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Supporting Information

A General Pathway to Heterobimetallic Triple-Decker Complexes

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1. Synthetic procedures and experimental details

Synthetic Procedures: All manipulations were performed under an atmosphere of dry argon using standard glove-box and Schlenk techniques. All solvents were degassed and purified by standard procedures. The compounds $[(Cp'''Co)_2(\mu,\eta^4:\eta^4\text{-}C_7H_8)]$ (**A**)[1], $[Cp^*Fe(\eta^5\text{-}P_5)]$ (**B**)[2], $[Cp'''Co(\eta^4\text{-}P_4)]$ (**C**)[3], $[Cp'''Ni(\eta^3\text{-}P_3)]$ (**E**)[4], $[K_2(dme)_3][(Cp^*Fe)_2(\mu,\eta^4:\eta^4\text{-}P_{10})]$[5] and $[(Cp'''CoCl)_2]$[6] were prepared according to literature procedures.

The NMR spectra were recorded with a Bruker Avance 400 spectrometer (^{1}H: 400.13 MHz, ^{31}P: 161.976 MHz). The chemical shifts are given in ppm referenced to external $SiMe_4$ (^{1}H) and H_3PO_4 (^{31}P). Elemental analyses were determined with an Elementar Vario EL III apparatus. All mass spectra were recorded with a Finnigan MAT 95 mass spectrometer (LIFDI-MS and EI-MS).

1.1 Synthesis of $[(Cp^*Fe)(Cp'''Co)(\mu,\eta^5:\eta^4\text{-}P_5)]$ (1)

A solution of **A** (2.93 g, 4.336 mmol, 1 eq) in 100 mL hexane was added dropwise to a stirred solution of **B** (3.00 g, 8.672 mmol, 2 eq) in 200 mL hexane at room temperature. Thereby, the reaction mixture turned violet. After stirring the mixture for 2 hours, the solvent was removed under reduces pressure. The residue was dissolved in 20 mL CH_2Cl_2, mixed with silica and dried *in vacuo*. The preabsorbed crude mixture was purified by column chromatography (SiO_2, hexane, 15 x 4 cm). Compound **1** can be eluted using toluene as a strong dark red/violet fraction. After removing the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2, layered with acetonitrile and storage at -30 °C. After a few days, **1** can be obtained as dark violet blocks. The supernatant was decanted off and dried *in vacuo*.

Yield: 4.88 g (88 %).

^{1}H NMR (toluene-d_8, 293 K): δ [ppm] = 3.68 (s, 2H, $C_5H_2{}^t\text{Bu}_3$), 1.39 (s, 18H, $C_5H_2{}^t\textit{Bu}_3$), 1.31 (s, 9H, $C_5H_2{}^t\textit{Bu}_3$), 1.30 (s, 15H, $C_5\textit{Me}_5$).

^{1}H NMR (toluene-d_8, 213 K): δ [ppm] = 3.77 (s, 2H, $C_5H_2{}^t\text{Bu}_3$), 1.45 (s, 18H, $C_5H_2{}^t\textit{Bu}_3$), 1.34 (s, 9H, $C_5H_2{}^t\textit{Bu}_3$), 1.27 (s, 15H, $C_5\textit{Me}_5$).

^{31}P{^{1}H} NMR (toluene-d_8, 363 K): δ [ppm] = -115.3 (s, $\omega_{1/2}$ = 500 Hz).

^{31}P{^{1}H} NMR (toluene-d_8, 293 K): δ [ppm] = -164.7 (s, $\omega_{1/2}$ = 16000 Hz).

^{31}P{^{1}H} NMR (toluene-d_8, 213 K): δ [ppm] = 289.3 (t, 1P; P_A), −205.8 (m, 2P; $P_M/P_{M'}$), −249.1 (m, 2P; $P_X/P_{X'}$). Corresponding coupling constants are taken from the simulation (Figure S1) and given in table S1.

LIFDI-MS (toluene): *m/z* = 638.2 (100 %, $[M]^+$).

EA: $C_{27}H_{44}CoFeP_5$: calc [%]: C: 50.81; H: 6.95; found [%]: C: 50.97; H: 6.90.

Alternative procedure:

A solution of $[(Cp'''CoCl)_2]$ (73 mg, 0.10 mmol, 1 eq) in dme was added to a stirred solution of $[K_2(dme)_3][(Cp^*Fe)_2(\mu,\eta^4:\eta^4\text{-}P_{10})]$ (112 mg, 0.10 mmol eq) in dme at room temperature and stirred overnight. A color change from dark brown to violet was observed. The solvent was removed *in vacuo*, the residue extracted with hexane and filtered over diatomaceous earth. After removing the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2, layered with acetonitrile and storage at -30 °C. After a few days, **1** can be obtained as dark violet blocks. The supernatant was decanted off and dried *in vacuo*.

Yield: 58 mg (41 %).

1.2 Reaction of [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-P$_5$)] (1) with [W(CO)$_5$(thf)]

A solution of W(CO)$_6$ (246 mg, 0.70 mmol, 2.2 eq) in 50 mL thf was radiated for 3 hours, while the color changed to yellow. The W(CO)$_5$(thf) solution was added to a stirred solution of **1** (200 mg, 0.3133, 1 eq) in 20 mL thf. After stirring for 1 h (solution turned from red/violet to brown) the solvent was removed *in vacuo*. The residue was dissolved in 10 mL hexane and purified by a short column chromatography (SiO$_2$, hexane, 12x3 cm) to remove remaining [W(CO)$_6$]/[W(CO)$_5$(thf)]. Using hexane/toluene (1:1) a dark brown fraction can be eluted. Removing the solvent *in vacuo* yields as dark brown powder (220 mg). The ^{31}P{^{1}H} NMR spectrum and mass spectrum both reveal a mixture of [(Cp*Fe)(Cp'''Co)(μ$_3$,η^5:η^4:η^1-P$_5$){W(CO)$_5$}] (**2a**) and [(Cp*Fe)(Cp'''Co)(μ$_4$,η^5:η^4:η^1:η^1-P$_5$){W(CO)$_5$}$_2$] (**2b**). By slow evaporation of solution in toluene very few crystals of **2b** could be obtained. The crude product was further purified by preparative thin layer chromatography (SiO$_2$,1mm 20x20 cm, hexane). The first strong dark brown and second very weak brown fraction were scratched of the plate, extracted with Et$_2$O and filtered over diatomaceous earth. The solvent was removed *in vacuo*. A concentrated solution of the first fraction in pentane was stored at -30°C. After a few days, **2a** can be obtained as black blocks. The supernatant (only **2a** according to ^{31}P{^{1}H} NMR) was decanted off and the crystals dried *in vacuo*. NMR spectra of fraction two reveals **2b**.

Crude reaction mixture:

^{31}P{^{1}H} NMR (C$_6$D$_6$, 293 K): δ [ppm] = 235.9 (t, 1P, P$_A$, **2b**), 190.1(br, **2a**), -110.7 (br, **2a**), -157.8 (m, 2P, P$_{M/M'}$, **2b**),-176.2 (t(br), **2a**), -182.3 (m, 2P, P$_{X/X'}$, **2b**), -209.8 (br, **2a**).

The spectrum is depicted in Figure S3.

LIFDI-MS (toluene): *m/z* = 1286.00 (100 %, [**2b**]$^+$), 962.06 (95 %, [**2a**]$^+$).

Compound **2a**: Yield: 46 mg (12 %).

^{1}H NMR (toluene-d$_8$, 293 K): δ [ppm] = 3.98 (br, 2H, , C$_5$*H*$_2$^{t}Bu$_3$), 1.50 (br, 18H, C$_5$H$_2$^{t}*Bu*$_3$), 1.31 (s, 9H, C$_5$H$_2$^{t}*Bu*$_3$), 1.28 (s, 15H, C$_5$*Me*$_5$).

^{31}P{^{1}H} NMR (toluene-d$_8$, 293 K): δ [ppm] = 187.7 (br, 1P, P$_A$), -109.3 (br, 1P, P$_M$), -175.5 (t, 1P, P$_N$), -208.4 (br, 2P, P$_X$/P$_Y$).

^{1}H NMR (toluene-d$_8$, 193 K): δ [ppm] = 4.38 (s, 1H, C$_5$*H*$_2$^{t}Bu$_3$), 3.66 (s, 1H, C$_5$*H*$_2$^{t}Bu$_3$), 2.08 (s, 9H, C$_5$H$_2$^{t}*Bu*$_3$), 1.31 (s, 9H, C$_5$H$_2$^{t}*Bu*$_3$), 1.18 (s, 15H, C$_5$*Me*$_5$), 1.08 (s, 9H, C$_5$H$_2$^{t}*Bu*$_3$).

^{31}P{^{1}H} NMR (toluene-d$_8$, 193 K): δ [ppm] = 249.9 (m, 1P; P$_A$), −-112.2 (m, 1P; P$_M$), −192.6 (m, 1P; P$_N$), −234.6 (m, 1P; P$_X$), −242.0 (m, 1P; P$_Y$). Corresponding coupling constants are taken from the simulation (Figure S6) and given in table S3.

LIFDI-MS (toluene): *m/z* = 961.97 (100 %, [M]$^+$).

EA C$_{32}$H$_{44}$O$_5$FeCoP$_5$W: calc [%]: C: 39.95; H: 4.61; found [%]: C: 40.27; H: 4.64.

ATR-IR (Ge crystal): $\bar{\nu}$ = 2065 (s, CO), 1990 (w, CO), 1972 (w, CO), 1943 (s, CO), 1905 (vs, CO), 1862 (w, CO) cm^{-1}.

Compound **2b**: Yield: only few crystals.

^{1}H NMR (C$_6$D$_6$, 293 K): δ [ppm] = 4.26 (s, 2H, , C$_5$*H*$_2$^{t}Bu$_3$), 1.37 (s, 9H, C$_5$H$_2$^{t}*Bu*$_3$), 1.30 (s, 18H, C$_5$H$_2$^{t}*Bu*$_3$), 1.23 (s, 15H, C$_5$*Me*$_5$).

^{31}P{^{1}H} NMR (C$_6$D$_6$, 293 K): δ [ppm] = 236.0 (t, 1P; P$_A$), −157.7 (m, 2P; P$_M$/P$_{M'}$), −181.9 (m, 2P; P$_X$/P$_{X'}$). Corresponding coupling constants are taken from the simulation (Figure S6) and given in table S3.

LIFDI-MS (toluene): *m/z* = 1286.00 (100 %, [M]$^+$).

1.3 Synthesis of [(Cp'''Co)(Cp'''Ni)(μ,η^3:η^3-P$_3$] (3)

A solution of **A** (1.76 g, 2.60 mmol, 2 eq) in 100 mL pentane was added dropwise to a stirred solution of **E** (2.00 g, 5.20 mmol, 1 eq) in 200 mL hexane at room temperature. Thereby, the reaction mixture turned brown. After stirring the mixture for 2 hours, the solvent was removed under reduces pressure. The residue was dissolved in 20 mL CH_2Cl_2, mixed with silica and dried *in vacuo*. The preabsorbed crude mixture was purified by column chromatography (SiO_2, hexane, 15 x 4.5 cm). Using hexane, a weak brown fraction was eluted. Compound **3** can be eluted using hexane/toluene 1:1 as a dark brown fraction. After removing the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2, layered with MeCN and storage at -30 °C. After a few days, **3** can be obtained as dark brown rods. The supernatant was decanted off and dried in vacuo.

Yield: 3.06 g (87 %).

^{1}H NMR (C_6D_6, 293 K): δ [ppm] = 4.96 (s, 2H, $C_5H_2{}^tBu_3$), 4.85 (s, 2H, $C_5H_2{}^tBu_3$), 1.42 (s, 18H, $C_5H_2{}^tBu_3$), 1.37 (s, 18H, $C_5H_2{}^tBu_3$), 1.12 (s, 18H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (C_6D_6, 293 K): δ [ppm] = 376.5 (s, $\omega_{1/2}$ = 20 Hz, 2P, *chain-P*$_3$), 248.6 (br, $\omega_{1/2}$ = 148 Hz, 10P, *cyclo-P*$_3$), 132.3 (s, $\omega_{1/2}$ = 11 Hz, 1P, *chain-P*$_3$).

^{1}H NMR (toluene-d$_8$, 223 K): δ [ppm] = 5.24 (s, 2H, $C_5H_2{}^tBu_3$), 5.21 (s, 2H, $C_5H_2{}^tBu_3$), 4.99 (s, 2H, $C_5H_2{}^tBu_3$), 4.66 (s, 2H, $C_5H_2{}^tBu_3$), 1.40 (s, 18H, $C_5H_2{}^tBu_3$), 1.36 (s, 18H, $C_5H_2{}^tBu_3$), 1.33 (s, 18H, $C_5H_2{}^tBu_3$), 1.31 (s, 9H, $C_5H_2{}^tBu_3$), 1.29 (s, 18H, $C_5H_2{}^tBu_3$), 1.27 (s, 9H, $C_5H_2{}^tBu_3$), 0.98 (s, 9H, $C_5H_2{}^tBu_3$), 0.94 (s, 9H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (toluene-d$_8$, 223 K): δ [ppm] = 373.2 (d,$^1J_{PP}$ = 359 Hz ,2P, *chain-P*$_3$), 239.4 (s, 3P, *cyclo-P*$_3$), 130.6 (t, $^1J_{PP}$ = 359 Hz, 1P, *chain-P*$_3$).

LIFDI-MS (toluene): *m/z* = 676.2 (100 %, $[M]^+$).

EA: $C_{34}H_{58}CoNiP_3$: calc [%]: C: 60.29; H: 8.63; found [%]: C: 60.17; H: 8.63.

1.4 Synthesis of [(Cp'''Co)(Cp'''Ni)(μ$_3$,η^3:η^2:η^1-P$_5$){W(CO)$_5$}] (4)

A solution of $W(CO)_6$ (229 mg, 0.65 mmol, 2.2 eq) in 50 mL thf was radiated for 3 hours, while the color changed to yellow. The $W(CO)_5$(thf) solution was added to a stirred solution of **3** (200 mg, 0.295, 1 eq) in 10 mL thf. After stirring for 1 h the solvent of the resulting brown solution was removed *in vacuo*. The residue was dissolved in CH_2Cl_2, SiO_2 added and the solvent removed *in vacuo*. The preabsorbed product was purified by column chromatography (SiO_2, hexane, 15 x 2.5 cm). Using hexane as an eluent a red to brown fraction (**4**) can be obtained. The solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and layered with acetonitrile at room temperature. After a few days **4** can be obtained in form of dark brown blocks. The supernatant was decanted off and the remaining crystals were dried *in vacuo*.

Yield: 81 mg (27 %).

^{1}H NMR (C_6D_6, 293 K): δ [ppm] = 4.99 (s, 2H, $C_5H_2{}^tBu_3$), 4.91 (s, 2H, $C_5H_2{}^tBu_3$), 1.45 (s, 18H, $C_5H_2{}^tBu_3$), 1.31 (s, 18H, $C_5H_2{}^tBu_3$), 1.30 (s, 9H, $C_5H_2{}^tBu_3$), 1.22 (s, 9H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (C_6D_6, 293 K): δ [ppm] = 354.3 (d, $^1J_{PP}$ = 408 Hz, 2P, P_A), 114.6 (t, $^1J_{PP}$ = 408 Hz, $^1J_{PW}$ = 203 Hz, 1P, P_X).

^{31}P NMR (C_6D_6, 293 K): δ [ppm] = 354.3 (d, $^1J_{PP}$ = 408 Hz, 2P, P_A), 114.6 (t, $^1J_{PP}$ = 408 Hz, $^1J_{PW}$ = 203 Hz, 1P, P_X).

LIFDI-MS (toluene/CH_2Cl_2): *m/z* = 1000.2 (100 %, $[M]^+$).

EA $C_{39}H_{58}O_5CoNiP_3W$: calc [%]: C: 46.78; H: 5.84; found [%]: C: 46.71; H: 5.64.

ATR-IR (Ge crystal): $\bar{\nu}$ = 2064 (s, CO), 1986 (m, CO), 1977 (m, CO), 1929 (vs, CO), 1916 (s, CO), 1892 (w, CO) cm^{-1}.

1.5 Synthesis of [(Cp'''Ni)$_2$(μ,η^2:η^2-P$_2$)] (5)

A solution of **3** (70 mg, 0.104 mmol) in 20 mL toluene was stirred heated under reflux for one day. The solvent was removed under reduced pressure and the resulting brown solid was purified by a short column chromatography (SiO_2, hexane, 12 x 2 cm) using hexane/toluene 6:1 as an eluent. At first a red fraction of **5** was eluted, followed by a violet fraction of **D**. The solvent of the red fraction was removed *in vacuo*, the residue was dissolved in a small amount hexane and stored at -30 °C. After a few days **5** can be obtained as red blocks. The supernatant was decanted off and dried *in vacuo*.

Yield: 17 mg (51 %).

^{1}H NMR (C_6D_6, 293 K): δ [ppm] = 5.34 (s, 2H, $C_5H_2^tBu_3$), 1.38 (s, 18H, $C_5H_2{}^tBu_3$), 1.34 (s, 9H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (C_6D_6, 293 K): δ [ppm] = 282.7 (s, Ni_2P_2).

LIFDI-MS (toluene): *m/z* = 644.5 (100 %, $[M]^+$).

EI-MS (70 eV, toluene): *m/z* = 644.2 (100 %, $[M]^+$).

3. NMR studies

3.1 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-P$_5$)] (1)

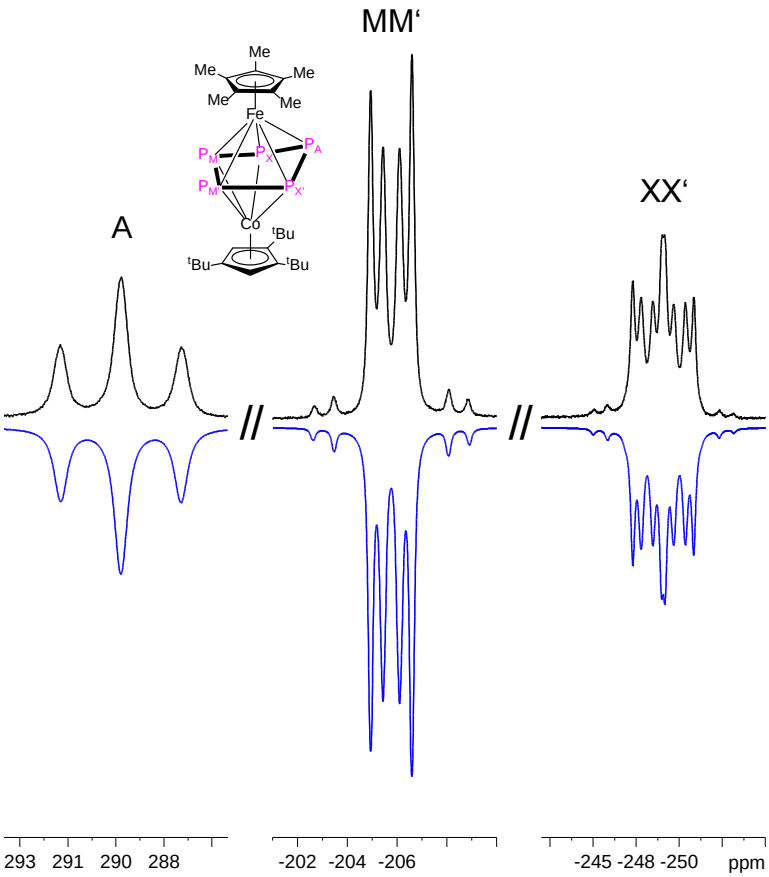


Figure S1: $^{31}P\{^1H\}$ NMR spectrum of **1** in toluene-d$_8$ at 213 K (measured top (black) and simulated bottom (blue)).

Table S1: Coupling constants obtained from the simulation in Figure **S1**.

J [Hz]		δ [ppm]	
$^1J_{P_AP_X} = {}^1J_{P_AP_{X'}}$	304.86	P_A	289.4
$^1J_{P_MP_X} = {}^1J_{P_{M'}P_{X'}}$	286.90	$P_{M/M'}$	-205.8
$^1J_{P_MP_{M'}}$	-386.68	$P_{X/X'}$	-249.1
$^1J_{P_XP_{X'}}$	76.73		
$^2J_{P_AP_M} = {}^2J_{P_AP_{M'}}$	13.27		
$^2J_{P_MP_{X'}} = {}^2J_{P_{M'}P_X}$	-18.19		
R-factor [%]	0.45		

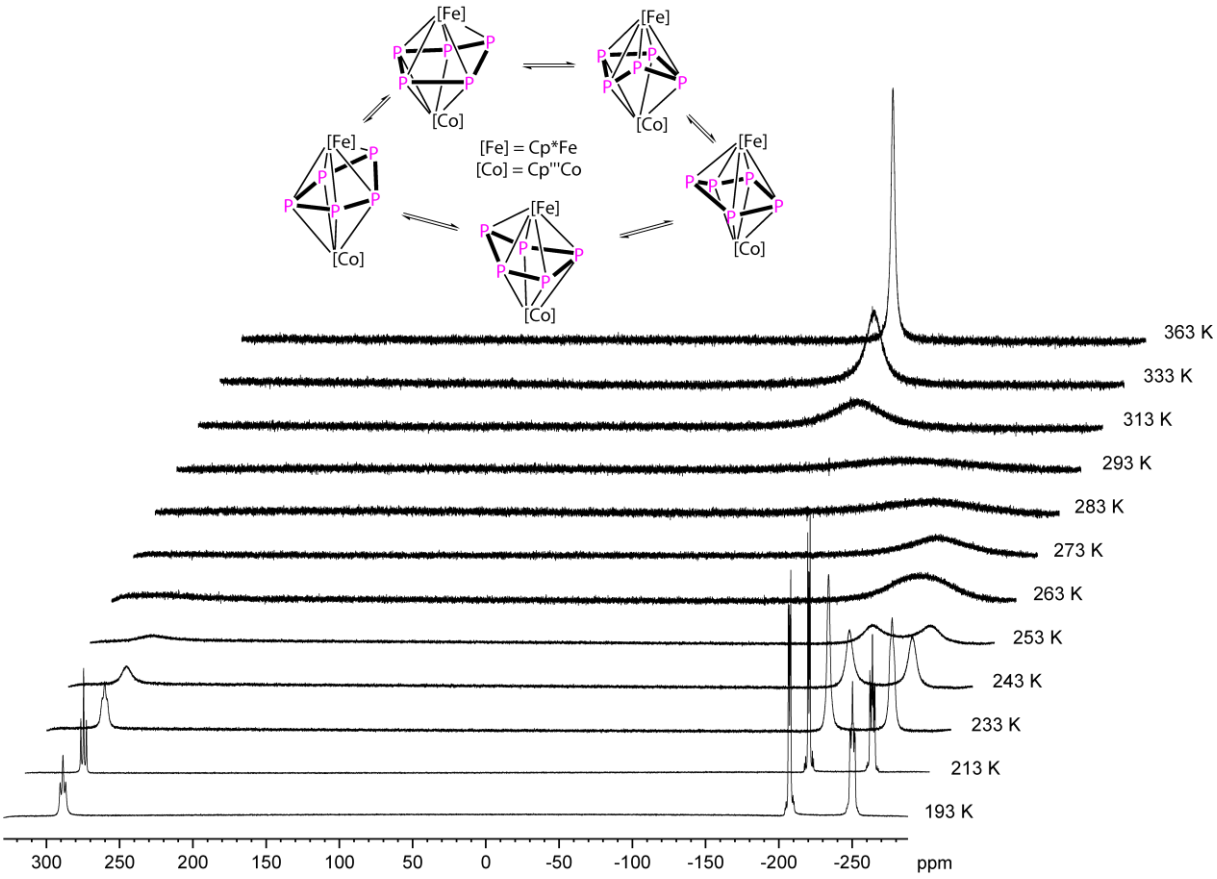


Figure S2:$^{31}P\{^{1}H\}$ NMR spectra of **1** in toluene-d_8 at different temperatures between 193 and 363 K and the proposed dynamic process.

Determination of activation barrier of the dynamic process illustrated in Figure S2.

The free activation enthalpy $\Delta G^{\ddagger}_{T_c}$ of this process can be calculated using the coalescence temperature T_c and the rate constant k_c at this temperature.[7] The rate constant k_c can be determined from the distance $\Delta\nu$ of the signals at δ = -205.8 and -249.1 ppm and their coupling constant J. Thereby, the distance of the two signals is calculated at a temperature, which is as far as possible below the coalescence temperature.

$$k_c = 2.22\sqrt{\Delta\nu^2 + 6J^2}$$

Moreover, the free activation enthalpy $\Delta G^{\ddagger}_{T_c}$ can be determined with the aid of the Eyring equation.

$$k = \chi \frac{k_B T}{h} e^{-\frac{\Delta G^{\ddagger}_{T_c}}{RT}}$$

$$\Delta G^{\ddagger}_{T_c} = -RT_c \ln\left(\frac{hk_c}{\chi k_B T_c}\right)$$

k_B = 1.3805 · 10^{-23} J K^{-1} (Boltzmann constant)

R = 8.3145 J K^{-1} mol^{-1} (universal gas constant)

h = 6.6261 · 10^{-34} J s

χ = transmission coefficient, generally equal to 1

The distance $\Delta\nu$ of the signals was calculated to be 6959.9 Hz with a coupling constant J of 286.6 Hz, which enables the calculation of the rate constant k_c to be 15529.5 s^{-1}. By entering this value into the Eyring equation the free activation enthalpy $\Delta G^{\ddagger}_{T_c}$ is 48.2 kJ mol^{-1}.

3.2 Reaction of [(Cp*Fe)(Cp’’’Co)(μ,η^5:η^4-P$_5$)] (1) with [W(CO)$_5$(thf)]

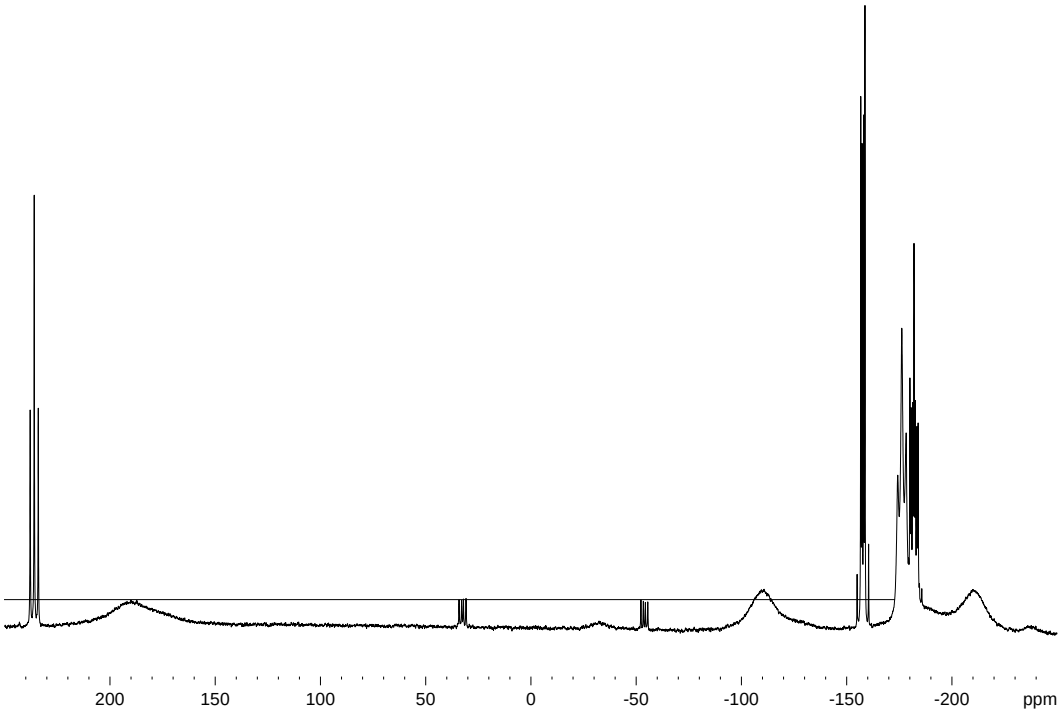


Figure S3: $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture of the reaction of **1** with [W(CO)$_5$(thf)].

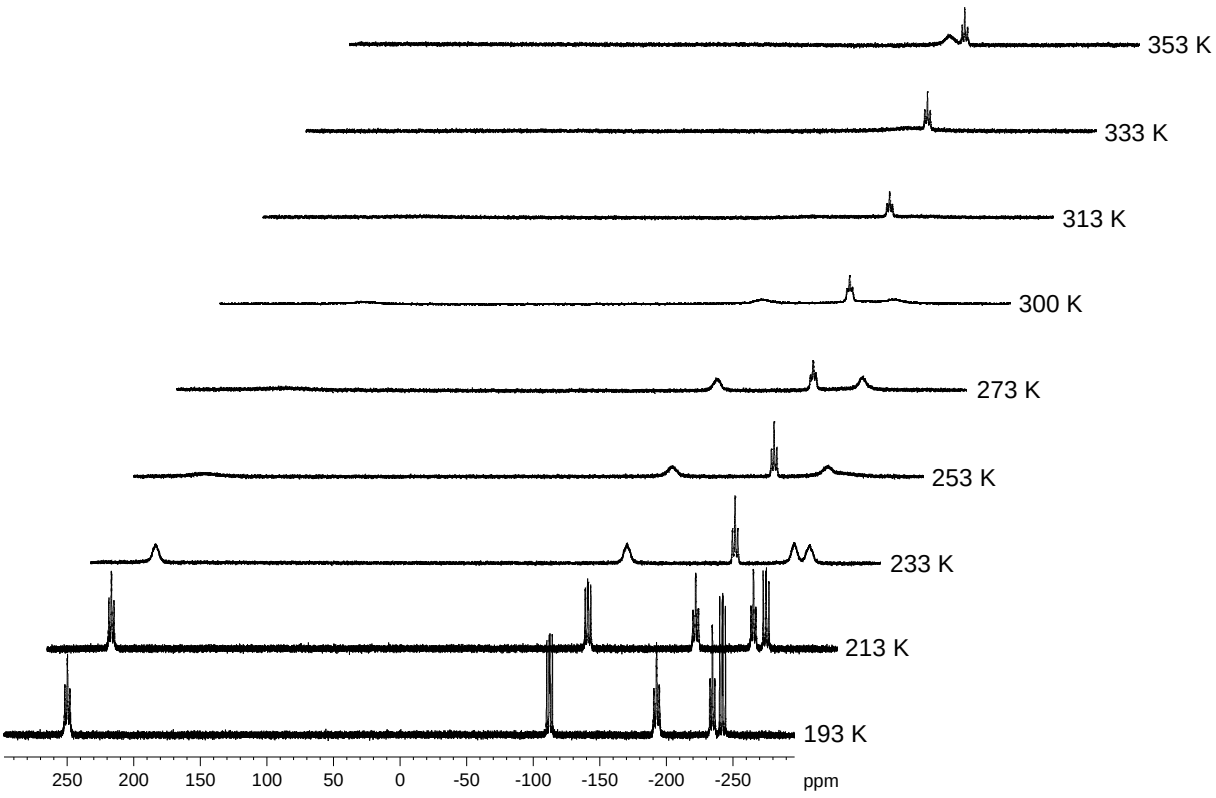


Figure S4:^{1}H NMR spectra of **2a** in toluene-d$_8$ at different temperatures between 193 and 353 K.

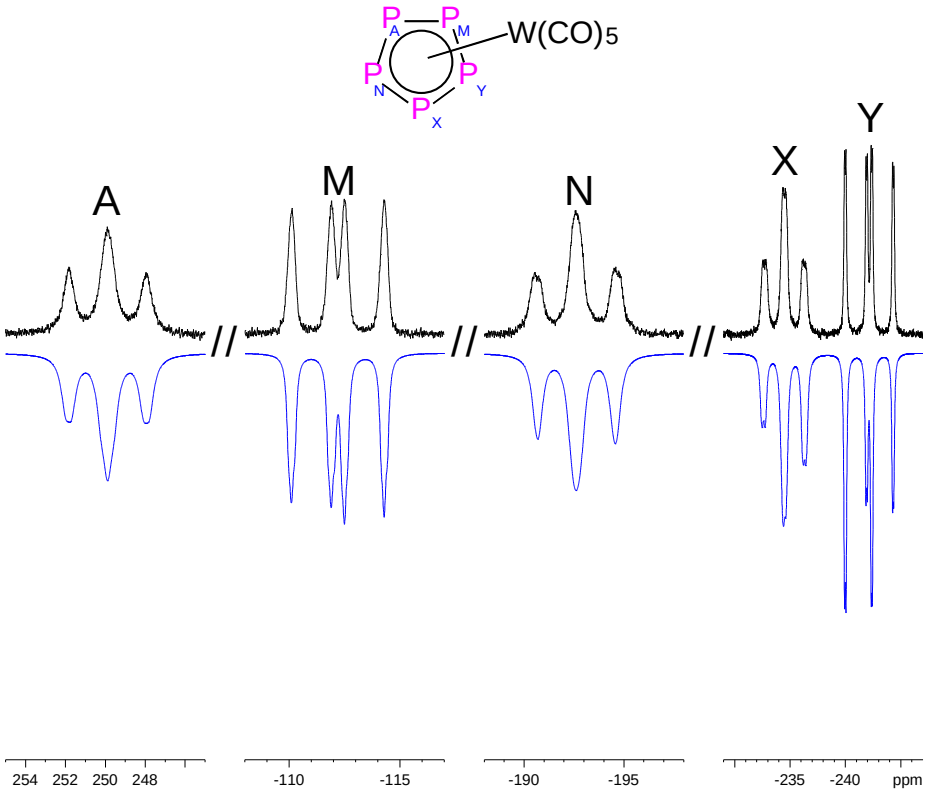


Figure S5: $^{31}P\{^{1}H\}$ NMR spectrum of **2a** in toluene-d_8 at 193 K (measured top (black) and simulated bottom (blue)).

Table S2: Coupling constants obtained from the simulation in Figure **S5**.

J [Hz]		δ [ppm]	
	290.22		
$^{1}J_{P_AP_M}$			
$^{1}J_{P_AP_N}$	342.91		
$^{2}J_{P_AP_X}$	50.52	P_A	249.9
$^{2}J_{P_AP_Y}$	2.46	P_M	-112.2
$^{2}J_{P_MP_N}$	20.98	P_N	-192.6
$^{2}J_{P_MP_X}$	20.51	P_X	-234.6
$^{2}J_{P_MP_Y}$	393.49	P_Y	-242.0
$^{1}J_{P_NP_X}$	293.79		
$^{2}J_{P_NP_Y}$	14.93		
$^{1}J_{P_XP_Y}$	312.23		
R-factor [%]	2.56		

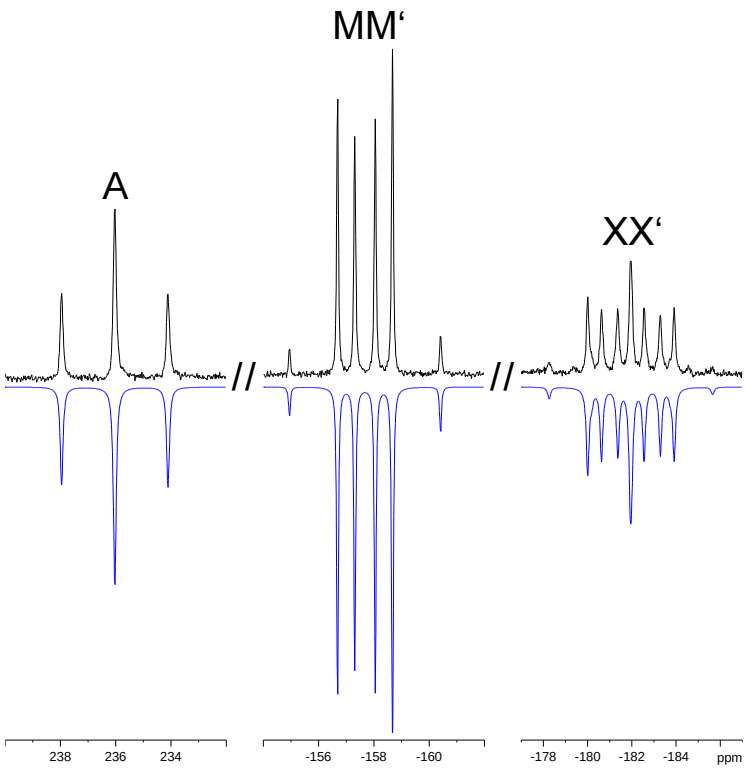


Figure S6: $^{31}P\{^{1}H\}$ NMR spectrum of **2b** in C_6D_6 at 293 K (measured top (black) and simulated bottom (blue)).

Table S3: Coupling constants obtained from the simulation in Figure **S5**.

J [Hz]		δ [ppm]	
$^{1}J_{P_AP_X} = {}^{1}J_{P_AP_X'}$	312.04	P_A	236.0
$^{1}J_{P_MP_X} = {}^{1}J_{P_M'P_X'}$	323.11	$P_{M/M'}$	-157.7
$^{1}J_{P_MP_M'}$	-384.20	$P_{X/X'}$	-181.9
$^{1}J_{P_XP_X'}$	2.63		
$^{2}J_{P_AP_M} = {}^{2}J_{P_AP_M'}$	2.82		
$^{2}J_{P_MP_X'} = {}^{2}J_{P_M'P_X}$	-0.87		
R-factor [%]	0.82		

3.3 [(Cp’’’Co)(Cp’’’Ni)(μ,η^3:η^3-P$_3$] (3)

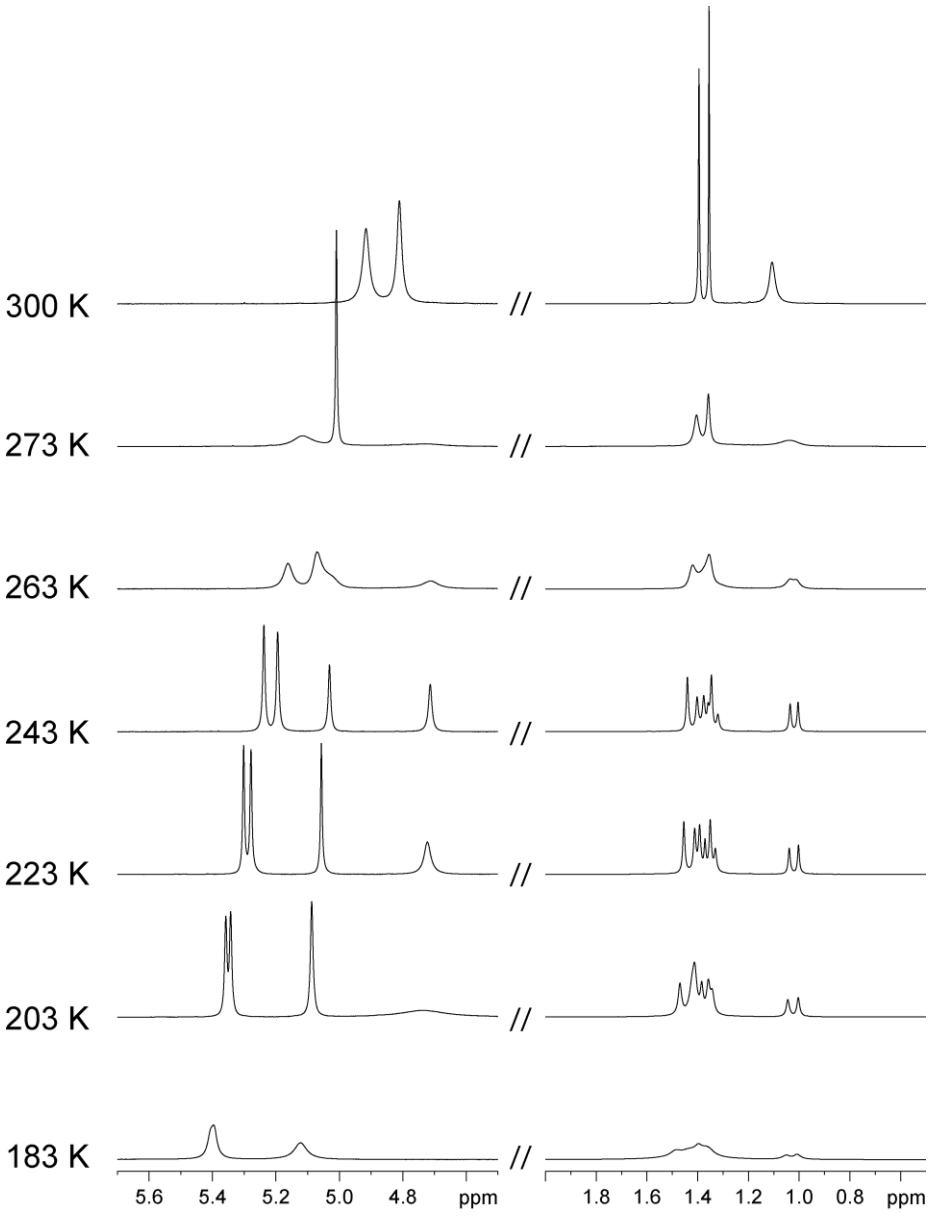


Figure S7:^{1}H NMR spectra of **3** in toluene-d$_8$ at different temperatures between 183 and 300 K (left part zoomed in).

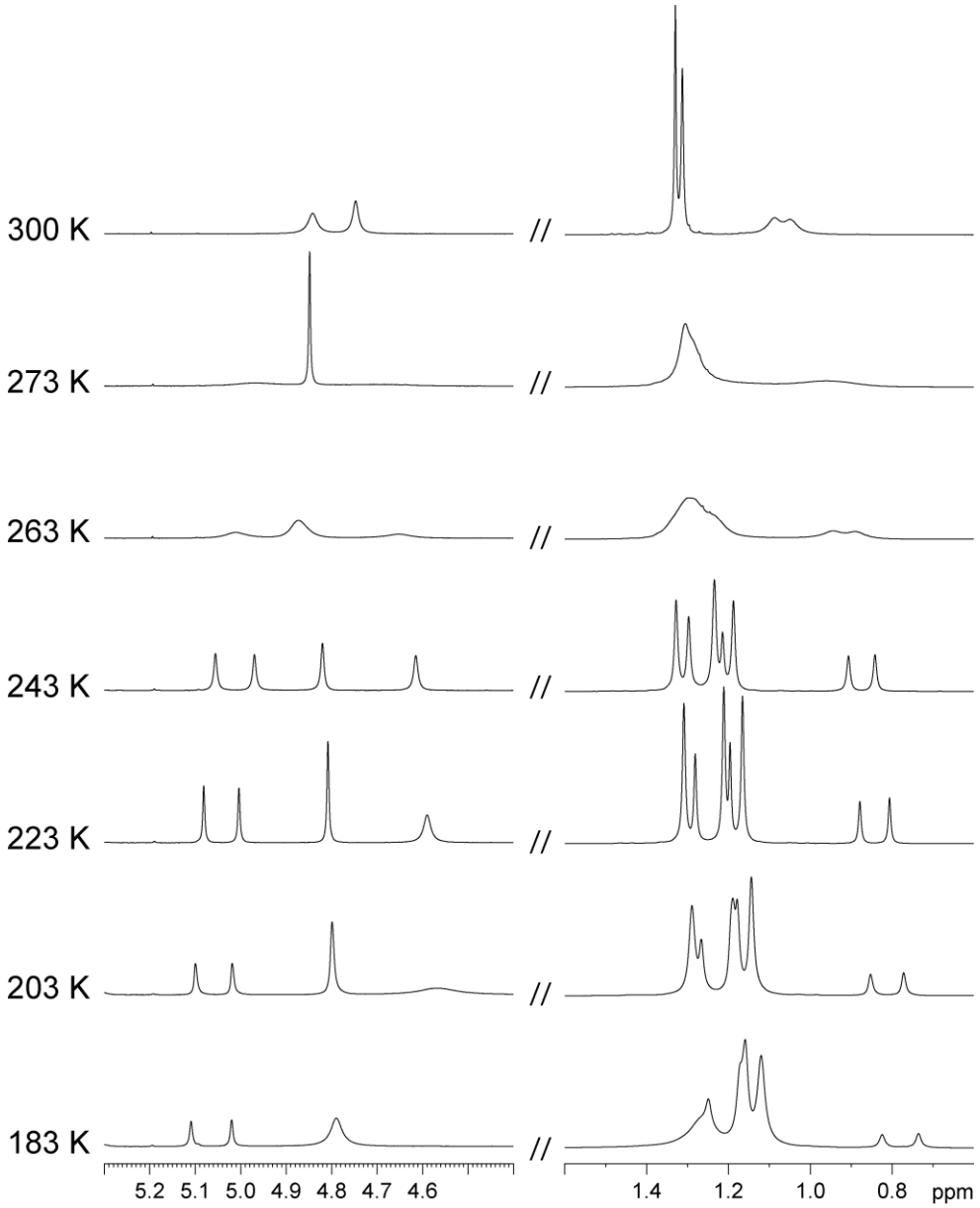


Figure S8:[1]H NMR spectra of **3** in CD_2Cl_2 at different temperatures between 183 and 300 K (left part zoomed in).

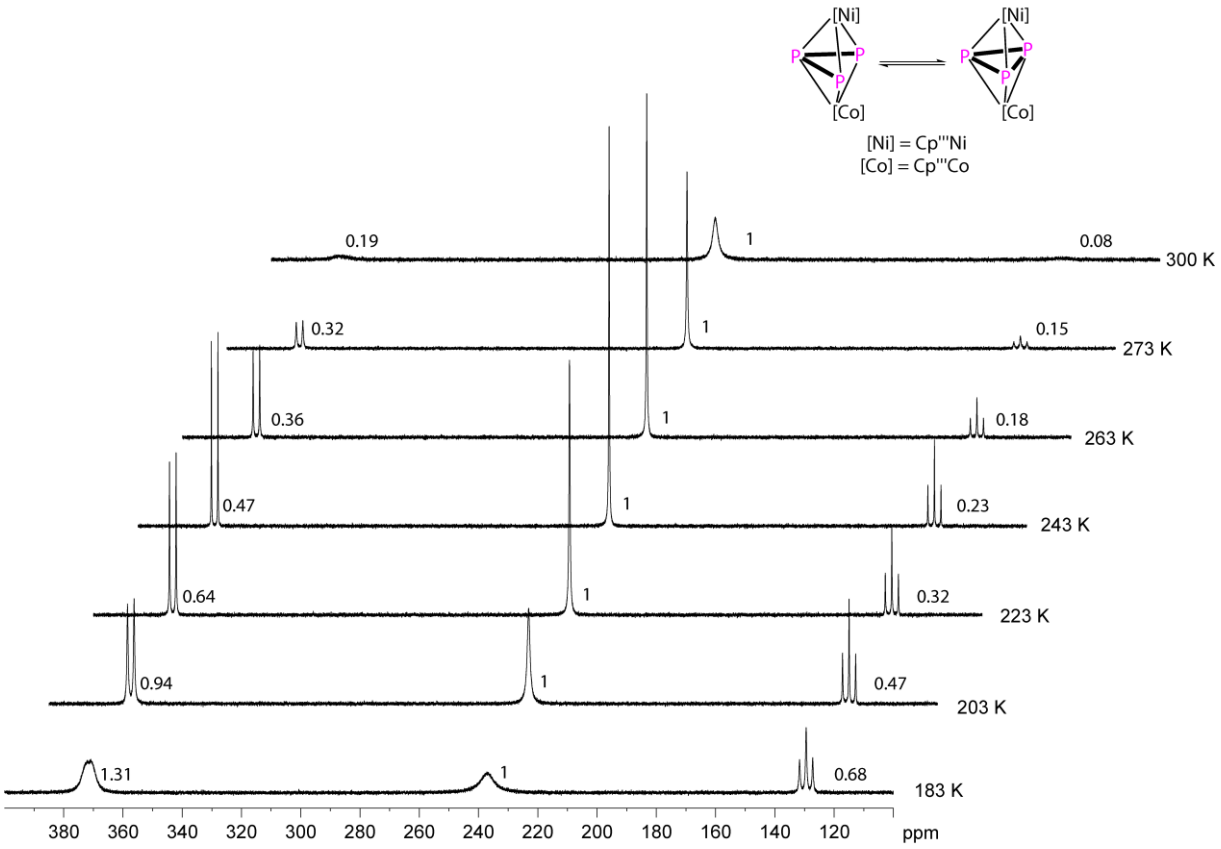


Figure S9:$^{31}P\{^{1}H\}$ NMR spectra of **3** in toluene-d_8 at different temperatures between 183 and 300 K and the proposed temperature dependent equilibrium (integrals given in the spectra).

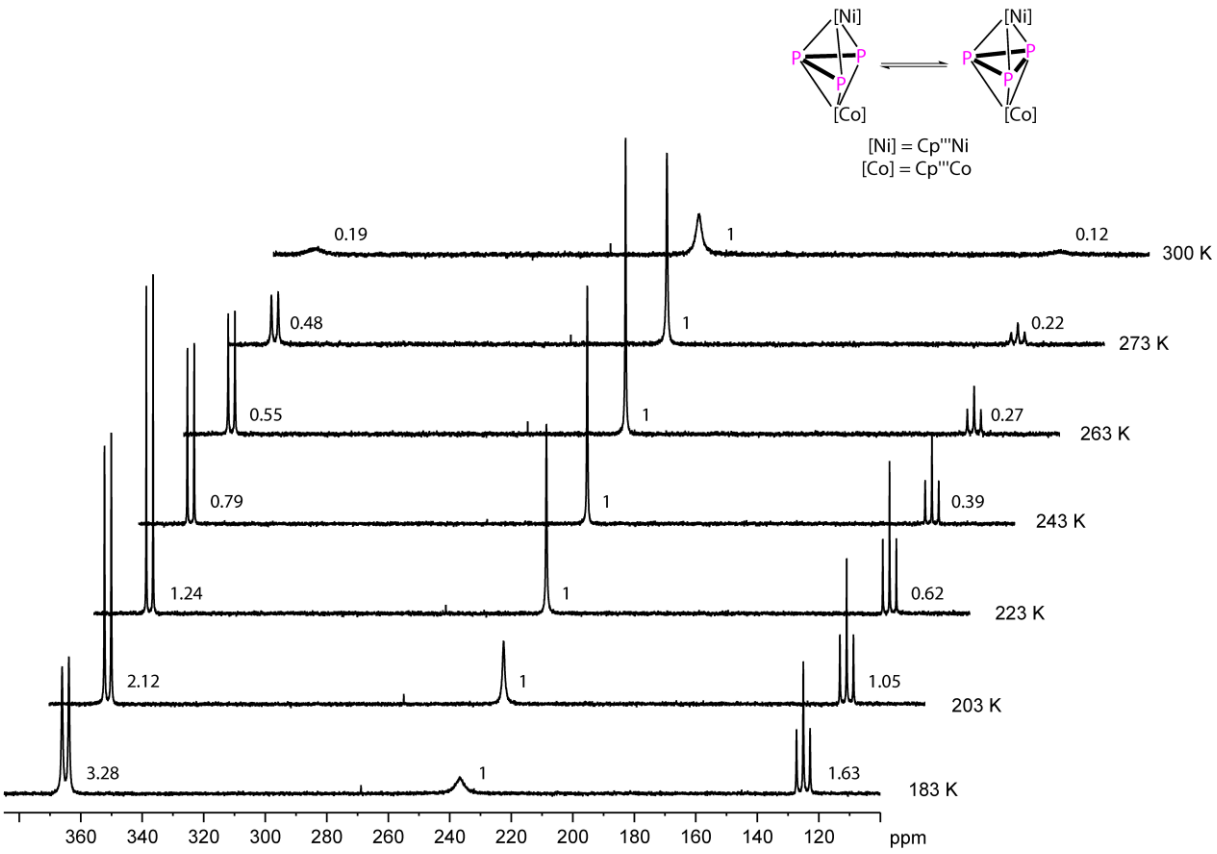


Figure S10:$^{31}P\{^{1}H\}$ NMR spectra of **3** in CD_2Cl_2 at different temperatures between 183 and 300 K and the proposed temperature dependent equilibrium (integrals given in the spectra).

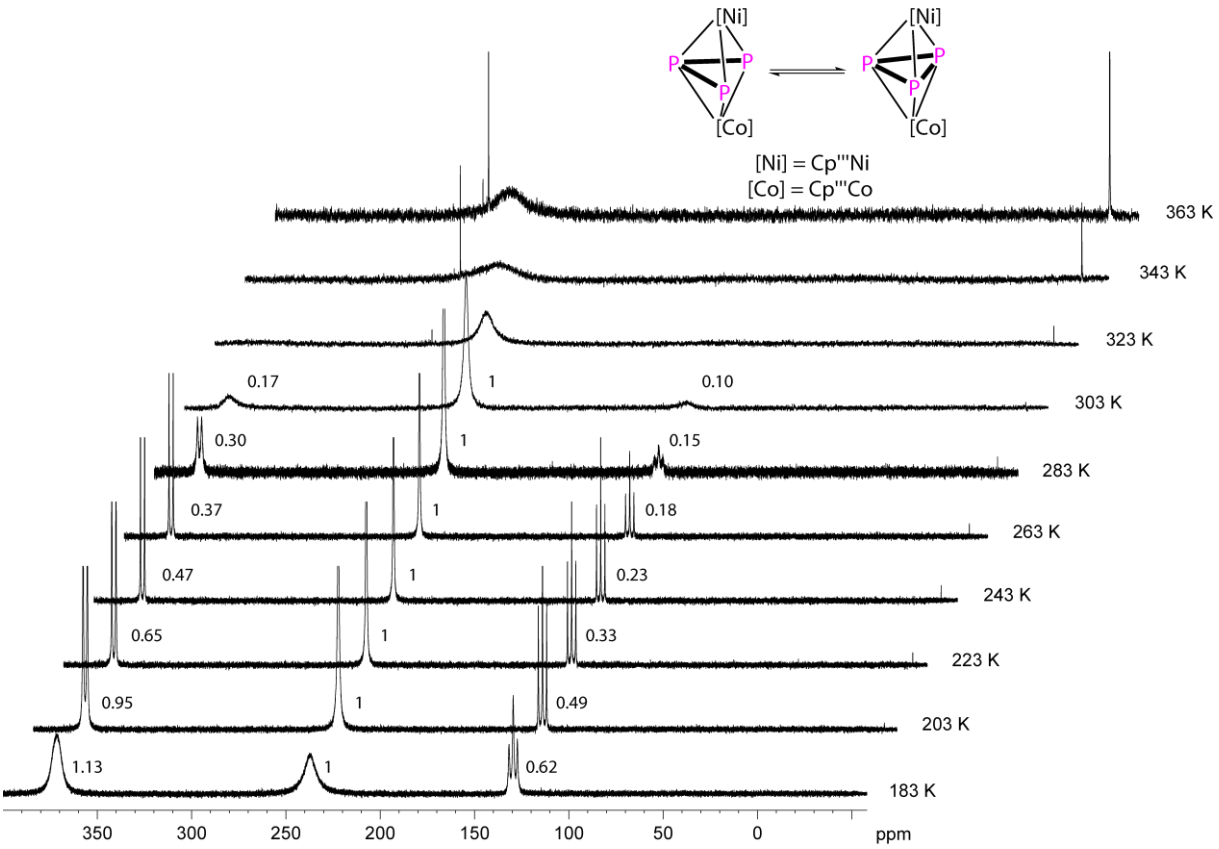


Figure S11:$^{31}P\{^{1}H\}$ NMR spectra of **3** in toluene-d_8 at different temperatures between 183 and 363 K and the proposed temperature dependent equilibrium (integrals given in the spectra).

3.4 [(Cp’’’Co)(Cp’’’Ni)(μ$_3$,η^3:η^2:η^1-P$_3$){W(CO)$_5$}] (4)

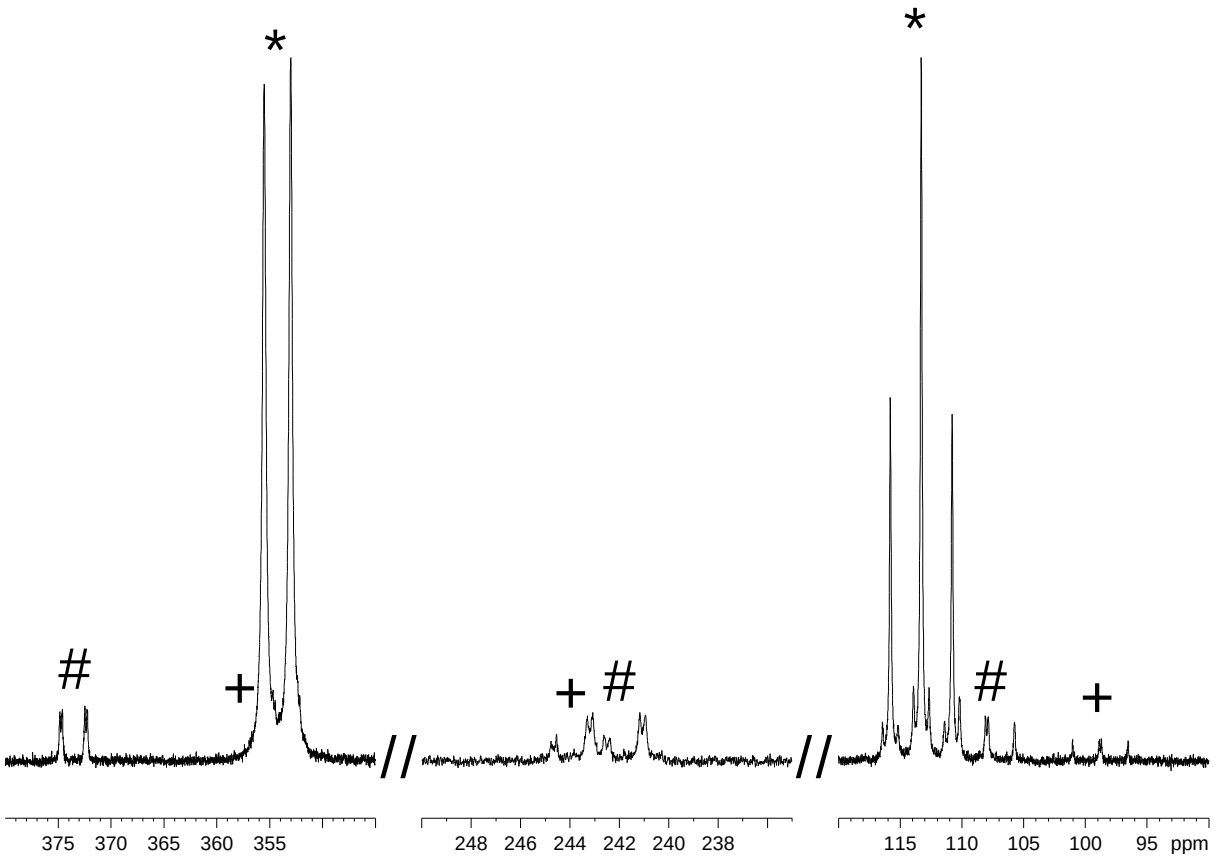


Figure S12: $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture from the reaction of **3** with [W(CO)$_5$(thf)] in C_6D_6 at 293 K. Signals marked with * belong to **4**, marked with # belong to isomer **I4-C** and + to isomer **I4-B**.

Compound **4**:

$^{31}P\{^1H\}$ NMR (C_6D_6, 293 K): δ [ppm] = 354.3 (d, $^1J_{PP}$ = 404 Hz, 2P, P_A), 113.3 (d, $^1J_{PP}$ = 406 Hz, $^1J_{PW}$ = 199 Hz, 1P, P_X).

Compound **I4-C**:

$^{31}P\{^1H\}$ NMR (C_6D_6, 293 K): δ [ppm] = 373.5 (dd, $^1J_{PP}$ = 386 Hz, $^2J_{PP}$ = 36 Hz, 0.1P, P_A), 242.1 (dd, $^1J_{PP}$ = 344 Hz, $^2J_{PP}$ = 36 Hz, 0.1P, P_M), 108.0 (dd, $^1J_{PP}$ = 386 Hz, $^1J_{PP}$ = 344 Hz 0.1P, P_X).

Compound **I4-B**:

$^{31}P\{^1H\}$ NMR (C_6D_6, 293 K): δ [ppm] = approx. 353 (overlapped by signal of **4**), 243.6 (dd, $^1J_{PP}$ = 345 Hz, $^2J_{PP}$ = 33 Hz, 0.04P, P_M), 98.8 (dd, $^1J_{PP}$ = 380 Hz, $^1J_{PP}$ = 345 Hz 0.04P, P_X).

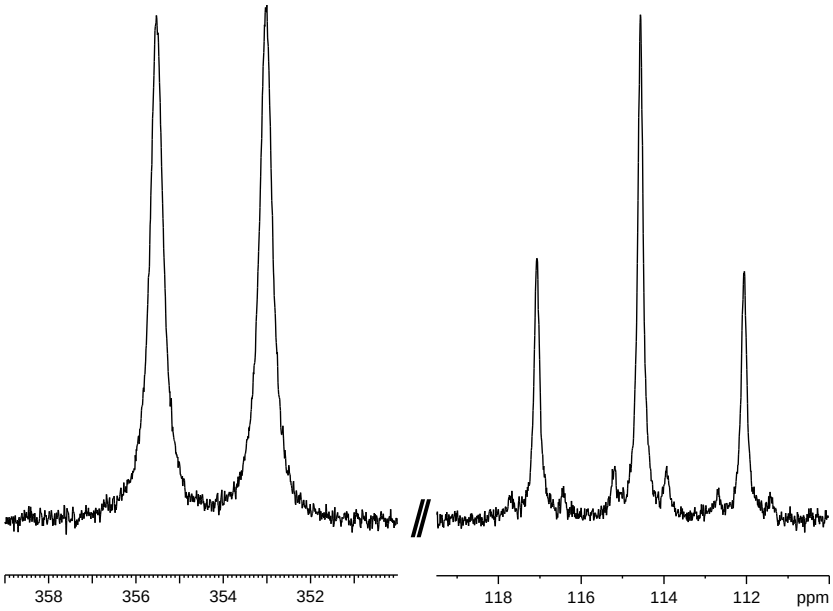


Figure S13: $^{31}P\{^{1}H\}$ NMR spectrum of **4** in C_6D_6 at 293 K.

4. Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on either an Gemini Ultra diffractometer (Oxford diffraction) with an AtlasS2 detector Mo radiation (λ = 0.71073 Å) (**1**), a GV 50 diffractometer (Rigaku, formerly Agilent Technologies) with TitanS2 detector from applying applying Cu-K*α* radiation (λ = 1.54178 Å) (**2a**) or Cu-K*β* radiation (λ = 1.39222 Å) (**3**) or SuperNova (Agilent Technologies) with an Atlas detector applying Cu-K*α* radiation (λ = 1.54178 Å) (**2b**, **4**, **5**). All measurements were performed at 123 K. An analytical numeric absorption correction[8] using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid using spherical harmonicsas implemented in SACLE3 ABSPACK was applied (**1**, **2a**, **3**, **4**, **5**).[9] A numerical absorption correction based on gaussian integration over a multifaceted crystal model using *CrysAlisPro* using spherical harmonicsas implemented in SACLE3 ABSPACK was applied (**2b**). All structures were solved by direct methods with ShelXT[10] and Olex2[11] and refined by full-matrix least-squares method against F^2 in anisotropic approximation using ShelXL.[10] Hydrogen atoms were refined in calculated positions using riding on pivot atom model.

CCDC-1965029 (**1**), CCDC-1965030 (**2a**), CCDC-1965031 (**2b**), CCDC-1965032 (**3**), CCDC-1965033 (**4**) and CCDC-1965034 (**5**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

4.1 [(Cp*Fe)(Cp’’’Co)(μ,η^5:η^4-P_5)] (1)

Compound **1** crystallizes from a concentrated solution in ortho-difluoro benzene layered with hexane at -30 °C in the triclinic space group $P\bar{1}$ as dark violet plates. The asymmetric unit contains five molecules **1** while three of them are heavily disordered. The P_5 ligand of two molecules is disordered over two positions (occupancy of 0.95 and 0.05) and of one molecule disordered over four positions (occupancy of 0.40, 0.35, 0.15 and 0.10) and two ^{t}Bu groups of the latter molecule is disordered over two positions (occupancy of 0.50 and 0.50). The restrains SADI, SIMU and ISOR were applied to describe the disorder. Bond lengths and distances are given of one non-disordered molecule. The complete structure in solid state is depicted in Figure S14 and S15.

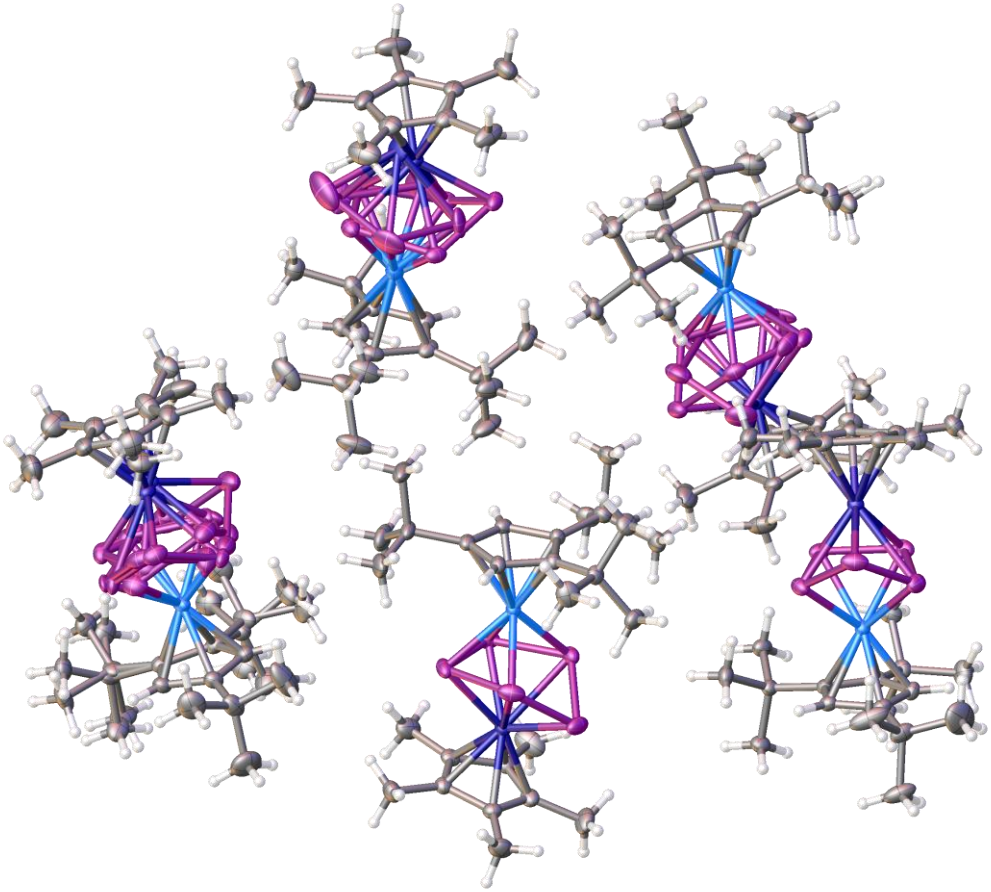


Figure S14: Molecular structure of **1** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

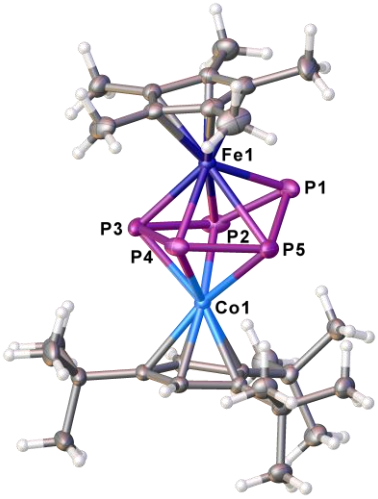


Figure S15: Molecular structure of **1** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Depicted is one of the non-disordered molecules within the asymmetric unit. Selected bond lengths [Å] and angles [°]: P1-P2 2.1519(11), P2-P3 (2.2307(11), P3-P4 2.1266(10), P4-P5 2.2459(10), P1-P5 2.1505(11), Co1-P1 3.3325(8), Co1-P2 2.2991(8), Co1-P3 2.3228(7), Co1-P4 2.3159(7), Co1-P5 2.3088(7), Fe1-P1 2.2697(8), Fe1-P2 2.5299(8), Fe1-P3 2.3481(7), Fe1-P4 2.3396(7), Fe1-P5 2.5056(7), P1-P2-P3 112.96(4), P2-P3-P4 100.27(4), P3-P4-P5 100.06(4), P4-P5-P1 112.90(4), P2-P1-P5 85.37(4), Cp*-Fe-Co-Cp''' 13.161 (166.839).

4.2 [(Cp*Fe)(Cp’’’Co)(μ$_3$,η^5:η^4:η^1-P$_5$){W(CO)$_5$}] (2a)

Compound **2a** crystallized from a concentrated solution in pentane at -30 °C in the monoclinic space group $P2_1/n$ as black blocks. The asymmetric contains one molecule of **2a**. The structure in solid state is given in Figure S16.

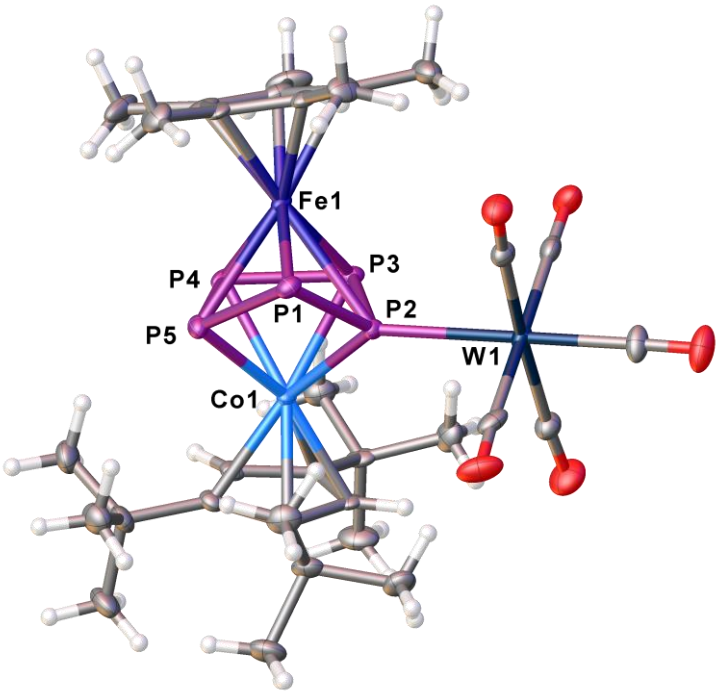


Figure S16: Molecular structure of **1** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.1350(13), P2-P3 2.2476(14), P3-P4 2.1269(16), P4-P5 2.2504(16), P1-P5 2.1720(16), P2-W1 2.5537(10), P1-P2-P3 112.60(6), P2-P3-P4 98.52(6). P3-P4-P5 101.18(6), P1-P5-P4 111.68(6), P2-P1-P5 84.61(5), Cp*-Fe-Co-Cp’’’ 22.276 (157.724), P2-P4-P5-P1 34.695, P2-P3-P5-P1 34.110.

4.3 [(Cp*Fe)(Cp’’’Co)(μ$_4$,η^5:η^4:η^1:η^1-P$_5$){W(CO)$_5$}$_2$] (2b)

Compound **2b** crystalizes from a concentrated solution in toluene while the solvent is slowly removed *in vacuo* in the orthorhombic space group *Pca2$_1$* as dark brown plates. The asymmetric unit contains two molecules of **2b**. A refinement as an inverse twin was carried out. The restraint ISOR was applied to two carbon atoms. The structure in solid state is shown in Figure S17 and S18.

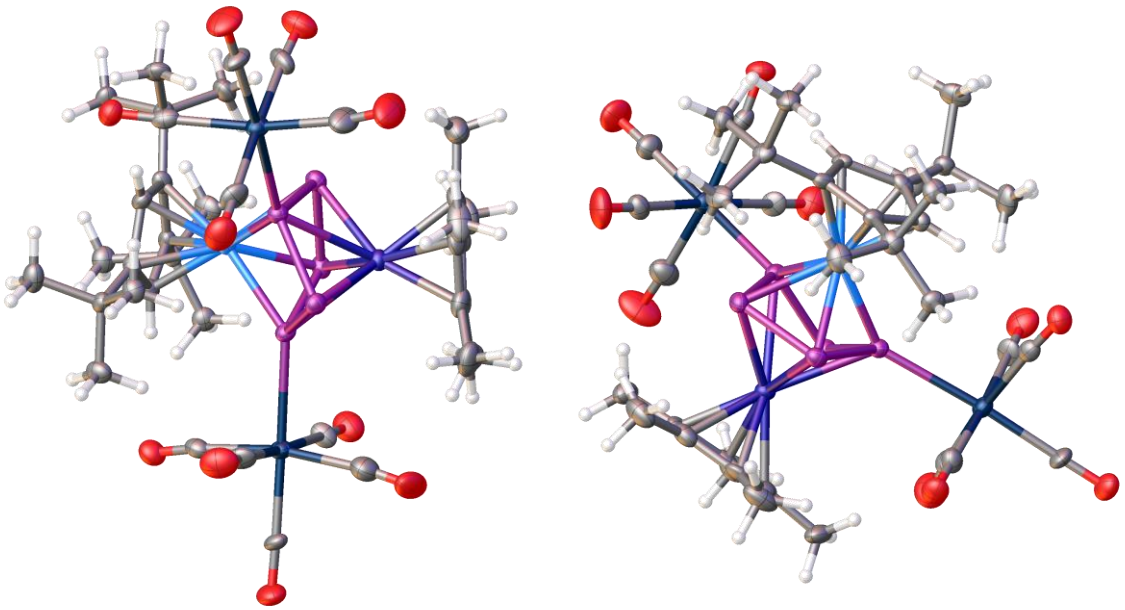


Figure S17: Molecular structure of **2a** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

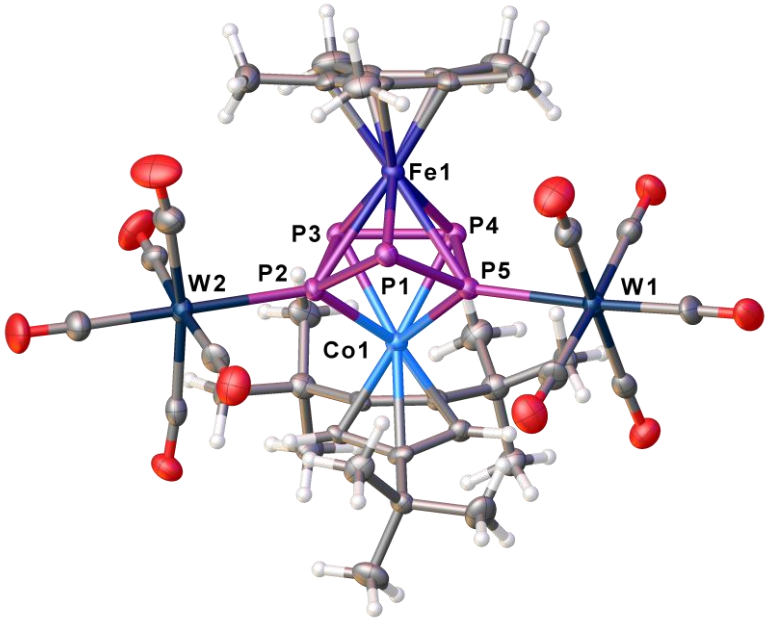


Figure S18: Molecular structure of **2a** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.148(4), P2-P3 2.236(4), P3-P4 2.136(4), P4-P5 2.263(4), P1-P5 2.154(4), P2-W2 2.564(3), P5-W1 2.551(2), P1-P2-P3 110.79(15), P2-P3-P4 100.04(15), P3-P4-P5 98.68(15), P1-P5-P4 111.13(15), P2-P1-P5 83.62(13), Cp*-Fe-Co-Cp’’’ 25.659 (154.341), P2-P4-P5-P1 37.833, P2-P3-P5-P1 36.159.

4.4 [(Cp’’’Co)(Cp’’’Ni)(μ,η^3:η^3-P_3)] (3)

Compound **3** crystallizes from a concentrated solution in ortho-difluoro benzene layered with acetonitrile at -30 °C in the monoclinic space group $P2_1/c$ as dark brown needles. The asymmetric unit contains one molecule **3**. The structure in solid state is shown in figure S19.

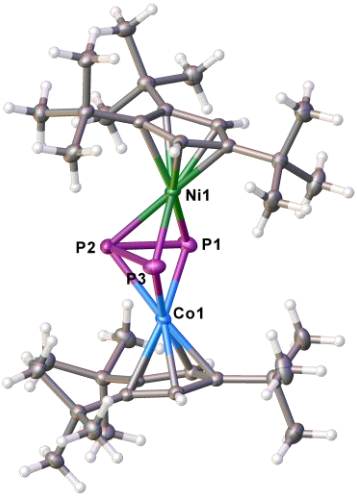


Figure S19: Molecular structure of **3** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.1895(6), P2-P3 2.1945(6), P1-P3 2.7619(6), Co1-Ni1 3.3941(5), Ni1-P1 2.1826(5), Ni1-P2 2.3538(5), Ni1-P3 2.1931(5), Co1-P1 2.1965(5), Co1-P2 2.3457(4), Co1-P3 2.1849(5), Ni1-Co1 3.3941(5), P1-P2-P3 78.10(2), Ni1-P1-Co1 101.620(18), Ni1-P2-Co1 92.476(15), Ni1-P3-Co1 101.661(19), Cp’’’-Ni-Co-Cp’’’ 18.064(161.936).

4.5 [(Cp’’’Co)(Cp’’’Ni)(μ$_3$,η^3:η^2:η^1-P$_3$){W(CO)$_5$}] (4)

Compound **4** crystallizes from a concentrated solution in CH_2Cl_2 layered with MeCN at room temperature in the triclinic space group $P\bar{1}$ in form of dark brown blocks. The asymmetric unit contains two molecules of **4**. The structure in solid state is shown in Figure S20 and S21.

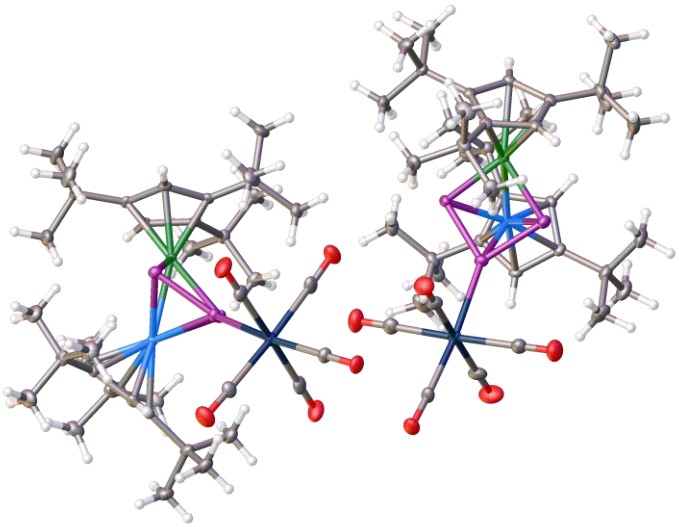


Figure S20: Molecular structure of **4** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

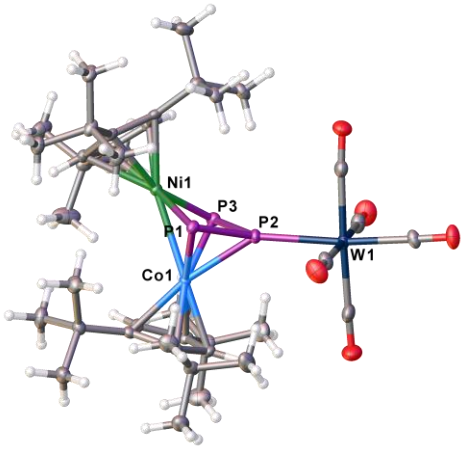


Figure S21: Molecular structure of **4** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.1213(9), P2-P3 2.1238(10), P1-P3 3.0005(11), Ni1-P1 2.1928(8), Ni1-P2 3.0425(9), Ni1-P3 2.1882(8), Ni1-Co1 2.6182(6), Co1-P1 2.2397(8), Co1-P2 2.3277(8), Co1-P3 2.2362(8), W1-P2 2.4846(7), P1-P2-P3 89.95(4), Cp’’’-Ni-Co-Cp’’’ 52.364.

4.6 [(Cp'''Ni)$_2$(μ,η^2:η^2-P$_2$)] (5)

Compound **5** crystallizes from a concentrated solution in hexane stored at -30 °C in the triclinic space group $P\bar{1}$ as red blocks. The asymmetric unit contains one molecule **5**. The structure in solid state is shown in figure S22.

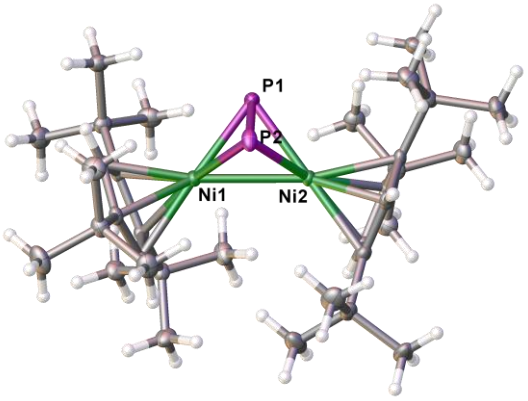


Figure S22: Molecular structure of **5** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ni1-Ni2 2.5848(5), P1-P2 2.0805(8), Ni1-P1 2.1995(6), Ni1-P2 2.2066(6), Ni2-P1 2.1983(6), Ni2-P2 2.1987(6), Ni2-Ni1-P1 53.982(17), Ni2-Ni1-P2 53.933(16), Ni1-Ni2-P1 54.023(16), Ni1-Ni2-P2 54.216(16), P1-Ni1-P2 56.35(2), P1-Ni1-P2 56.48(2), Ni1-P1-P2 62.00(1), Ni1-P2-P1 61.65(2), Ni2-P1-P2 61.77(2), Ni2-P2-P1 61.75(2), Ni1-P1-Ni2 71.99(2), Ni1-P2-Ni2 71.851(19).

4.7 Crystallographic information

Table S4: Crystallographic data for all compounds

	1	**2a**	**2b**	**3**
CCDC	1965029	1965030	1965031	1965032
Formula	$C_{135}H_{220}Co_5Fe_5P_{25}$	$C_{32}H_{44}CoFeO_5P_5W$	$C_{74}H_{88}Co_2Fe_2O_{20}P_{10}W_4$	$C_{34}H_{58}CoNiP_3$
$D_{calc.}$/ g cm^{-3}	1.407	1.717	1.947	1.270
μ/mm^{-1}	1.312	14.455	17.120	7.061
Formula Weight	3191.25	962.15	2572.10	677.35
Colour	dark black	dark black	clear brown	clear dark brown
Shape	plate	block	block	needle
Size/mm^3	0.65×0.32×0.04	0.21×0.13×0.07	0.39×0.21×0.15	0.27×0.05×0.03
T/K	123.01(10)	123.00(10)	123.00(10)	123.02(13)
Crystal System	triclinic	monoclinic	orthorhombic	monoclinic
Flack Parameter			0.503(8)	
Hooft Parameter			0.498(5)	
Space Group	P-1	$P2_1/n$	$Pca2_1$	$P2_1/c$
a/Å	11.91379(19)	10.04893(15)	12.3918(3)	14.2229(5)
b/Å	22.7577(5)	31.8158(5)	40.0229(7)	19.1947(4)
c/Å	29.2373(5)	11.94872(18)	17.6945(4)	14.6893(5)
α/°	107.5943(17)	90	90	90
β/°	94.0464(14)	102.9845(15)	90	117.956(4)
γ/°	90.3095(15)	90	90	90
V/Å^3	7534.5(3)	3722.50(10)	8775.7(3)	3542.3(2)
Z	2	4	4	4
Z'	1	1	1	1
Wavelength/Å	0.71073	1.54184	1.54184	1.39222
Radiation type	Mo K_α	Cu K_α	Cu K_α	Cu K_β
θ_{min}/°	3.339	4.043	3.734	3.713
θ_{max}/°	30.508	73.909	73.679	74.009
Measured Refl.	94291	13945	18946	24385
Independent Refl.	45861	7242	12534	9639
Reflections with I > 2(I)	36206	6591	12153	7922
R_{int}	0.0292	0.0485	0.0310	0.0347
Parameters	1814	421	1038	370
Restraints	144	0	13	0
Largest Peak	1.937	1.547	1.822	0.373
Deepest Hole	-0.760	-3.036	-1.254	-0.432
GooF	1.051	1.070	1.068	1.016
wR_2 (all data)	0.1211	0.1018	0.0899	0.0815
wR_2	0.1113	0.0986	0.0891	0.0759
R_1 (all data)	0.0661	0.0465	0.0356	0.0434
R_1	0.0480	0.0422	0.0341	0.0325

	4	**5**
CCDC	1965033	1965034
Formula	$C_{78}H_{116}Co_2Ni_2O_{10}P_6W_2$	$C_{34}H_{58}Ni_2P_2$
$D_{calc.}$/ g cm^{-3}	1.582	1.249
μ/mm^{-1}	9.910	2.371
Formula Weight	2002.50	646.16
Colour	clear dark brown	clear dark red
Shape	block	block
Size/mm^3	0.24×0.15×0.12	0.15×0.06×0.03
T/K	123.01(10)	123(1)
Crystal System	triclinic	triclinic
Space Group	*P*-1	*P*-1
a/Å	11.7671(3)	8.7286(5)
b/Å	11.8506(3)	12.1860(5)
c/Å	35.0039(6)	17.2330(9)
α/°	83.149(2)	81.990(4)
β/°	84.296(2)	88.160(4)
γ/°	60.283(2)	71.242(4)
V/Å^3	4204.39(18)	1718.57(16)
Z	2	2
Z'	1	1
Wavelength/Å	1.54184	1.54184
Radiation type	Cu K$_\alpha$	Cu K$_\alpha$
θ_{min}/°	3.820	3.867
θ_{max}/°	73.824	76.583
Measured Refl.	47322	11343
Independent Refl.	16650	6907
Reflections with I > 2(I)	15916	6103
R_{int}	0.0251	0.0415
Parameters	937	361
Restraints	0	0
Largest Peak	0.999	0.451
Deepest Hole	-0.658	-0.478
GooF	1.121	1.018
wR_2 (all data)	0.0593	0.1170
wR_2	0.0585	0.1107
R_1 (all data)	0.0299	0.0487
R_1	0.0273	0.0431

5. Computational Details

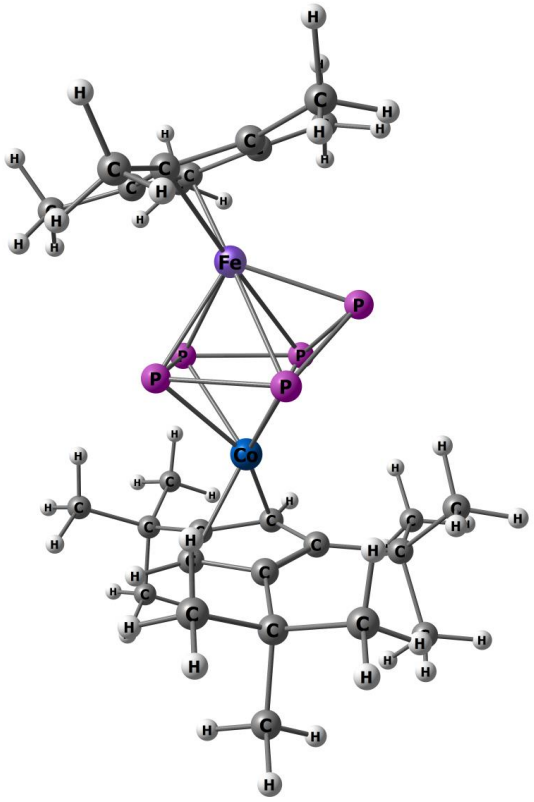
Gaussian 09 program package was used throughout.[12] Density functional theory (DFT) in form of Becke's three-parameter hybrid functioncal B3LYP[13] with def2-SVP all electron basis set[14] was employed. The Natural Bond Orbital (NBO) analysis has been performed with the NBO3.1 program implemented in Gaussian 09 program package. The figures for the energy schemata were created using OLEX2.[11] The figures for the supporting information concerning the DFT calculations were created with Chemcraft.[15]

5.1 Computations for [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-P$_5$] (1) and the reaction with [W(CO)$_5$(thf)]

Table S5: Total energies for all optimized geometries (B3LYP/def2-SVP level of theory).

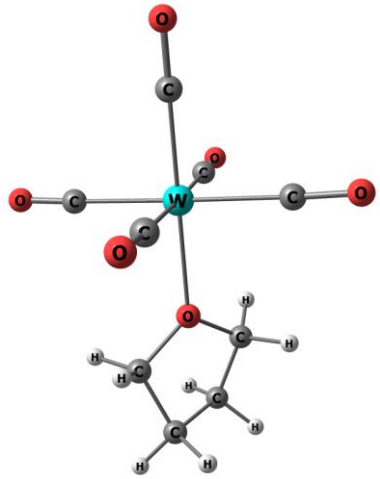
	total energy [Ha]
1 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-P$_5$]	-5407.2923483
[W(CO)$_5$(thf)]	-865.7468723
thf	-232.2786488
I2a [(Cp*Fe)(Cp'''Co)(μ$_3$,η^5:η^4:η^1-P$_5$){W(CO)$_5$}]	-6040.7694041
2a [(Cp*Fe)(Cp'''Co)(μ$_3$,η^5:η^4:η^1-P$_5$){W(CO)$_5$}]	-6040.7694595
2b [(Cp*Fe)(Cp'''Co)(μ$_4$,η^5:η^4:η^1:η^1-P$_5$){W(CO)$_5$}$_2$]	-6674.2315986

Table S6: Optimized geometries of **1**. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



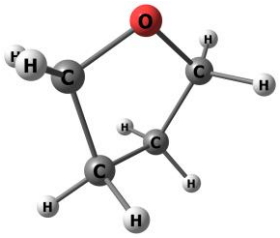
C	4.278226000	-0.413393000	-0.943268000	H	-5.404207000	-1.448600000	1.281596000
C	4.090072000	0.968651000	-0.605668000	H	-4.996592000	-0.160167000	2.433822000
C	3.924161000	1.062103000	0.818337000	C	-2.526943000	-1.092275000	3.214594000
C	3.980655000	-0.269075000	1.356288000	H	-2.840608000	-1.784091000	4.011968000
C	4.213687000	-1.178836000	0.271203000	H	-2.739455000	-0.075859000	3.574413000
C	4.458671000	-2.652751000	0.407048000	H	-1.439093000	-1.194510000	3.091486000
H	5.527218000	-2.847573000	0.609660000	C	-3.260995000	-1.687169000	-1.699773000
H	4.185933000	-3.198641000	-0.506387000	C	-2.347687000	-2.928991000	-1.642192000
H	3.882726000	-3.087587000	1.237056000	H	-1.318175000	-2.668517000	-1.922705000
C	3.901571000	-0.645904000	2.806173000	H	-2.710902000	-3.688428000	-2.354082000
H	4.911407000	-0.714374000	3.248303000	H	-2.311219000	-3.391834000	-0.652518000
H	3.411761000	-1.620779000	2.944975000	C	-3.175375000	-1.159312000	-3.151785000
H	3.332730000	0.091939000	3.389535000	H	-2.162816000	-0.809543000	-3.404027000
C	3.783776000	2.329140000	1.606502000	H	-3.884794000	-0.339134000	-3.340586000
H	4.775768000	2.750377000	1.847102000	H	-3.424980000	-1.975167000	-3.847616000
H	3.255193000	2.161384000	2.555969000	C	-4.736332000	-2.094666000	-1.468365000
H	3.223642000	3.097204000	1.052375000	H	-5.400814000	-1.216723000	-1.510505000
C	4.151530000	2.116942000	-1.568881000	H	-4.890501000	-2.586340000	-0.499553000
H	5.197831000	2.425334000	-1.742387000	H	-5.059485000	-2.800575000	-2.250881000
H	3.604544000	2.993703000	-1.194478000	C	-2.637259000	3.224383000	-0.154339000
H	3.717426000	1.851541000	-2.543997000	C	-2.058780000	3.745660000	-1.483471000
C	4.591365000	-0.941253000	-2.312140000	H	-1.001630000	3.465957000	-1.602629000
H	5.678566000	-0.897645000	-2.503918000	H	-2.125475000	4.844969000	-1.516590000
H	4.094889000	-0.353721000	-3.098354000	H	-2.616387000	3.359716000	-2.351215000
H	4.272500000	-1.986005000	-2.429141000	C	-1.883159000	3.873618000	1.022003000
C	-2.592000000	1.700517000	-0.076255000	H	-0.815423000	3.609753000	1.009423000
C	-2.659615000	0.781101000	-1.162109000	H	-2.298746000	3.565064000	1.993934000
H	-2.590597000	1.067312000	-2.206193000	H	-1.965405000	4.971087000	0.964789000
C	-2.881934000	-0.566730000	-0.699248000	C	-4.131081000	3.630499000	-0.074956000
C	-2.876256000	-0.482790000	0.762815000	H	-4.585538000	3.296597000	0.871012000
C	-2.683987000	0.907644000	1.092669000	H	-4.708442000	3.186247000	-0.901210000
H	-2.643033000	1.295909000	2.105752000	H	-4.235937000	4.726585000	-0.136155000
C	-3.284101000	-1.442203000	1.909694000	Co	-1.013337000	0.191930000	-0.035003000
C	-3.049989000	-2.943776000	1.668037000	Fe	2.408661000	-0.144459000	-0.026642000
H	-3.335173000	-3.500305000	2.574880000	P	0.830617000	1.625493000	-0.338055000
H	-1.991129000	-3.159046000	1.466002000	P	0.698436000	0.548745000	1.530759000
H	-3.655022000	-3.342732000	0.845846000	P	0.329167000	-1.550704000	0.798647000
C	-4.796403000	-1.209190000	2.165959000	P	1.346152000	-1.889035000	-1.106841000
H	-5.142969000	-1.843800000	2.998411000	P	0.476056000	-0.020287000	-1.838419000

Table S7: Optimized geometries of $[W(CO)_5(thf)]$. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



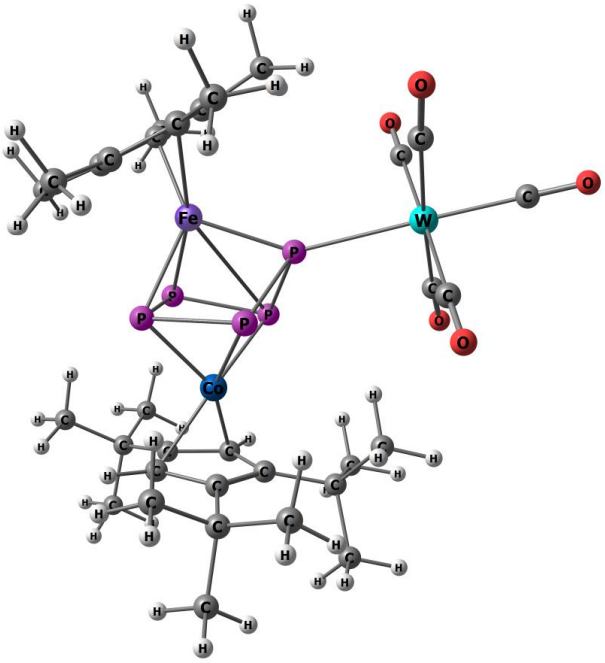
W	1.603117000	2.337707000	0.651551000
C	2.670206000	4.022345000	0.585305000
O	3.289051000	4.999227000	0.546999000
C	3.306423000	1.306739000	1.251011000
O	4.267990000	0.769036000	1.582154000
C	2.092034000	1.995139000	-1.339133000
O	2.386946000	1.842036000	-2.440829000
C	-0.078309000	3.402929000	0.050399000
O	-0.987268000	4.023395000	-0.284638000
C	1.155405000	2.745516000	2.639637000
O	0.930297000	3.008866000	3.736952000
H	-1.682819000	0.772799000	0.682919000
O	0.354506000	0.365764000	0.729898000
C	0.788996000	-0.899005000	0.180426000
C	-0.455461000	-1.782674000	0.193042000
C	-1.222789000	-1.248813000	1.410543000
C	-0.955977000	0.251720000	1.329657000
H	1.196914000	-0.715604000	-0.823981000
H	1.594405000	-1.299193000	0.820104000
H	-0.207593000	-2.851395000	0.268099000
H	-1.041663000	-1.634239000	-0.728241000
H	-0.805537000	-1.663692000	2.342322000
H	-2.296806000	-1.483650000	1.386422000
H	-0.931597000	0.755067000	2.306834000

Table S8: Optimized geometries of thf. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



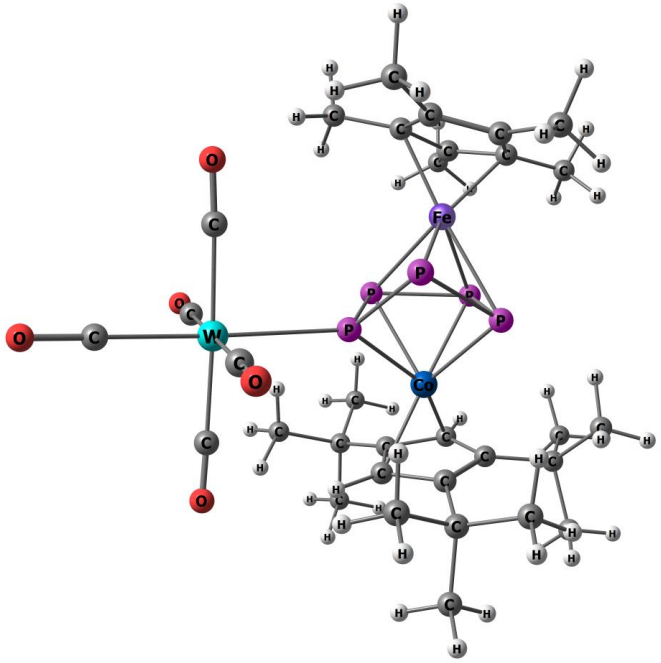
H	-1.554550000	0.701872000	0.072534000
O	0.424896000	0.505342000	0.680570000
C	1.008258000	-0.785702000	0.547777000
C	-0.159254000	-1.774905000	0.458258000
C	-1.220182000	-1.070459000	1.313617000
C	-0.965896000	0.399717000	0.962133000
H	1.657812000	-0.801659000	-0.344159000
H	1.645551000	-1.003722000	1.428413000
H	0.101206000	-2.782462000	0.816188000
H	-0.507821000	-1.866248000	-0.584237000
H	-1.027843000	-1.249354000	2.384897000
H	-2.249798000	-1.393363000	1.097403000
H	-1.224848000	1.091325000	1.782100000

Table S9: Optimized geometries of **I2a**. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



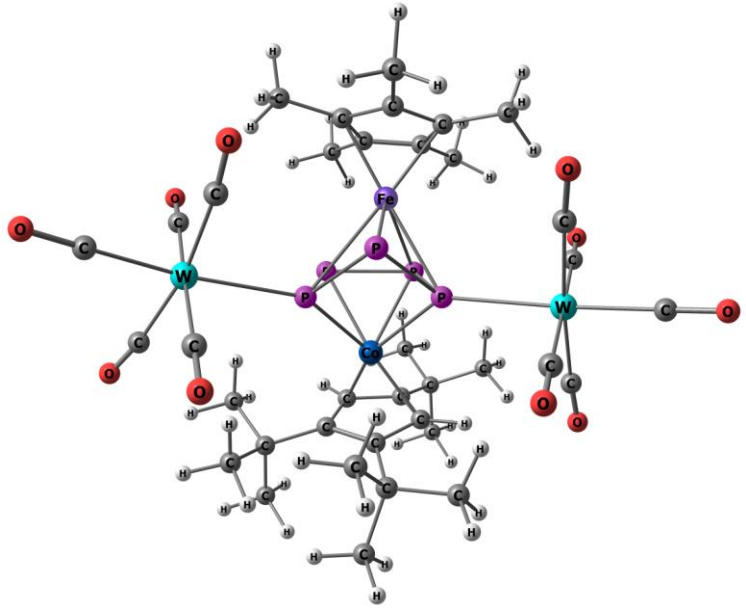
C	2.222874000	3.469066000	0.022890000
C	1.183512000	4.039885000	-0.785904000
C	0.125728000	4.473180000	0.091376000
C	0.488939000	4.114654000	1.428836000
C	1.781791000	3.481389000	1.383839000
C	2.555658000	3.032841000	2.588438000
H	3.020559000	3.899978000	3.090730000
H	3.359950000	2.332638000	2.331916000
H	1.907293000	2.538824000	3.327782000
C	-0.268434000	4.441149000	2.681933000
H	0.107713000	5.379234000	3.127090000
H	-0.160076000	3.652080000	3.440723000
H	-1.343138000	4.570322000	2.491945000
C	-1.098081000	5.230608000	-0.328616000
H	-0.874387000	6.308668000	-0.412283000
H	-1.920051000	5.118331000	0.393151000
H	-1.469365000	4.895141000	-1.308449000
C	1.258649000	4.280741000	-2.264872000
H	1.770830000	5.235974000	-2.479424000
H	0.259884000	4.332388000	-2.721171000
H	1.816919000	3.485395000	-2.779512000
C	3.573321000	3.058193000	-0.477124000
H	4.239016000	3.939250000	-0.511600000
H	3.530254000	2.641957000	-1.492171000
H	4.051442000	2.314606000	0.171372000
C	-4.213103000	-0.254181000	-0.899856000
C	-3.432479000	-1.375540000	-1.296494000
H	-3.231034000	-1.645933000	-2.327076000
C	-2.965238000	-2.114806000	-0.152200000
C	-3.462620000	-1.385480000	1.022445000
C	-4.193309000	-0.256334000	0.521576000
H	-4.685370000	0.483821000	1.144178000
C	-3.553254000	-1.702527000	2.535468000
C	-2.401260000	-2.528980000	3.134294000
H	-2.559719000	-2.627126000	4.219557000
H	-1.428114000	-2.040829000	2.984257000
H	-2.349727000	-3.545158000	2.727793000
C	-4.885425000	-2.472256000	2.742653000
H	-5.028900000	-2.691963000	3.813259000
H	-4.900585000	-3.425924000	2.197056000
H	-5.746188000	-1.876678000	2.400955000
C	-3.636376000	-0.398846000	3.366781000
H	-3.687541000	-0.656225000	4.435742000
H	-4.532020000	0.197231000	3.141330000
H	-2.752520000	0.238586000	3.218937000
C	-2.278923000	-3.489662000	-0.334210000
C	-0.878511000	-3.574939000	0.303251000
H	-0.208176000	-2.831348000	-0.146633000
H	-0.447165000	-4.571751000	0.119409000
H	-0.879351000	-3.408858000	1.383080000
C	-2.093390000	-3.800653000	-1.838572000
H	-1.460844000	-3.053402000	-2.339950000
H	-3.054299000	-3.865694000	-2.371883000
H	-1.592112000	-4.774371000	-1.944928000
C	-3.197890000	-4.598920000	0.232664000
H	-4.203593000	-4.548439000	-0.214563000
H	-3.309109000	-4.542205000	1.322549000
H	-2.774524000	-5.588267000	-0.003014000
C	-5.085032000	0.616159000	-1.799009000
C	-4.526702000	0.693093000	-3.231888000
H	-3.522282000	1.141628000	-3.245700000
H	-5.185710000	1.314931000	-3.858170000
H	-4.470547000	-0.299776000	-3.704546000
C	-5.251500000	2.039122000	-1.234072000
H	-4.286615000	2.564089000	-1.185721000
H	-5.691355000	2.032121000	-0.224550000
H	-5.926848000	2.622276000	-1.880105000
C	-6.475207000	-0.071060000	-1.841719000
H	-6.924133000	-0.131059000	-0.837856000
H	-6.402563000	-1.094721000	-2.241594000
H	-7.161398000	0.499575000	-2.488630000
Co	-2.195327000	-0.149028000	-0.170818000
Fe	0.384814000	2.387345000	0.213570000
P	-1.426722000	1.790503000	-1.420301000
P	-1.702053000	1.879451000	0.857873000
P	-0.393623000	0.212991000	1.467710000
P	1.100748000	0.275556000	-0.216484000
P	-0.475794000	-0.159793000	-1.705483000
W	3.167181000	-1.365038000	-0.199897000
C	4.725935000	-2.652311000	-0.259895000
O	5.614950000	-3.388618000	-0.294652000
C	3.979367000	-0.282448000	-1.772804000
O	4.436142000	0.311959000	-2.646174000
C	4.228718000	-0.236536000	1.164635000
O	4.861785000	0.358355000	1.923396000
C	2.328743000	-2.418775000	1.384610000
O	1.874522000	-3.002008000	2.265439000
C	2.197266000	-2.588712000	-1.577948000
O	1.705328000	-3.296814000	-2.338556000

Table S10: Optimized geometries of **2a**. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



C	0.658347000	4.639179000	0.927982000
C	1.500782000	4.591854000	-0.238917000
C	0.662111000	4.358451000	-1.380592000
C	-0.694846000	4.250157000	-0.914807000
C	-0.700147000	4.455440000	0.503584000
C	-1.914146000	4.570596000	1.376370000
H	-2.261133000	5.619419000	1.397582000
H	-1.703567000	4.270808000	2.412142000
H	-2.747275000	3.954122000	1.014931000
C	-1.902206000	4.066621000	-1.786426000
H	-2.246895000	5.040582000	-2.177879000
H	-2.740405000	3.617195000	-1.237394000
H	-1.686491000	3.423979000	-2.652586000
C	1.093199000	4.307372000	-2.815777000
H	0.923508000	5.280163000	-3.309845000
H	0.531129000	3.549496000	-3.382798000
H	2.161679000	4.067637000	-2.916114000
C	2.977565000	4.853385000	-0.256879000
H	3.177315000	5.938600000	-0.301158000
H	3.465888000	4.390181000	-1.125946000
H	3.471429000	4.463576000	0.645332000
C	1.110842000	4.933870000	2.328165000
H	1.071156000	6.018861000	2.531571000
H	2.145390000	4.603467000	2.499556000
H	0.475884000	4.436010000	3.075492000
C	1.814508000	-2.372496000	-1.521705000
C	3.061939000	-1.729244000	-1.306814000
H	3.673710000	-1.308356000	-2.096089000
C	3.406790000	-1.717356000	0.079542000
C	2.277119000	-2.342263000	0.793261000
C	1.336486000	-2.727626000	-0.226606000
H	0.407080000	-3.254675000	-0.037929000
C	2.057912000	-2.851173000	2.237451000
C	2.808440000	-2.084637000	3.339989000
H	2.516517000	-2.491371000	4.320696000
H	2.549908000	-1.015654000	3.334100000
H	3.897689000	-2.183502000	3.265346000
C	2.494304000	-4.339698000	2.270829000
H	2.335995000	-4.758433000	3.277953000
H	3.557099000	-4.463620000	2.017409000
H	1.907844000	-4.941686000	1.559638000
C	0.559512000	-2.787253000	2.614594000
H	0.423095000	-3.181141000	3.633649000
H	-0.077610000	-3.389363000	1.953154000
H	0.190038000	-1.751829000	2.604884000
C	4.853751000	-1.332589000	0.497089000
C	4.992461000	-0.219039000	1.555740000
H	4.691231000	0.754299000	1.144831000
H	6.050506000	-0.139687000	1.854407000
H	4.401254000	-0.389888000	2.458260000
C	5.652846000	-0.835710000	-0.732343000
H	5.192663000	0.054314000	-1.187942000
H	5.759909000	-1.610718000	-1.506003000
H	6.666710000	-0.553912000	-0.409554000
C	5.558159000	-2.622051000	0.987601000
H	5.471698000	-3.429011000	0.242723000
H	5.148561000	-2.992534000	1.935819000
H	6.630203000	-2.422367000	1.146130000
C	1.263760000	-2.816491000	-2.873374000
C	1.688162000	-1.859140000	-4.003352000
H	1.300425000	-0.843280000	-3.835898000
H	1.293114000	-2.219869000	-4.966115000
H	2.783162000	-1.798976000	-4.103590000
C	-0.268130000	-2.936096000	-2.853851000
H	-0.738644000	-1.974428000	-2.608443000
H	-0.612272000	-3.684821000	-2.125846000
H	-0.636147000	-3.247847000	-3.843879000
C	1.872766000	-4.215657000	-3.150094000
H	1.589204000	-4.936851000	-2.367657000
H	2.972681000	-4.172994000	-3.189599000
H	1.511626000	-4.603313000	-4.116739000
Co	1.547847000	-0.657194000	-0.230190000
Fe	0.503318000	2.776749000	-0.009362000
P	2.161745000	1.511447000	-0.883072000
P	0.241803000	0.800148000	-1.675390000
P	-0.617880000	-0.058159000	0.188345000
P	-0.246830000	1.440762000	1.725454000
P	1.908249000	1.162494000	1.348162000
W	-3.074079000	-1.000538000	0.182706000
C	-4.992354000	-1.636916000	0.283928000
O	-6.087305000	-1.997533000	0.342468000
C	-3.768265000	0.952265000	0.287233000
O	-4.199496000	2.019176000	0.334433000
C	-3.209530000	-0.905877000	-1.888685000
O	-3.312608000	-0.853881000	-3.032514000
C	-2.463421000	-2.973798000	0.082081000
O	-2.146686000	-4.081787000	0.041135000
C	-2.942517000	-1.086958000	2.258461000
O	-2.888233000	-1.149360000	3.404121000

Table S11: Optimized geometries of **2b**. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



C	1.375171000	-3.919624000	1.244115000	C	1.850228000	3.671031000	-2.057620000
C	1.106936000	-3.405522000	2.558889000	H	2.249551000	2.658803000	-1.923095000
C	-0.312546000	-3.393161000	2.741094000	H	2.490160000	4.373095000	-1.502142000
C	-0.920956000	-3.888133000	1.536787000	H	1.936932000	3.917167000	-3.126365000
C	0.127678000	-4.215935000	0.609205000	C	-0.035402000	5.243271000	-1.832040000
C	-0.050179000	-4.880142000	-0.724273000	H	0.541275000	5.900952000	-1.162222000
H	-0.033887000	-5.978440000	-0.608523000	H	-1.100017000	5.430879000	-1.653159000
H	0.749290000	-4.608040000	-1.427639000	H	0.182077000	5.548174000	-2.868062000
H	-1.005542000	-4.607614000	-1.191905000	C	2.028259000	3.073768000	3.231881000
C	-2.372947000	-4.215070000	1.369516000	C	3.387649000	2.424800000	2.913681000
H	-2.562223000	-5.242314000	1.730123000	H	3.285043000	1.354250000	2.685455000
H	-2.690118000	-4.178050000	0.320353000	H	4.057322000	2.519416000	3.783007000
H	-3.020653000	-3.546142000	1.948623000	H	3.887159000	2.913115000	2.064201000
C	-1.031335000	-3.033182000	4.007213000	C	1.425156000	2.432530000	4.496059000
H	-1.086180000	-3.910158000	4.676245000	H	1.221320000	1.362241000	4.348635000
H	-2.060047000	-2.697262000	3.816039000	H	0.486334000	2.923170000	4.796566000
H	-0.517917000	-2.231652000	4.558483000	H	2.128379000	2.531417000	5.337910000
C	2.141094000	-3.105878000	3.603908000	C	2.261438000	4.583351000	3.505725000
H	2.402780000	-4.028303000	4.152370000	H	1.320367000	5.095478000	3.760710000
H	1.780789000	-2.376582000	4.343646000	H	2.694794000	5.086666000	2.627270000
H	3.068185000	-2.707710000	3.167761000	H	2.958881000	4.712016000	4.349524000
C	2.735313000	-4.271886000	0.725961000	Co	0.063079000	1.488208000	0.836333000
H	3.086946000	-5.190565000	1.228656000	Fe	0.179803000	-2.156104000	1.091627000
H	3.480299000	-3.492830000	0.929664000	P	1.115592000	-0.308483000	2.049640000
H	2.728792000	-4.470690000	-0.351399000	P	-1.068256000	-0.180987000	2.126927000
C	1.062666000	3.011486000	2.050167000	P	-1.565598000	0.012076000	-0.034966000
C	1.384980000	3.082039000	0.662550000	P	-0.174254000	-1.335448000	-1.070099000
H	2.390210000	2.985901000	0.270524000	P	1.456177000	-0.175737000	-0.178366000
C	0.224275000	3.377666000	-0.139053000	W	-4.081165000	-0.489998000	-0.855083000
C	-0.894963000	3.410129000	0.800792000	C	-5.858138000	-1.092263000	-1.590194000
C	-0.344537000	3.146171000	2.105876000	O	-6.869626000	-1.451749000	-2.014203000
H	-0.931721000	3.106629000	3.017705000	C	-3.604270000	0.456524000	-2.648889000
C	-2.348738000	3.921559000	0.730171000	O	-3.354047000	0.989725000	-3.634852000
C	-3.053313000	3.753478000	-0.624089000	C	-3.385826000	-2.287298000	-1.618722000
H	-4.096678000	4.089580000	-0.536395000	O	-3.121136000	-3.310007000	-2.077275000
H	-3.068026000	2.702550000	-0.936686000	C	-4.503279000	-1.331426000	0.989560000
H	-2.590026000	4.344071000	-1.420763000	O	-4.750955000	-1.765931000	2.026175000
C	-2.301701000	5.432653000	1.084337000	C	-5.132876000	1.176068000	-0.205466000
H	-3.324235000	5.843566000	1.095315000	O	-5.840519000	2.025455000	0.114057000
H	-1.713214000	6.008276000	0.356147000	W	3.880226000	-0.336585000	-1.250902000
H	-1.860623000	5.597400000	2.079695000	C	5.695601000	-0.572795000	-2.105635000
C	-3.218363000	3.218896000	1.800831000	C	4.500714000	1.548269000	-0.673418000
H	-4.264238000	3.539728000	1.695014000	C	4.600783000	-1.073855000	0.544214000
H	-2.909353000	3.468796000	2.825543000	C	3.393267000	-2.218636000	-1.987158000
H	-3.191396000	2.124732000	1.693709000	C	3.123154000	0.418778000	-3.039408000
C	0.369198000	3.762272000	-1.631149000	O	6.733836000	-0.718711000	-2.587132000
C	-0.421669000	2.838088000	-2.580754000	O	4.901226000	2.590255000	-0.385829000
H	-0.062778000	1.801362000	-2.499650000	O	5.002639000	-1.468014000	1.549165000

H	-0.276940000	3.160945000	-3.623941000	O	3.168287000	-3.241824000	-2.461680000
H	-1.496474000	2.835280000	-2.382030000	O	2.724901000	0.817732000	-4.039714000

5.2 Computations for the reaction of [(Cp'''Co)(Cp'''Ni)(μ,η^3:η^3-P$_3$)] (3) and [W(CO)$_5$(thf)]

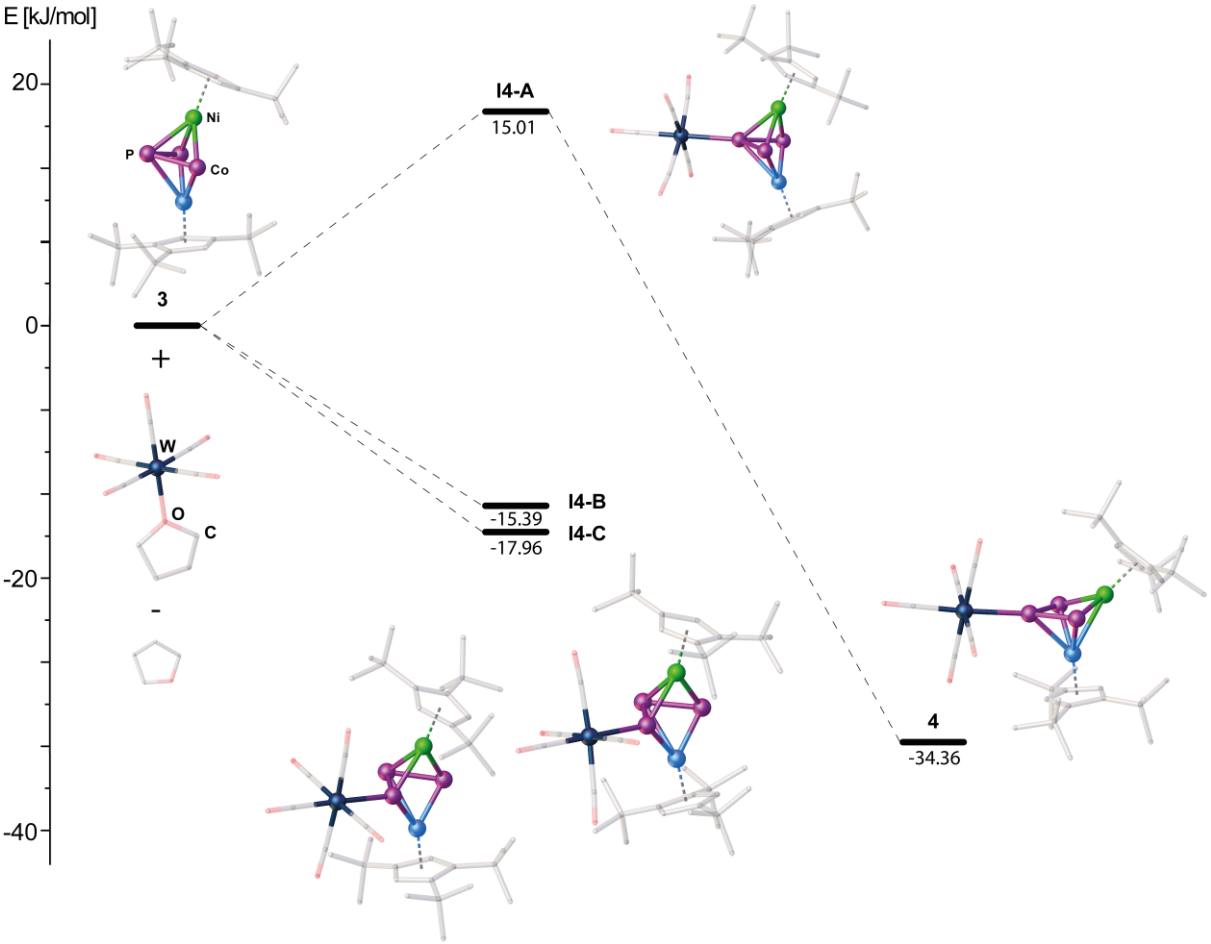


Figure S23: Energetic profile of the reaction of **3** and [W(CO)$_5$(thf)].

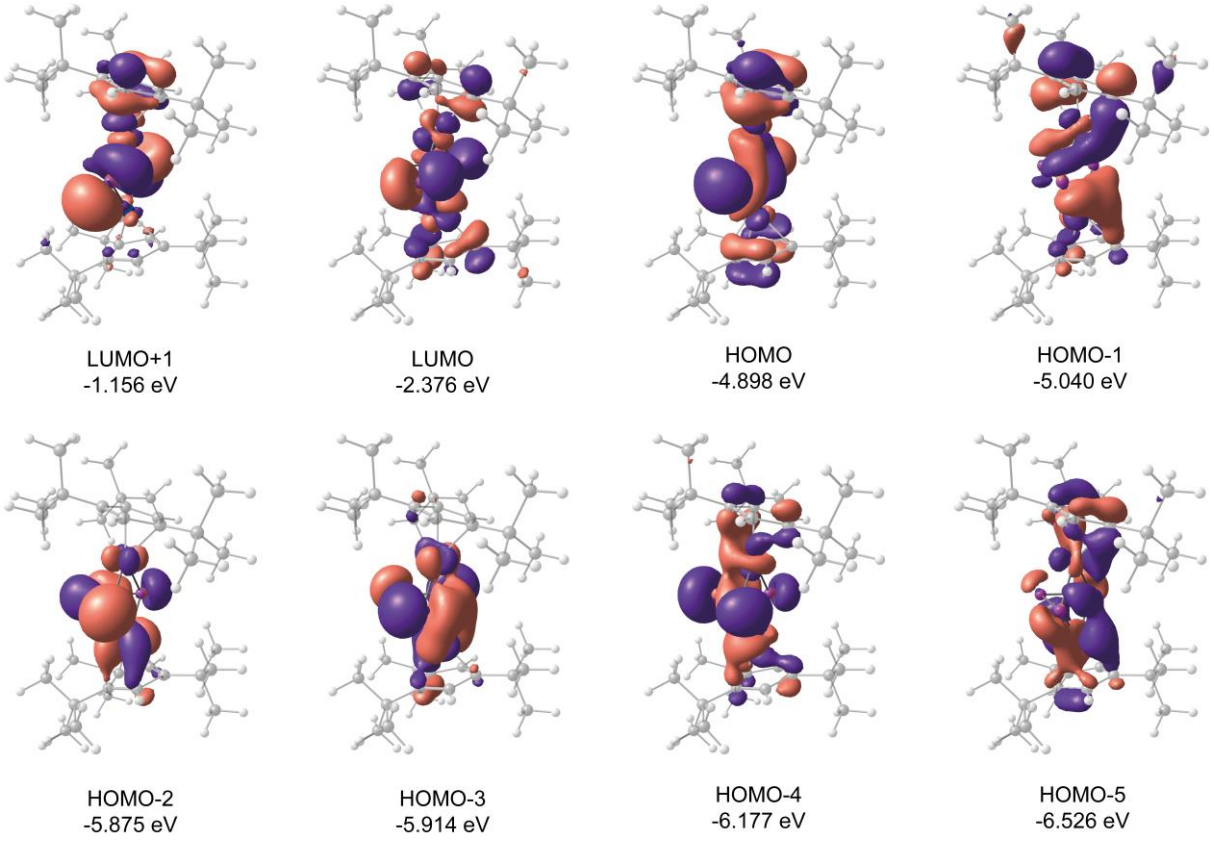


Figure S24: Frontier orbitals of **3** (B3LYP/def2-SVP level of theory).

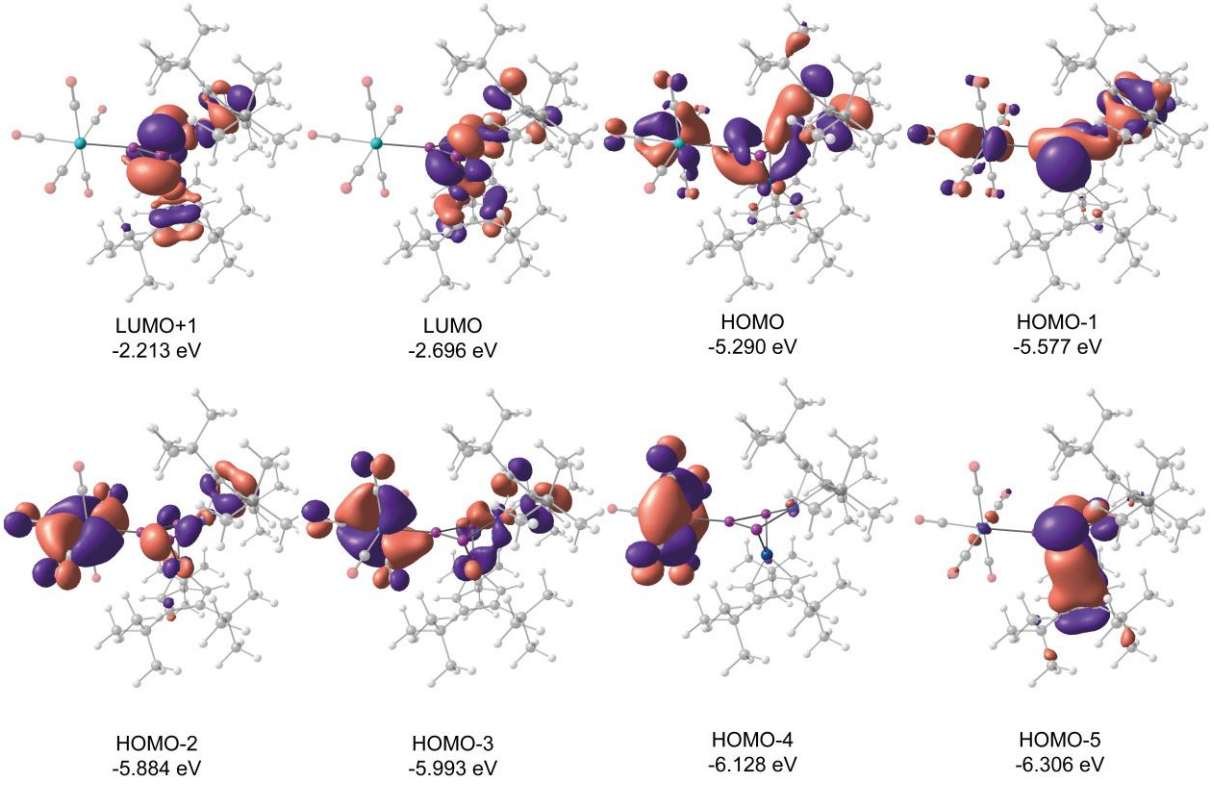
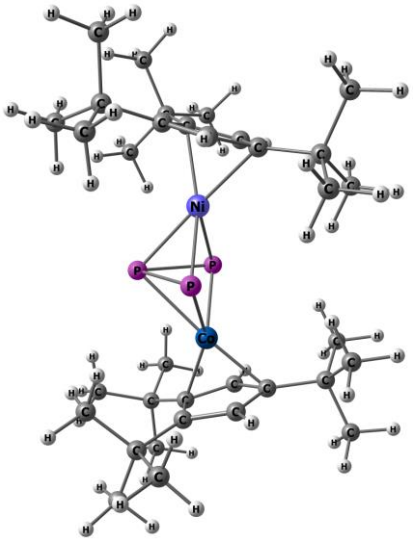


Figure S25: Frontier orbitals of **4** (B3LYP/def2-SVP level of theory).

Table S12: Total energies for all optimized geometries (B3LYP/def2-SVP level of theory).

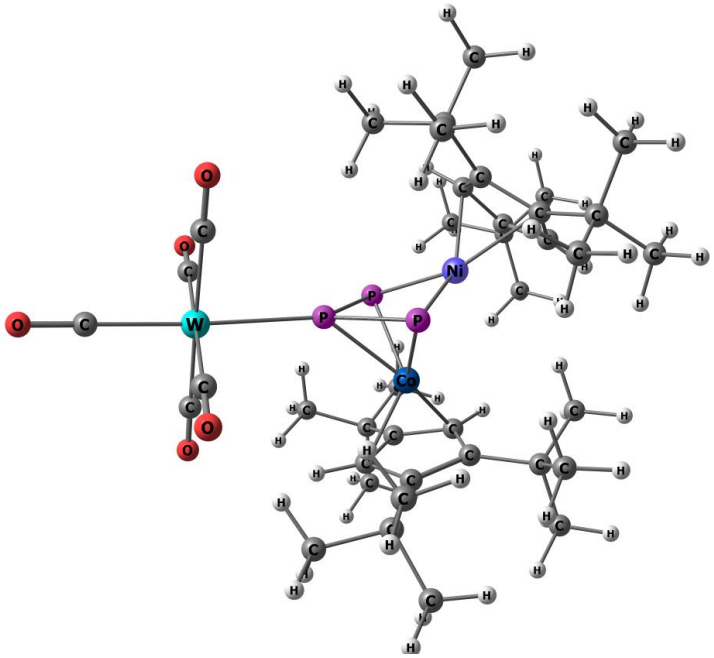
	total energy [Ha]
3 [(Cp'''Co)(Cp'''Ni)(μ,η^3:η^3-P$_3$]	-5244.2879391
4 [Cp'''CoCp'''Ni(μ$_3$,η^3:η^2:η^1-P$_3$){W(CO)$_5$}]	-5877.7692497
I4-A	-5877.7504461
I4-B	-5877.7620250
I4-C	-5877.7630013
[Cp'''NiCp'''Co(μ$_3$,η^3:η^2:η^1-P$_3$){W(CO)$_5$}] (position of Co and Ni exchanged)	-5877.7519902

Table S12: Optimized geometries of **3**. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



Ni	1.654055000	0.043408000	-0.059502000	H	-3.762722000	-4.089090000	1.670398000
Co	-1.735203000	0.092584000	0.045493000	H	-2.000148000	-1.946002000	-2.593762000
P	-0.032924000	0.056960000	1.418957000	H	-3.308290000	-3.003483000	-3.177997000
P	0.056081000	-1.627553000	-0.030659000	H	-2.793738000	-3.067976000	-1.480311000
P	-0.124309000	0.088991000	-1.434047000	H	-5.450179000	-2.669334000	-1.053263000
C	-3.619021000	-0.700074000	0.665609000	H	-5.719714000	-2.413348000	-2.783863000
C	-3.650876000	-0.427984000	-0.785026000	H	-6.163994000	-1.142518000	-1.618297000
C	-3.353313000	0.959686000	-0.931951000	H	-4.835550000	0.387453000	-3.193747000
C	-3.141095000	1.574898000	0.343126000	H	-4.351094000	-1.029196000	-4.150380000
C	-3.342245000	0.545586000	1.309209000	H	-3.108027000	0.061418000	-3.513285000
C	-3.959625000	-1.933575000	1.534818000	H	-2.840005000	2.910473000	2.802172000
C	-5.489213000	-1.931991000	1.787212000	H	-2.146283000	4.397107000	2.127504000
C	-3.264428000	-1.831039000	2.914802000	H	-1.266911000	2.851169000	1.972110000
C	-3.536015000	-3.291999000	0.944571000	H	-1.170860000	3.298682000	-0.615397000
C	-4.008757000	-1.293271000	-2.019320000	H	-2.054106000	4.819309000	-0.307101000
C	-2.967775000	-2.393721000	-2.324509000	H	-2.678805000	3.654776000	-1.490483000
C	-5.414078000	-1.915823000	-1.849230000	H	-4.927206000	3.536300000	-0.284663000
C	-4.077589000	-0.405805000	-3.285051000	H	-4.331856000	4.767729000	0.859407000
C	-2.971072000	3.065412000	0.610587000	H	-4.992534000	3.226279000	1.466613000
C	-2.264259000	3.315289000	1.955287000	H	3.217734000	0.749948000	-2.364972000
C	-2.171476000	3.744167000	-0.517335000	H	3.125737000	1.514904000	1.895065000
C	-4.390499000	3.683916000	0.665782000	H	6.218077000	-0.887119000	1.700933000
C	3.673285000	-0.349308000	0.785740000	H	5.633241000	-2.444199000	1.075729000
C	3.700348000	-0.606625000	-0.655587000	H	5.825488000	-2.215230000	2.820645000
C	3.298089000	0.611556000	-1.291735000	H	3.435542000	-2.943857000	3.166677000
C	3.016931000	1.626231000	-0.326595000	H	3.012303000	-3.054958000	1.445372000
C	3.244481000	1.010406000	0.942629000	H	2.086173000	-1.985105000	2.509217000
C	4.068195000	-1.193859000	2.022619000	H	3.035913000	0.071202000	3.509859000
C	5.516942000	-1.716264000	1.887488000	H	4.737614000	0.535595000	3.224939000
C	3.095112000	-2.365415000	2.291379000	H	4.350324000	-0.923254000	4.162321000
C	4.043364000	-0.315848000	3.296664000	H	6.042773000	-2.476913000	-2.426006000
C	4.160553000	-1.794209000	-1.532101000	H	6.252409000	-1.749774000	-0.814738000
C	5.689816000	-1.675502000	-1.755396000	H	5.942739000	-0.709395000	-2.219520000
C	3.830149000	-3.189739000	-0.969158000	H	2.748823000	-3.305327000	-0.799469000
C	3.481141000	-1.725343000	-2.922700000	H	4.351450000	-3.409694000	-0.030750000
C	2.790853000	3.109879000	-0.592961000	H	4.139582000	-3.958527000	-1.695231000
C	2.051083000	3.333464000	-1.924987000	H	3.750855000	-2.618562000	-3.507555000
C	1.989109000	3.761118000	0.549387000	H	3.804178000	-0.852747000	-3.508808000
C	4.183729000	3.783953000	-0.675840000	H	2.384445000	-1.691905000	-2.835116000
H	-3.278813000	1.481059000	-1.879745000	H	1.063897000	2.847345000	-1.920577000
H	-3.252914000	0.682617000	2.381660000	H	2.618159000	2.933709000	-2.779987000
H	-6.064269000	-2.031487000	0.856789000	H	1.905430000	4.411022000	-2.103977000
H	-5.803694000	-0.996257000	2.275249000	H	1.008542000	3.277813000	0.672334000
H	-5.766570000	-2.769444000	2.448755000	H	1.823638000	4.830087000	0.339423000
H	-3.471570000	-2.743273000	3.495557000	H	2.521692000	3.695590000	1.510885000
H	-3.632104000	-0.984668000	3.512700000	H	4.081818000	4.865499000	-0.865789000
H	-2.173051000	-1.732493000	2.814473000	H	4.786325000	3.349916000	-1.489238000
H	-2.454326000	-3.321864000	0.743981000	H	4.744096000	3.653672000	0.263331000
H	-4.066515000	-3.543850000	0.019336000				

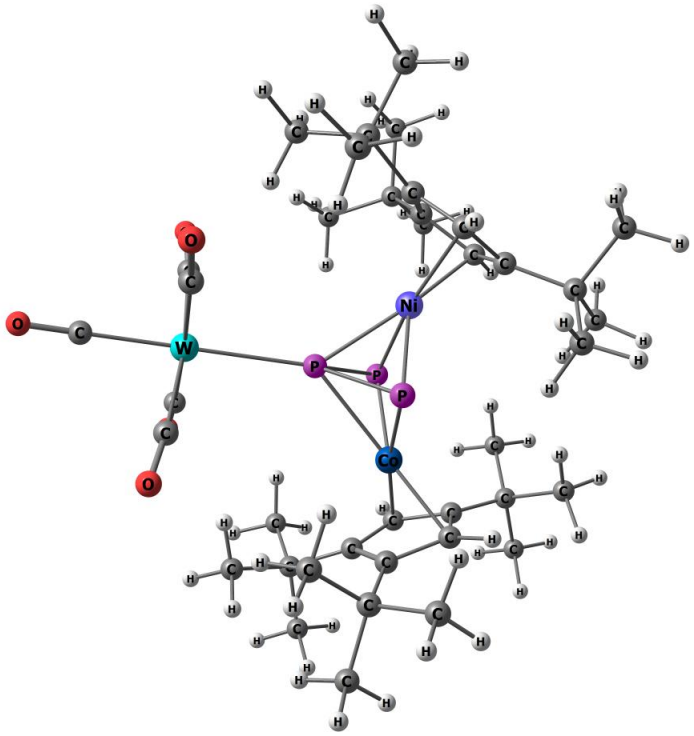
Table S14: Optimized geometries of **4**. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



W	-3.644355000	-1.114928000	0.041640000	H	4.524911000	2.982809000	-1.619184000
Ni	1.922319000	-0.698321000	0.233965000	H	3.544809000	1.724914000	-0.818921000
Co	0.314353000	1.356558000	0.087355000	C	-0.278188000	3.302693000	2.807325000
P	0.303920000	-0.257958000	1.656640000	C	-0.495514000	4.831151000	2.954976000
P	-1.128736000	-0.529890000	0.077683000	H	0.401126000	5.393131000	2.648925000
P	0.454998000	-0.364598000	-1.373676000	H	-0.716717000	5.085659000	4.004270000
O	-2.791162000	-4.042020000	-1.040331000	H	-1.338710000	5.176477000	2.336539000
O	-3.365721000	-2.148752000	3.090503000	C	-1.558316000	2.573751000	3.257363000
O	-4.441474000	1.812307000	1.123841000	H	-2.437711000	2.872181000	2.667945000
O	-3.942027000	-0.105302000	-3.007673000	H	-1.774033000	2.813624000	4.310688000
O	-6.702426000	-1.996880000	0.034890000	H	-1.446431000	1.481982000	3.176336000
C	-3.092285000	-3.002131000	-0.657022000	C	0.891179000	2.880255000	3.712789000
C	-3.457741000	-1.779609000	2.007064000	H	1.085558000	1.800659000	3.636474000
C	-4.160957000	0.762920000	0.739166000	H	0.652394000	3.106598000	4.763914000
C	-3.826779000	-0.462394000	-1.920442000	H	1.819399000	3.418441000	3.465647000
C	-5.593617000	-1.678886000	0.037605000	C	4.270396000	-1.703732000	-2.203333000
C	-0.285115000	3.092842000	-1.015975000	C	3.233321000	-1.375626000	-3.297310000
C	1.148298000	3.118894000	-0.750153000	H	2.379638000	-2.060410000	-3.307607000
C	1.295967000	3.075598000	0.688418000	H	3.711919000	-1.418513000	-4.289517000
H	2.249873000	3.091230000	1.205562000	H	2.838073000	-0.358820000	-3.161558000
C	0.029162000	3.060768000	1.332062000	C	5.380547000	-0.632827000	-2.329446000
C	-0.922634000	3.006965000	0.273481000	H	5.001157000	0.381873000	-2.143086000
H	-1.994599000	2.944204000	0.424849000	H	5.783139000	-0.648597000	-3.353999000
C	3.689972000	-1.710847000	-0.764413000	H	6.219144000	-0.821978000	-1.642289000
C	2.775649000	-2.630641000	-0.062371000	C	4.954387000	-3.058291000	-2.506182000
C	2.821274000	-2.244015000	1.323184000	H	5.698996000	-3.305371000	-1.732964000
H	2.294472000	-2.755932000	2.121959000	H	5.479339000	-3.002776000	-3.473662000
C	3.702560000	-1.136754000	1.512117000	H	4.243457000	-3.890060000	-2.568850000
C	4.210260000	-0.824689000	0.228532000	C	2.061332000	-3.949658000	-0.443222000
H	4.919662000	-0.028159000	0.030630000	C	1.520010000	-4.015593000	-1.882819000
C	-1.141675000	3.295903000	-2.294281000	H	0.817536000	-3.192079000	-2.081128000
C	-0.811327000	4.674497000	-2.917719000	H	0.972822000	-4.960776000	-2.024105000
H	-0.890366000	5.478845000	-2.169194000	H	2.309466000	-3.986394000	-2.642481000
H	-1.527562000	4.896016000	-3.724761000	C	0.842964000	-4.187043000	0.483352000
H	0.193736000	4.715431000	-3.354725000	H	1.129773000	-4.330881000	1.535011000
C	-2.643451000	3.341579000	-1.926721000	H	0.314414000	-5.099736000	0.168413000
H	-2.983823000	2.406910000	-1.461250000	H	0.130698000	-3.351326000	0.433722000
H	-3.235154000	3.481120000	-2.843858000	C	3.051475000	-5.120024000	-0.208009000
H	-2.882384000	4.174768000	-1.248535000	H	3.944278000	-5.044068000	-0.842973000
C	-0.991321000	2.184040000	-3.353731000	H	2.561015000	-6.083013000	-0.426443000
H	0.043937000	2.016443000	-3.663188000	H	3.388777000	-5.142928000	0.839975000
H	-1.575270000	2.448273000	-4.250193000	C	4.191924000	-0.558662000	2.837248000
H	-1.380619000	1.229059000	-2.975770000	C	4.321474000	0.974653000	2.753834000
C	2.392900000	3.413477000	-1.615120000	H	5.029676000	1.281575000	1.968450000
C	2.339811000	2.872637000	-3.054077000	H	4.689659000	1.383385000	3.708788000
H	2.159924000	1.787802000	-3.065087000	H	3.349268000	1.437949000	2.533319000
H	3.305094000	3.059105000	-3.550374000	C	5.587287000	-1.165323000	3.126559000

H	1.568760000	3.354732000	-3.664953000	H	5.536746000	-2.264132000	3.182670000
C	2.580636000	4.952948000	-1.645406000	H	5.981129000	-0.792997000	4.087210000
H	1.728678000	5.466237000	-2.110392000	H	6.308913000	-0.902195000	2.337431000
H	3.487105000	5.212336000	-2.216661000	C	3.246388000	-0.928039000	3.995253000
H	2.697573000	5.354712000	-0.626751000	H	2.222679000	-0.564334000	3.819580000
C	3.657178000	2.807476000	-0.964886000	H	3.608033000	-0.484629000	4.936641000
H	3.895868000	3.262285000	0.007087000	H	3.195731000	-2.017767000	4.145795000

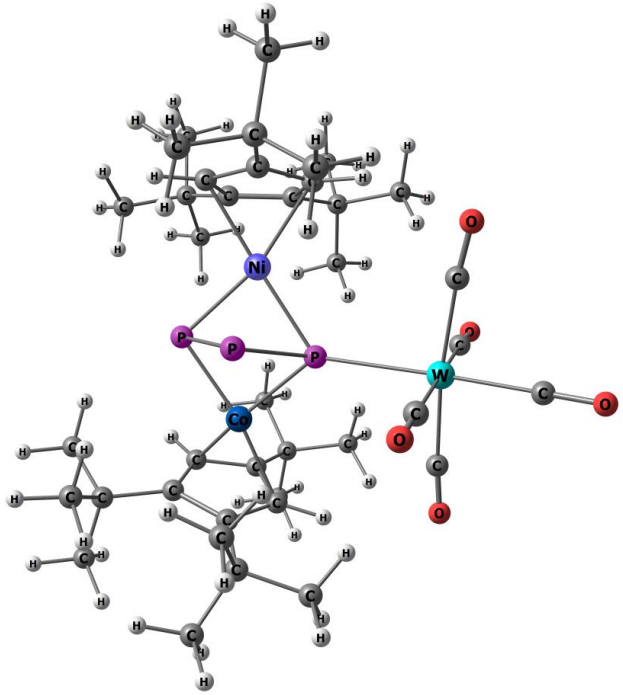
Table S15: Optimized geometries of **I4-A**. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



Ni	2.286873549	-2.040665455	-1.482162575	H	-5.086895451	-4.497421455	-4.206523575
Co	-1.102384451	-1.991489455	-1.377167575	H	-5.531175451	-3.226591455	-3.040957575
P	0.599894549	-2.027113455	-0.003703575	H	-4.202731451	-1.696620455	-4.616407575
P	0.688899549	-3.711626455	-1.453319575	H	-3.718275451	-3.113269455	-5.573040575
P	0.508509549	-1.995082455	-2.856707575	H	-2.475208451	-2.022655455	-4.935945575
C	-2.986202451	-2.784147455	-0.757051575	H	-2.207186451	0.826399545	1.379511425
C	-3.018057451	-2.512057455	-2.207686575	H	-1.513464451	2.313033545	0.704843425
C	-2.720494451	-1.124387455	-2.354611575	H	-0.634092451	0.767095545	0.549449425
C	-2.508276451	-0.509175455	-1.079534575	H	-0.538041451	1.214608545	-2.038057575
C	-2.709426451	-1.538487455	-0.113451575	H	-1.421287451	2.735235545	-1.729761575
C	-3.326806451	-4.017648455	0.112157425	H	-2.045986451	1.570702545	-2.913143575
C	-4.856394451	-4.016064455	0.364551425	H	-4.294387451	1.452226545	-1.707323575
C	-2.631609451	-3.915112455	1.492141425	H	-3.699037451	2.683655545	-0.563253575
C	-2.903196451	-5.376072455	-0.478089575	H	-4.359715451	1.142205545	0.043952425
C	-3.375938451	-3.377344455	-3.441980575	H	3.850552549	-1.334125455	-3.787632575
C	-2.334956451	-4.477794455	-3.747169575	H	3.758555549	-0.569169455	0.472404425
C	-4.781259451	-3.999896455	-3.271890575	H	6.850895549	-2.971192455	0.278272425
C	-3.444770451	-2.489878455	-4.707711575	H	6.266059549	-4.528272455	-0.346931575
C	-2.338253451	0.981338545	-0.812073575	H	6.458306549	-4.299303455	1.397984425
C	-1.631440451	1.231215545	0.532626425	H	4.068360549	-5.027930455	1.744016425
C	-1.538657451	1.660093545	-1.939995575	H	3.645121549	-5.139031455	0.022711425
C	-3.757680451	1.599842545	-0.756878575	H	2.718991549	-4.069178455	1.086556425
C	4.306103549	-2.433381455	-0.636920575	H	3.668731549	-2.012871455	2.087198425
C	4.333166549	-2.690698455	-2.078247575	H	5.370432549	-1.548478455	1.802278425
C	3.930907549	-1.472517455	-2.714395575	H	4.983142549	-3.007327455	2.739660425
C	3.649749549	-0.457842455	-1.749255575	H	6.675591549	-4.560986455	-3.848666575
C	3.877299549	-1.073667455	-0.480031575	H	6.885227549	-3.833847455	-2.237398575
C	4.701013549	-3.277932455	0.599958425	H	6.575557549	-2.793468455	-3.642180575
C	6.149760549	-3.800337455	0.464827425	H	3.381641549	-5.389400455	-2.222129575
C	3.727930549	-4.449488455	0.868718425	H	4.984268549	-5.493767455	-1.453410575
C	4.676182549	-2.399921455	1.874003425	H	4.772400549	-6.042600455	-3.117891575
C	4.793371549	-3.878282455	-2.954761575	H	4.383673549	-4.702635455	-4.930215575
C	6.322634549	-3.759575455	-3.178056575	H	4.436996549	-2.936820455	-4.931468575
C	4.462967549	-5.273812455	-2.391818575	H	3.017263549	-3.775978455	-4.257776575
C	4.113959549	-3.809416455	-4.345360575	H	1.696715549	0.763271545	-3.343237575
C	3.423671549	1.025805545	-2.015621575	H	3.250977549	0.849635545	-4.202647575
C	2.683901549	1.249390545	-3.347647575	H	2.538248549	2.326948545	-3.526637575
C	2.621927549	1.677044545	-0.873273575	H	1.641360549	1.193739545	-0.750326575
C	4.816547549	1.699879545	-2.098500575	H	2.456456549	2.746013545	-1.083237575
H	-2.645994451	-0.603014455	-3.302405575	H	3.154510549	1.611516545	0.088224425
H	-2.620095451	-1.401456455	0.958999425	H	4.714636549	2.781425545	-2.288449575
H	-5.431450451	-4.115560455	-0.565871575	H	5.419143549	1.265842545	-2.911898575

H	-5.170875451	-3.080330455	0.852588425	H	5.376914549	1.569598545	-1.159329575
H	-5.133751451	-4.853517455	1.026094425	W	0.991569591	-6.479707207	-1.746781320
H	-2.838751451	-4.827346455	2.072896425	C	0.964999227	-8.464003048	-1.408357087
H	-2.999285451	-3.068741455	2.090039425	O	0.916973271	-9.580102765	-1.200424262
H	-1.540232451	-3.816566455	1.391812425	C	1.127982230	-6.130719688	0.276334550
H	-1.821507451	-5.405937455	-0.678679575	O	1.213997363	-5.940254011	1.384806901
H	-3.433696451	-5.627923455	-1.403324575	C	-1.030698687	-6.705837532	-1.567263202
H	-3.129903451	-6.173163455	0.247737425	O	-2.138276174	-6.947189237	-1.685730394
H	-1.367329451	-4.030075455	-4.016422575	C	0.831325923	-6.847767086	-3.782979511
H	-2.675471451	-5.087556455	-4.600657575	O	0.739302213	-7.079205019	-4.867197911
H	-2.160919451	-5.152049455	-2.902971575	C	3.010112811	-6.680085825	-1.855498983
H	-4.817360451	-4.753407455	-2.475923575	O	4.118105351	-6.903596775	-1.911335506

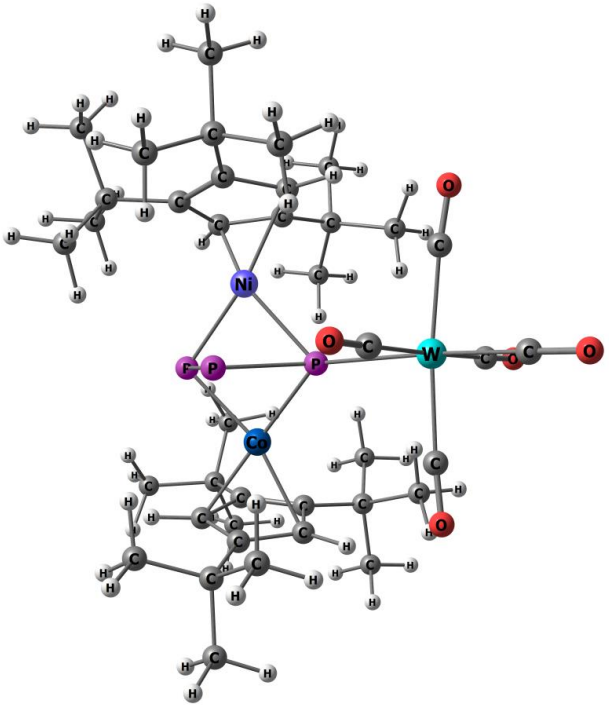
Table S16: Optimized geometries of **I4-B**. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



Ni	1.604396000	-1.127041000	-0.433380000	H	-6.354637000	0.322699000	-2.598906000
Co	-1.713703000	-0.999935000	0.063839000	H	-6.487875000	-0.404156000	-0.980774000
P	-0.205992000	-2.472423000	-0.528053000	H	-5.264054000	1.776290000	-0.298603000
P	-0.152671000	-0.755107000	-1.899478000	H	-5.063971000	2.195851000	-2.013175000
P	-0.021475000	0.415100000	-0.001325000	H	-3.645360000	2.125344000	-0.958164000
C	-3.569844000	-2.071939000	-0.193790000	H	-1.895800000	-2.728118000	3.645221000
C	-3.816944000	-0.635624000	-0.396843000	H	-1.319363000	-1.505635000	4.792490000
C	-3.418050000	0.024936000	0.806096000	H	-0.596170000	-1.606521000	3.166114000
C	-2.911237000	-0.916709000	1.752360000	H	-1.134726000	0.936060000	2.889854000
C	-3.013879000	-2.193688000	1.118961000	H	-1.828767000	0.893741000	4.528995000
C	-3.977963000	-3.349162000	-0.968403000	H	-2.793257000	1.513638000	3.175689000
C	-5.469581000	-3.639942000	-0.656970000	H	-4.667391000	-0.151735000	3.680153000
C	-3.182151000	-4.578817000	-0.466482000	H	-3.726134000	-0.708319000	5.087911000
C	-3.760891000	-3.284993000	-2.492453000	H	-4.302137000	-1.883457000	3.876949000
C	-4.443869000	0.162677000	-1.568176000	H	2.993172000	-3.299504000	-1.711160000
C	-3.577556000	0.149001000	-2.847939000	H	3.820976000	0.742764000	-0.449496000
C	-5.863990000	-0.360343000	-1.887449000	H	5.598523000	-1.237258000	2.415124000
C	-4.609634000	1.647434000	-1.174027000	H	4.366440000	-2.155951000	3.314540000
C	-2.578969000	-0.676362000	3.220383000	H	4.889321000	-0.573818000	3.905151000
C	-1.537203000	-1.690442000	3.728725000	H	2.448184000	0.099710000	3.983038000
C	-2.055574000	0.749285000	3.460899000	H	1.842459000	-1.372051000	3.191608000
C	-3.898438000	-0.867412000	4.010852000	H	1.498136000	0.210795000	2.481332000
C	3.368771000	-1.078769000	0.789983000	H	3.333197000	1.651351000	1.470189000
C	3.103014000	-2.449065000	0.360359000	H	5.021902000	1.086757000	1.501535000
C	3.172193000	-2.431634000	-1.085201000	H	4.179282000	1.487007000	3.014278000
C	3.530593000	-1.151481000	-1.571109000	H	4.509743000	-5.266475000	1.829419000
C	3.590382000	-0.316295000	-0.424755000	H	5.038373000	-3.583121000	2.046088000
C	3.566078000	-0.426388000	2.182029000	H	5.083111000	-4.321907000	0.433533000
C	4.665463000	-1.151046000	2.993814000	H	1.201293000	-3.482383000	2.214955000
C	2.262153000	-0.377326000	3.007308000	H	2.670889000	-3.177068000	3.171889000
C	4.052608000	1.032022000	2.020333000	H	2.194282000	-4.837640000	2.803808000
C	3.049452000	-3.813639000	1.088759000	H	2.363551000	-5.847866000	0.745452000
C	4.507569000	-4.263834000	1.370606000	H	3.046046000	-5.108877000	-0.706732000
C	2.234892000	-3.815504000	2.395166000	H	1.418242000	-4.638357000	-0.156136000
C	2.430158000	-4.904811000	0.181121000	H	2.162876000	-1.843896000	-3.906632000
C	3.868421000	-0.786250000	-3.012836000	H	3.654934000	-2.818369000	-3.836103000
C	3.259679000	-1.803215000	-3.997038000	H	3.504005000	-1.518671000	-5.032701000
C	3.367064000	0.624334000	-3.374883000	H	2.272319000	0.695251000	-3.280565000
C	5.411513000	-0.820664000	-3.148594000	H	3.634443000	0.864611000	-4.416553000
H	-3.484812000	1.092254000	0.977390000	H	3.813757000	1.397577000	-2.734363000
H	-2.716494000	-3.130126000	1.578377000	H	5.714011000	-0.577361000	-4.180618000
H	-6.139102000	-2.843231000	-1.002249000	H	5.810328000	-1.817498000	-2.902067000

H	-5.622878000	-3.759085000	0.427055000	H	5.886211000	-0.090876000	-2.474146000
H	-5.779700000	-4.577978000	-1.146340000	W	0.166855000	3.068435000	0.033861000
H	-3.480383000	-5.462493000	-1.051392000	C	0.249465000	5.085966000	-0.026621000
H	-3.389509000	-4.812420000	0.588110000	O	0.294617000	6.238763000	-0.070888000
H	-2.096909000	-4.447570000	-0.587106000	C	2.110240000	3.079373000	-0.682954000
H	-2.710577000	-3.063503000	-2.736523000	O	3.196040000	3.175893000	-1.054958000
H	-4.394583000	-2.538577000	-2.984470000	C	-0.582354000	3.029982000	-1.906356000
H	-4.009633000	-4.260925000	-2.938483000	O	-1.007535000	3.013250000	-2.973938000
H	-2.637542000	0.694785000	-2.689369000	C	-1.734152000	3.287422000	0.811770000
H	-4.117651000	0.654155000	-3.665200000	O	-2.773291000	3.493724000	1.266731000
H	-3.323203000	-0.860092000	-3.187901000	C	0.869027000	3.081047000	1.987448000
H	-5.858135000	-1.355453000	-2.347361000	O	1.236889000	3.117946000	3.076881000

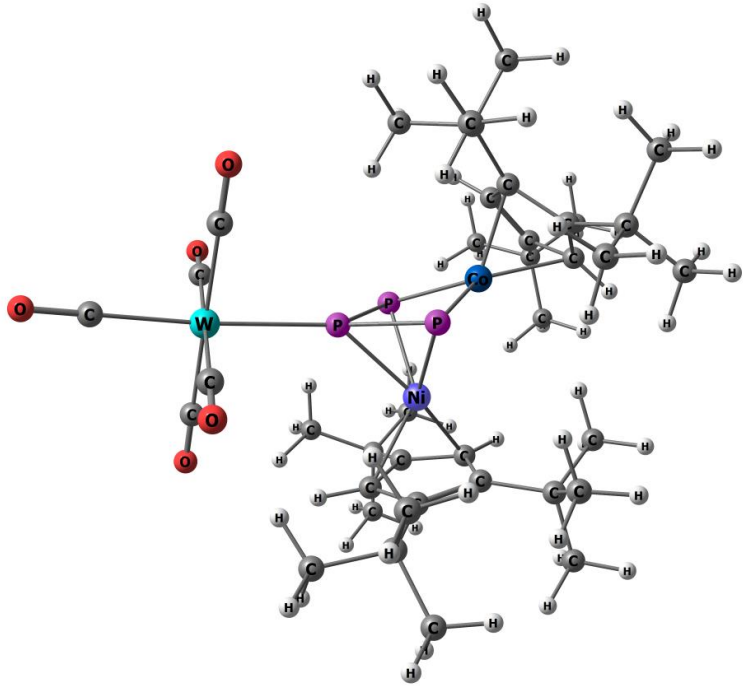
Table S17: Optimized geometries of **I4-C**. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



Ni	1.630781000	-0.985922000	0.032633000	H	-4.453851000	-5.056477000	2.172452000
Co	-1.675525000	-1.119070000	-0.395467000	H	-5.287946000	-3.960049000	1.045382000
P	0.050647000	-2.465639000	-0.574949000	H	-3.697005000	-5.042903000	-0.647562000
P	0.302845000	-0.695270000	-1.848765000	H	-2.804910000	-5.875490000	0.639994000
P	-0.152295000	0.424847000	0.038552000	H	-1.929746000	-4.826394000	-0.490729000
C	-3.488507000	-1.040746000	0.680355000	H	-3.595217000	1.452963000	-2.804923000
C	-3.182888000	-2.422954000	0.276914000	H	-3.222693000	0.958252000	-4.467381000
C	-3.131572000	-2.409755000	-1.156932000	H	-1.988743000	0.792822000	-3.194888000
C	-3.404224000	-1.106714000	-1.664482000	H	-1.760368000	-1.747473000	-3.841175000
C	-3.616184000	-0.277944000	-0.533642000	H	-2.964601000	-1.409944000	-5.106598000
C	-3.913900000	-0.390801000	2.016111000	H	-3.238734000	-2.737443000	-3.964040000
C	-5.450052000	-0.566308000	2.144009000	H	-5.496390000	-1.793813000	-3.244732000
C	-3.623554000	1.125111000	1.992391000	H	-5.278621000	-0.538178000	-4.492745000
C	-3.227495000	-0.942374000	3.277608000	H	-5.652935000	-0.072763000	-2.813231000
C	-3.096827000	-3.762839000	1.054500000	H	3.483188000	0.999350000	1.041254000
C	-1.946893000	-3.840239000	2.083613000	H	2.478709000	-3.166948000	1.627443000
C	-4.449652000	-4.036438000	1.755844000	H	5.908980000	-3.499775000	-0.067251000
C	-2.869776000	-4.935544000	0.070586000	H	5.819869000	-2.811940000	-1.703647000
C	-3.573483000	-0.725241000	-3.131106000	H	5.648233000	-4.559020000	-1.474396000
C	-3.064665000	0.701987000	-3.407677000	H	3.512150000	-4.461290000	-2.775017000
C	-2.839545000	-1.715260000	-4.055921000	H	3.379669000	-2.696387000	-2.904030000
C	-5.091782000	-0.787237000	-3.435346000	H	2.079765000	-3.623331000	-2.137271000
C	3.522285000	-2.160140000	-0.089605000	H	2.327594000	-4.717744000	0.080240000
C	3.874530000	-0.762849000	-0.275056000	H	3.914521000	-4.767215000	0.900844000
C	3.370377000	-0.065313000	0.872798000	H	3.679233000	-5.605830000	-0.645938000
C	2.765901000	-0.968460000	1.806548000	H	6.816420000	0.560263000	-1.573216000
C	2.837365000	-2.245046000	1.183475000	H	6.596658000	-1.052832000	-0.853411000
C	3.865493000	-3.452203000	-0.876120000	H	6.315338000	0.400308000	0.128351000
C	5.398759000	-3.577069000	-1.040625000	H	3.547425000	-0.491914000	-3.113239000
C	3.170879000	-3.551289000	-2.254427000	H	4.991717000	-1.515493000	-2.903933000
C	3.415882000	-4.699925000	-0.078329000	H	5.168726000	0.158014000	-3.435300000
C	4.711128000	0.008443000	-1.321979000	H	4.837603000	2.012597000	-2.159929000
C	6.196452000	-0.030080000	-0.878186000	H	4.493353000	2.026723000	-0.427948000
C	4.593129000	-0.504030000	-2.769414000	H	3.208324000	1.595023000	-1.582636000
C	4.281679000	1.493785000	-1.363961000	H	1.169351000	1.095517000	2.833181000
C	2.365872000	-0.690937000	3.251735000	H	2.864756000	1.452856000	3.238216000
C	2.015617000	0.790949000	3.465550000	H	1.733674000	0.967277000	4.515577000
C	1.161298000	-1.556567000	3.666527000	H	0.284247000	-1.333927000	3.040214000
C	3.581661000	-1.051316000	4.142068000	H	0.895837000	-1.361910000	4.717943000
H	-2.902057000	-3.269296000	-1.776496000	H	1.376028000	-2.632779000	3.576730000
H	-3.848103000	0.780199000	-0.577872000	H	3.352643000	-0.860743000	5.203538000
H	-5.748028000	-1.621930000	2.195718000	H	4.463560000	-0.449678000	3.871297000
H	-5.968649000	-0.113057000	1.285098000	H	3.852795000	-2.113606000	4.037029000

H	-5.809723000	-0.066558000	3.058287000	W	-0.092199000	3.092488000	0.023585000
H	-3.870985000	1.564512000	2.970443000	C	-0.129674000	5.106945000	-0.106907000
H	-4.216688000	1.662486000	1.240148000	O	-0.157198000	6.258230000	-0.192004000
H	-2.561607000	1.316577000	1.794292000	C	1.858780000	3.275392000	0.691205000
H	-2.132624000	-0.864213000	3.203725000	O	2.922609000	3.464645000	1.091307000
H	-3.490635000	-1.985055000	3.488689000	C	0.553182000	2.970863000	-1.951038000
H	-3.545033000	-0.349451000	4.149347000	O	0.916568000	2.913581000	-3.039519000
H	-0.971234000	-3.825420000	1.578072000	C	-2.068943000	3.130107000	-0.585544000
H	-2.021025000	-4.785749000	2.645512000	O	-3.171399000	3.224771000	-0.908687000
H	-1.954496000	-3.020829000	2.806897000	C	-0.685988000	3.193790000	2.008648000
H	-4.643154000	-3.344812000	2.584904000	O	-0.994390000	3.278891000	3.113848000

Table S18: Optimized geometries of [Cp'''NiCp'''Co(μ_3,η^3:η^2:η^1-P_3){$W(CO)_5$}] (position of Co and Ni exchanged). Xyz coordinates in angstroms. B3LYP/def2-SVP level of theory.

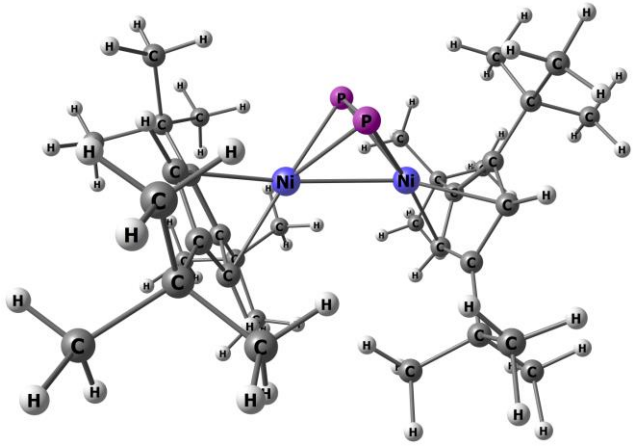


W	-3.571909000	-1.236548000	0.045119000	H	4.316405000	3.193102000	-1.658890000
Co	2.029998000	-0.714324000	0.242231000	H	3.393676000	1.900979000	-0.845334000
Ni	0.190559000	1.360779000	0.093888000	C	-0.438263000	3.275333000	2.824538000
P	0.367180000	-0.368154000	1.638044000	C	-0.717298000	4.787931000	3.020598000
P	-1.099683000	-0.551102000	0.066853000	H	0.150141000	5.395930000	2.718109000
P	0.527496000	-0.441035000	-1.355357000	H	-0.932059000	5.003029000	4.080174000
O	-2.575154000	-4.124597000	-1.016986000	H	-1.583762000	5.115078000	2.424944000
O	-3.219068000	-2.215169000	3.104018000	C	-1.677120000	2.475234000	3.269720000
O	-4.531245000	1.649636000	1.112811000	H	-2.579542000	2.759151000	2.708585000
O	-3.949129000	-0.281931000	-3.014062000	H	-1.882042000	2.663060000	4.335771000
O	-6.577553000	-2.297036000	0.069802000	H	-1.516979000	1.394272000	3.139614000
C	-2.927785000	-3.098301000	-0.640728000	C	0.760650000	2.875774000	3.701586000
C	-3.337970000	-1.865506000	2.016953000	H	0.993081000	1.806572000	3.591764000
C	-4.191669000	0.617378000	0.731724000	H	0.529216000	3.065020000	4.761734000
C	-3.802721000	-0.616733000	-1.924048000	H	1.663611000	3.456136000	3.456158000
C	-5.490105000	-1.914206000	0.060874000	C	4.330661000	-1.572121000	-2.242732000
C	-0.498463000	3.133193000	-0.991492000	C	3.263856000	-1.335410000	-3.331945000
C	0.949734000	3.202016000	-0.744488000	H	2.449525000	-2.065732000	-3.307506000
C	1.119060000	3.158436000	0.682655000	H	3.732798000	-1.385794000	-4.328413000
H	2.074525000	3.222518000	1.191912000	H	2.813844000	-0.338038000	-3.224992000
C	-0.146211000	3.078924000	1.339266000	C	5.362665000	-0.429367000	-2.395820000
C	-1.117894000	3.047602000	0.298249000	H	4.914202000	0.559838000	-2.224331000
H	-2.187039000	2.987946000	0.467399000	H	5.758289000	-0.434432000	-3.423174000
C	3.775284000	-1.598582000	-0.794871000	H	6.216973000	-0.547838000	-1.711815000
C	2.927220000	-2.548691000	-0.053787000	C	5.101666000	-2.883464000	-2.527137000
C	3.013564000	-2.163012000	1.340458000	H	5.866445000	-3.066967000	-1.755789000
H	2.525371000	-2.694477000	2.151205000	H	5.614258000	-2.812674000	-3.500201000
C	3.795825000	-0.996607000	1.492548000	H	4.445673000	-3.761162000	-2.567848000
C	4.216085000	-0.652629000	0.171064000	C	2.270369000	-3.905148000	-0.400250000
H	4.825051000	0.216091000	-0.058514000	C	1.729347000	-4.031703000	-1.835282000
C	-1.365974000	3.294099000	-2.266385000	H	0.987834000	-3.248475000	-2.053054000
C	-1.083982000	4.665404000	-2.926687000	H	1.226529000	-5.004646000	-1.950049000
H	-1.198433000	5.486724000	-2.201430000	H	2.515562000	-3.985471000	-2.597438000
H	-1.802339000	4.836808000	-3.744158000	C	1.069417000	-4.184028000	0.537035000
H	-0.078479000	4.732371000	-3.358925000	H	1.361462000	-4.270635000	1.593438000
C	-2.866164000	3.298637000	-1.891199000	H	0.601355000	-5.139523000	0.255210000
H	-3.172842000	2.358423000	-1.413314000	H	0.306320000	-3.397519000	0.456075000
H	-3.466765000	3.409628000	-2.806531000	C	3.324773000	-5.014106000	-0.146690000
H	-3.127212000	4.131312000	-1.220658000	H	4.207886000	-4.899589000	-0.789839000
C	-1.184758000	2.158224000	-3.295706000	H	2.887047000	-6.006292000	-0.344482000
H	-0.150906000	2.037863000	-3.630184000	H	3.669011000	-4.999463000	0.899229000
H	-1.808556000	2.359150000	-4.181673000	C	4.275760000	-0.348699000	2.787098000
H	-1.505045000	1.196443000	-2.873921000	C	4.268797000	1.187607000	2.668607000
C	2.167651000	3.535529000	-1.633332000	H	4.928060000	1.538126000	1.859031000

C	2.117857000	2.966675000	-3.062229000	H	4.624745000	1.647157000	3.604750000
H	1.971683000	1.876478000	-3.049305000	H	3.254681000	1.560732000	2.466839000
H	3.071430000	3.175719000	-3.572143000	C	5.726674000	-0.826199000	3.041505000
H	1.325545000	3.411684000	-3.673882000	H	5.772332000	-1.922956000	3.131851000
C	2.298973000	5.080344000	-1.691610000	H	6.120941000	-0.390123000	3.974562000
H	1.419977000	5.554775000	-2.147385000	H	6.396467000	-0.528946000	2.219033000
H	3.183756000	5.363174000	-2.285505000	C	3.399050000	-0.771909000	3.980083000
H	2.420610000	5.501812000	-0.681584000	H	2.345651000	-0.487982000	3.834108000
C	3.463299000	2.986950000	-0.994310000	H	3.756486000	-0.289096000	4.903548000
H	3.693678000	3.454310000	-0.026454000	H	3.436650000	-1.860134000	4.145082000

5.3 Computations for [(Cp'''Ni)$_2$(μ,η^2:η^2-P$_2$)] (5)

Table S19: Optimized geometries of **I4-C**. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



Ni	-1.290409000	0.089755000	-0.548508000	H	-4.689771000	3.057200000	1.089838000
Ni	1.231106000	0.212902000	-0.370127000	C	-2.239658000	3.759768000	0.009010000
P	0.046023000	0.937036000	-2.107544000	H	-1.238635000	3.532124000	-0.385323000
P	0.120827000	-1.129807000	-1.759631000	H	-2.199400000	3.677415000	1.106047000
C	-2.658614000	-0.600849000	1.016383000	H	-2.475277000	4.808903000	-0.232903000
C	-3.137352000	-1.000061000	-0.298714000	C	-3.340699000	3.034998000	-2.122742000
C	-3.314219000	0.222337000	-1.047345000	H	-4.137908000	2.441045000	-2.596361000
H	-3.662573000	0.268367000	-2.073829000	H	-2.384771000	2.762388000	-2.595496000
C	-3.010065000	1.362662000	-0.249609000	H	-3.545247000	4.093691000	-2.349278000
C	-2.573763000	0.842789000	0.996627000	C	3.188023000	-2.190239000	1.134195000
H	-2.261813000	1.451201000	1.838357000	C	2.761281000	-2.356192000	2.612244000
C	2.925482000	-0.736181000	0.664491000	H	3.314549000	-1.675845000	3.277845000
C	3.342559000	0.021408000	-0.521537000	H	2.973493000	-3.386369000	2.938380000
C	2.973596000	1.396758000	-0.275237000	H	1.686399000	-2.185073000	2.756705000
H	3.170810000	2.215720000	-0.958752000	C	4.700904000	-2.509180000	1.098812000
C	2.325859000	1.528115000	0.975089000	H	5.275822000	-1.761127000	1.667561000
C	2.272306000	0.206340000	1.522164000	H	5.106684000	-2.545817000	0.081475000
H	1.841806000	-0.036642000	2.488318000	H	4.884572000	-3.494071000	1.557913000
C	-2.359842000	-1.388305000	2.313021000	C	2.402451000	-3.247280000	0.326060000
C	-2.023456000	-0.414592000	3.466912000	H	2.639547000	-4.258228000	0.697957000
H	-1.128648000	0.186663000	3.250232000	H	2.630861000	-3.220322000	-0.744708000
H	-1.820075000	-0.991705000	4.382385000	H	1.319921000	-3.089321000	0.434988000
H	-2.856245000	0.270680000	3.687416000	C	4.205861000	-0.307138000	-1.761645000
C	-1.137537000	-2.317437000	2.161062000	C	5.696011000	-0.107828000	-1.378139000
H	-0.265027000	-1.731334000	1.842038000	H	6.341424000	-0.284688000	-2.254623000
H	-1.289211000	-3.105331000	1.416506000	H	6.016127000	-0.789858000	-0.579753000
H	-0.904240000	-2.804088000	3.122746000	H	5.874754000	0.921362000	-1.029393000
C	-3.597352000	-2.192040000	2.773350000	C	3.901260000	0.679827000	-2.916183000
H	-4.473015000	-1.534332000	2.892941000	H	4.494715000	0.398622000	-3.800084000
H	-3.396744000	-2.665871000	3.748189000	H	4.170852000	1.717019000	-2.670409000
H	-3.869037000	-2.990455000	2.072638000	H	2.838854000	0.659177000	-3.200177000
C	-3.642209000	-2.326361000	-0.914869000	C	4.004106000	-1.717949000	-2.346518000
C	-2.852183000	-3.585742000	-0.513716000	H	4.614018000	-1.825485000	-3.257546000
H	-1.787303000	-3.484063000	-0.771778000	H	2.952483000	-1.887319000	-2.623847000
H	-3.249605000	-4.455585000	-1.060666000	H	4.310268000	-2.516255000	-1.661609000
H	-2.931081000	-3.819125000	0.554113000	C	1.974575000	2.827651000	1.689137000
C	-5.130990000	-2.499526000	-0.514568000	C	0.691623000	2.672366000	2.525144000
H	-5.548238000	-3.408073000	-0.979968000	H	-0.157283000	2.397545000	1.884515000
H	-5.729890000	-1.640031000	-0.854511000	H	0.450880000	3.616521000	3.040323000
H	-5.261628000	-2.586275000	0.572570000	H	0.800923000	1.896027000	3.298587000
C	-3.592024000	-2.264079000	-2.461616000	C	3.150416000	3.177118000	2.635133000
H	-2.575771000	-2.054018000	-2.827116000	H	4.089541000	3.297596000	2.072384000
H	-4.272671000	-1.506821000	-2.876350000	H	3.307922000	2.386151000	3.385474000
H	-3.906814000	-3.234463000	-2.875963000	H	2.950202000	4.119774000	3.171618000
C	-3.296451000	2.820290000	-0.597869000	C	1.791290000	3.976404000	0.680263000
C	-4.683803000	3.173118000	-0.005474000	H	1.015286000	3.736247000	-0.061558000
H	-5.468623000	2.518568000	-0.416570000	H	2.724327000	4.191640000	0.136612000
H	-4.952630000	4.216770000	-0.239869000	H	1.495514000	4.900931000	1.201254000

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