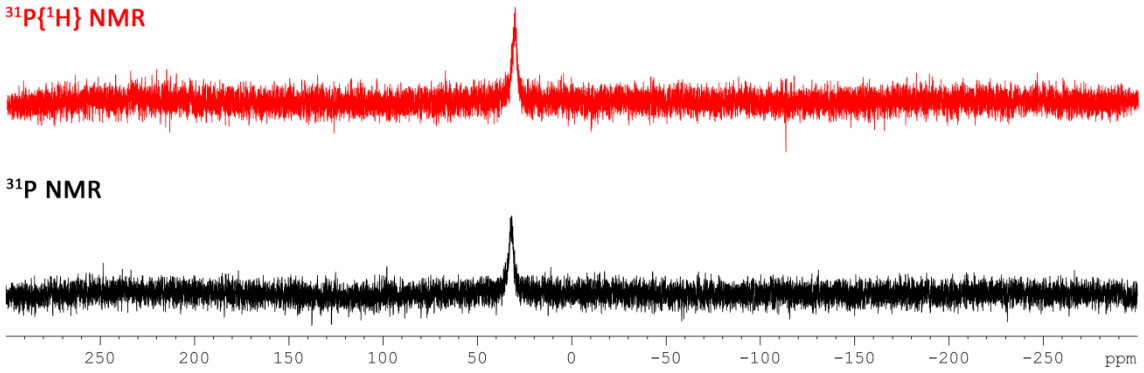


Fig. S10 ^{31}P (black) and $^{31}P\{^{1}H\}$ (red) NMR spectra of **7a** in a CD_2Cl_2/CD_3CN mixture at 300 K.

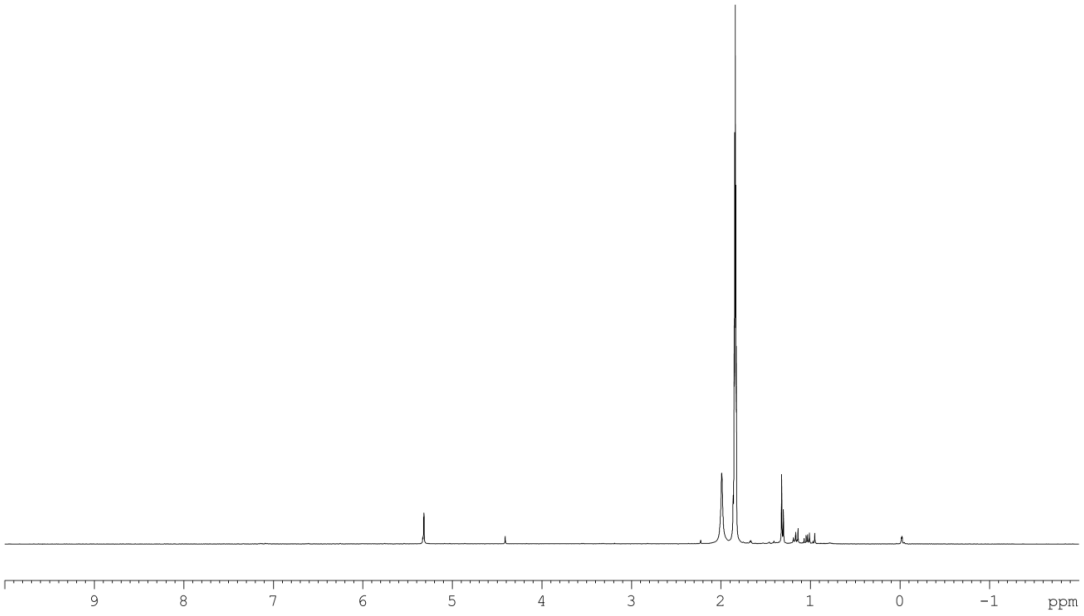


Fig. S11 ^{1}H NMR spectrum of **7b** in a CD_2Cl_2/CD_3CN mixture at 300 K.

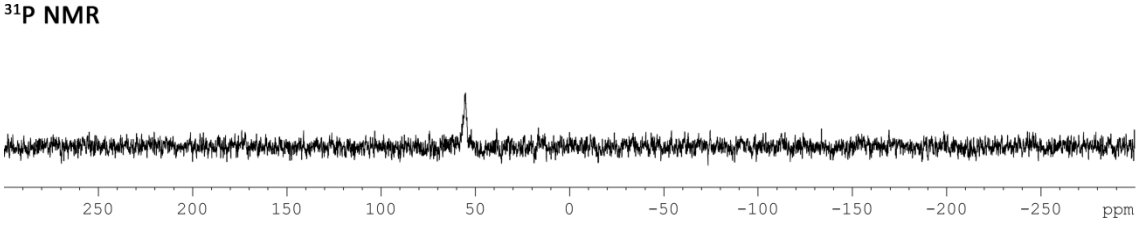


Fig. S12 ^{31}P NMR spectrum of **7b** in a CD_2Cl_2/CD_3CN mixture with a C_6D_6 capillary at 300 K.

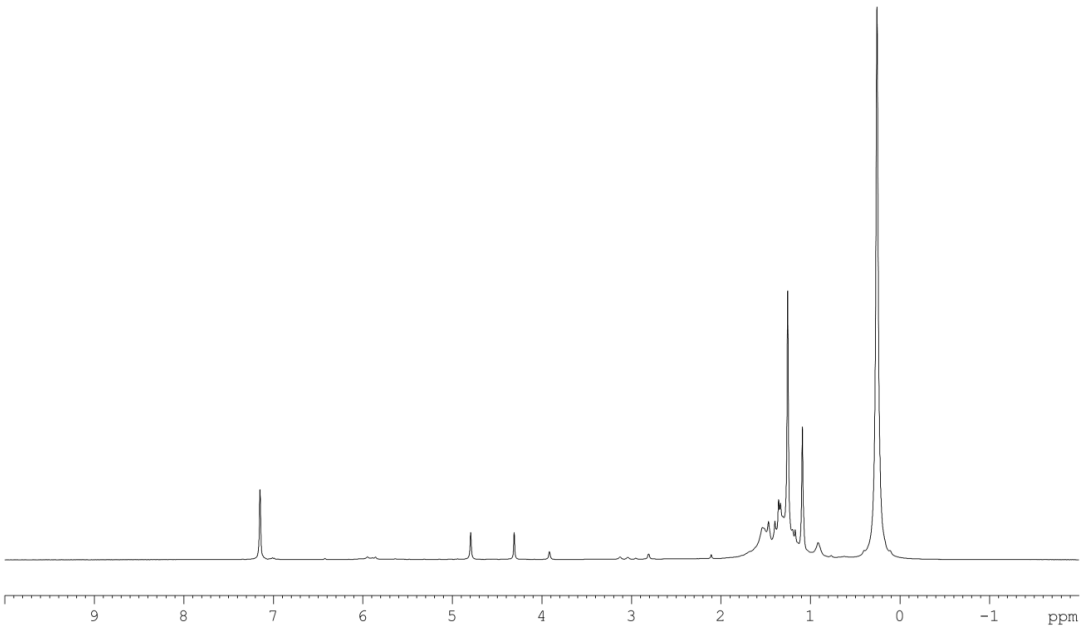


Fig. S13 ^{1}H NMR spectra of **8** in C_6D_6 at r.t.

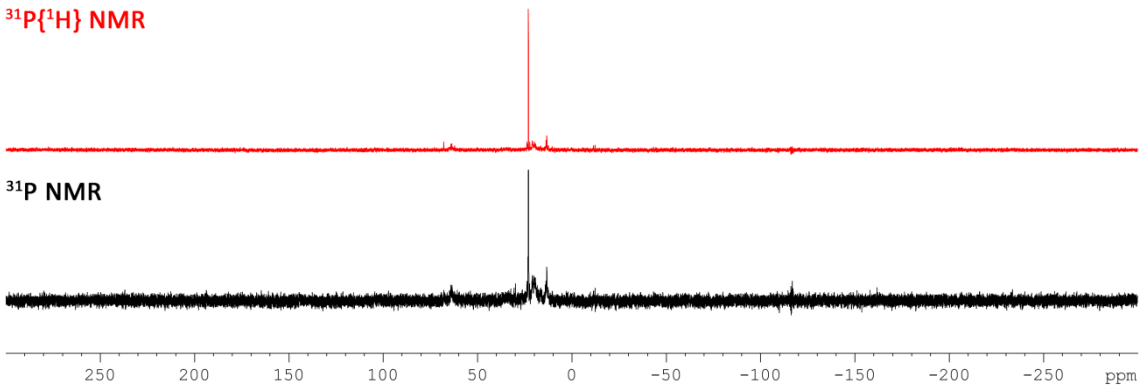


Fig. S14 ^{31}P (black) and ^{31}P{^{1}H} (red) NMR spectra of **8** in C_6D_6 at 300 K.

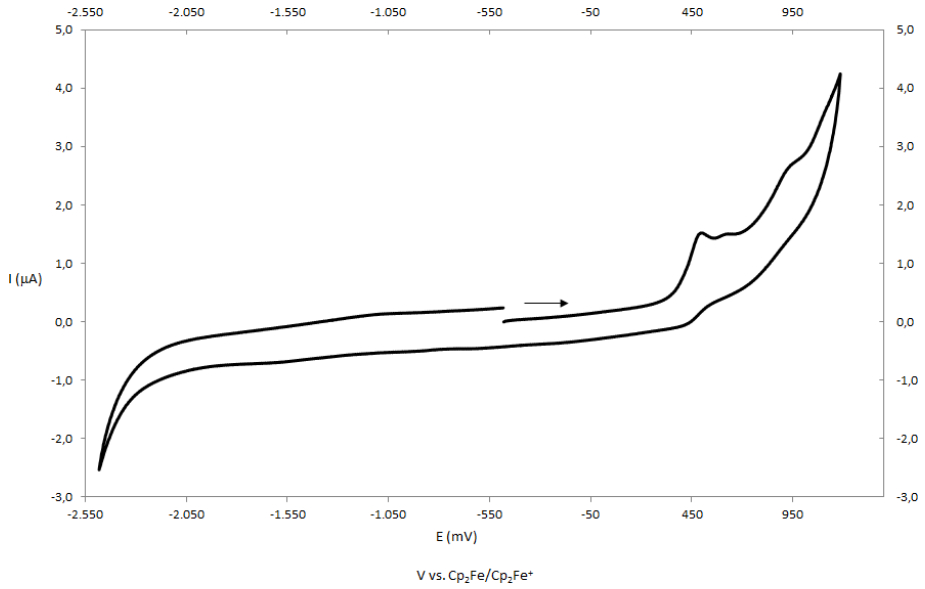


Fig. S15 Cyclovoltammogram of **1** recorded at a platinum disc electrode in CH_2Cl_2, referenced against Cp_2Fe/Cp_2Fe^+. Supporting electrolyte $[Bu_4N][PF_6]$ (0.1 mol/L). Regardless of potential rates, only an irreversible oxidation could be observed in the solvent window.

For **1**, One reversible oxidation at $E_{1/2}$ = -0.8 V ($i_{p(reverse)}/i_{p(forward)}$ = 0.83), one reversible reduction $E_{1/2}$ = -1.85 V ($i_{p(reverse)}/i_{p(forward)}$ = 0.93) and one irreversible reduction at $E_{1/2}$ = -2.3 V ($i_{p(reverse)}/i_{p(forward)}$ = 0.21) can be observed in the solvent window.

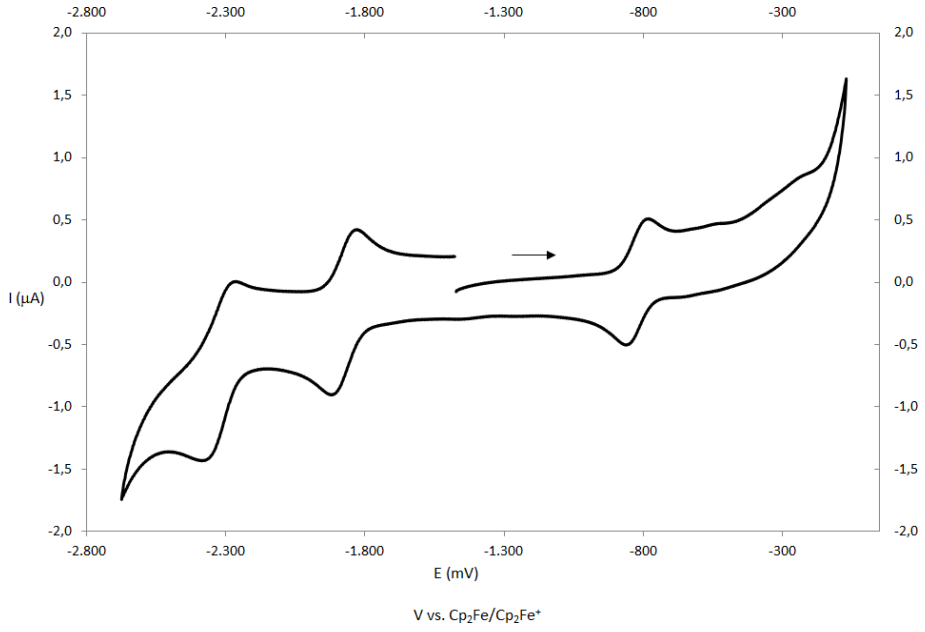


Fig. S16 Cyclovoltammogram of **2** recorded at a platinum disc electrode in THF at 200 mV/s, referenced against Cp_2Fe/Cp_2Fe^+. Supporting electrolyte $[Bu_4N][PF_6]$ (0.1 mol/L).

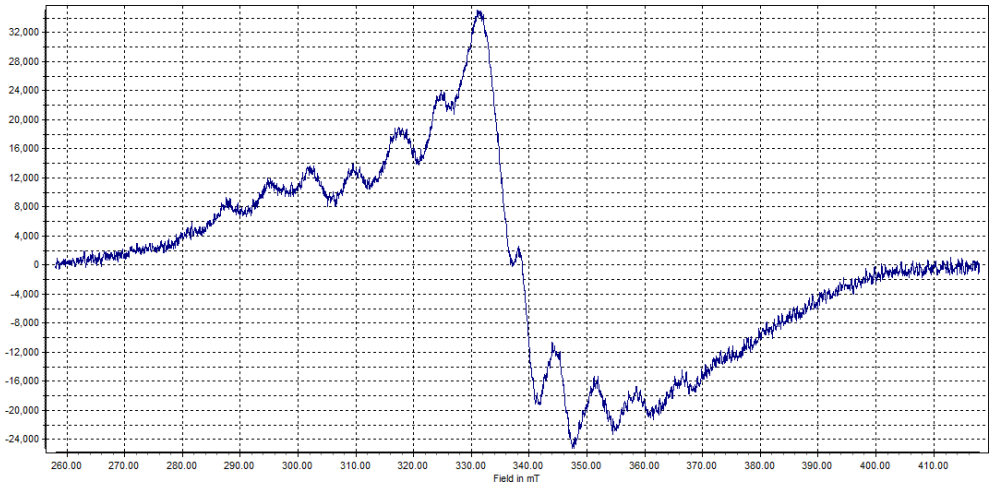


Fig. S17 Baseline corrected EPR spectrum of **3**. A g value of 2 could be determined, indicating one unpaired electron. Hyperfine structure indicates the electron is ^{59}Co centred. Spectrum recorded at 77.4 K in CH_2Cl_2.

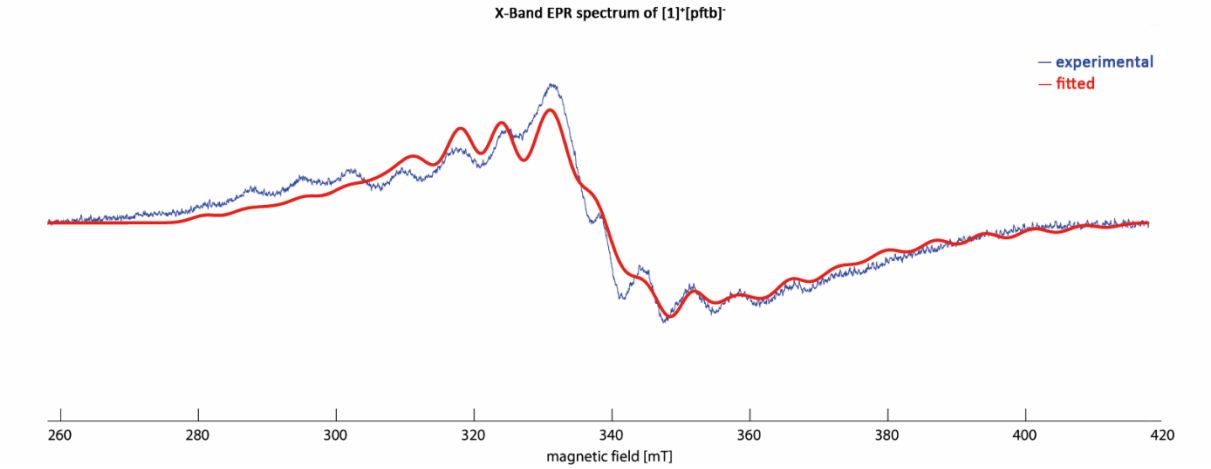


Fig. S18 Experimental (blue) and simulated (red) X-band EPR spectrum of **3** in CH_2Cl_2 at 77K. Parameters used for fitting: g_x = 1.858, g_y = 1.995, g_z = 2.079; A_{1x} = 170.58, A_{1y} = 34.56, A_{1z} = 145.29, A_{2x} = 191.95, A_{2y} = 14.18, A_{2z} = 213.82.

3. Crystallographic details

Crystals suitable for single crystal X-ray structure analysis were obtained for **1**-**6**, **7a**, **7b**, **8** and as described above. The crystals of each compound were taken out of the Schlenk tube under argon or nitrogen atmosphere and placed into the degassed mineral or perfluorinated oil to slow down the decomposition. This the thin needle the appropriate crystal was selected under visual control with the microscope. All crystals found in this way, were mounted on a MiTeGen micro mount or a Mylar loop, placed under a stream of cold nitrogen on a goniometer of a diffractometer and checked for quality. For every crystal with high indexation percentage of reflections in the found unit cell (usually more than 90 %) the diffraction experiment was performed (Tables S1-S3).

Diffraction intensities for selected single crystals of all structurally characterized compounds **1**-**6**, **7a**, **7b**, **8** were acquired according to the strategies individually found in each case with the CrysAlis Pro software using an Agilent Technologies Gemini R Ultra diffractometer (**7b**) using microfocus CuKα source (λ = 1.54178 Å) and a Ruby CCD detector, an Agilent Technologies SuperNova diffractometer equipped with a microfocus CuKα source and with either an Atlas CCD (**8**) or CCD Titan^{S2} detectors (**6** and **7a**). The data collection strategy consisted of a few scans depending on the symmetry and covered sufficient sector of a reciprocal space. The number of 0.5-degree of 1-degree ϕ-scans covering the required part of reciprocal space were performed in each diffraction experiment depending on the length of the unit cell constants. The data processing was performed with the CrysAlisPro software package.[8] A semi-empirical multi-scan absorption correction using equivalent reflections (**2**, **5**, **7b**), a semi-empirical numerical absorption correction (**6**, **7a**) based on gaussian integration over a multifaceted crystal model or an analytical absorption correction from crystal faces (**1**, **8**) was applied in each case. The crystal structures were solved by direct methods using programs SIR-92 (**8**),[9] SHELXS (**1**, **6** and **7a**)[10] or SUPERFLIP (**7b**).[11] All structures were refined by full-matrix least-squares based on F^2 with the program SHELXL-97 or its multi-processor versions SHELXL-14 and SHELXT.[12] All fully occupied non-hydrogen atoms were refined in anisotropic approximation. The disorder of the particular fragments was treated in a usual way for each of the compounds: the site occupancy factors for each position of a disordered atom were refined and fixed at the obtained value. After that the atomic displacement parameters were refined in isotropic and then in anisotropic approximation. In case of the closely located positions the refinement was performed with restrained or constrained geometry using standard SHELX procedures. This especially applies to the refinement of the TEF anions. The detailed information can be found in the provided CIF files deposited as follows. Hydrogen atoms were placed in idealized positions and refined with isotropic displacement parameters according to the riding model.

ORTEP plots were obtained with OLEX program.[13]

CCDC reference numbers CCDC-2381406 (**1**), CCDC-2381407 (**2**), CCDC-2381408 (**3**), CCDC-2381409 (**5**), CCDC-2239459 (**6**), CCDC-2239463 (**7a**), CCDC-2239462 (**7b**), CCDC-2239461 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retreving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table S1. Crystal data and structure refinement for compounds **1**-**3**.

Compound	**1**	**2**	**3**
CCDC Code	CCDC-**2381406**	CCDC-**2381407**	CCDC-**2381408**
Empirical formula	$C_{21}H_{35}CoP_2$	$C_{38}H_{64}Co_2P_2$	$C_{54}H_{64}AlCo_2F_{36}O_4P_2$
Formula weight	408.36	700.69	1667.83
Temperature/K	182.9(6)	123.0(1)	123.5(9)
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/Å	9.25753(14)	8.6880(2)	10.4962(3)
b/Å	9.93611(13)	11.8823(2)	12.6761(4)
c/Å	11.86967(16)	17.8344(3)	25.5265(5)
α/°	82.9524(11)	90	83.317(2)
β/°	89.1001(12)	91.643(2)	89.0423(18)
γ/°	83.3831(12)	90	89.363(2)
Volume/Å^3	1076.35(3)	1840.35(6)	3372.64(16)
Z	2	2	2
D_x / g·cm^{-3}	1.260	1.265	1.642
μ/mm^{-1}	7.632	8.044	5.742
F(000)	436	752.0	1682.0
Crystal habit and colour	light orange prism	green plate	dark green prism
Crystal size/mm^3	0.201 × 0.118 × 0.040	0.13 × 0.07 × 0.02	0.377 × 0.222 × 0.077
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54178)	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.513 to 66.772	8.94 to 141.42	6.974 to 130.176
Index ranges	-11 ≤ *h* ≤ 10, -11 ≤ *k* ≤ 11, -11 ≤ *l* ≤ 14	-8 ≤ *h* ≤ 10, -14 ≤ *k* ≤ 12, -17 ≤ *l* ≤ 21	-12 ≤ *h* ≤ 12, -11 ≤ *k* ≤ 14, -29 ≤ *l* ≤ 30
Reflections collected	11359	6866	26034
Independent reflections	3767 [R_{int} = 0.0220, R_{sigma} = 0.0224]	3431 [R_{int} = 0.0390, R_{sigma} = 0.0470]	11168 [R_{int} = 0.0531, R_{sigma} = 0.0558]
Data/restraints/parameters	3767/0/228	3431/0/200	11168/1747/1453
Goodness-of-fit on F^2	1.024	1.021	1.082
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0236, wR_2 = 0.0587	R_1 = 0.0489, wR_2 = 0.1223	R_1 = 0.0892, wR_2 = 0.2530
Final *R* indexes [all data]	R_1 = 0.0251, wR_2 = 0.0591	R_1 = 0.0524, wR_2 = 0.1263	R_1 = 0.1069, wR_2 = 0.2670
Largest diff. peak/hole / e Å^{-3}	0.19/-0.30	0.80/-0.81	1.49/-1.21

Table S2. Crystal data and structure refinement for compounds **5**-**6**.

Compound	**5**	**6**
CCDC Code	CCDC-**2381409**	CCDC-**2239459**
Empirical formula	$C_{105.5}H_{127}Al_2Cl_3Co_4F_{72}O_{12}P_2$	$C_{39.5}H_{67.5}P_2Cl_2Co_2Cu_2$
Formula weight	3413.03	920.21
Temperature/K	182.9(6)	122.95(16)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
a/Å	15.6948(4)	26.6988(9)
b/Å	20.5290(7)	24.0162(4)
c/Å	22.3059(7)	19.3413(11)
α/°	76.935(3)	90
β/°	80.111(3)	133.198(6)
γ/°	81.106(3)	90
Volume/Å^3	6846.5(4)	9040.7(9)
Z	2	8
D_x / g·cm^{-3}	1.656	1.352
μ/mm^{-1}	6.006	8.634
F(000)	3438.0	3844.0
Crystal habit and colour	green rod	black rod
Crystal size/mm^3	0.45 × 0.34 × 0.20	0.305 × 0.042 × 0.025
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.842 to 134.09	9.158 to 146.318
Index ranges	$-18 \le h \le 13$, $-24 \le k \le 24$, $-26 \le l \le 26$	$-32 \le h \le 32$, $-29 \le k \le 19$, $-23 \le l \le 16$
Reflections collected	41916	14527
Independent reflections	23556 [R_{int} = 0.0270, R_{sigma} = 0.0397]	8702 [R_{int} = 0.0372, R_{sigma} = 0.0429]
Data/restraints/parameters	23556/2072/2649	8702/22/512
Goodness-of-fit on F^2	0.908	0.998
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0426, wR_2 = 0.1056	R_1 = 0.0457, wR_2 = 0.1322
Final R indexes [all data]	R_1 = 0.0572, wR_2 = 0.1103	R_1 = 0.0546, wR_2 = 0.1354
Largest diff. peak/hole / e Å^{-3}	0.41/-0.29	0.91/-0.72

Table S3. Crystal data and structure refinement for compounds **7**-**8**.

Compound	**7a**	**7b**	**8**
CCDC Code	CCDC-**2239463**	CCDC-**2239462**	CCDC-**2239461**
Empirical formula	$C_{23.9}H_{39.8}Br_2CoCu_2NP_2Cl_{1.8}$	$C_{46}H_{76}Co_2Cu_4I_4P_4ClN_2$	$C_{75}H_{105}O_{12}P_6Co_3W_3$
Formula weight	812.75	1660.58	2112.74
Temperature/K	123(2)	123(2)	123(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	17.9871(7)	12.6970(6)	10.34490(10)
b/Å	9.7704(2)	16.4574(6)	24.9146(2)
c/Å	20.8995(6)	15.5867(5)	32.2794(3)
β/°	106.194(4)	96.667(3)	94.5370(10)
Volume/Å^3	3527.15(19)	3235.0(2)	8293.59(13)
Z	4	2	4
D_x/ g·cm^{-3}	1.531	1.705	1.692
μ/mm^{-1}	9.898	21.486	13.568
F(000)	1623.0	1616.0	4176.0
Crystal habit and colour	red-orange plate	orange prism	orange needle
Crystal size/mm^3	0.238 × 0.048 × 0.031	0.12 × 0.11 × 0.09	0.229 × 0.035 × 0.016
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.744 to 148.06	7.84 to 124.666	6.54 to 132.782
Index ranges	-22 ≤ h ≤ 22, -12 ≤ k ≤ 11, -16 ≤ l ≤ 26	-14 ≤ h ≤ 7, -18 ≤ k ≤ 17, -17 ≤ l ≤ 16	-11 ≤ h ≤ 12, -21 ≤ k ≤ 29, -27 ≤ l ≤ 37
Reflections collected	20909	15292	29666
Independent reflections	7007 [R_{int} = 0.0419, R_{sigma} = 0.0423]	5012 [R_{int} = 0.0313, R_{sigma} = 0.0305]	13943 [R_{int} = 0.0419, R_{sigma} = 0.0477]
Data/restraints/parameters	7007/9/380	5012/0/292	13943/0/925
Goodness-of-fit on F^2	0.992	0.971	1.031
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0511, wR_2 = 0.1562	R_1 = 0.0246, wR_2 = 0.0577	R_1 = 0.0394, wR_2 = 0.1001
Final R indexes [all data]	R_1 = 0.0623, wR_2 = 0.1626	R_1 = 0.0296, wR_2 = 0.0588	R_1 = 0.0473, wR_2 = 0.1058
Largest diff. peak/hole / e Å^{-3}	1.34/-1.13	0.77/-0.55	1.99/-1.70

Crystal structure of compound 1

The crystal was kept at *T* = 182.9(6) K during data collection as the crystals lost crystallinity below this temperature presumably due to the first order phase transition accompanied by an increase in volume.

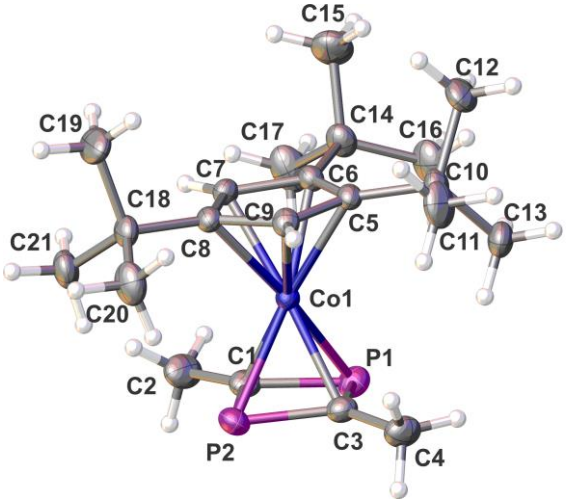


Fig. S19. Molecular structure of compound **1** in the solid state showing the atom-labelling scheme. Atomic displacement ellipsoids are drawn at the 50% probability level.

Table S4. Selected geometric parameters for compound **1** (Å, °)

Co1—P1	2.2483 (4)	C8—C9	1.426 (2)
Co1—P2	2.2435 (4)	C5—C6	1.463 (2)
Co1—C3	2.0656 (14)	C5—C10	1.5408 (19)
Co1—C8	2.0718 (13)	C5—C9	1.429 (2)
Co1—C5	2.0928 (13)	C6—C7	1.437 (2)
Co1—C6	2.0764 (14)	C6—C14	1.537 (2)
Co1—C7	2.0532 (14)	C1—C2	1.496 (2)
Co1—C1	2.0529 (14)	C14—C17	1.536 (2)
Co1—C9	2.0506 (13)	C14—C16	1.532 (2)
P1—C3	1.7926 (16)	C14—C15	1.538 (2)
P1—C1	1.7911 (16)	C10—C13	1.537 (2)
P2—C3	1.7857 (16)	C10—C11	1.539 (2)
P2—C1	1.7903 (17)	C10—C12	1.540 (2)
C3—C4	1.489 (2)	C18—C21	1.531 (2)
C8—C7	1.420 (2)	C18—C20	1.527 (2)
C8—C18	1.5190 (19)	C18—C19	1.543 (2)
C1—P1—C3	81.00 (7)	C4—C3—P2	128.89 (12)
C3—P2—C1	81.21 (7)	P2—C1—P1	98.54 (8)
P2—C3—P1	98.66 (8)	C2—C1—P1	130.66 (13)
C4—C3—P1	131.51 (12)	C2—C1—P2	130.01 (13)

Crystal structure of compound 2

Complex **2** occupies an inversion centre in the space group $P2_1/n$.

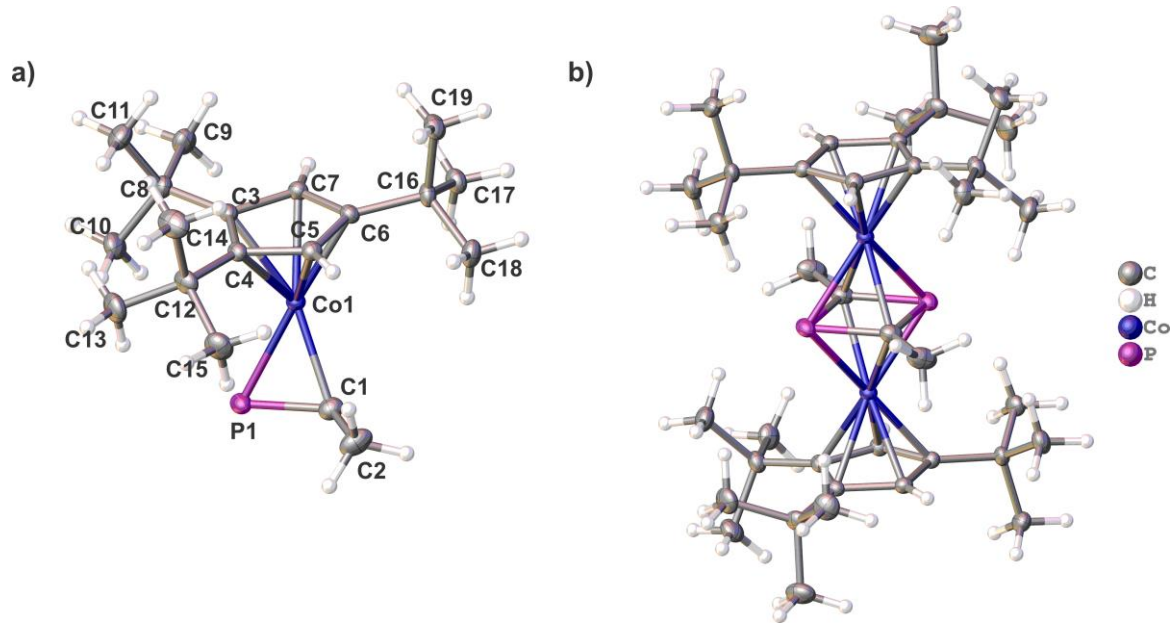


Fig. S20. a) Asymmetric unit of **2** showing the atom-labelling scheme; b) Molecular structure of compound **2** in the solid state. Atomic displacement ellipsoids are drawn at the 50% probability level.

Table S5. Selected geometric parameters for compound **2** (Å, °)

Co1—P1	2.2596 (7)	Co1—C7	2.100 (2)
Co1—C1	2.130 (2)	Co1—P1^{i}	2.2855 (6)
Co1—C3	2.129 (2)	Co1—C1^{i}	2.128 (2)
Co1—C4	2.126 (2)	P1—C1	1.838 (3)
Co1—C5	2.101 (2)	P1—C1^{i}	1.839 (2)
Co1—C6	2.117 (2)		
C1—P1—C1^{i}	79.20 (11)	P1—C1—P1^{i}	100.80 (13)

Symmetry code: (i) -*x*+2, -*y*, -*z*+2.

Crystal structure of compound 3

Cations occupy inversion centres, whereas TEF anion lies in a general position of the $P\bar{1}$ space group.

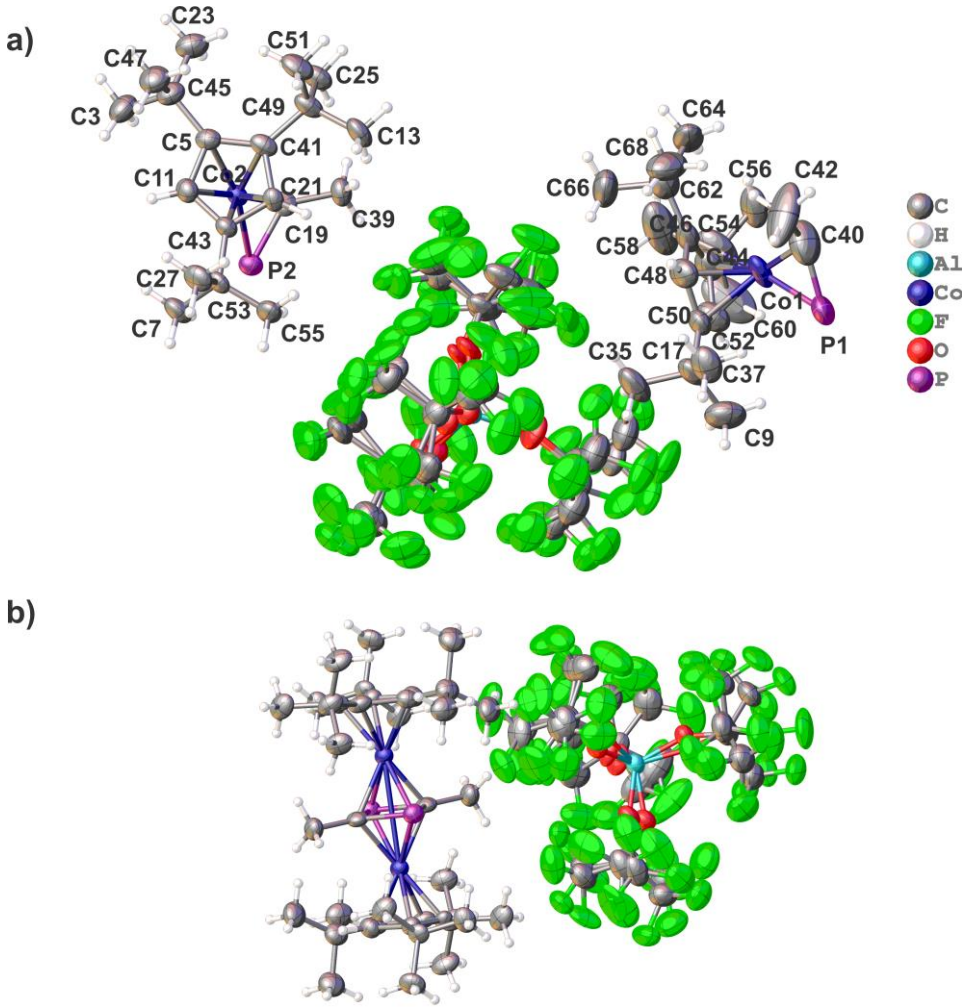


Fig. S21. a) Asymmetric unit of **3** in the solid state showing the atom-labelling scheme; b) Molecular structure of one unique complex of compound **3** in the solid state. Disorder of the *t*Bu groups was omitted for clarity. Atomic displacement ellipsoids are drawn at the 50% probability level.

Table S6. Selected geometric parameters for compound **3** (Å, °)

Co1—P1	2.220(2)	P1—C40^{i}	1.920(12)
Co1—P1^{i}	2.2222(19)	C40—C42	1.516(15)
Co1—C40	2.023(9)	C44—C54	1.557(13)
Co1—C40^{i}	2.062(10)	C46—C48	1.452(10)
Co1—C44	2.046(7)	C48—C50	1.372(10)
Co1—C46	2.139(7)	C50—C52	1.414(10)
Co1—C48	2.073(7)	C54—C56	1.53(2)
Co1—C50	2.069(6)	C5—C45	1.535(8)
Co1—C52	2.013(8)	C41—C21	1.460(8)
P1—C40	1.843(13)	C21—C43	1.408(7)

C45—C3	1.510(9)	Co2—C19^{ii}	2.074(5)
C49—C25	1.542(8)	Co2—C5	2.119(5)
Co2—Co2$^{i\,i}$	3.4525(15)	P2—C19^{ii}	1.866(6)
Co2—P2$^{i\,i}$	2.2420(15)	P2—C19	1.841(6)
Co2—P2	2.2459(16)	Co2—C41	2.103(5)
Co2—C19	2.102(5)	Co2—C21	2.049(5)
P1—Co1—P1^{i}	82.66(8)	C40—P1—C40^{i}	77.6 (5)
P1—C40—P1^{i}	102.4(5)	C19—P2—C19^{ii}	78.7 (3)
P2—Co2—Co2^{ii}	39.67(4)	P2—C19—P2^{ii}	101.3 (3)

Symmetry codes: (i) *-x, -y+2, -z* and (ii) *-x, -y, -z*+1.

Crystal structure of compound 4

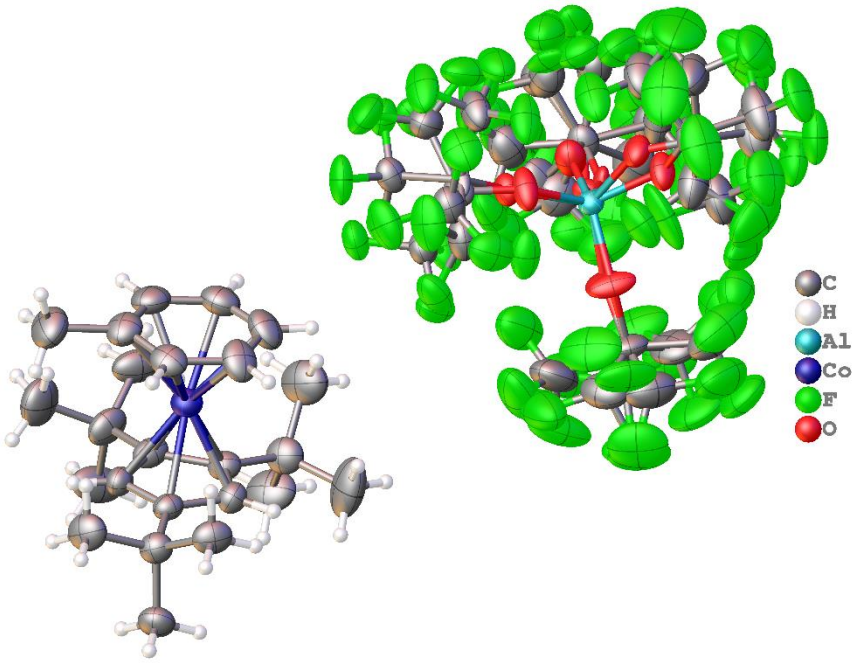


Fig. S22. Preliminary data on molecular structure of compound **4** in the solid state.

Crystal structure of compound 5

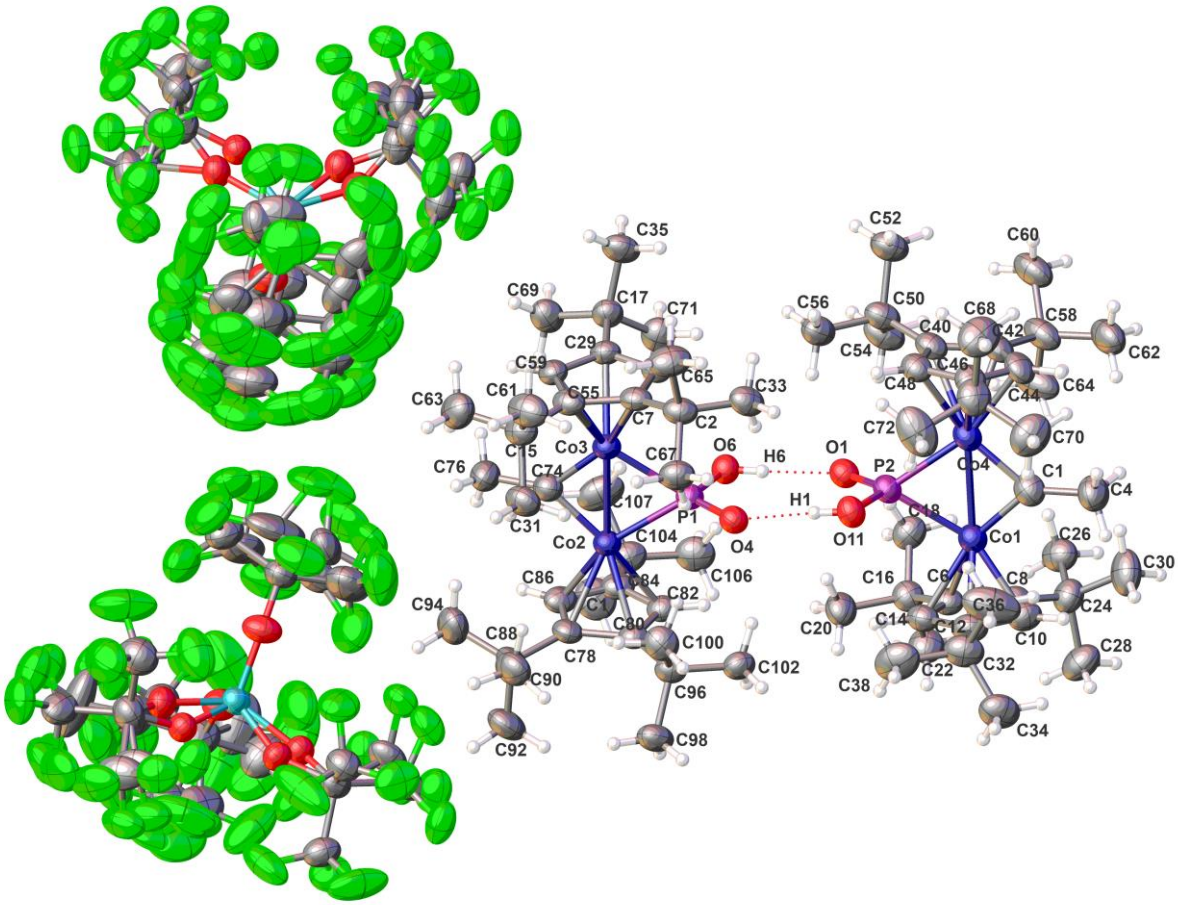


Fig. S23. Asymmetric unit of **5** in the solid state showing the atom-labelling scheme. Disorder of the *t*Bu groups (denoted by an addition of A in the atom label in Table S7) was omitted for clarity. Atomic displacement ellipsoids are drawn at the 50% probability level.

Table S7. Selected geometric parameters for compound **5** (Å, °)

Co1—Co4	2.3843 (6)	Co3—C29	2.077 (3)
Co1—C1	1.781 (3)	Co3—C59	2.059 (3)
Co1—C6	2.145 (3)	P1—O4	1.4901 (19)
Co1—C8	2.123 (3)	P1—O6	1.5687 (19)
Co1—C10	2.054 (3)	C74—C76	1.475 (4)
Co1—C12	2.078 (3)	C78—C80	1.469 (4)
Co1—C14	2.077 (3)	C78—C86	1.432 (4)
Co1—P2	2.1793 (8)	C78—C88	1.530 (5)
Co4—C1	1.803 (3)	C78—C88A	1.575 (17)
Co4—C40	2.154 (3)	C80—C82	1.428 (4)
Co4—C42	2.095 (3)	C80—C96	1.534 (4)
Co4—C44	2.048 (3)	C82—C84	1.425 (4)
Co4—C46	2.083 (3)	C84—C86	1.416 (4)
Co4—C48	2.089 (3)	C84—C104	1.520 (4)
Co4—P2	2.1701 (8)	C88—C90	1.510 (6)
O1—P2	1.4888 (19)	C88—C92	1.553 (6)
C1—C4	1.481 (4)	C88—C94	1.540 (6)
C6—C8	1.466 (4)	C96—C98	1.533 (4)
C6—C14	1.429 (4)	C96—C100	1.535 (4)
C6—C16	1.533 (4)	C96—C102	1.532 (4)
C8—C10	1.423 (4)	C104—C106	1.520 (5)
C8—C24	1.544 (4)	C104—C107	1.532 (5)
C10—C12	1.409 (5)	C104—C27	1.540 (5)
C12—C14	1.421 (4)	C55—C7	1.470 (4)
C12—C32	1.516 (4)	C55—C59	1.432 (4)
C16—C18	1.538 (4)	C55—C15	1.539 (5)
C16—C20	1.542 (4)	C55—C15A	1.549 (16)
C16—C22	1.532 (4)	C7—C57	1.424 (4)
C24—C26	1.523 (5)	C7—C2	1.535 (4)
C24—C28	1.548 (5)	C57—C29	1.426 (4)
C24—C30	1.527 (5)	C29—C59	1.411 (4)
C32—C34	1.532 (5)	C29—C17	1.517 (4)
C32—C36	1.529 (5)	C15—C61	1.540 (7)
C32—C38	1.525 (6)	C15—C31	1.541 (7)
C40—C42	1.462 (4)	C15—C63	1.529 (8)
C40—C48	1.429 (4)	C2—C65	1.542 (4)
C40—C50	1.533 (4)	C2—C33	1.541 (4)
C42—C44	1.432 (4)	C2—C67	1.533 (4)
C42—C58	1.540 (4)	C17—C69	1.529 (4)
C44—C46	1.417 (4)	C17—C35	1.532 (4)
C46—C48	1.420 (4)	C17—C71	1.529 (5)
C46—C66	1.519 (4)	C9—C73	1.516 (7)
C50—C52	1.544 (4)	C9—C37	1.572 (10)
C50—C54	1.529 (4)	C9—C75	1.584 (8)

C50—C56	1.536 (5)	C9—C73A	1.565 (12)
C58—C60	1.535 (5)	C9—C37A	1.509 (15)
C58—C62	1.535 (5)	C9—C75A	1.541 (14)
C58—C64	1.543 (5)	C19—C85	1.577 (8)
C66—C68	1.537 (5)	C19—C43	1.557 (8)
C66—C70	1.518 (5)	C19—C87	1.527 (8)
C66—C72	1.519 (5)	C19—C11	1.575 (14)
Co2—Co3	2.3793 (6)	C19—C89	1.538 (14)
Co2—P1	2.1734 (8)	C19—C45	1.577 (11)
Co2—C74	1.794 (3)	C77—C39	1.511 (12)
Co2—C78	2.116 (3)	C77—C79	1.589 (6)
Co2—C80	2.140 (3)	C77—C5	1.65 (3)
Co2—C82	2.085 (3)	C77—C39A	1.575 (10)
Co2—C84	2.088 (3)	C77—C110	1.41 (4)
Co2—C86	2.050 (3)	C81—C83	1.538 (5)
Co3—P1	2.1724 (8)	C81—C21	1.547 (5)
Co3—C74	1.790 (3)	C81—C41	1.595 (12)
Co3—C55	2.107 (3)	C81—C41A	1.535 (10)
Co3—C7	2.147 (3)	P2—O11	1.567 (2)
Co3—C57	2.081 (3)		

C1—Co1—C4	48.68(11)	C10—Co1—P2	153.10(9)
C1—Co1—P2	104.77(11)	C12—Co1—P2	113.87(10)
C6—Co1—P2	100.90(8)	C14—Co1—P2	88.97(9)
C8—Co1—P2	139.65(8)	P2—Co1—Co4	56.57(2)
C1—Co4—P2	104.37(10)	C42—Co4—P2	134.16(9)
C40—Co4—P2	98.74(8)	P1—Co2—Co3	56.78(2)
C44—Co4—P2	159.92(10)	C74—Co2—Co3	48.35(9)
C46—Co4—P2	122.56(9)	C74—Co2—P1	104.29(9)
C48—Co4—P2	93.65(8)	Co3—P1—Co2	66.39(2)
P2—Co4—Co1	56.94(2)	O4—P1—Co2	125.56(8)
Co3—C74—Co2	83.17(12)	O4—P1—Co3	124.66(8)
C76—C74—Co2	138.7(2)	O4—P1—O6	109.79(10)
C76—C74—Co3	137.5(2)	O6—P1—Co2	111.50(7)
Co4—P2—Co1	66.49(3)	O6—P1—Co3	112.81(8)
O1—P2—Co1	124.78(8)	O11—P2—Co1	111.88(8)
O1—P2—Co4	124.72(8)	O11—P2—Co4	112.46(8)
O1—P2—O11	110.22(10)		

Crystal structure of compound 6

Centres of the $\{CuCl\}_2$ groups are situated on two different 2-fold axes of the space group *C*2/*c*. One of two unique Cl bridges (Cl1) is disordered over four close positions. The occupancy factors were refined to 0.400/0.300/0.175/0.125 for A/B/C/D position respectively and fixed at the resulting values. The minor position was not included in anisotropic refinement because it led to inappropriate displacement parameters.

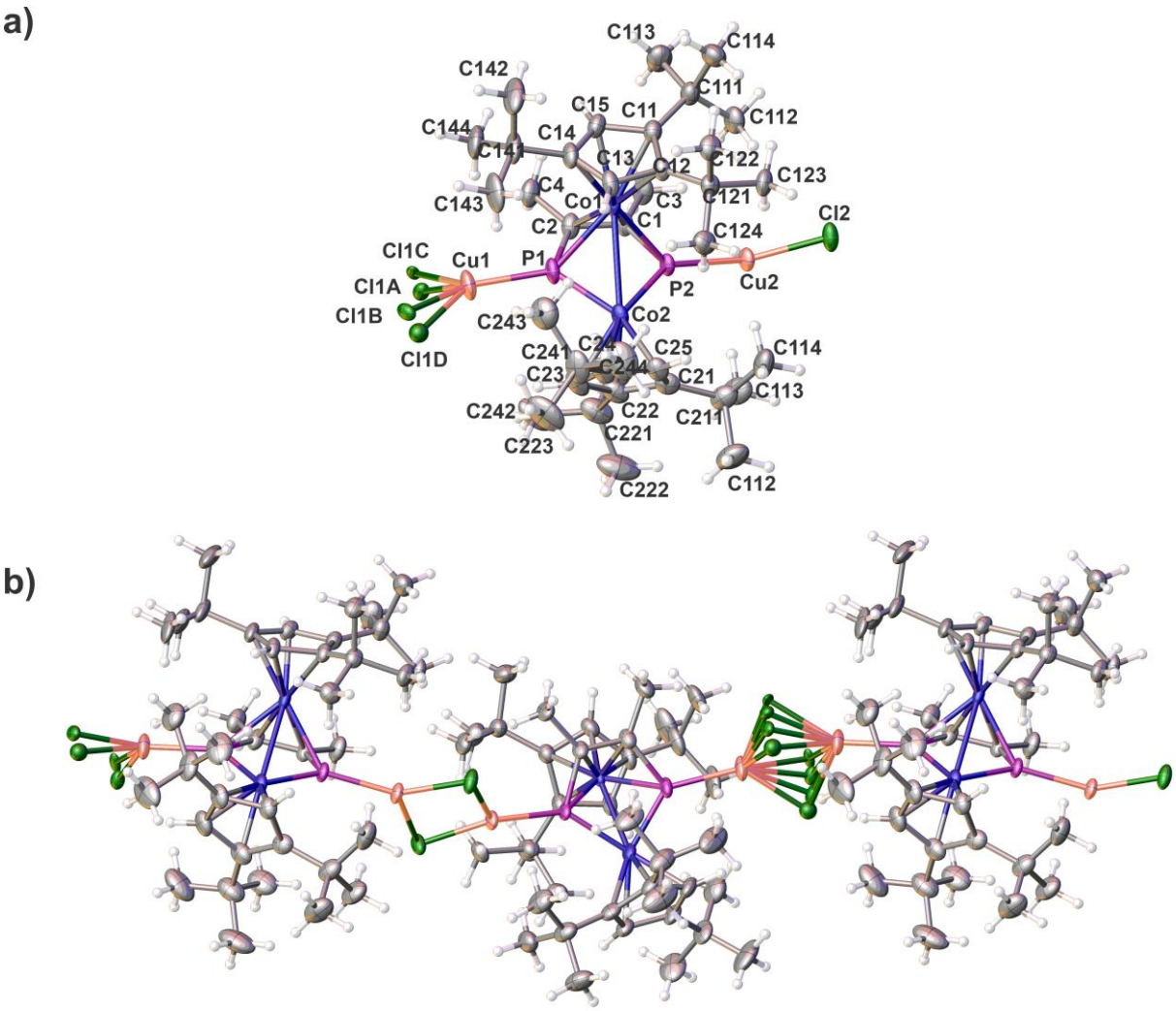


Fig. S24. a) Asymmetric unit of **6** showing the atom-labelling scheme; b) Section of the 1D polymer **6** in the solid state. One of two unique Cl bridges is disordered. Disorder of the *t*Bu groups and solvent molecules are omitted for clarity. Atomic displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) -*x*, *y*, -*z*+3/2 and (ii) -*x*+1, *y*, -*z*+5/2.

Table S8. Selected bond distances for Compound **6** (Å)

Cu1—P1	2.1713 (9)	Co1—C13	2.055 (3)
Cu1—Cl1B	2.251 (5)	Co1—C15	2.073 (4)
Cu1—Cl1D	2.252 (9)	Co1—C2	2.103 (3)
Cu1—Cl1A^{i}	2.256 (4)	Co1—C14	2.111 (3)
Cu1—Cl1C^{i}	2.308 (9)	Co1—C12	2.118 (3)
Cu1—Cl1A	2.358 (4)	Co1—C1	2.141 (3)
Cu1—Cl1B^{i}	2.384 (7)	Co1—C11	2.157 (4)

Cu1—Cl1C	2.413 (13)	Co1—P2	2.3096 (10)
Cu1—Cl1D^{i}	2.497 (9)	Co1—P1	2.3171 (10)
Cu1—Cu1^{i}	2.9597 (11)	Co1—Co2	2.8137 (8)
Cu2—P2	2.1701 (9)	Co2—C22	2.040 (4)
Cu2—Cl2	2.2275 (10)	Co2—C23	2.065 (4)
Cu2—Cl2^{ii}	2.3772 (9)	Co2—C21	2.105 (4)
Cu2—Cu2^{ii}	3.0424 (10)	Co2—P1	2.1234 (11)
Cl1A—Cu1^{i}	2.256 (4)	Co2—C25	2.127 (4)
Cl1B—Cu1^{i}	2.384 (7)	Co2—P2	2.1414 (9)
Cl1C—Cu1^{i}	2.308 (9)	Co2—C24	2.175 (3)
Cl1D—Cu1^{i}	2.497 (9)	P1—C2	1.772 (4)
Cl2—Cu2^{ii}	2.3771 (9)	P2—C1	1.788 (3)

Symmetry code(s): (i) -*x*, *y*, -*z*+3/2; (ii) -*x*+1, *y*, -*z*+5/2.

Crystal structure of compounds 7a and 7b

In **7a**, complex occupies an inversion centre of the $P2_1/n$ space group. Solvent CH_2Cl_2 molecules occupy general position and are positionally disordered over several close positions with a maximal occupancy factor of 0.25. For this reason, most of the atoms of the solvent molecules are refined isotropically.

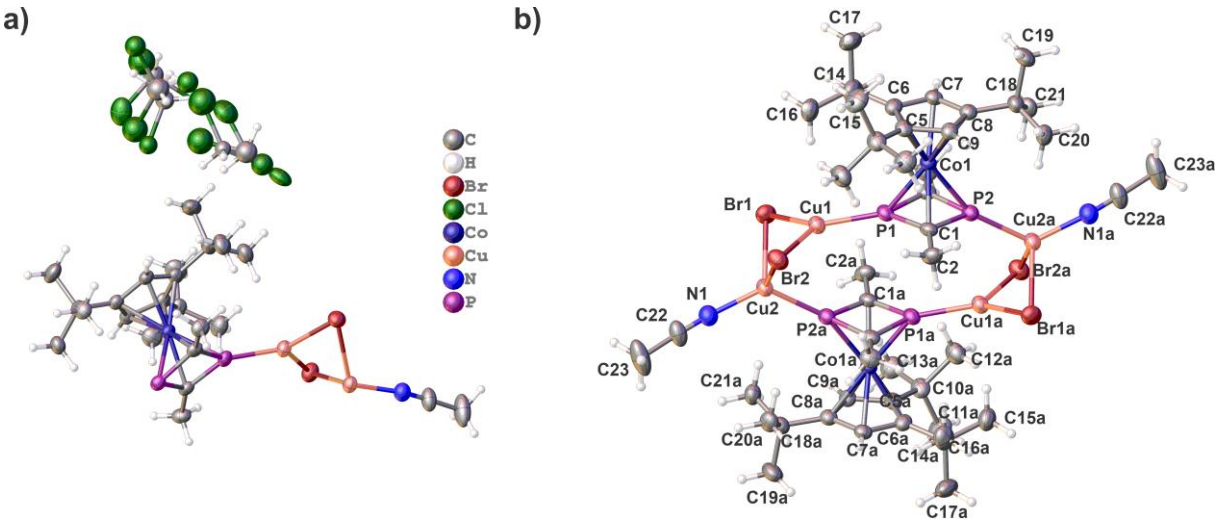


Fig. S25. a) Asymmetric unit of **7a**; b) Molecular structure of compound **7a** in the solid state showing the atom-labelling scheme. Atomic displacement ellipsoids are drawn at the 50% probability level. Symmetry code -*x*, -*y*+1, -*z*+2 is used for generating symmetry-related atoms with index *a*.

Table S9. Selected geometric parameters for Compound **7a** (Å, °)

Cu1—P1	2.1609 (15)	P2—Cu2^{i}	2.2175 (15)
Cu1—Br2	2.3973 (9)	C1—C2	1.490 (7)

Cu1—Br1	2.4092 (9)	C3—C4	1.496 (7)
Cu1—Cu2	2.6090 (10)	C5—C9	1.418 (7)
Cu2—N1	1.960 (5)	C5—C6	1.474 (8)
Cu2—P2^{i}	2.2175 (15)	C5—C10	1.538 (8)
Cu2—Br2	2.5529 (9)	C6—C7	1.428 (8)
Cu2—Br1	2.5698 (10)	C6—C14	1.538 (7)
Co1—C9	2.052 (5)	C7—C8	1.410 (7)
Co1—C7	2.054 (5)	C8—C9	1.436 (7)
Co1—C6	2.070 (5)	C8—C18	1.511 (7)
Co1—C3	2.073 (4)	C10—C11	1.539 (8)
Co1—C8	2.074 (5)	C10—C13	1.544 (9)
Co1—C5	2.080 (5)	C10—C12	1.563 (8)
Co1—C1	2.082 (5)	C14—C15	1.529 (9)
Co1—P1	2.2134 (14)	C14—C17	1.532 (8)
Co1—P2	2.2320 (15)	C14—C16	1.540 (9)
P1—C3	1.773 (5)	C18—C20	1.532 (8)
P1—C1	1.775 (5)	C18—C21	1.536 (8)
P1—P2	2.6434 (18)	C18—C19	1.551 (8)
P2—C3	1.779 (5)	N1—C22	1.132 (8)
P2—C1	1.787 (5)	C22—C23	1.465 (9)
P1—Cu1—Br2	123.42 (5)	N1—Cu2—Br1	115.90 (16)
P1—Cu1—Br1	130.60 (5)	P2^{i}—Cu2—Br1	102.70 (5)
Br2—Cu1—Br1	105.77 (4)	Br2—Cu2—Br1	96.87 (3)
P1—Cu1—Cu2	138.56 (5)	N1—Cu2—Cu1	150.80 (15)
Br2—Cu1—Cu2	61.14 (3)	P2^{i}—Cu2—Cu1	79.99 (4)
Br1—Cu1—Cu2	61.45 (3)	Br2—Cu2—Cu1	55.33 (3)
N1—Cu2—P2^{i}	128.05 (16)	Br1—Cu2—Cu1	55.44 (3)
N1—Cu2—Br2	103.53 (14)	Cu1—Br1—Cu2	63.11 (3)
P2^{i}—Cu2—Br2	104.93 (5)	Cu1—Br2—Cu2	63.52 (3)

Symmetry code: (i) *-x*, *-y*+1, *-z*+2.

Complex **7b** occupies an inversion centre of the $P2_1/n$ space group. Due to the disorder, unidentified solvent molecules were treated with SQUEEZE procedure implemented in *PLATON* program.[12]

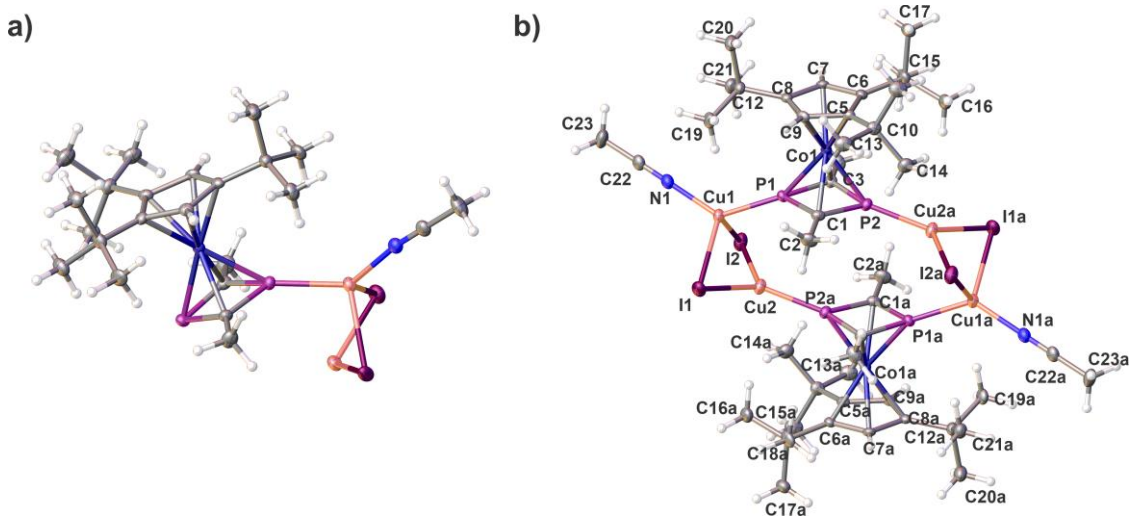


Fig. S26. a) Asymmetric unit of **7b**; b) Molecular structure of compound **7b** in the solid state showing the atom-labelling scheme. Atomic displacement ellipsoids are drawn at the 50% probability level. Symmetry code -*x*+1, -*y*+2, -*z*+1 is used for generating symmetry-related atoms with index *a*.

Table S10. Selected geometric parameters for Compound **7b** (Å, °)

C1—C2	1.505 (5)	C10—C14	1.538 (5)
C1—P2	1.776 (4)	C10—C15	1.542 (5)
C1—P1	1.779 (3)	C11—C16	1.525 (5)
C1—Co1	2.077 (3)	C11—C18	1.538 (5)
C3—C4	1.502 (5)	C11—C17	1.548 (5)
C3—P1	1.771 (4)	C12—C21	1.526 (5)
C3—P2	1.780 (3)	C12—C19	1.535 (5)
C3—Co1	2.085 (3)	C12—C20	1.542 (5)
C5—C9	1.415 (5)	C22—N1	1.137 (5)
C5—C6	1.470 (5)	C22—C23	1.456 (5)
C5—C10	1.547 (5)	Co1—P2	2.2195 (10)
C5—Co1	2.089 (3)	Co1—P1	2.2327 (10)
C6—C7	1.430 (5)	Cu1—N1	1.961 (3)
C6—C11	1.543 (5)	Cu1—P1	2.2304 (10)
C6—Co1	2.080 (3)	Cu1—Cu2	2.5913 (7)
C7—C8	1.410 (5)	Cu1—I1	2.6794 (5)
C7—Co1	2.054 (3)	Cu1—I2	2.7363 (5)
C8—C9	1.427 (5)	Cu2—P2^{i}	2.1878 (10)
C8—C12	1.519 (5)	Cu2—I1	2.5560 (6)
C8—Co1	2.083 (3)	Cu2—I2	2.5814 (6)
C9—Co1	2.056 (3)	P2—Cu2^{i}	2.1878 (10)

C10—C13	1.533 (5)	P2—P1	2.6503 (13)
N1—Cu1—P1	130.25 (9)	I1—Cu2—I2	112.19 (2)
N1—Cu1—Cu2	146.85 (9)	P2^{i}—Cu2—Cu1	139.44 (4)
P1—Cu1—Cu2	81.51 (3)	I1—Cu2—Cu1	62.733 (17)
N1—Cu1—I1	111.38 (9)	I2—Cu2—Cu1	63.873 (17)
P1—Cu1—I1	105.89 (3)	Cu2—I2—Cu1	58.239 (16)
Cu2—Cu1—I1	57.990 (17)	Cu2—I1—Cu1	59.277 (16)
N1—Cu1—I2	100.88 (9)	C1—P2—C3	83.23 (16)
P1—Cu1—I2	100.90 (3)	C1—P2—P1	41.83 (11)
Cu2—Cu1—I2	57.888 (16)	C3—P2—P1	41.61 (12)
I1—Cu1—I2	103.865 (18)	C3—P1—C1	83.40 (16)
P2^{i}—Cu2—I1	129.75 (3)	C3—P1—P2	41.84 (11)
P2^{i}—Cu2—I2	117.88 (3)	C1—P1—P2	41.77 (12)

Symmetry code: (i) -*x*+1, -*y*+2, -*z*+1.

Crystal structure of compound 8

In the crystal structure, complex **8** occupies a general position. Enumerating scheme and corresponding bond distances are shown in Figure S26 and Table S11, respectively.

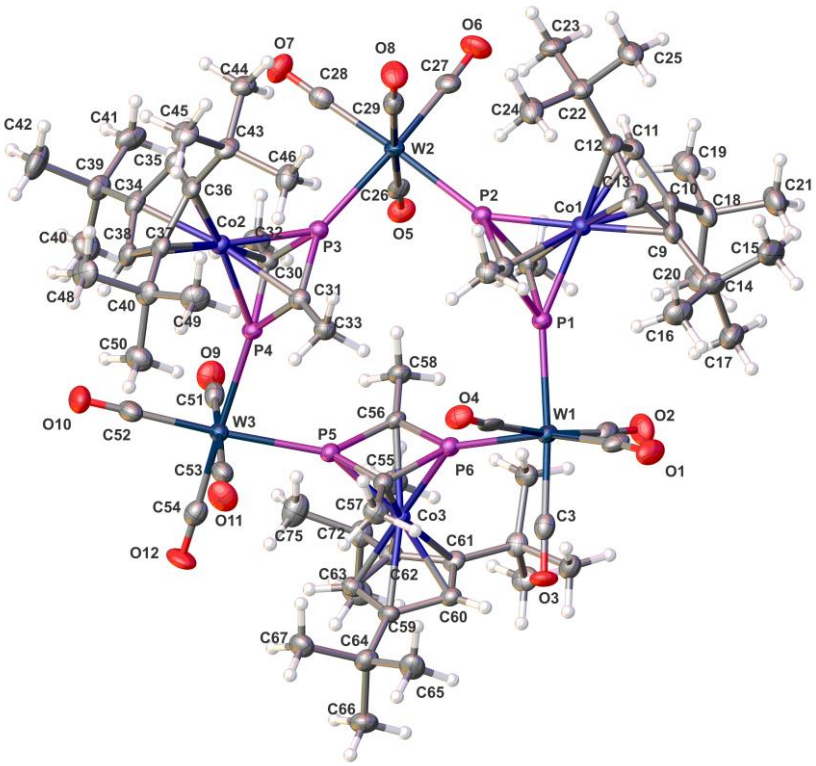


Fig. S27. Molecular structure of compound **8** in the solid state showing the atom-labelling scheme. Atomic displacement ellipsoids are drawn at the 50% probability level.

Table S10. Selected geometric parameters for compound **8** (Å, °)

W2—C27	2.009 (6)	O7—C28	1.152 (7)
W2—C28	2.010 (6)	O8—C29	1.154 (7)
W2—C26	2.027 (6)	C16—C14	1.545 (10)
W2—C29	2.047 (6)	O4—C4	1.155 (8)
W2—P3	2.4763 (13)	O9—C51	1.137 (8)
W2—P2	2.4766 (14)	O11—C53	1.132 (8)
W3—C54	1.996 (7)	O3—C3	1.142 (7)
W3—C52	2.002 (6)	C25—C22	1.540 (8)
W3—C51	2.049 (7)	C12—C13	1.407 (9)
W3—C53	2.056 (7)	C12—C11	1.425 (8)
W3—P4	2.4563 (13)	C12—C22	1.537 (8)
W3—P5	2.4581 (13)	C18—C19	1.537 (10)
W1—C3	2.016 (7)	C18—C21	1.541 (9)
W1—C1	2.022 (6)	C18—C10	1.545 (8)
W1—C4	2.027 (7)	C18—C20	1.545 (9)
W1—C2	2.054 (7)	O10—C52	1.149 (8)
W1—P1	2.4733 (14)	C14—C17	1.537 (9)
W1—P6	2.4871 (14)	C14—C15	1.547 (9)
Co3—C60	2.064 (5)	C14—C9	1.548 (9)
Co3—C63	2.074 (5)	O2—C2	1.150 (8)
Co3—C61	2.101 (5)	O6—C27	1.139 (7)
Co3—C62	2.102 (5)	O12—C54	1.156 (8)
Co3—C55	2.109 (5)	C72—C73	1.530 (8)
Co3—C56	2.114 (5)	C72—C75	1.541 (9)
Co3—C59	2.119 (5)	C72—C74	1.546 (8)
Co3—P5	2.2154 (16)	C9—C13	1.427 (8)
Co3—P6	2.2355 (16)	C9—C10	1.449 (9)
Co1—C11	2.062 (6)	C50—C47	1.541 (9)
Co1—C13	2.070 (6)	C23—C22	1.511 (9)
Co1—C6	2.080 (5)	C39—C41	1.510 (9)
Co1—C12	2.096 (5)	C39—C34	1.527 (8)
Co1—C10	2.099 (5)	C39—C40	1.535 (9)
Co1—C5	2.110 (6)	C39—C42	1.541 (9)
Co1—C9	2.113 (6)	C68—C71	1.523 (8)
Co1—P2	2.2425 (16)	C68—C61	1.533 (8)
Co1—P1	2.2462 (16)	C68—C70	1.544 (8)
Co2—C35	2.055 (6)	C68—C69	1.552 (7)
Co2—C38	2.070 (5)	C61—C60	1.444 (8)
Co2—C36	2.087 (5)	C36—C35	1.428 (8)
Co2—C37	2.099 (5)	C36—C37	1.465 (8)

Co2—C34	2.107 (6)	C36—C43	1.537 (8)
Co2—C30	2.113 (5)	C65—C64	1.537 (9)
Co2—C31	2.115 (6)	C66—C64	1.550 (9)
Co2—P4	2.2147 (15)	C37—C38	1.439 (8)
Co2—P3	2.2286 (15)	C37—C47	1.533 (8)
P3—C30	1.784 (5)	C49—C47	1.532 (9)
P3—C31	1.790 (6)	C59—C63	1.411 (8)
P3—P4	2.6412 (18)	C59—C60	1.425 (8)
P4—C30	1.767 (6)	C59—C64	1.512 (8)
P4—C31	1.782 (6)	C44—C43	1.530 (8)
P5—C55	1.773 (6)	C45—C43	1.539 (8)
P5—C56	1.776 (6)	C46—C43	1.536 (8)
P5—P6	2.6465 (19)	C57—C55	1.479 (8)
P6—C55	1.789 (5)	C34—C38	1.410 (8)
P6—C56	1.799 (6)	C34—C35	1.413 (8)
P1—C5	1.779 (6)	C48—C47	1.546 (8)
P1—C6	1.782 (5)	C6—C8	1.492 (8)
P1—P2	2.6407 (19)	C64—C67	1.535 (8)
P2—C5	1.768 (5)	C24—C22	1.537 (9)
P2—C6	1.789 (6)	C58—C56	1.488 (8)
O1—C1	1.128 (7)	C10—C11	1.429 (8)
O5—C26	1.145 (7)	C33—C31	1.487 (8)
C62—C63	1.442 (8)	C32—C30	1.491 (8)
C62—C61	1.456 (8)	C5—C7	1.496 (8)
C62—C72	1.537 (8)		

P3—W2—P2	92.24 (5)	W3—P5—P6	162.03 (6)
P4—W3—P5	83.50 (4)	C55—P6—C56	83.6 (3)
P1—W1—P6	93.46 (5)	C55—P6—Co3	62.05 (18)
C30—P3—C31	83.8 (3)	C56—P6—Co3	62.08 (17)
C30—P3—Co2	62.39 (17)	C55—P6—W1	122.37 (19)
C31—P3—Co2	62.38 (18)	C56—P6—W1	150.36 (19)
C30—P3—W2	123.09 (19)	Co3—P6—W1	139.96 (6)
C31—P3—W2	148.2 (2)	C55—P6—P5	41.77 (19)
Co2—P3—W2	142.14 (7)	C56—P6—P5	41.92 (18)
C30—P3—P4	41.69 (18)	Co3—P6—P5	53.17 (5)
C31—P3—P4	42.20 (18)	W1—P6—P5	158.89 (7)
Co2—P3—P4	53.29 (5)	C5—P1—C6	83.8 (3)
W2—P3—P4	158.12 (6)	C5—P1—Co1	61.94 (18)
C30—P4—C31	84.6 (3)	C6—P1—Co1	60.91 (18)
C30—P4—Co2	62.93 (17)	C5—P1—W1	135.55 (19)

C31—P4—Co2	62.80 (18)	C6—P1—W1	130.56 (19)
C30—P4—W3	132.86 (19)	Co1—P1—W1	153.21 (7)
C31—P4—W3	137.9 (2)	C5—P1—P2	41.73 (18)
Co2—P4—W3	143.76 (6)	C6—P1—P2	42.41 (19)
C30—P4—P3	42.20 (18)	Co1—P1—P2	53.90 (5)
C31—P4—P3	42.45 (19)	W1—P1—P2	152.60 (6)
Co2—P4—P3	53.77 (4)	C5—P2—C6	84.0 (3)
W3—P4—P3	162.18 (6)	C5—P2—Co1	62.15 (19)
C55—P5—C56	84.7 (3)	C6—P2—Co1	60.91 (17)
C55—P5—Co3	62.71 (18)	C5—P2—W2	128.7 (2)
C56—P5—Co3	62.82 (17)	C6—P2—W2	140.02 (18)
C55—P5—W3	133.10 (19)	Co1—P2—W2	149.21 (7)
C56—P5—W3	137.58 (19)	C5—P2—P1	42.05 (19)
Co3—P5—W3	143.87 (7)	C6—P2—P1	42.21 (17)
C55—P5—P6	42.25 (18)	Co1—P2—P1	54.03 (5)
C56—P5—P6	42.58 (18)	W2—P2—P1	155.65 (7)
Co3—P5—P6	53.87 (5)		

4. Computational Data

The geometries of the compounds have been fully optimized with gradient-corrected density functional theory (DFT) in form of Becke's three-parameter hybrid method B3LYP[14] with pVDZ all electron basis set.[15] Gaussian 09 program package[16] was used throughout. All structures correspond to minima on their respective potential energy surfaces.

At B3LYP/pVDZ level of theory, in the gas phase $[(Cp'''Co)_2(\eta^4\text{-}P_2C_2Me_2)]$ **2** has a triplet ground state, the singlet state is 68 kJ mol^{-1} higher in energy. The spin density in the triplet state of **2** is located predominantly on both Co atoms, with much smaller contributions of the opposite spin from C and P atoms of the ring. SOMOs and LUMOS of **2**(triplet) are quite delocalized, with comparable contributions from the Cp''', C_2P_2 ring and Co atoms. The gaps between HOMO(SOMO) and LUMO are quite small: 10.3 kJ mol^{-1} for **2**(triplet), 6.7 kJ mol^{-1} for **2**(singlet), and 6.9 kJ mol^{-1} for $\mathbf{2}^+$(doublet). Oxidation of **2**(triplet state) to $\mathbf{2}^+$(doublet state) in the gas phase requires 506 kJ mol^{-1}. The spin density of $\mathbf{2}^+$ is also predominantly located on both Co atoms.

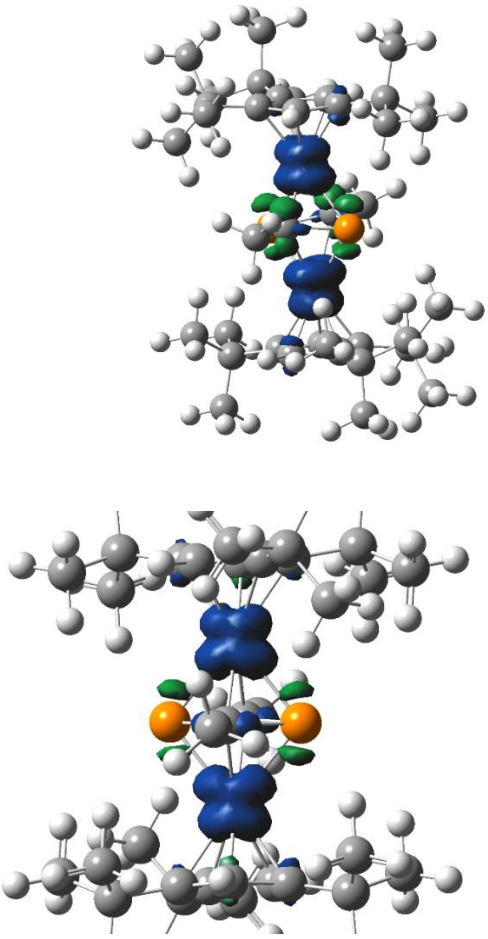
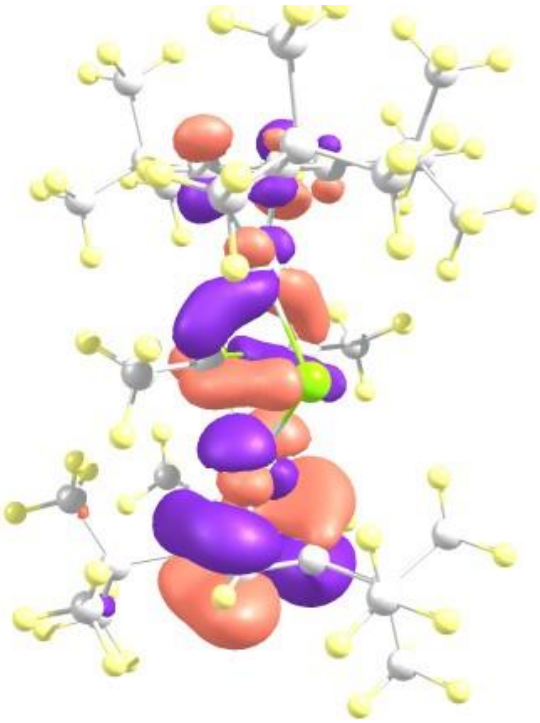
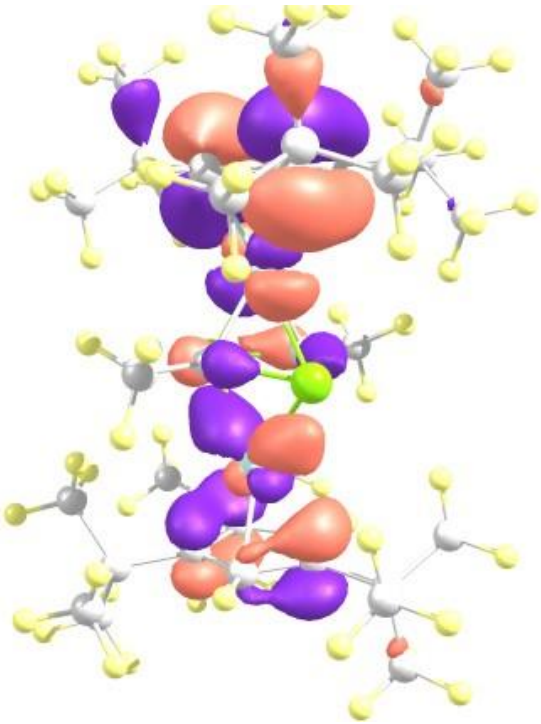


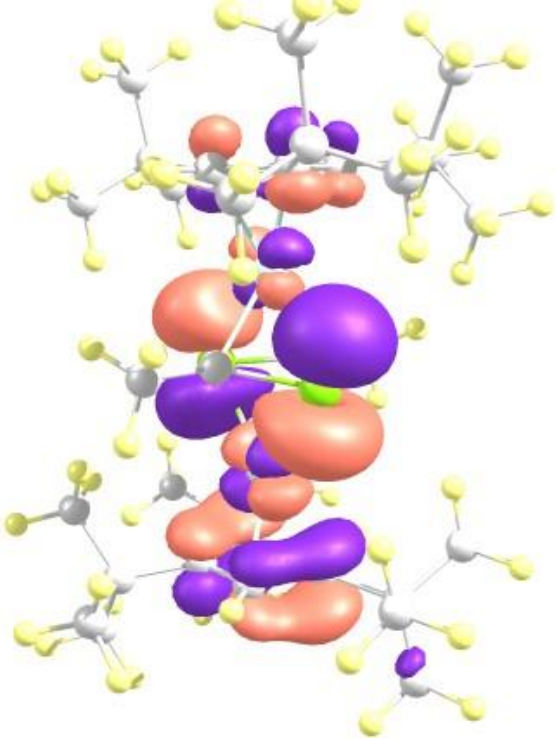
Fig. S28. Spin density plots: **2** in triplet electronic state (up); cationic $\mathbf{2}^+$ in the doublet electronic state (down).



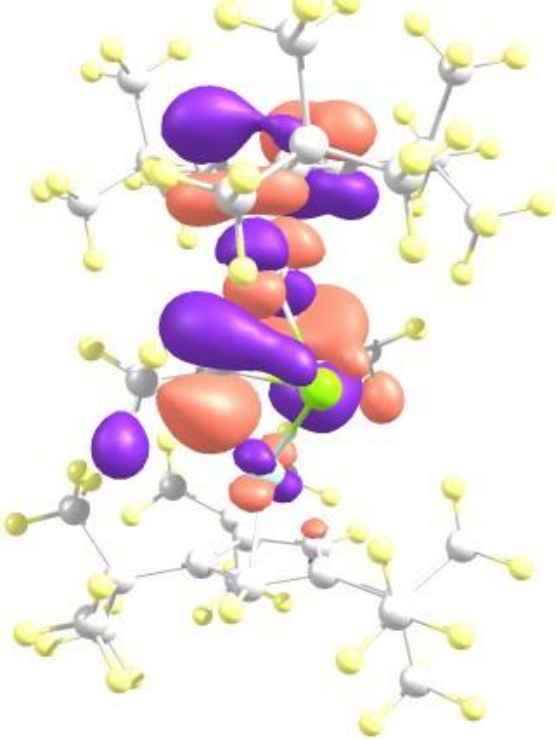
Triplet_**2**_alpha_SOMO_188



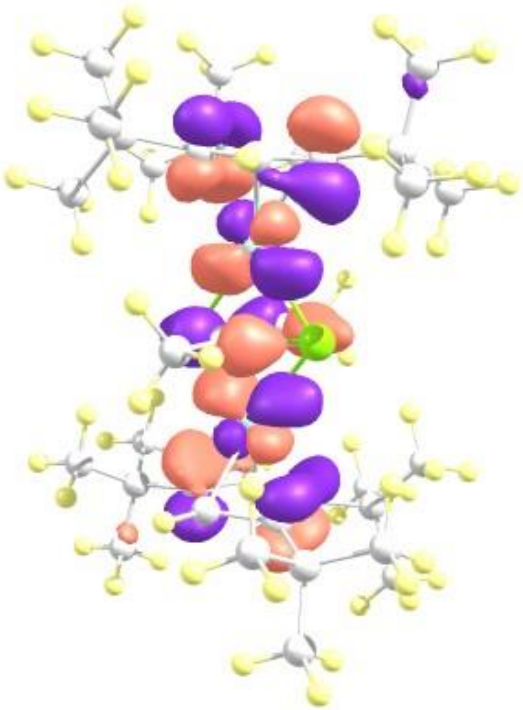
Triplet_**2**_alpha_SOMO_189



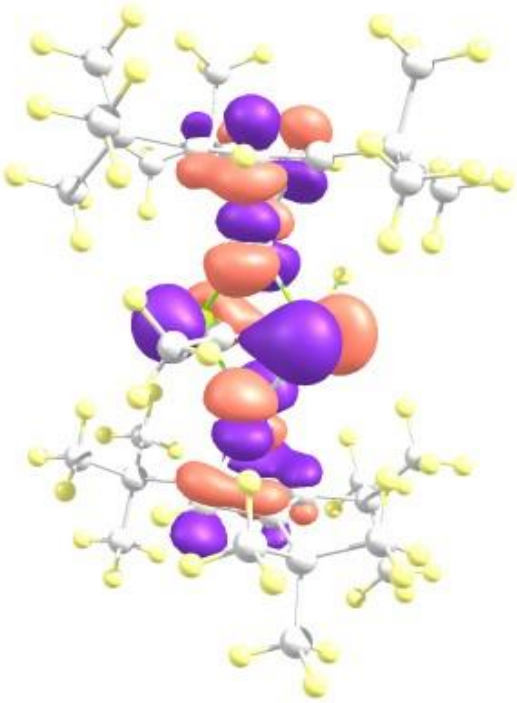
Triplet_**2**_alpha_LUMO_190



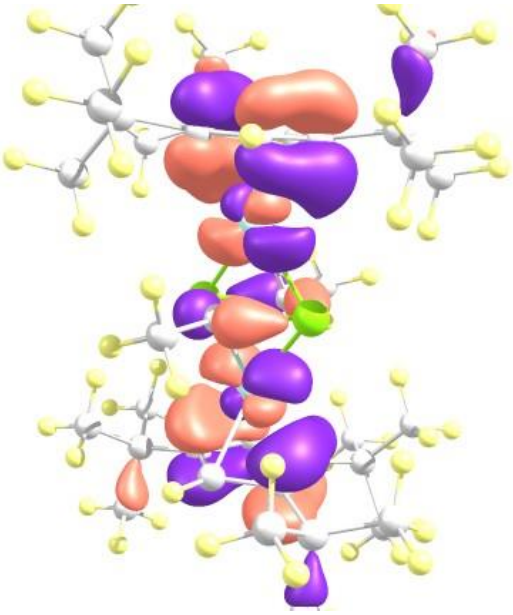
Triplet_**2**_alpha_LUMO_191



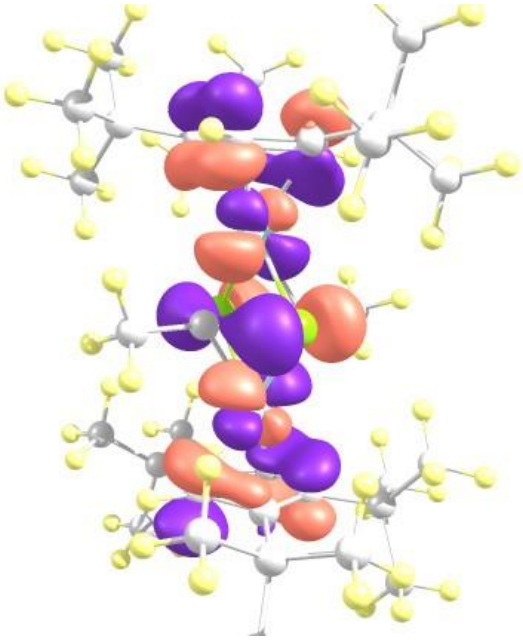
HOMO_**2**_singlet
On carbon atoms of C_2P_2 ring



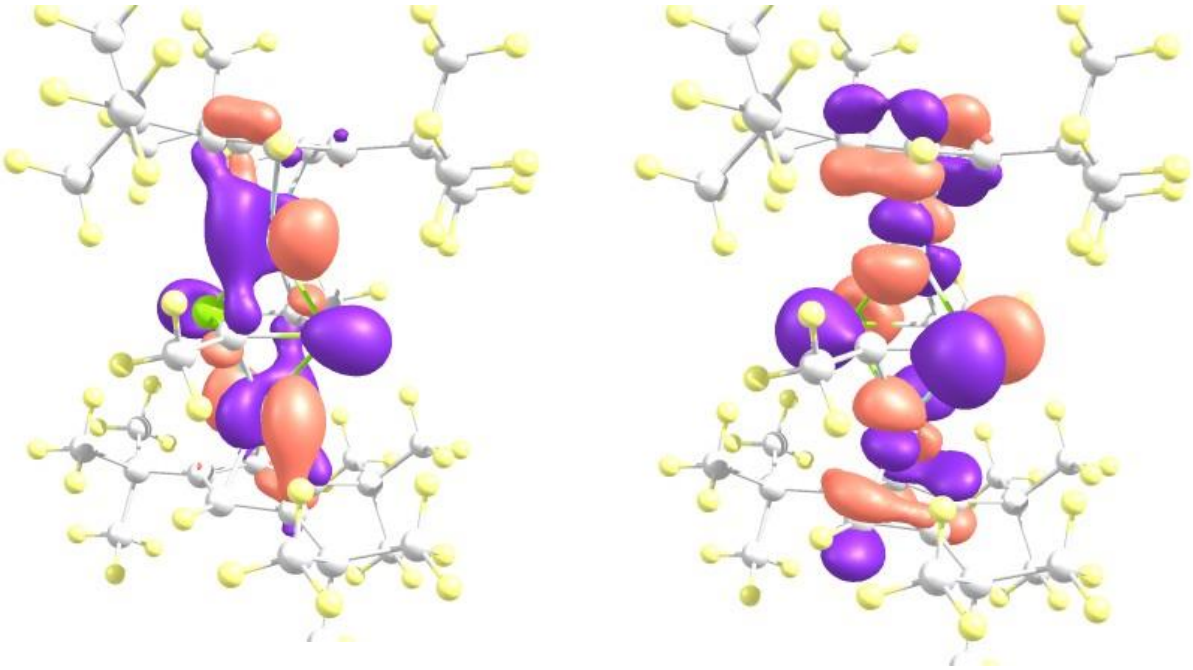
LUMO_**2**_singlet
On phosphorus atoms of C_2P_2 ring



SOMO_doublet_$\mathbf{2}^{+}$



LUMO_doublet_$\mathbf{2}^{+}$



HOMO_doublet_**2**$^{+}$_beta LUMO_doublet_**2**$^{+}$_beta

Fig. S29. Selected MO of **2** and **2**$^{+}$.

Sandwich 1,3-diphosphete complex [Cp'''Co(η^4-$P_2C_2Me_2$)] **1** has a singlet ground state in the gas phase, which is by 43.6 kJ mol^{-1} lower in energy than the triplet state. Note that [Cp'''Co(toluene)] has a triplet ground state which lies 68 kJ mol^{-1} below the singlet state.

The gas phase reaction of the **2** with toluene to yield **1** and Cp'''Co(toluene):

2(triplet) + toluene = **1**(singlet) + Cp'''Co(toluene)(triplet)

is endothermic by 27 kJ mol^{-1} and endergonic by 30 kJ mol^{-1}. Therefore, the reverse reaction is exergonic by 29.6 kJ mol^{-1} and formation of **2** from **1** and [Cp'''Co(toluene)] is thermodynamically favorable in the gas phase.

Table S11. Total energies E^{o}_{0}, sum of electronic and thermal enthalpies H^{o}_{298} (Hartree) and standard entropies S^{o}_{298} (cal mol^{-1}K^{-1}) for studied compounds. B3LYP/pVDZ level of theory.

Compound	E^{o}_{0}	H^{o}_{298}	S^{o}_{298}
P≡CMe	-419.176808	-419.129967	60.899
Toluene C_7H_8	-271.373458	-271.238700	81.457
[Cp'''Co(Toluene)], singlet state	-2318.788187	-2318.210997	176.509
[Cp'''Co(Toluene)], triplet state	-2318.813919	-2318.237026	185.141
2, singlet state	-4933.321743	-4932.338093	280.766
2, triplet state	-4933.347673	-4932.364164	285.89
2^{+}, doublet state	-4933.156829	-4932.171299	281.168
1,3 [Cp'''Co(η^4-$P_2C_2Me_2$)] **1**, singlet state	-2885.896432	-2885.355532	180.164
1,3 [Cp'''Co(η^4-$P_2C_2Me_2$)] **1**, triplet state	-2885.861708	-2885.322469	187.386
1,2 [Cp'''Co(η^4-$P_2C_2Me_2$)], singlet state	-2885.9120528	-2885.37058	180.729
1,2 [Cp'''Co(η^4-$P_2C_2Me_2$)], triplet state	-2885.8801054	-2885.339902	194.059
trans-[Cp'''Co(PC≡Me)$_2$] singlet state	-2885.826650	-2885.286949	184.679
trans-[Cp'''Co(PC≡Me)$_2$] triplet state	-2885.810028	-2885.271745	197.230
cis-[Cp'''Co(PC≡Me)$_2$] singlet state	-2885.8203943	-2885.280606	187.199
cis-[Cp'''Co(PC≡Me)$_2$] triplet state	-2885.8047371	-2885.266148	198.218

Table S12. Reaction energies ΔE°_{0}, standard enthalpies ΔH°_{298}, Gibbs energies ΔG°_{298} (kJ mol^{-1}) and standard entropies ΔS°_{298} (J mol^{-1} K^{-1}) for the considered gas phase processes. All compounds in their respective ground electronic states. B3LYP/pVDZ level of theory.

Process	ΔE°_{0}	ΔH°_{298}	ΔS°_{298}	ΔG°_{298}
2(triplet) + C_7H_8 = **1** + [Cp'''Co(C_7H_8)]	28.3	27.1	-8.5	29.6
[Cp'''Co(C_7H_8)] + 2 P≡CMe = *trans*-[Cp'''Co(P≡CMe)$_2$] + C_7H_8	-85.5	-75.3	-170.7	-24.4
Cp'''Co(C_7H_8)] + 2 P≡CMe = *cis*-[Cp'''Co(P≡CMe)$_2$] + C_7H_8	-69.1	-58.7	-160.2	-10.9
[Cp'''Co(C_7H_8)] + 2 P≡CMe = 1,3 [Cp'''Co(η^4-$P_2C_2Me_2$)] **1** + C_7H_8	-268.7	-255.4	-189.6	-198.9
Cp'''Co(C_7H_8)] + 2 P≡CMe = 1,2 [Cp'''Co(η^4-$P_2C_2Me_2$)] + C_7H_8	-309.7	-294.9	-187.2	-239.1

Table S13. Optimized geometries of studied compounds (xyz coordinates in Å), B3LYP/pVDZ level of theory.

P≡CMe			
6	0.000000000	0.000000000	-0.296986000
15	0.000000000	0.000000000	1.252852000
6	0.000000000	0.000000000	-1.757302000
1	0.000000000	1.029406000	-2.155684000
1	0.891492000	-0.514703000	-2.155684000
1	-0.891492000	-0.514703000	-2.155684000
Toluene			
6	-2.427422000	-0.000118000	0.009509000
6	-0.917465000	-0.000241000	-0.012418000
6	1.908148000	0.000164000	0.008853000
6	-0.195009000	1.204094000	-0.009519000
6	-0.194669000	-1.204267000	-0.009398000
6	1.202982000	-1.206822000	0.002091000
6	1.202553000	1.207075000	0.002166000
1	-0.736863000	2.154677000	-0.018528000
1	-0.736211000	-2.155008000	-0.018534000
1	1.743743000	-2.157131000	0.002289000
1	1.743105000	2.157488000	0.002451000
1	3.001117000	0.000375000	0.015211000
1	-2.809543000	0.012712000	1.045680000
1	-2.839933000	-0.897262000	-0.477232000
1	-2.840120000	0.884842000	-0.499034000
[Cp"'Co(Toluene)], singlet state			
6	-2.041017000	-1.041306000	1.776659000
6	-1.220231000	-0.064444000	0.893153000
6	-1.492973000	0.614879000	-0.356216000
1	0.520569000	0.155752000	2.304244000
6	-2.692070000	0.651386000	-1.331037000
6	-0.362872000	1.474561000	-0.591789000
1	-0.253246000	2.114523000	-1.462277000
6	0.560753000	1.446390000	0.504814000
6	1.717872000	2.404035000	0.773938000
6	0.045931000	0.461841000	1.377914000
6	2.808925000	1.727683000	1.625607000
6	1.146833000	3.614861000	1.552510000
6	2.349046000	2.914197000	-0.535140000
6	-3.392289000	-0.704534000	-1.544080000
6	-2.237603000	1.123364000	-2.734254000
6	-3.718544000	1.692158000	-0.816172000
6	-2.180600000	-2.457334000	1.172775000
6	-3.439587000	-0.454201000	2.077945000
6	-1.355648000	-1.230171000	3.151356000
1	-4.182177000	-0.599103000	-2.305212000
1	-3.873418000	-1.084495000	-0.635763000
1	-2.682626000	-1.466981000	-1.901104000
1	-3.092085000	1.088870000	-3.428243000
1	-1.443405000	0.480085000	-3.141787000
1	-1.870630000	2.159815000	-2.732501000
1	-4.564737000	1.780898000	-1.518513000

1	-3.250613000	2.684773000	-0.723207000
1	-4.123258000	1.423345000	0.168438000
1	-2.838455000	-3.074879000	1.807121000
1	-1.201623000	-2.956742000	1.129189000
1	-2.599627000	-2.451862000	0.161151000
1	-3.962792000	-1.085408000	2.814990000
1	-4.078330000	-0.396588000	1.188326000
1	-3.357803000	0.559900000	2.500144000
1	-1.959138000	-1.913923000	3.768793000
1	-1.262617000	-0.281038000	3.700865000
1	-0.353449000	-1.673967000	3.056740000
1	3.224158000	0.848885000	1.110050000
1	2.418410000	1.400970000	2.602198000
1	3.631387000	2.434497000	1.823140000
1	0.696699000	3.295721000	2.505788000
1	0.366055000	4.129024000	0.969458000
1	1.941400000	4.346330000	1.777399000
1	2.780805000	2.088427000	-1.118548000
1	3.154542000	3.632830000	-0.312785000
1	1.613277000	3.434728000	-1.168233000
27	0.457667000	-0.424765000	-0.462550000
6	4.097099000	-2.307779000	0.553772000
6	2.977236000	-1.745835000	-0.271449000
6	0.816371000	-1.436163000	-2.152207000
6	3.118025000	-0.897928000	-1.317893000
6	1.576341000	-2.122496000	0.024842000
6	0.656400000	-2.323149000	-1.059342000
6	1.879445000	-0.484767000	-1.999443000
1	4.092163000	-0.542751000	-1.667359000
1	1.385999000	-2.667450000	0.954849000
1	-0.168146000	-3.036613000	-1.012908000
1	1.940767000	0.323543000	-2.733468000
1	0.124375000	-1.427417000	-2.997410000
1	3.960457000	-2.063749000	1.623057000
1	5.074226000	-1.912984000	0.237202000
1	4.134822000	-3.409793000	0.487433000

[Cp"'Co(Toluene)] triplet state

6	-2.013666000	-0.424387000	1.974454000
6	-1.107652000	0.279820000	0.931384000
6	-1.317251000	0.686953000	-0.453888000
1	0.623295000	0.684084000	2.296353000
6	-2.528879000	0.652531000	-1.417786000
6	-0.153970000	1.436591000	-0.834150000
1	-0.014300000	1.911630000	-1.801238000
6	0.763867000	1.528666000	0.244790000
6	1.990144000	2.437206000	0.315782000
6	0.177194000	0.796615000	1.312981000
6	3.030230000	1.904726000	1.319288000
6	1.524958000	3.836897000	0.788107000
6	2.658867000	2.585184000	-1.065234000
6	-3.382111000	-0.629886000	-1.359760000
6	-2.059681000	0.782065000	-2.888583000

6	-3.434118000	1.877574000	-1.128839000
6	-2.307388000	-1.907163000	1.646410000
6	-3.344705000	0.342576000	2.156399000
6	-1.333997000	-0.427538000	3.364345000
1	-4.168860000	-0.588373000	-2.130685000
1	-3.886750000	-0.763957000	-0.396110000
1	-2.772115000	-1.525809000	-1.554983000
1	-2.925785000	0.693835000	-3.564043000
1	-1.339103000	-0.005290000	-3.156345000
1	-1.590410000	1.753889000	-3.096596000
1	-4.284619000	1.912232000	-1.831912000
1	-2.862833000	2.812233000	-1.239800000
1	-3.839373000	1.858246000	-0.108463000
1	-3.018979000	-2.327318000	2.377540000
1	-1.385041000	-2.503623000	1.704076000
1	-2.733089000	-2.046504000	0.647539000
1	-3.925094000	-0.090296000	2.988532000
1	-3.980632000	0.306196000	1.263358000
1	-3.154729000	1.401850000	2.390551000
1	-1.987634000	-0.933435000	4.093031000
1	-1.148018000	0.591921000	3.734202000
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1	3.394264000	0.907946000	1.027818000
1	2.612558000	1.826206000	2.334940000
1	3.898733000	2.581888000	1.373105000
1	1.053210000	3.778878000	1.781503000
1	0.784035000	4.259384000	0.091549000
1	2.375558000	4.537664000	0.851862000
1	2.991114000	1.611546000	-1.457416000
1	3.539390000	3.245539000	-1.000273000
1	1.972346000	3.026847000	-1.803980000
27	0.588505000	-0.644550000	-0.386710000
6	3.184184000	-2.163566000	1.401360000
6	2.291999000	-2.107232000	0.188647000
6	0.621330000	-2.081736000	-2.122390000
6	2.675058000	-1.404435000	-0.978525000
6	1.045996000	-2.782840000	0.182852000
6	0.217126000	-2.774465000	-0.960490000
6	1.847611000	-1.385233000	-2.123181000
1	3.617282000	-0.853207000	-0.986739000
1	0.721687000	-3.314635000	1.079509000
1	-0.741909000	-3.294296000	-0.937781000
1	2.151491000	-0.815425000	-3.003048000
1	-0.021838000	-2.065054000	-3.003263000
1	2.602697000	-2.063773000	2.330648000
1	3.939888000	-1.365435000	1.385706000
1	3.718031000	-3.128481000	1.446368000
2 singlet state			
27	1.778747000	0.246847000	0.005049000
15	0.223447000	-1.376922000	-0.173531000
15	-0.223437000	1.376851000	0.173487000
6	-0.017759000	0.159296000	-1.176375000

6	0.017725000	-0.159393000	1.176332000
6	3.681388000	-0.419944000	0.726831000
6	3.677608000	-0.389879000	-0.724573000
6	3.377686000	0.981418000	-1.093005000
6	3.266021000	1.819887000	0.047835000
6	3.364249000	0.929775000	1.152723000
1	3.297601000	1.330941000	-2.118946000
1	3.261607000	1.233420000	2.189980000
27	-1.778738000	-0.246855000	-0.005068000
6	-0.042952000	0.320099000	-2.673472000
6	0.042944000	-0.320260000	2.673422000
6	4.086275000	-1.498382000	1.765152000
6	4.105309000	-1.384201000	-1.829459000
6	3.211120000	3.343588000	0.079282000
6	-3.681374000	0.419905000	-0.726863000
6	-3.677548000	0.389933000	0.724555000
6	-3.377638000	-0.981357000	1.093051000
6	-3.266015000	-1.819895000	-0.047743000
6	-3.364273000	-0.929854000	-1.152676000
1	-3.297525000	-1.330828000	2.119008000
1	-3.261643000	-1.233548000	-2.189918000
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1	-0.976303000	0.789544000	-3.020315000
1	0.031192000	-0.655586000	-3.182792000
1	-0.788619000	-0.944298000	3.037865000
1	0.976366000	-0.789570000	3.020238000
1	-0.031360000	0.655382000	3.182798000
6	4.102168000	-0.896096000	3.190706000
6	3.130469000	-2.710962000	1.812579000
6	5.533306000	-1.976297000	1.495986000
6	3.788653000	-2.864564000	-1.546121000
6	5.628439000	-1.213467000	-2.062511000
6	3.398907000	-1.052445000	-3.165309000
6	2.567660000	3.853619000	1.382527000
6	2.427053000	3.901980000	-1.123753000
6	4.669729000	3.861240000	0.009165000
6	-4.086323000	1.498289000	-1.765247000
6	-4.105215000	1.384352000	1.829400000
6	-3.211150000	-3.343599000	-0.079101000
1	4.820172000	-0.066734000	3.280482000
1	4.400989000	-1.673531000	3.911169000
1	3.113610000	-0.527084000	3.500823000
1	2.128362000	-2.407465000	2.147192000
1	3.507580000	-3.461463000	2.527500000
1	3.013717000	-3.199579000	0.841016000
1	5.628380000	-2.535986000	0.557898000
1	5.868070000	-2.641391000	2.308935000
1	6.227621000	-1.122286000	1.451309000
1	4.346048000	-3.267846000	-0.693279000
1	4.063364000	-3.472280000	-2.423309000
1	2.714385000	-3.011191000	-1.357485000
1	6.213434000	-1.452567000	-1.164258000
1	5.865342000	-0.176167000	-2.347002000

1	5.969989000	-1.874350000	-2.876915000
1	3.695558000	-1.787680000	-3.929634000
1	3.668250000	-0.060997000	-3.556517000
1	2.306391000	-1.096032000	-3.060304000
1	1.536067000	3.485823000	1.488383000
1	2.540856000	4.955287000	1.388487000
1	3.138927000	3.536552000	2.269226000
1	2.877331000	3.597482000	-2.081616000
1	2.424207000	5.003908000	-1.100059000
1	1.381626000	3.558781000	-1.111238000
1	5.263902000	3.485499000	0.857195000
1	4.695496000	4.963779000	0.035750000
1	5.163461000	3.530602000	-0.918288000
6	-4.102264000	0.896000000	-3.190795000
6	-3.130566000	2.710903000	-1.812796000
6	-5.533361000	1.976148000	-1.496060000
6	-3.788698000	2.864718000	1.545941000
6	-5.628310000	1.213535000	2.062582000
6	-3.398692000	1.052893000	3.165249000
6	-2.567775000	-3.853723000	-1.382351000
6	-2.427037000	-3.901944000	1.123924000
6	-4.669772000	-3.861208000	-0.008876000
1	-4.820257000	0.066625000	-3.280551000
1	-4.401110000	1.673432000	-3.911248000
1	-3.113702000	0.527019000	-3.500944000
1	-2.128449000	2.407403000	-2.147379000
1	-3.507704000	3.461317000	-2.527794000
1	-3.013830000	3.199631000	-0.841289000
1	-5.628462000	2.535747000	-0.557923000
1	-5.868134000	2.641301000	-2.308957000
1	-6.227652000	1.122113000	-1.451459000
1	-4.346345000	3.267968000	0.693249000
1	-4.063210000	3.472433000	2.423195000
1	-2.714485000	3.011387000	1.357033000
1	-6.213374000	1.452295000	1.164283000
1	-5.865093000	0.176291000	2.347379000
1	-5.969901000	1.874614000	2.876811000
1	-3.695260000	1.788323000	3.929421000
1	-3.667991000	0.061553000	3.556739000
1	-2.306186000	1.096472000	3.060102000
1	-1.536180000	-3.485956000	-1.488288000
1	-2.540996000	-4.955392000	-1.388248000
1	-3.139086000	-3.536694000	-2.269036000
1	-2.877242000	-3.597359000	2.081793000
1	-2.424244000	-5.003874000	1.100305000
1	-1.381594000	-3.558798000	1.111321000
1	-5.263979000	-3.485499000	-0.856895000
1	-4.695569000	-4.963748000	-0.035398000
1	-5.163443000	-3.530505000	0.918585000
2 triplet state			
27	1.855283000	0.288557000	0.045963000
15	0.299041000	-1.333723000	-0.311555000

15	-0.125817000	1.368403000	0.441888000
6	-0.147497000	0.296583000	-1.082701000
6	-0.164253000	-0.333948000	1.184917000
6	3.790612000	-0.393550000	0.741687000
6	3.741873000	-0.371381000	-0.737720000
6	3.523412000	0.993398000	-1.116382000
6	3.362059000	1.809432000	0.034336000
6	3.542384000	0.945202000	1.164138000
1	3.465395000	1.352180000	-2.139929000
1	3.495526000	1.275481000	2.196317000
27	-1.802037000	-0.246788000	-0.001256000
6	-0.127422000	0.669386000	-2.540560000
6	-0.111843000	-0.736229000	2.632681000
6	4.180009000	-1.489456000	1.765427000
6	4.100824000	-1.398223000	-1.839581000
6	3.285342000	3.334593000	0.057557000
6	-3.735219000	0.448064000	-0.723138000
6	-3.768500000	0.353139000	0.726836000
6	-3.458491000	-1.021653000	1.042456000
6	-3.304310000	-1.800522000	-0.138949000
6	-3.417733000	-0.877563000	-1.210176000
1	-3.411015000	-1.422711000	2.051186000
1	-3.316182000	-1.140533000	-2.257854000
1	0.885376000	0.917931000	-2.893164000
1	-0.765165000	1.542554000	-2.742769000
1	-0.500533000	-0.162052000	-3.161038000
1	-0.390119000	-1.795044000	2.760749000
1	0.893966000	-0.604066000	3.062265000
1	-0.807298000	-0.138299000	3.240376000
6	4.228926000	-0.893271000	3.192449000
6	3.184129000	-2.669195000	1.828364000
6	5.607754000	-2.010113000	1.474191000
6	3.767298000	-2.867746000	-1.523340000
6	5.617422000	-1.271269000	-2.134344000
6	3.343012000	-1.068977000	-3.148592000
6	2.725026000	3.853702000	1.395335000
6	2.413970000	3.869779000	-1.095046000
6	4.728602000	3.870299000	-0.115549000
6	-4.134371000	1.569916000	-1.715260000
6	-4.246643000	1.284231000	1.868746000
6	-3.205697000	-3.320951000	-0.230848000
1	4.973423000	-0.087581000	3.278710000
1	4.507364000	-1.682024000	3.908818000
1	3.253376000	-0.493999000	3.508247000
1	2.201837000	-2.328167000	2.184631000
1	3.548230000	-3.432787000	2.536130000
1	3.032445000	-3.155697000	0.860709000
1	5.676890000	-2.558021000	0.526547000
1	5.931139000	-2.697003000	2.273673000
1	6.326762000	-1.176519000	1.433594000
1	4.347009000	-3.268941000	-0.684691000
1	4.002149000	-3.490911000	-2.401217000
1	2.697788000	-2.995670000	-1.299812000

1	6.228397000	-1.499869000	-1.250085000
1	5.868325000	-0.248470000	-2.455508000
1	5.913399000	-1.964213000	-2.939924000
1	3.587131000	-1.820372000	-3.916013000
1	3.615566000	-0.088719000	-3.564231000
1	2.254213000	-1.086084000	-2.992831000
1	1.710931000	3.470144000	1.583422000
1	2.676316000	4.954601000	1.383914000
1	3.364045000	3.564508000	2.244249000
1	2.793742000	3.550146000	-2.077914000
1	2.405025000	4.971950000	-1.089122000
1	1.373707000	3.522523000	-1.002435000
1	5.384881000	3.504043000	0.689672000
1	4.740854000	4.972987000	-0.091185000
1	5.160718000	3.544582000	-1.074609000
6	-4.003937000	1.073218000	-3.175414000
6	-3.268304000	2.844702000	-1.614118000
6	-5.628158000	1.924529000	-1.518411000
6	-4.069084000	2.796233000	1.639127000
6	-5.748029000	0.984795000	2.113644000
6	-3.484308000	0.980228000	3.179739000
6	-2.590265000	-3.761604000	-1.572594000
6	-2.367689000	-3.904472000	0.923239000
6	-4.645753000	-3.883459000	-0.135728000
1	-4.670928000	0.223537000	-3.384725000
1	-4.283043000	1.887114000	-3.862686000
1	-2.975697000	0.772184000	-3.421772000
1	-2.212727000	2.617861000	-1.817069000
1	-3.602506000	3.584955000	-2.359880000
1	-3.313997000	3.319512000	-0.631267000
1	-5.832883000	2.368046000	-0.536346000
1	-5.950755000	2.650744000	-2.282862000
1	-6.258594000	1.026686000	-1.618339000
1	-4.684774000	3.181251000	0.818526000
1	-4.377037000	3.337034000	2.548358000
1	-3.017458000	3.050556000	1.440175000
1	-6.355862000	1.193054000	1.221322000
1	-5.900123000	-0.073286000	2.377868000
1	-6.136850000	1.601442000	2.941539000
1	-3.866491000	1.626156000	3.985846000
1	-3.600791000	-0.058103000	3.519424000
1	-2.410865000	1.189220000	3.063582000
1	-1.576940000	-3.352112000	-1.701783000
1	-2.522578000	-4.860612000	-1.617822000
1	-3.204168000	-3.437159000	-2.427521000
1	-2.784182000	-3.638044000	1.907325000
1	-2.348655000	-5.004845000	0.863076000
1	-1.328427000	-3.545354000	0.881291000
1	-5.277707000	-3.489619000	-0.947306000
1	-4.641036000	-4.984079000	-0.208886000
1	-5.117429000	-3.607068000	0.820464000

2^+ doublet state

27	-1.757956000	0.266841000	0.038308000
27	1.757949000	-0.266844000	-0.038311000
15	0.223105000	1.345250000	0.459026000
15	-0.223111000	-1.345253000	-0.459035000
6	-0.000830000	-0.379121000	1.117018000
6	0.000820000	0.379117000	-1.117025000
6	0.001414000	-0.859099000	2.544964000
6	-0.001431000	0.859089000	-2.544974000
1	0.148851000	-1.948826000	2.598719000
1	-0.148829000	1.948821000	-2.598732000
1	-0.940429000	-0.626894000	3.061918000
1	0.940394000	0.626846000	-3.061943000
1	0.813638000	-0.392096000	3.120207000
1	-0.813683000	0.392114000	-3.120200000
6	-3.660092000	-0.361422000	-0.727162000
6	3.660086000	0.361423000	0.727160000
6	-3.661315000	-0.422782000	0.727187000
6	3.661315000	0.422772000	-0.727192000
6	-3.354698000	0.915578000	1.192737000
6	3.354693000	-0.915593000	-1.192730000
1	-3.266109000	1.195610000	2.237301000
1	3.266107000	-1.195635000	-2.237291000
6	-3.220564000	1.819691000	0.108351000
6	3.220554000	-1.819697000	-0.108338000
6	-3.334908000	1.006468000	-1.058673000
6	3.334896000	-1.006465000	1.058680000
1	-3.236117000	1.380603000	-2.073993000
1	3.236102000	-1.380593000	2.074001000
6	-4.096237000	-1.321315000	-1.859818000
6	4.096240000	1.321329000	1.859812000
6	-3.872420000	-2.822688000	-1.603736000
6	3.872592000	2.822713000	1.603656000
1	-4.471664000	-3.214749000	-0.775277000
1	4.471964000	3.214689000	0.775249000
1	-2.812788000	-3.045149000	-1.407037000
1	2.813002000	3.045268000	1.406834000
1	-4.166760000	-3.386032000	-2.502240000
1	4.166889000	3.386058000	2.502173000
6	-5.605110000	-1.058098000	-2.108996000
6	5.605068000	1.057979000	2.109121000
1	-6.214366000	-1.274361000	-1.220925000
1	6.214416000	1.274134000	1.221087000
1	-5.968179000	-1.693806000	-2.932211000
1	5.968135000	1.693694000	2.932332000
1	-5.784178000	-0.008593000	-2.389780000
1	5.784010000	0.008470000	2.389974000
6	-3.343661000	-1.003899000	-3.173942000
6	3.343553000	1.004066000	3.173907000
1	-3.513706000	0.018545000	-3.539016000
1	3.513489000	-0.018364000	3.539067000
1	-3.695563000	-1.682619000	-3.964846000
1	3.695460000	1.682813000	3.964786000
1	-2.260226000	-1.163237000	-3.064168000

1	2.260138000	1.163490000	3.064052000
6	-4.069475000	-1.525587000	1.735362000
6	4.069493000	1.525575000	-1.735376000
6	-3.154122000	-2.768980000	1.707910000
6	3.154196000	2.769008000	-1.707899000
1	-3.096116000	-3.239286000	0.722672000
1	3.096193000	3.239281000	-0.722646000
1	-3.532449000	-3.522818000	2.416139000
1	3.532570000	3.522855000	-2.416095000
1	-2.133088000	-2.508925000	2.018864000
1	2.133160000	2.509012000	-2.018881000
6	-5.540474000	-1.932190000	1.471690000
6	5.540512000	1.932127000	-1.471749000
1	-5.676085000	-2.446608000	0.513525000
1	5.676162000	2.446569000	-0.513604000
1	-6.202699000	-1.052427000	1.481724000
1	6.202700000	1.052337000	-1.481771000
1	-5.882142000	-2.617163000	2.263267000
1	5.882189000	2.617063000	-2.263355000
6	-4.032997000	-0.977486000	3.182111000
6	4.032976000	0.977510000	-3.182137000
1	-3.029067000	-0.643035000	3.483692000
1	3.029028000	0.643113000	-3.483717000
1	-4.329271000	-1.776452000	3.877741000
1	4.329279000	1.776478000	-3.877754000
1	-4.732576000	-0.140872000	3.327969000
1	4.732516000	0.140867000	-3.328021000
6	-3.142468000	3.340937000	0.163909000
6	3.142455000	-3.340943000	-0.163885000
6	-4.588855000	3.860202000	-0.045125000
6	4.588839000	-3.860210000	0.045168000
1	-5.266807000	3.476751000	0.733195000
1	5.266799000	-3.476767000	-0.733148000
1	-4.989022000	3.553693000	-1.024139000
1	4.988997000	-3.553694000	1.024184000
1	-4.608122000	4.960724000	-0.000272000
1	4.608104000	-4.960732000	0.000324000
6	-2.631054000	3.829940000	1.531516000
6	2.631053000	-3.829955000	-1.531493000
1	-3.295366000	3.518847000	2.352509000
1	3.295373000	-3.518871000	-2.352482000
1	-2.592556000	4.929907000	1.546120000
1	2.592553000	-4.929923000	-1.546088000
1	-1.618061000	3.455703000	1.745864000
1	1.618062000	-3.455719000	-1.745853000
6	-2.243843000	3.906379000	-0.952392000
6	2.243818000	-3.906373000	0.952412000
1	-2.259300000	5.006796000	-0.927845000
1	2.259273000	-5.006790000	0.927875000
1	-2.583495000	3.599618000	-1.953805000
1	2.583459000	-3.599603000	1.953826000
1	-1.198115000	3.585517000	-0.827979000
1	1.198091000	-3.585510000	0.827985000

1,3 [Cp'''Co(η^4-$P_2C_2Me_2$)] **1** singlet state			
15	-2.422452000	-1.669554000	-0.168098000
15	-0.014423000	-2.672339000	0.695065000
6	-0.898701000	-2.346188000	-0.852423000
6	-1.448994000	-1.781911000	1.348563000
27	-0.454095000	-0.534480000	0.045197000
6	-0.637715000	-2.792080000	-2.258949000
6	-1.874345000	-1.509556000	2.759335000
6	1.158654000	0.553740000	-0.775043000
6	1.077217000	0.770079000	0.677353000
6	-0.223527000	1.329168000	0.927443000
6	-0.955665000	1.481213000	-0.283409000
6	-0.101849000	0.982038000	-1.313259000
1	-0.596618000	1.602290000	1.909759000
1	-0.374435000	0.936987000	-2.361853000
1	-1.058507000	-3.798178000	-2.434852000
1	0.436998000	-2.849131000	-2.491992000
1	-1.104685000	-2.112671000	-2.992550000
1	-2.539749000	-0.631986000	2.823678000
1	-2.430315000	-2.369536000	3.173482000
1	-1.017102000	-1.327921000	3.426836000
6	2.321764000	0.157184000	-1.719283000
6	2.109167000	0.750719000	1.831682000
6	-2.269035000	2.237128000	-0.464288000
6	1.851699000	0.197386000	-3.193097000
6	2.881697000	-1.262499000	-1.484496000
6	3.457094000	1.202399000	-1.599927000
6	3.241055000	-0.284696000	1.713783000
6	2.726862000	2.171044000	1.914444000
6	1.414333000	0.459760000	3.181748000
6	-2.973551000	1.848636000	-1.777371000
6	-3.229471000	1.994458000	0.714789000
6	-1.910360000	3.744034000	-0.519121000
1	1.527090000	1.203877000	-3.497525000
1	2.688240000	-0.090225000	-3.848623000
1	1.027343000	-0.504780000	-3.384225000
1	2.105886000	-2.020590000	-1.654401000
1	3.704526000	-1.457697000	-2.191894000
1	3.268830000	-1.414082000	-0.474193000
1	3.936085000	1.195621000	-0.613037000
1	4.240382000	0.996019000	-2.347546000
1	3.076067000	2.219762000	-1.783052000
1	3.908736000	-0.090998000	0.867063000
1	3.860855000	-0.246271000	2.623764000
1	2.840762000	-1.305073000	1.622577000
1	3.250014000	2.445425000	0.987393000
1	1.949269000	2.929521000	2.094798000
1	3.453077000	2.225234000	2.742393000
1	2.163838000	0.471895000	3.988397000
1	0.650426000	1.204850000	3.444665000
1	0.942171000	-0.532867000	3.174668000
1	-3.224596000	0.777611000	-1.793728000

1	-3.908515000	2.421184000	-1.886726000
1	-2.349949000	2.072238000	-2.657178000
1	-2.782076000	2.288149000	1.677228000
1	-4.147599000	2.589913000	0.585580000
1	-3.516367000	0.934249000	0.777544000
1	-1.221373000	3.958661000	-1.351371000
1	-2.818582000	4.352168000	-0.663546000
1	-1.424416000	4.073367000	0.412806000

1,3 [Cp'''Co(η^4-$P_2C_2Me_2$)] **1** triplet state

15	-2.960713000	-1.158509000	-0.094686000
15	-0.735224000	-2.831811000	0.198772000
6	-1.663361000	-1.951406000	-1.100310000
6	-1.842961000	-1.780547000	1.196736000
27	-0.657102000	-0.456280000	0.018560000
6	-1.608477000	-2.102730000	-2.588813000
6	-2.011379000	-1.723877000	2.682749000
6	1.371713000	0.474332000	-0.725708000
6	1.346546000	0.526579000	0.714443000
6	0.155355000	1.271185000	1.074078000
6	-0.517261000	1.746657000	-0.084643000
6	0.191510000	1.183168000	-1.178293000
1	-0.125628000	1.520006000	2.093161000
1	-0.067908000	1.339138000	-2.220350000
1	-2.249210000	-2.944857000	-2.907021000
1	-0.590150000	-2.316868000	-2.951587000
1	-1.976433000	-1.201159000	-3.106386000
1	-2.389799000	-0.744556000	3.019326000
1	-2.744079000	-2.484958000	3.006447000
1	-1.071168000	-1.933927000	3.217447000
6	2.386679000	-0.087066000	-1.754497000
6	2.337243000	0.107777000	1.826043000
6	-1.635782000	2.784454000	-0.143925000
6	1.992845000	0.344755000	-3.187350000
6	2.452553000	-1.631686000	-1.772303000
6	3.796360000	0.498376000	-1.505265000
6	3.054159000	-1.235269000	1.587197000
6	3.384223000	1.238834000	1.997363000
6	1.604582000	-0.036300000	3.181809000
6	-2.489956000	2.618437000	-1.415514000
6	-2.551139000	2.696273000	1.092347000
6	-0.965888000	4.180930000	-0.170812000
1	1.966359000	1.439687000	-3.297502000
1	2.736703000	-0.043099000	-3.900514000
1	1.013708000	-0.057199000	-3.487545000
1	1.487837000	-2.060188000	-2.080370000
1	3.214059000	-1.966054000	-2.496535000
1	2.700928000	-2.062079000	-0.797540000
1	4.238609000	0.154353000	-0.562945000
1	4.477368000	0.192394000	-2.316127000
1	3.769124000	1.599348000	-1.485232000
1	3.728865000	-1.212586000	0.723965000
1	3.668798000	-1.484539000	2.466986000

1	2.329565000	-2.050306000	1.437479000
1	3.982659000	1.392380000	1.089925000
1	2.890446000	2.193599000	2.237239000
1	4.074684000	0.997698000	2.822935000
1	2.316722000	-0.380545000	3.947690000
1	1.185320000	0.914318000	3.541170000
1	0.789420000	-0.771939000	3.123758000
1	-2.977511000	1.632123000	-1.440485000
1	-3.276154000	3.389903000	-1.447732000
1	-1.886498000	2.730771000	-2.330194000
1	-1.992730000	2.861828000	2.027227000
1	-3.334493000	3.469450000	1.039835000
1	-3.044643000	1.714492000	1.152471000
1	-0.307930000	4.288095000	-1.047722000
1	-1.727849000	4.977162000	-0.215677000
1	-0.353566000	4.345222000	0.730003000

1,2 [Cp'''Co(η^4-$P_2C_2Me_2$)] singlet state

6	-2.046675000	-1.097080000	-1.706534000
6	-0.948206000	-0.947617000	-0.625512000
6	-0.942651000	-0.740451000	0.824519000
1	0.731449000	-1.525136000	-1.993515000
6	-2.073144000	-0.575281000	1.871713000
6	0.413090000	-0.958242000	1.257935000
1	0.758724000	-0.868627000	2.281918000
6	1.243030000	-1.342168000	0.162942000
6	2.663142000	-1.898710000	0.227302000
6	0.402370000	-1.305074000	-0.982806000
6	3.497945000	-1.479266000	-0.997564000
6	2.531442000	-3.443217000	0.236267000
6	3.386482000	-1.457842000	1.512681000
6	-2.921704000	0.703459000	1.717929000
6	-1.481528000	-0.524012000	3.300540000
6	-2.986131000	-1.824419000	1.821635000
6	-1.505307000	-0.677987000	-3.095878000
6	-3.332002000	-0.281532000	-1.484785000
6	-2.418676000	-2.601072000	-1.783555000
1	-3.747638000	0.691205000	2.447938000
1	-3.358662000	0.815982000	0.722751000
1	-2.315864000	1.596316000	1.922444000
1	-2.298124000	-0.386631000	4.026326000
1	-0.782889000	0.316467000	3.426749000
1	-0.957769000	-1.453886000	3.567872000
1	-3.717893000	-1.790745000	2.645329000
1	-2.395582000	-2.747692000	1.931878000
1	-3.550184000	-1.896598000	0.883146000
1	-2.306924000	-0.773883000	-3.845034000
1	-0.673592000	-1.309885000	-3.437697000
1	-1.154886000	0.364478000	-3.097657000
1	-4.002128000	-0.421583000	-2.347639000
1	-3.119230000	0.793421000	-1.402057000
1	-3.890081000	-0.596847000	-0.595546000
1	-3.167929000	-2.769933000	-2.574789000

1	-2.838788000	-2.969275000	-0.836549000
1	-1.535648000	-3.215597000	-2.017484000
1	3.646866000	-0.389848000	-1.024489000
1	3.021864000	-1.782043000	-1.943116000
1	4.489836000	-1.958168000	-0.961195000
1	2.046748000	-3.808454000	-0.682893000
1	1.929810000	-3.786127000	1.093020000
1	3.525379000	-3.914924000	0.307372000
1	3.456531000	-0.361775000	1.573694000
1	4.408425000	-1.869188000	1.531171000
1	2.871275000	-1.823077000	2.415215000
27	0.441731000	0.572007000	-0.135284000
6	0.659730000	2.480417000	0.643043000
15	2.286104000	1.932418000	0.053468000
6	-0.107542000	2.534591000	-0.555525000
15	1.080552000	1.993057000	-1.822118000
6	0.308376000	2.984510000	2.011911000
6	-1.462277000	3.144611000	-0.767565000
1	-0.763267000	2.877826000	2.238424000
1	0.556152000	4.057406000	2.099413000
1	0.878458000	2.454553000	2.791420000
1	-2.149209000	2.956546000	0.070830000
1	-1.932681000	2.767927000	-1.688782000
1	-1.367705000	4.239769000	-0.878199000

1,2 [Cp'''Co(η^4-$P_2C_2Me_2$)] triplet state

6	-1.333116000	2.218775000	-1.502595000
6	-1.200458000	1.055267000	-0.492163000
6	-0.773854000	0.965253000	0.904856000
1	-2.153440000	-0.481973000	-1.814392000
6	-0.262753000	2.006532000	1.933559000
6	-1.013236000	-0.389370000	1.301088000
1	-0.812324000	-0.791242000	2.288486000
6	-1.637970000	-1.131280000	0.241034000
6	-2.243073000	-2.530162000	0.329056000
6	-1.742800000	-0.232713000	-0.840994000
6	-2.101256000	-3.280522000	-1.009632000
6	-3.747550000	-2.364525000	0.658570000
6	-1.580166000	-3.361120000	1.443905000
6	1.169713000	2.502161000	1.636948000
6	-0.214376000	1.377574000	3.346851000
6	-1.233509000	3.205479000	2.032621000
6	-1.340698000	1.677565000	-2.954070000
6	-0.201597000	3.261937000	-1.444207000
6	-2.698140000	2.914968000	-1.264482000
1	1.476584000	3.248155000	2.389005000
1	1.265723000	2.965559000	0.649543000
1	1.881093000	1.665036000	1.683177000
1	0.126604000	2.134597000	4.070041000
1	0.490851000	0.534627000	3.402171000
1	-1.203273000	1.023914000	3.676003000
1	-0.925303000	3.871795000	2.854713000
1	-2.260035000	2.865288000	2.241722000

1	-1.258715000	3.809623000	1.117834000
1	-1.373613000	2.523332000	-3.658493000
1	-2.220237000	1.053332000	-3.167128000
1	-0.437635000	1.086408000	-3.169564000
1	-0.349050000	4.007695000	-2.241452000
1	0.779866000	2.790803000	-1.607295000
1	-0.169164000	3.810213000	-0.496017000
1	-2.850833000	3.718495000	-2.004130000
1	-2.769917000	3.358875000	-0.262796000
1	-3.524787000	2.195411000	-1.370852000
1	-1.042410000	-3.417868000	-1.277596000
1	-2.595401000	-2.744382000	-1.834825000
1	-2.568302000	-4.276258000	-0.940126000
1	-4.265612000	-1.792796000	-0.127322000
1	-3.888793000	-1.829456000	1.611132000
1	-4.237042000	-3.349024000	0.744712000
1	-0.499966000	-3.477084000	1.267953000
1	-2.029406000	-4.366324000	1.484572000
1	-1.721535000	-2.901359000	2.434832000
27	0.424204000	-0.523181000	-0.333883000
6	2.877447000	-1.004284000	0.427451000
15	1.864985000	-2.329132000	-0.451526000
6	3.020445000	-0.049559000	-0.533794000
15	2.059409000	-0.758343000	-2.000963000
6	3.436340000	-1.080861000	1.814342000
6	3.814483000	1.218343000	-0.535758000
1	3.898657000	-0.132228000	2.130915000
1	4.205927000	-1.870596000	1.882668000
1	2.654411000	-1.341952000	2.548114000
1	4.206569000	1.471869000	0.461719000
1	3.214338000	2.070871000	-0.895909000
1	4.673502000	1.127915000	-1.224753000

trans-[Cp'''Co(PC≡Me)$_2$], singlet state

6	-2.176406000	0.955500000	1.600762000
6	-1.035203000	0.806595000	0.560085000
6	-1.006319000	0.576031000	-0.886227000
1	0.571917000	1.528516000	1.942538000
6	-2.108514000	0.274831000	-1.932176000
6	0.335480000	0.855509000	-1.292505000
1	0.706896000	0.756893000	-2.306871000
6	1.130060000	1.314665000	-0.194231000
6	2.481113000	2.025388000	-0.263978000
6	0.282979000	1.243983000	0.935553000
6	3.366613000	1.691694000	0.951476000
6	2.179178000	3.546337000	-0.254188000
6	3.237345000	1.691714000	-1.563693000
6	-2.774433000	-1.106426000	-1.750851000
6	-1.512468000	0.295408000	-3.360010000
6	-3.180576000	1.391183000	-1.913612000
6	-1.656444000	0.726540000	3.041687000
6	-3.385979000	0.017217000	1.430696000
6	-2.659348000	2.428383000	1.522450000

1	-3.577395000	-1.236364000	-2.495522000
1	-3.213384000	-1.241028000	-0.757781000
1	-2.042398000	-1.911778000	-1.896556000
1	-2.306935000	0.069413000	-4.088065000
1	-0.721409000	-0.455775000	-3.495058000
1	-1.096944000	1.280997000	-3.619740000
1	-3.886285000	1.246525000	-2.747795000
1	-2.717874000	2.383708000	-2.033243000
1	-3.768794000	1.403261000	-0.988694000
1	-2.492641000	0.845801000	3.748181000
1	-0.888064000	1.455070000	3.337051000
1	-1.248836000	-0.285522000	3.166384000
1	-4.098643000	0.197332000	2.251264000
1	-3.086023000	-1.039766000	1.478959000
1	-3.931007000	0.181359000	0.494676000
1	-3.448290000	2.607655000	2.271730000
1	-3.067101000	2.681941000	0.534852000
1	-1.831284000	3.123883000	1.729822000
1	3.628586000	0.624343000	0.974664000
1	2.865250000	1.938897000	1.900349000
1	4.301183000	2.274531000	0.912834000
1	1.675685000	3.848811000	0.677313000
1	1.526592000	3.827125000	-1.095960000
1	3.114422000	4.124185000	-0.340077000
1	3.428913000	0.612835000	-1.659550000
1	4.207781000	2.213163000	-1.578321000
1	2.676858000	2.018874000	-2.453589000
27	0.457516000	-0.728792000	0.119652000
15	2.563175000	-1.699617000	-0.352962000
6	0.536014000	-1.753252000	1.842397000
6	1.220002000	-2.093293000	-1.153143000
15	-0.685469000	-2.527971000	1.128923000
6	1.442381000	-1.590802000	2.998711000
6	0.595031000	-2.939838000	-2.192327000
1	-0.186901000	-3.580861000	-1.747067000
1	0.097664000	-2.334503000	-2.968168000
1	1.333843000	-3.590470000	-2.689312000
1	1.180612000	-2.270233000	3.827405000
1	2.486726000	-1.796363000	2.701181000
1	1.425737000	-0.555463000	3.380889000

trans-[Cp'''Co(PC≡Me)$_2$] triplet state

6	-2.393984000	0.737164000	1.551478000
6	-1.225371000	0.767983000	0.533701000
6	-1.121035000	0.531761000	-0.900125000
1	0.267067000	1.634071000	1.950639000
6	-2.143143000	0.065112000	-1.968206000
6	0.181109000	1.000461000	-1.294665000
1	0.559242000	0.990552000	-2.311569000
6	0.895425000	1.505631000	-0.181922000
6	2.150421000	2.379578000	-0.202435000
6	0.034967000	1.307736000	0.940696000
6	3.055123000	2.112836000	1.017184000

6	1.683394000	3.856862000	-0.151082000
6	2.959208000	2.173691000	-1.496617000
6	-2.566571000	-1.411993000	-1.799921000
6	-1.536622000	0.184625000	-3.386482000
6	-3.392263000	0.978249000	-1.968184000
6	-1.861058000	0.610227000	3.000530000
6	-3.412819000	-0.406354000	1.375054000
6	-3.137657000	2.096089000	1.463281000
1	-3.313459000	-1.682329000	-2.565318000
1	-3.002551000	-1.621865000	-0.818225000
1	-1.701210000	-2.078318000	-1.924838000
1	-2.273450000	-0.159300000	-4.129065000
1	-0.635616000	-0.434451000	-3.507435000
1	-1.272693000	1.223193000	-3.636610000
1	-4.052355000	0.713001000	-2.810378000
1	-3.104886000	2.035178000	-2.084391000
1	-3.984253000	0.888598000	-1.050121000
1	-2.711257000	0.567451000	3.699409000
1	-1.246710000	1.470750000	3.301925000
1	-1.269191000	-0.306505000	3.134514000
1	-4.158033000	-0.358435000	2.185227000
1	-2.927069000	-1.392190000	1.430483000
1	-3.965556000	-0.347135000	0.430779000
1	-3.950564000	2.138965000	2.208180000
1	-3.579171000	2.263643000	0.471750000
1	-2.448051000	2.930431000	1.665114000
1	3.451414000	1.086580000	1.011566000
1	2.513083000	2.260728000	1.964563000
1	3.911382000	2.807180000	1.018491000
1	1.126755000	4.067644000	0.775573000
1	1.021843000	4.090603000	-1.000024000
1	2.547814000	4.541085000	-0.192507000
1	3.273715000	1.126356000	-1.619544000
1	3.865378000	2.800802000	-1.484542000
1	2.375708000	2.458340000	-2.386241000
27	0.646939000	-0.734106000	0.129520000
15	2.944979000	-1.452060000	-0.439447000
6	0.759528000	-1.812707000	1.952120000
6	1.681320000	-2.046130000	-1.215639000
15	-0.324332000	-2.727004000	1.214737000
6	1.617057000	-1.402392000	3.079910000
6	1.057024000	-2.893713000	-2.249883000
1	0.333180000	-3.593797000	-1.798016000
1	0.498266000	-2.286709000	-2.981241000
1	1.812660000	-3.481032000	-2.798384000
1	1.513038000	-2.088242000	3.937891000
1	2.677636000	-1.383680000	2.774908000
1	1.366531000	-0.382629000	3.418296000

cis-[Cp'''Co(PC≡Me)$_2$] singlet state

6	-2.134375000	-1.365385000	-1.371317000
6	-0.957536000	-0.982760000	-0.436285000
6	-0.864495000	-0.572823000	0.954307000

1	0.633048000	-1.705678000	-1.840567000
6	-1.922615000	-0.277395000	2.048767000
6	0.531644000	-0.686509000	1.298691000
1	0.947658000	-0.438390000	2.269181000
6	1.294422000	-1.219167000	0.221284000
6	2.714373000	-1.782562000	0.261442000
6	0.378464000	-1.336449000	-0.851726000
6	3.506491000	-1.432730000	-1.013474000
6	2.581338000	-3.324219000	0.354333000
6	3.483706000	-1.288076000	1.500229000
6	-2.758805000	0.991250000	1.779798000
6	-1.234014000	-0.073594000	3.419611000
6	-2.861645000	-1.494357000	2.232505000
6	-1.724829000	-1.284597000	-2.862662000
6	-3.413763000	-0.520553000	-1.232341000
6	-2.472488000	-2.852659000	-1.082403000
1	-3.502167000	1.130211000	2.582322000
1	-3.301685000	0.945834000	0.830760000
1	-2.117303000	1.880942000	1.756903000
1	-1.996841000	0.156777000	4.179334000
1	-0.518032000	0.759844000	3.409127000
1	-0.700514000	-0.977244000	3.751077000
1	-3.509160000	-1.336560000	3.110408000
1	-2.284527000	-2.416961000	2.402468000
1	-3.519183000	-1.660030000	1.370741000
1	-2.589500000	-1.557908000	-3.487475000
1	-0.916993000	-1.984612000	-3.119152000
1	-1.403673000	-0.273162000	-3.145335000
1	-4.151628000	-0.856272000	-1.978124000
1	-3.217258000	0.544187000	-1.419587000
1	-3.889298000	-0.619127000	-0.250121000
1	-3.276697000	-3.194753000	-1.755067000
1	-2.804153000	-3.014200000	-0.048536000
1	-1.594015000	-3.493591000	-1.254731000
1	3.665957000	-0.348883000	-1.104650000
1	2.986285000	-1.773480000	-1.922184000
1	4.492649000	-1.924689000	-0.994072000
1	2.071863000	-3.736512000	-0.530768000
1	2.003220000	-3.620346000	1.244105000
1	3.576831000	-3.793659000	0.423022000
1	3.566464000	-0.191070000	1.517392000
1	4.503375000	-1.705432000	1.502774000
1	2.995239000	-1.608353000	2.434217000
27	0.454242000	0.730053000	-0.266289000
6	0.976470000	2.319856000	0.860744000
15	2.405224000	1.982319000	0.191954000
6	-0.459848000	1.974412000	-1.546807000
15	0.752757000	1.466940000	-2.483879000
6	-1.603399000	2.903516000	-1.392306000
1	-2.094368000	3.113035000	-2.358178000
1	-2.361328000	2.535164000	-0.685421000
1	-1.243460000	3.870629000	-0.997223000
6	0.241646000	3.217395000	1.783794000

1	0.866716000	4.065911000	2.109196000
1	-0.672002000	3.623709000	1.320219000
1	-0.084201000	2.678795000	2.689499000

cis-[Cp'''Co(PC≡Me)$_2$] triplet state

6	-2.416174000	-0.993433000	-1.391662000
6	-1.178209000	-0.904501000	-0.462808000
6	-0.991969000	-0.592247000	0.951239000
1	0.264652000	-1.744764000	-1.940333000
6	-1.971710000	-0.155958000	2.072692000
6	0.360714000	-0.960303000	1.272633000
1	0.806528000	-0.876950000	2.258109000
6	1.028973000	-1.471777000	0.134036000
6	2.343723000	-2.252565000	0.097270000
6	0.078629000	-1.394785000	-0.929206000
6	3.138042000	-1.970671000	-1.193770000
6	1.987356000	-3.760466000	0.134432000
6	3.223028000	-1.933757000	1.320890000
6	-2.472583000	1.296234000	1.907321000
6	-1.279415000	-0.226319000	3.454845000
6	-3.180728000	-1.115677000	2.166538000
6	-1.994696000	-0.975403000	-2.881805000
6	-3.443742000	0.143853000	-1.228419000
6	-3.112923000	-2.359061000	-1.153242000
1	-3.181021000	1.550571000	2.713499000
1	-2.983694000	1.459883000	0.952299000
1	-1.632688000	2.003029000	1.966131000
1	-1.988780000	0.089561000	4.235719000
1	-0.404706000	0.436586000	3.521030000
1	-0.950465000	-1.247832000	3.697420000
1	-3.784173000	-0.872013000	3.056391000
1	-2.847304000	-2.160806000	2.261511000
1	-3.845122000	-1.050016000	1.297496000
1	-2.895380000	-1.010993000	-3.514968000
1	-1.379426000	-1.844454000	-3.155695000
1	-1.436849000	-0.063687000	-3.139435000
1	-4.246789000	0.024947000	-1.973486000
1	-2.978925000	1.126595000	-1.396945000
1	-3.923868000	0.151851000	-0.243021000
1	-3.971286000	-2.475353000	-1.836704000
1	-3.482547000	-2.469320000	-0.126277000
1	-2.413063000	-3.187137000	-1.345287000
1	3.441262000	-0.915396000	-1.259678000
1	2.547958000	-2.205778000	-2.093264000
1	4.048695000	-2.591101000	-1.226634000
1	1.381972000	-4.048577000	-0.739247000
1	1.409208000	-4.006919000	1.038963000
1	2.902097000	-4.377210000	0.133609000
1	3.473362000	-0.863493000	1.377239000
1	4.167088000	-2.499975000	1.269576000
1	2.723439000	-2.214306000	2.261524000
27	0.628970000	0.735870000	-0.267269000
6	1.683089000	2.123159000	1.054278000

15	2.902451000	1.640688000	0.150735000
6	-0.141657000	2.345169000	-1.456724000
15	0.759964000	1.612788000	-2.553961000
6	-1.031744000	3.430203000	-0.995673000
1	-1.481934000	3.974734000	-1.843209000
1	-1.841948000	3.060793000	-0.348600000
1	-0.455139000	4.160502000	-0.400578000
6	1.085067000	2.866536000	2.182170000
1	1.822624000	3.538205000	2.653358000
1	0.221910000	3.474877000	1.866651000
1	0.717471000	2.173935000	2.957298000

Table S14. Calculated reaction energies (kJ·mol^{-1}) of different transformations at the B3LYP/def2-TZVP level of theory.

Transformation	**Reaction Energy (kJ·mol^{-1})**
2 MeCP = 1,3-$(MeCP)_2$	-6.56
2 MeCP = 1,2-$(MeCP)_2$	-54.91
2 *t*BuCP = 1,3-$(t$BuCP$)_2$	-1.42
2 tBuCP = 1,2-$(t$BuCP$)_2$	0.28
2 AdCP = 1,3-$(AdCP)_2$	0.16
2 AdCP = 1,2-$(AdCP)_2$	5.28
L_2Cr_2 + 2 MeCP = L_2Cr_2{1,3-$(MeCP)_2$}	-208.09
L_2Cr_2 + 2 MeCP = L_2Cr_2{1,2-$(MeCP)_2$}	-228.86
L_2Cr_2 + MeCP = L_2Cr_2(MeCP)	-81.63
L_2Cr_2(MeCP) + MeCP = L_2Cr_2{1,3-$(MeCP)_2$}	-126.45
L_2Cr_2(MeCP) + MeCP = L_2Cr_2{1,2-$(MeCP)_2$}	-147.23
L_2Cr_2 + 2 *t*BuCP = L_2Cr_2{1,3-$(t$BuCP$)_2$}	-76.35
L_2Cr_2 + 2 *t*BuCP = L_2Cr_2{1,2-$(t$BuCP$)_2$}	-43.39
L_2Cr_2 + *t*BuCP = L_2Cr_2(tBuCP)	-39.69
L_2Cr_2 + 2 AdCP = L_2Cr_2{1,3-$(AdCP)_2$}	-47.08
L_2Cr_2 + AdCP = L_2Cr_2(AdCP)	-33.07
L_2Cr_2(AdCP) + AdCP = L_2Cr_2{1,3-$(AdCP)_2$}	-14.01
L_2Cr_2(AdCP) + AdCP = L_2Cr_2{1,2-$(AdCP)_2$}	17.01

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