Chemistry–A European Journal

Supporting Information

Redox Chemistry of Heterobimetallic Polypnictogen Triple-Decker Complexes – Rearrangement, Fragmentation and Transfer

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1. EPR studies

1.1 [(Cp*Fe)(Cp’’’Co)(μ,η^5:η^5-P$_5$)][FAl] (3)

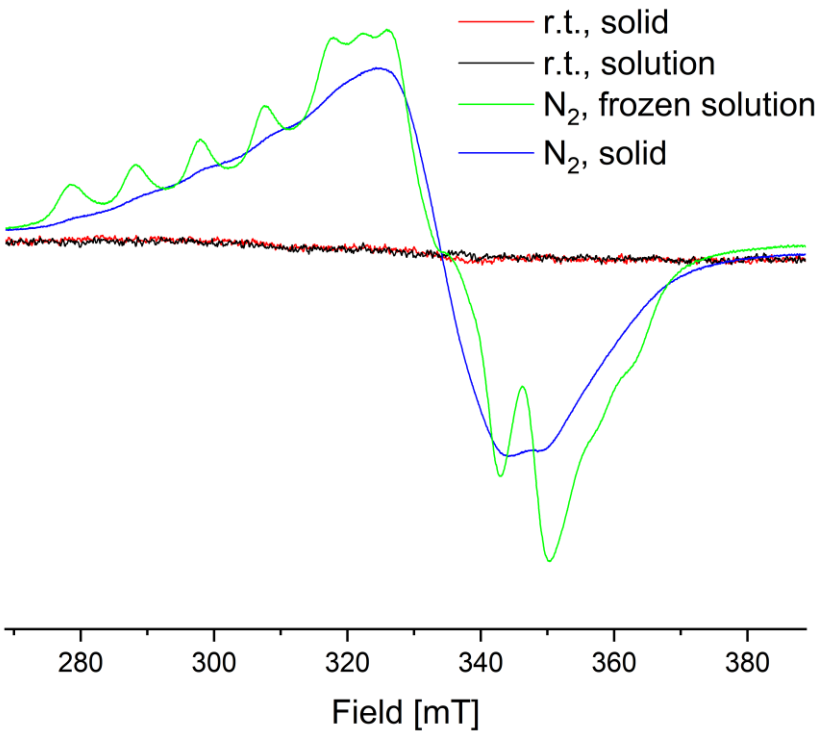


Figure S1: EPR spectra of **3** in solid state and frozen solution (*o*-$C_6H_4F_2$) at 77 K.

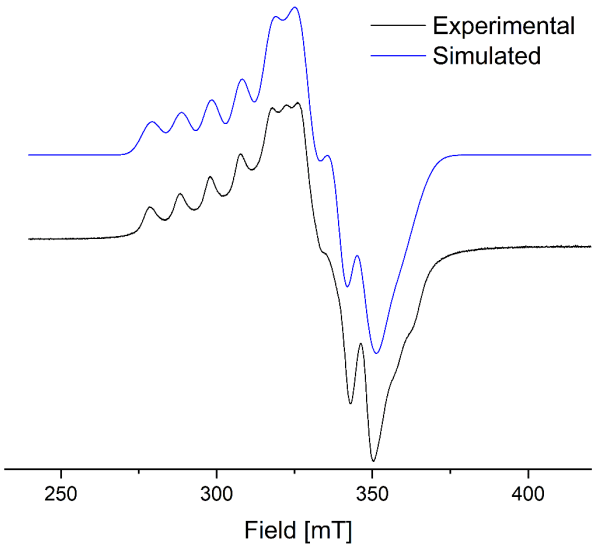


Figure S2: EPR spectra of **3** in solution (*o*-$C_6H_4F_2$) at 77 K (experimental (black) and simulated (blue). Parameters for the fitting: g_1 = 2.155, g_2 = 2.035, g_3 = 1.948, A_1^{Co} = 290.125, A_2^{Co} = 55.125, A_3^{Co} = 120.125 MHz.

The simulation has been performed with the EasySpin program.[1]

```
SysCo.Nucs = 'Co';
SysCo.S = 7/2;
SysCo.g = [ 2.15525 2.03525 1.948];
SysCo.lw = [ 5 ];
SysCo.A = [ 290.125 55.125 120.125];
SysCo.HStrain = [ 180.25 150.25 150.25  ];
SysCo.AStrain = [ 40.25 40.25 80.25  ];
Exp.mwFreq = 9.440920;
Exp.Range = [239.6630 420.2450];
Exp.nPoints = 4096;
Exp.Temperature = 77;
Exp.ModAmp = 0.2;
```

1.2 [(Cp*Fe)(Cp’’’Co)(μ,η^5:η^5-As$_5$)][FAl] (4)

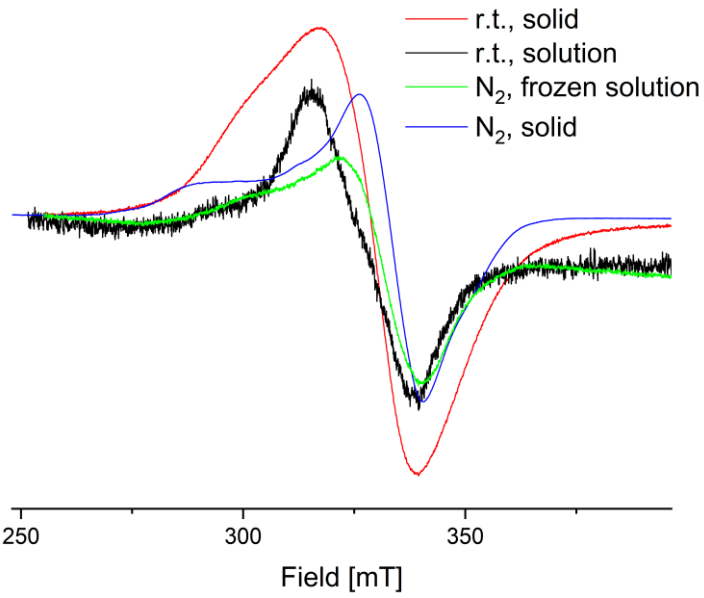


Figure S3: EPR spectra of **4** in solid state (r.t. (red), liquid nitrogen (blue) and in CH_2Cl_2 solution (r.t. (black), fozen solution in liquid nitrogen (green)).

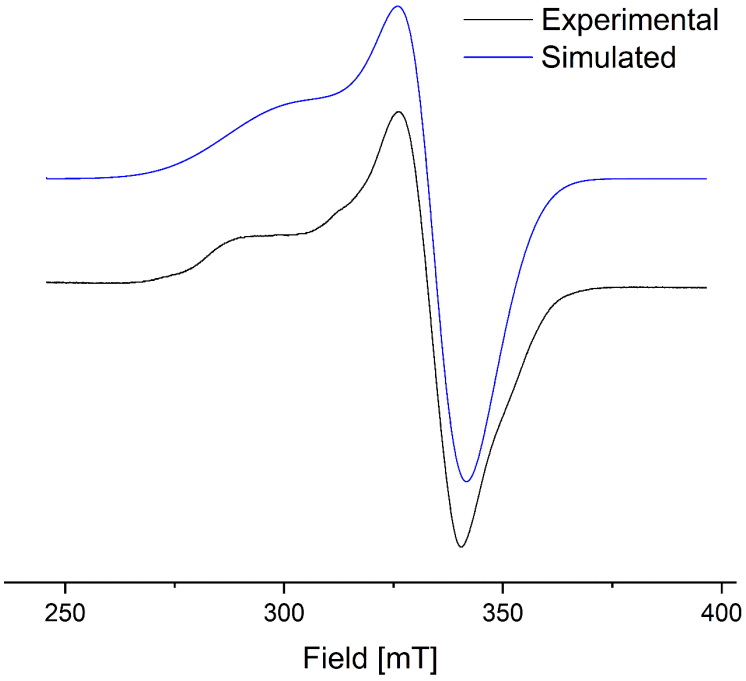


Figure S4: EPR spectra of **4** in solid state at 77 K (experimental (black) and simulated (blue). Parameters for the fitting: g_1 = 2.235, g_2 = 1.952, g_3 = 1.896.

The simulation has been performed with the EasySpin program.[1]
Sys.S = 1/2;
Sys.g = [2.23533 1.9518 1.89552];
SysCo.lw = [20];
Sys.HStrain = [1239 412 639];

Exp.mwFreq = 9.440920;
Exp.Range = [239.6630 420.2450];
Exp.nPoints = 4096;
Exp.Temperature = 77;
Exp.ModAmp = 0.2;

1.3 [K(18-c-6)(thf)$_2$][(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-P$_5$)] (7)

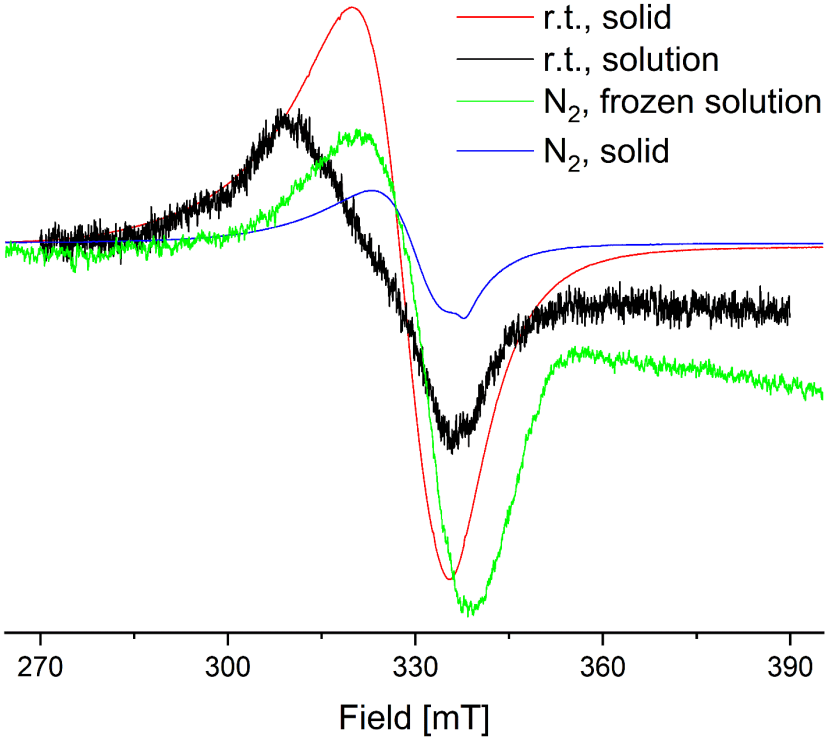


Figure S5: EPR spectra of **7** in solid state (r.t. (red), liquid nitrogen (blue) and in CH_2Cl_2 solution (r.t. (black), frozen solution in liquid nitrogen (green)).

1.4 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-As$_5$)] + KC$_8$ (precipitated crude reaction mixture)

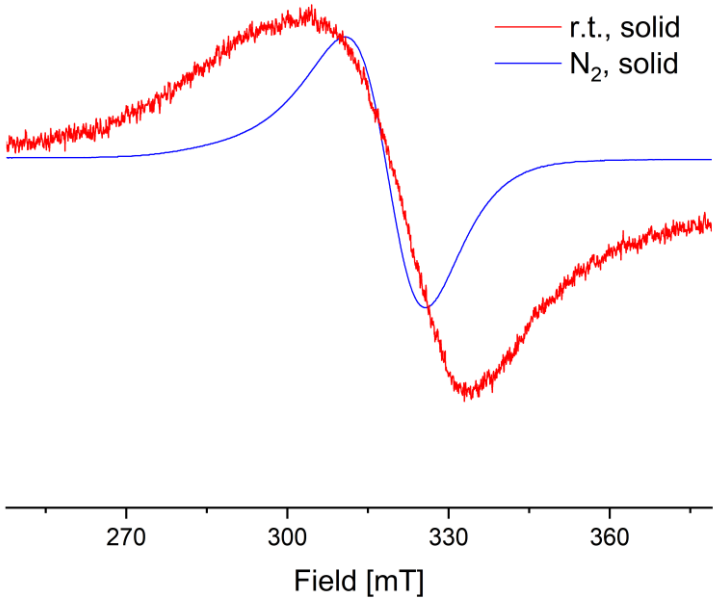


Figure S6: EPR spectra of precipitated solid obtained from the reaction of **2** with KC_8 in solid state (r.t. (black), liquid nitrogen (red).

1.5 [(Cp’’’Co)(Cp’’’Ni)(μ,η³:η³-P₃)][FAl] (12)

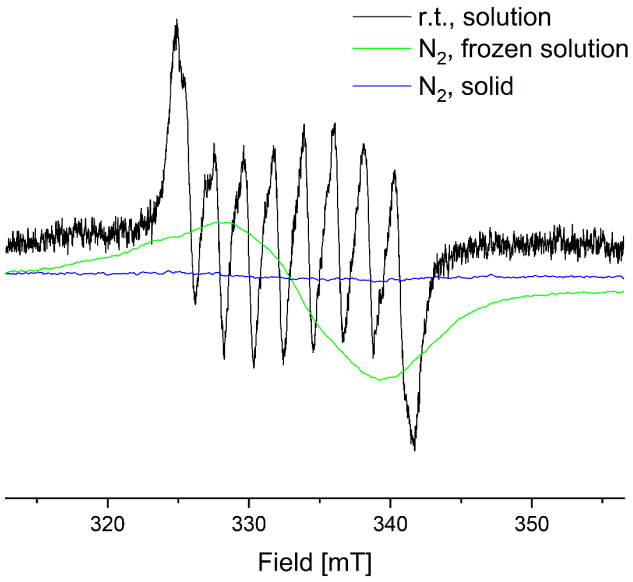


Figure S7: EPR spectra of **12** in solid state (liquid nitrogen (blue) and in CH_2Cl_2 solution (r.t. (black), frozen solution in liquid nitrogen (green)).

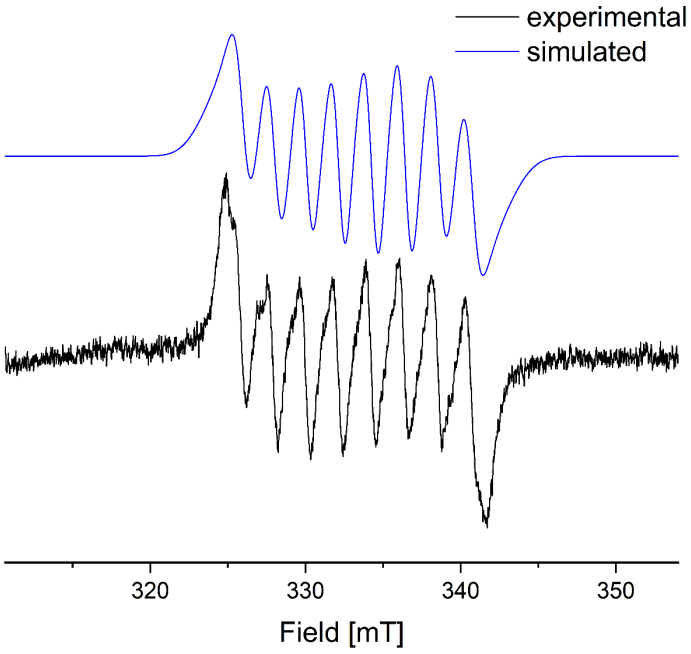


Figure S8: EPR spectra of **12** in CH_2Cl_2 solution at r.t. (experimental (black) and simulated (blue). Parameters for the fitting: g_1 = 2.023, g_2 = 2.031, g_3 = 2.014, A_1^{Co} = 59.5577, A_2^{Co} = 63.9666, A_3^{Co} = 62.8305.

The simulation has been performed with the EasySpin program.[1]
SysCo.S = 7/2;
SysCo.g = [2.02342 2.03139 2.04128];
SysCo.lw = [0.109269];
SysCo.A = [59.5577 63.9666 62.8305];
SysCo.HStrain = [26.6589 40.3355 49.2673];
SysCo.AStrain = [0.320737 21.6238 21.0745];

Exp.mwFreq = 9.440920;
Exp.Range = [303.6680 363.6840];
Exp.nPoints = 4096;
Exp.Temperature = 293;
Exp.ModAmp = 0.05;

1.6 [(Cp'''Co)(Cp'''Ni)(μ,η³:η³-As₃)][FAl] (13)

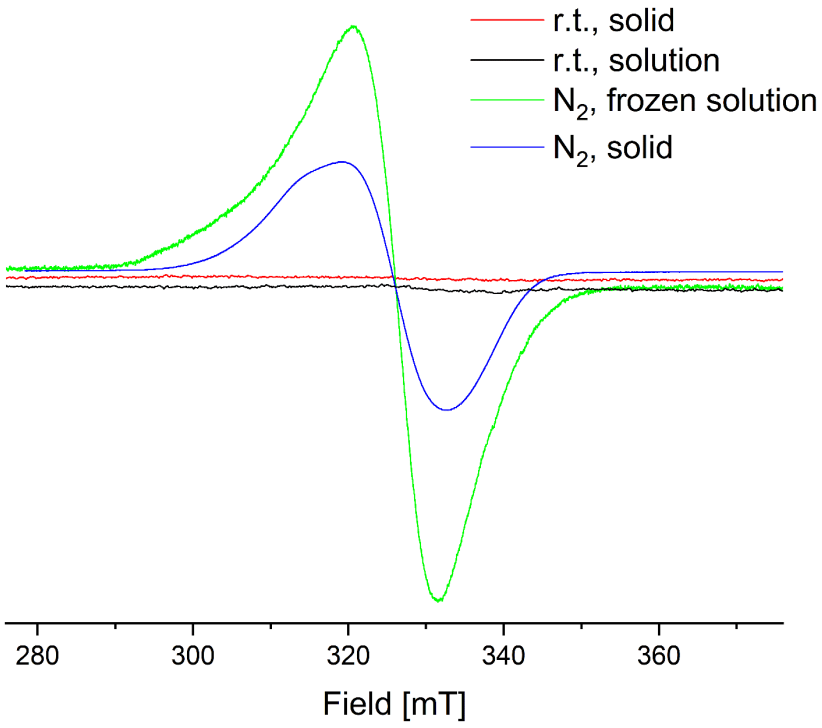


Figure S9: EPR spectra of **13** in solid state (r.t. (red), liquid nitrogen (blue) and in CH_2Cl_2 solution (r.t. (black), frozen solution in liquid nitrogen (green)).

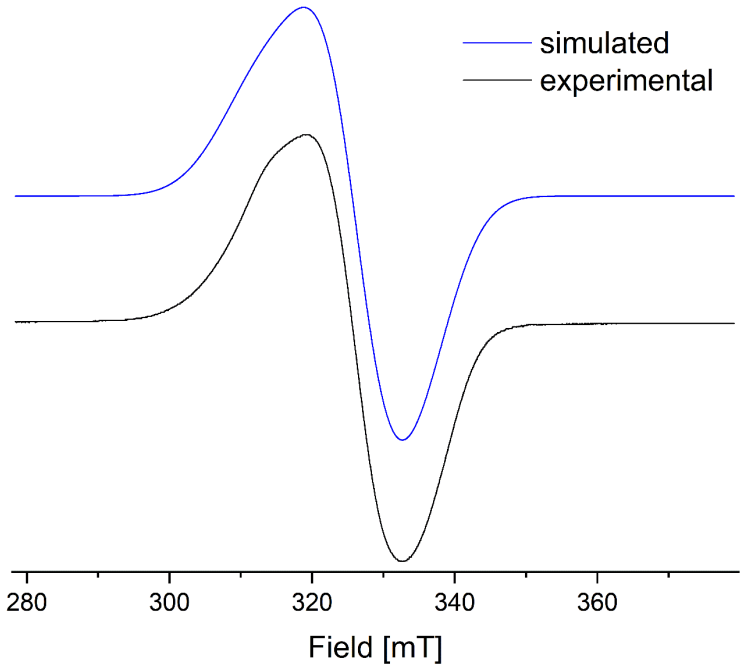


Figure S10: EPR spectra of **13** in solid state at 77 K (experimental (black) and simulated (blue). Parameters for the fitting: g_1 = 2.155, g_2 = 2.071, g_3 = 2.016.

The simulation has been performed with the EasySpin program.[1]
Sys.S = 1/2;
Sys.g = [2.15539 2.07055 2.01631];
SysCo.lw = [10];
Sys.HStrain = [330.7 76.5 202.5];

Exp.mwFreq = 9.440920;
Exp.Range = [278.3980 379.2020];
Exp.nPoints = 4096;
Exp.Temperature = 77;
Exp.ModAmp = 0.05;

1.7 [(Cp’’’Co)(Cp’’’Ni)(μ,η^3:η^3:η^1-P$_3$){W(CO)$_5$}][FAl] (21)

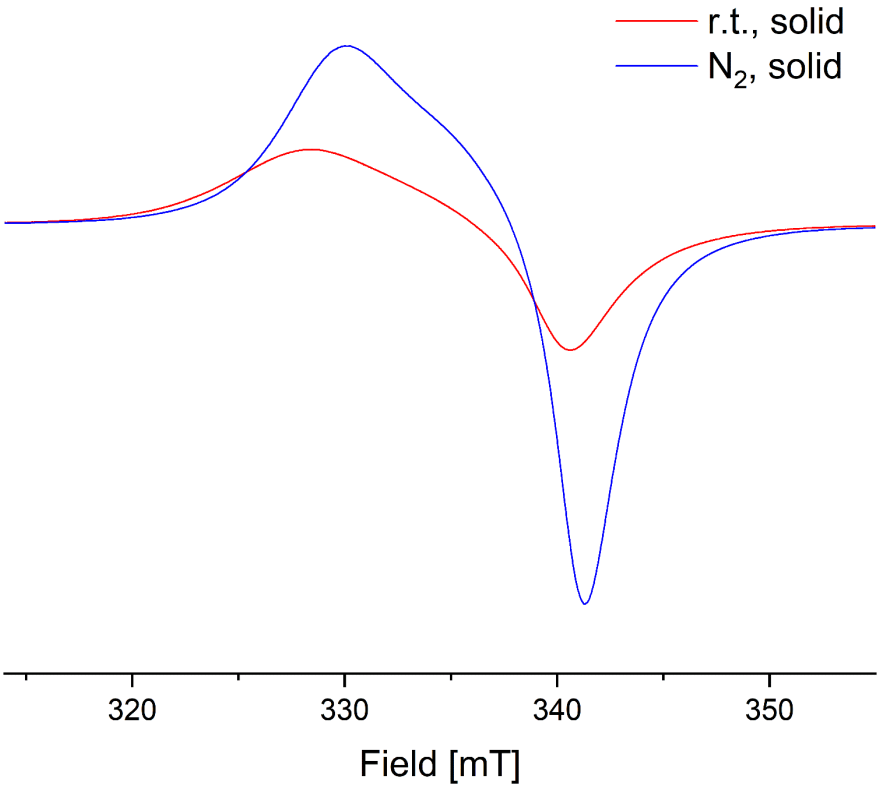


Figure S11: EPR spectra of **7** in solid state (r.t. (red), liquid nitrogen (blue).

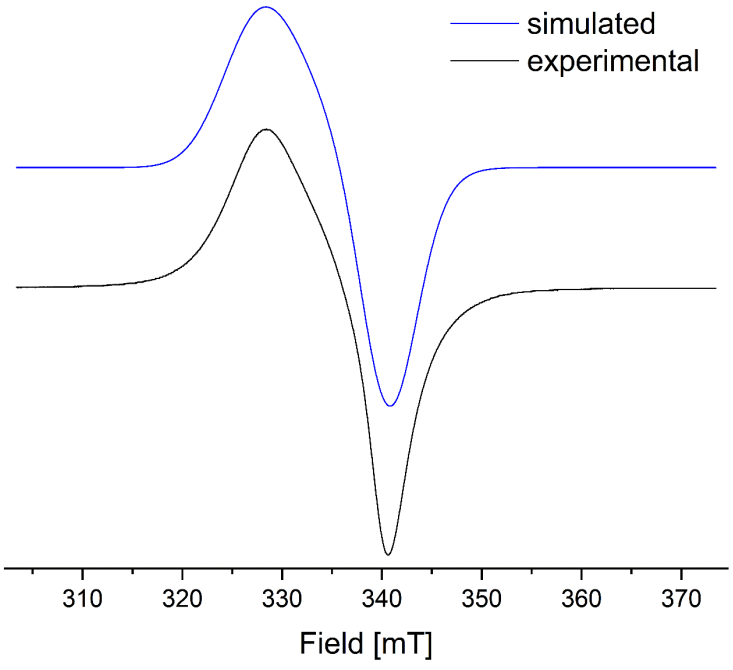


Figure S12: EPR spectra of **7** in solid state at 77 K (experimental (black) and simulated (blue). Parameters for the fitting: g_1 = 2.060, g_2 = 2.007, g_3 = 1.984.

The simulation has been performed with the EasySpin program.[1]
Sys.S = 1/2;
Sys.g = [2.060 2.0066 1.984];
SysCo.lw = [5];
Sys.HStrain = [190 280 90];

Exp.mwFreq = 9.440920;
Exp.Range = [303.3835 373.4645];
Exp.nPoints = 4096;
Exp.Temperature = 77;
Exp.ModAmp = 0.05;

1.8 [K(2,2,2-crypt)][(Cp'''Co)(Cp'''Ni)(μ,η^3:η^3-P$_3$)]

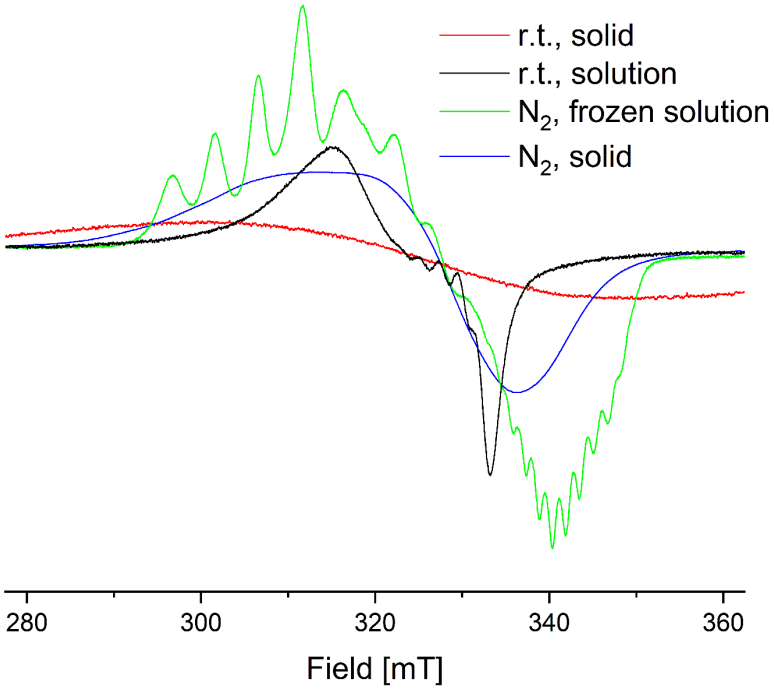


Figure S13: EPR spectra of **22** in solid state (r.t. (green), liquid nitrogen (blue)) and in thf solution (r.t. (black), frozen solution in liquid nitrogen (green)).

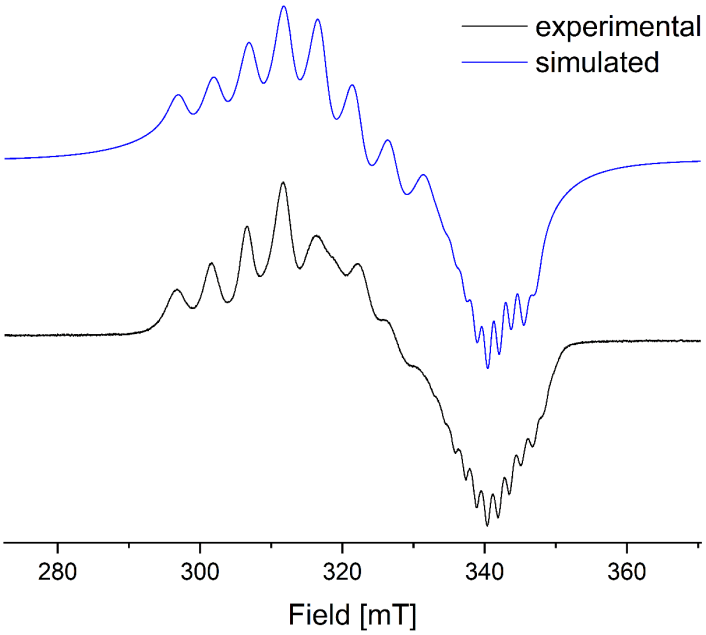


Figure S14: EPR spectra of **22** (crypt) in frozen thf solution at 77 K (experimental (black) and simulated (blue). Parameters for the fitting: g_1 = 2.143, g_2 = 2.120, g_3 = 1.980, A_1^{Co} = 148.53, A_2^{Co} = 50.32, A_3^{Co} = 42.72, A_1^{P} = 13.63, A_2^{P} = 35.94, A_3^{P} = 42.13 MHz.

```
The simulation has been performed with the EasySpin program.[1]
SysCo.Nucs = 'Co,P';
SysCo.g = [ 2.14301 2.1201 1.98022];
SysCo.lw = [ 1 ];
SysCo.A = [ 148.53 50.32 42.72; 13.63 35.94 42.13];
SysCo.HStrain = [50.13 500.92 15.21 ];
SysCo.AStrain = [ 1.13 389.27 2.16 ];

Exp.mwFreq = 9.440920;
Exp.Range = [268.7840 388.8160];
Exp.nPoints = 4096;
Exp.Temperature = 77;
Exp.ModAmp = 0.05;
```

1.9 [K(2,2,2-crypt)][(Cp'''Co)(Cp'''Ni)(μ,η^3:η^3-As$_3$)] (23)

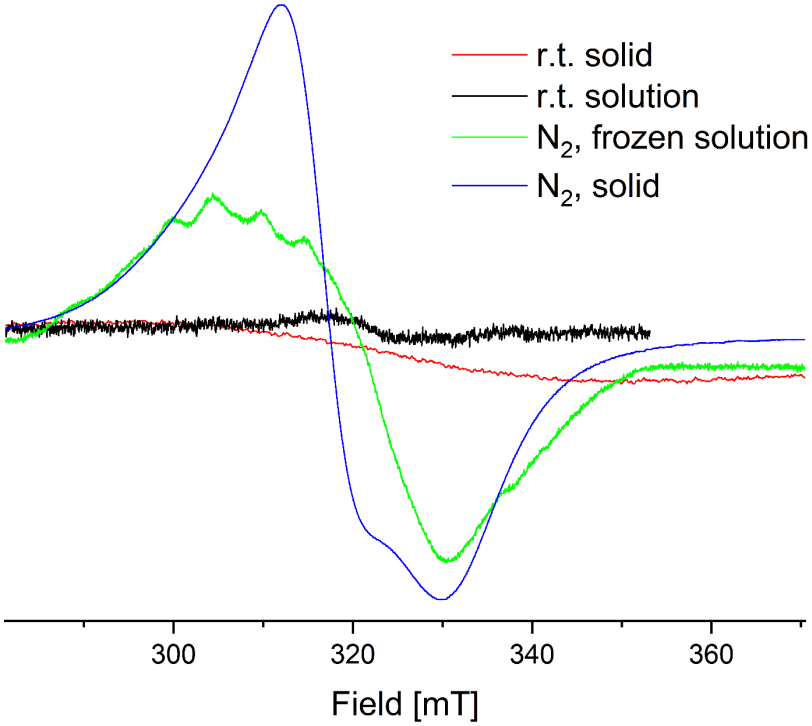


Figure S15: EPR spectra of **23** in solid state (r.t. (green), liquid nitrogen (blue)) and in thf solution (r.t. (black), frozen solution in liquid nitrogen (green)).

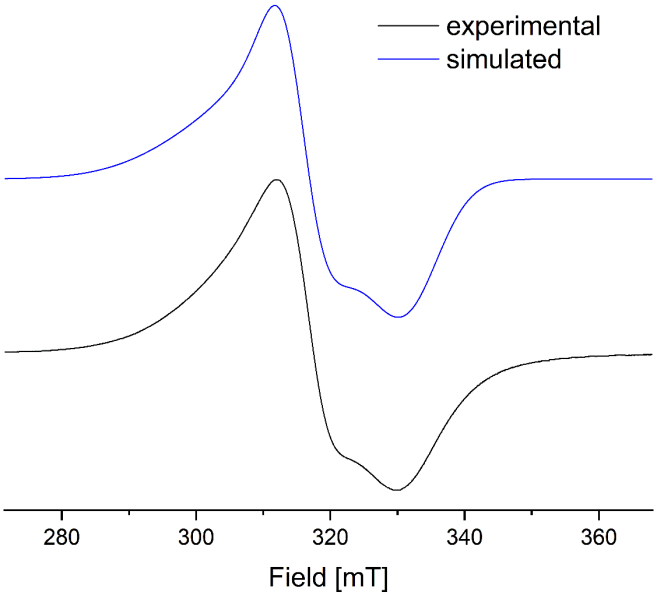


Figure S16: EPR spectra of **23** solid at 77 K (experimental (black) and simulated (blue). Parameters for the fitting: g_1 = 2.214 g_2 = 2.142, g_3 = 2.039.

The simulation has been performed with the EasySpin program.[1]
Sys.S = 1/2;
Sys.g = [2.214 2.142 2.039];
Sys.lw = [3];
Sys.HStrain = [800 190 300];

Exp.mwFreq = 9.440920;
Exp.Range = [269.6695 370.4745];
Exp.nPoints = 4096;
Exp.Temperature = 77;
Exp.ModAmp = 0.05;

2. NMR spectroscopic investigations

2.1 [(Cp*Fe)(Cp’’’Co)(μ,η^5:η^5-P$_5$)][FAl] (3)

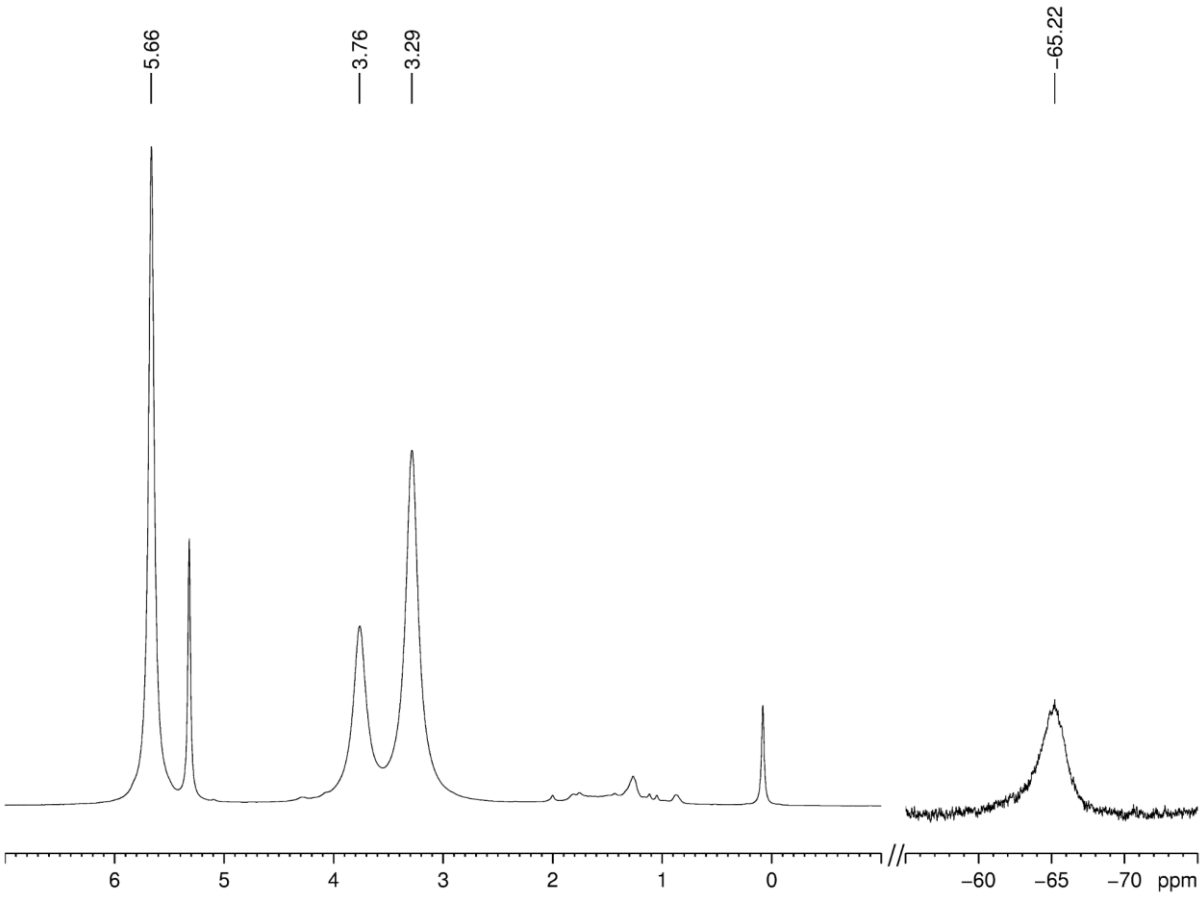


Figure S17: ^{1}H NMR spectrum of **3** in CD_2Cl_2.

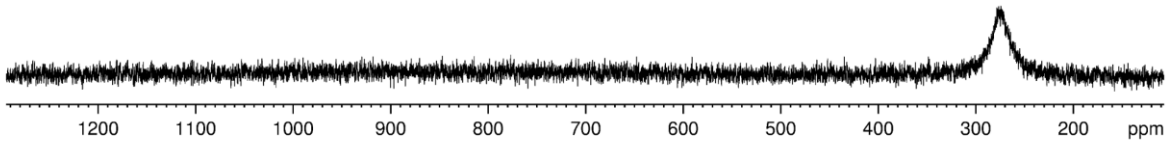


Figure S18: ^{1}H NMR spectrum of **3** in CD_2Cl_2.

2.2 [(Cp*Fe)(Cp’’’Co)(μ,η^5:η^5-As$_5$)][FAl] (4)

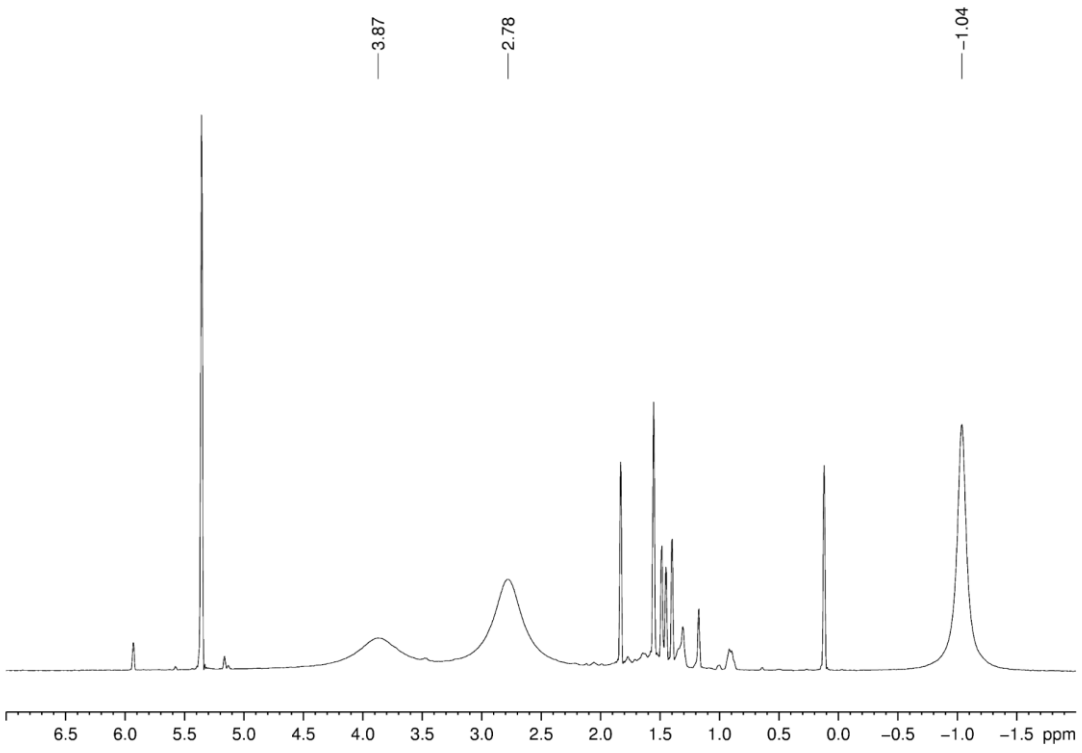


Figure S19: ^{1}H NMR spectrum of **4** in CD_2Cl_2.

2.3 [(Cp*Fe)(Cp’’’Co)(μ,η^5:η^5-P$_5$)][FAl]$_2$ (5)

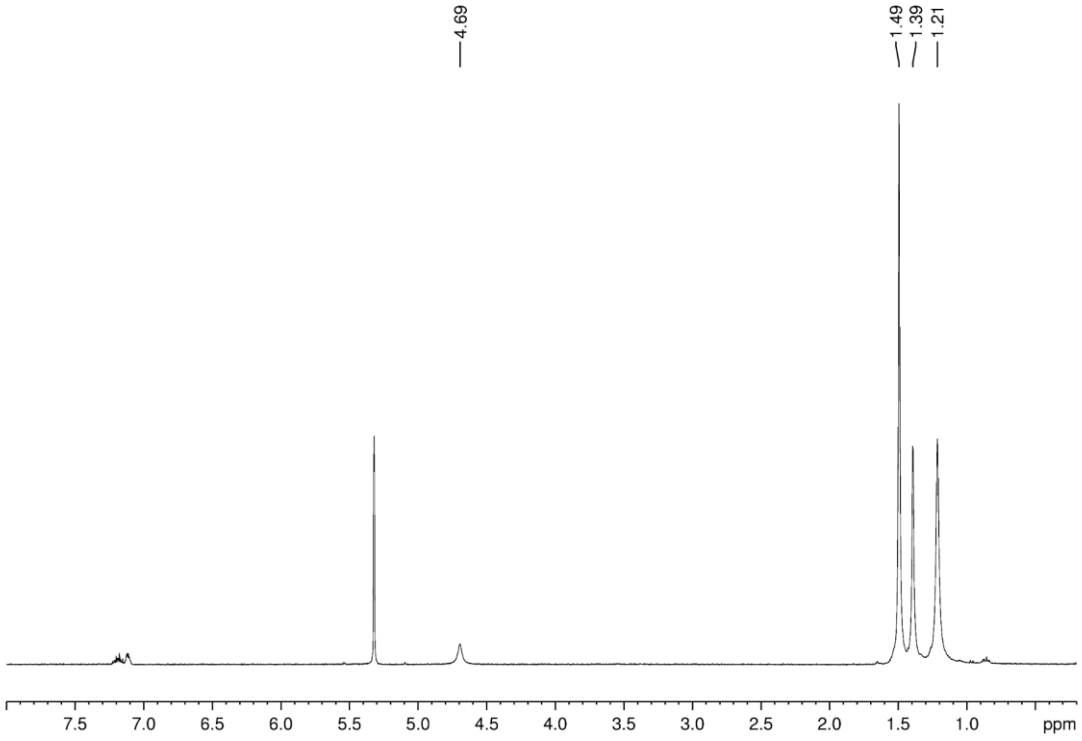


Figure S20: ^{1}H NMR spectrum of **5** in CD_2Cl_2.

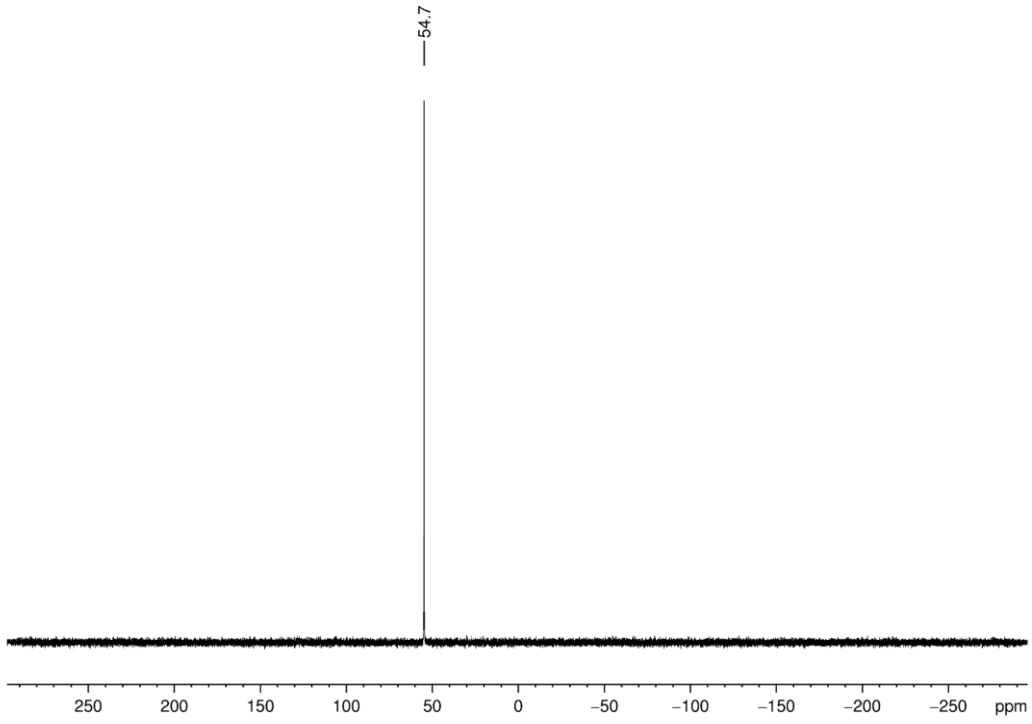


Figure S21: ^{31}P{^{1}H} NMR spectrum of **5** in CD_2Cl_2.

2.4 [(Cp*Fe)(Cp’’’Co)(μ,η^5:η^5-As$_5$)][FAl]$_2$ (6)

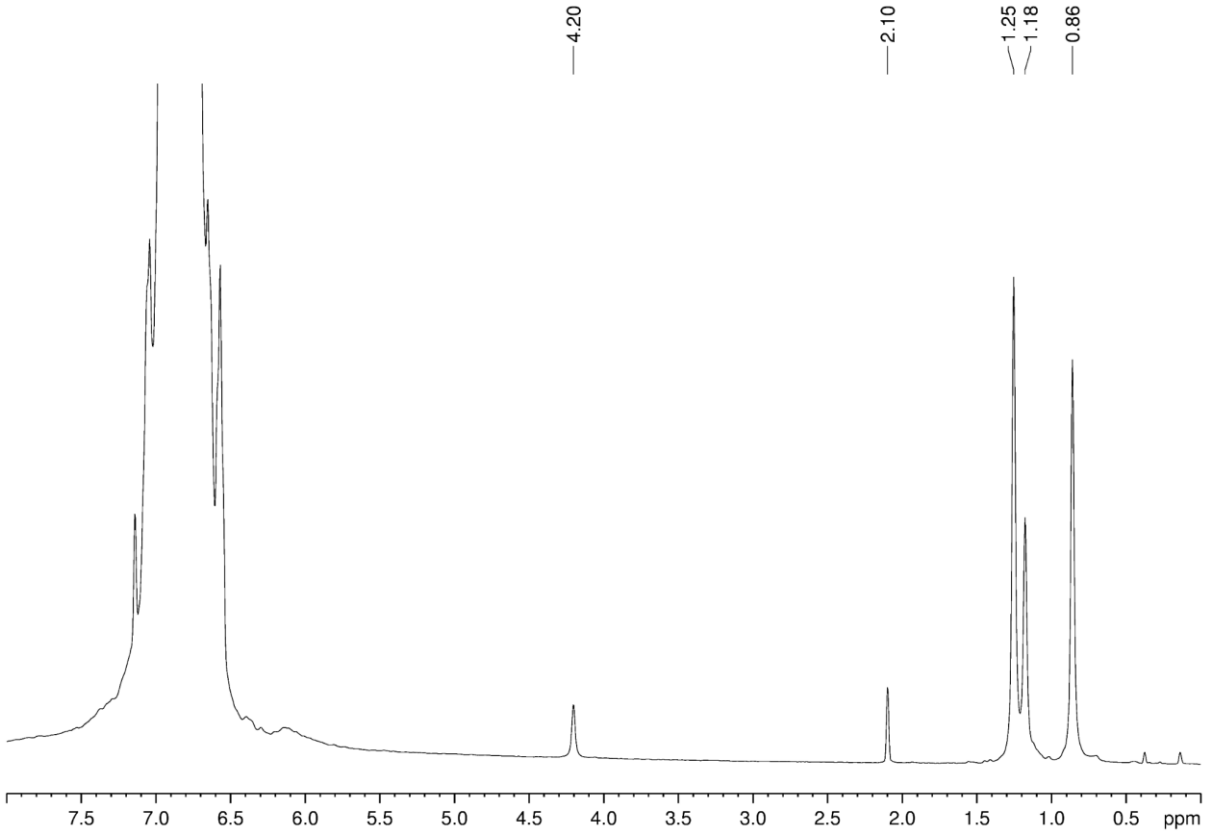


Figure S22: ^{1}H NMR spectrum of **6** in *o*-$C_6H_4F_2$ with C_6D_6 capillary.

2.5 [K(2,2,2-crypt)][(Cp*Fe)(Cp’’’Co)(μ,η^5:η^5-P$_5$)] (7)

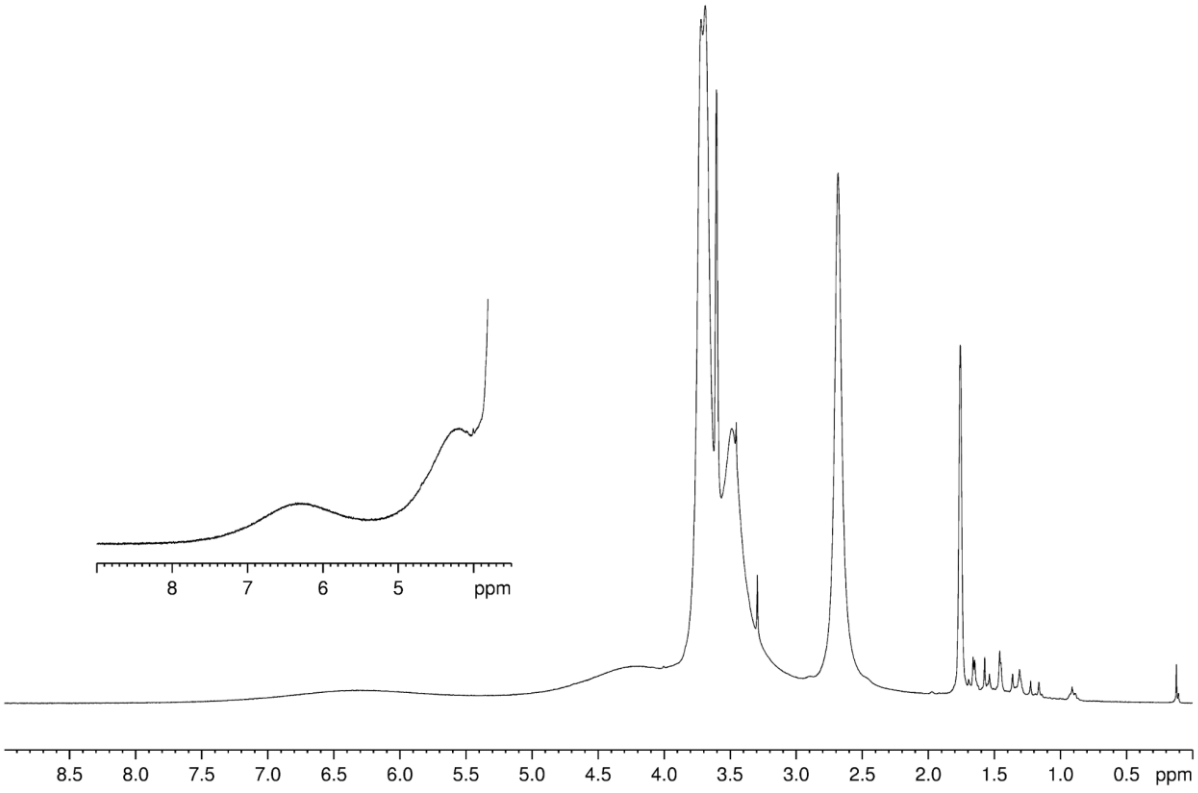


Figure S23: ^{1}H NMR spectrum of **7** in thf-d$_8$.

2.6 [(Cp*Fe)(Cp’’’Co)(μ,η^5:η^5-As$_5$)] (2) + KC$_8$/2,2,2-cryptand

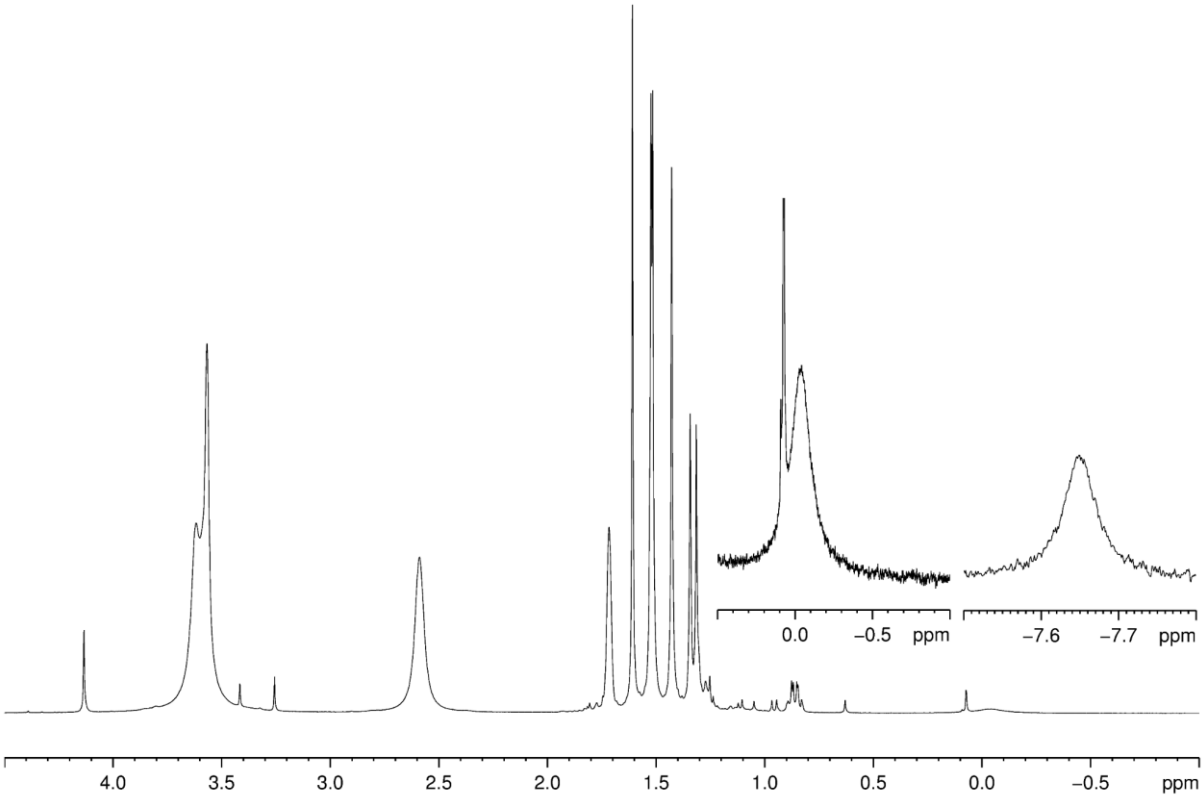


Figure S24: ^{1}H NMR spectrum of the reaction of **2** with KC_8 in the presence of 2,2,2-cryptand in thf-d_8.

2.7 [K(2,2,2-crypt)][(Cp*Fe)(Cp’’’Co)(μ,η^4:η^4-As$_6$)] (9)

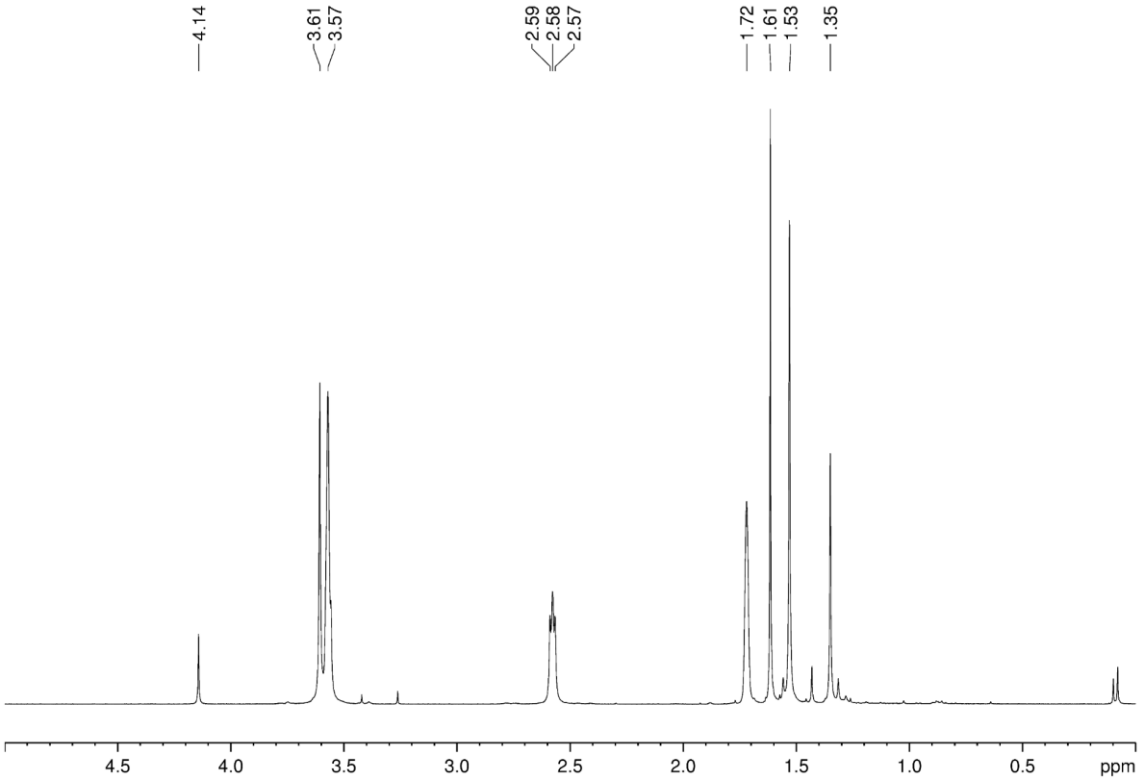


Figure S25: ^{1}H NMR spectrum of **9** in thf-d$_8$.

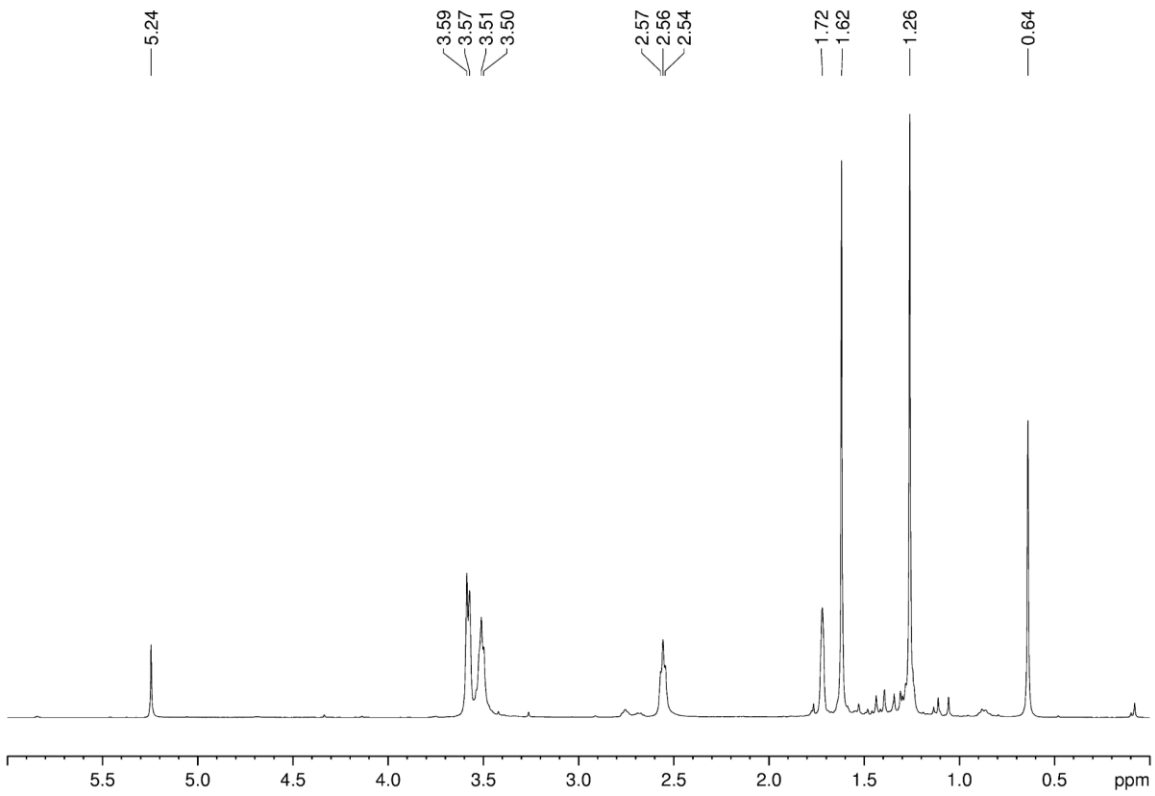


Figure S26: ^{1}H NMR spectrum of the mother liquor of the crystallization of **9** in thf-d$_8$.

2.8 Reaction of [(Cp’’’Co)(Cp’’’Ni)(μ,η^3:η^3-P$_3$)] (10) with Ag[FAl]

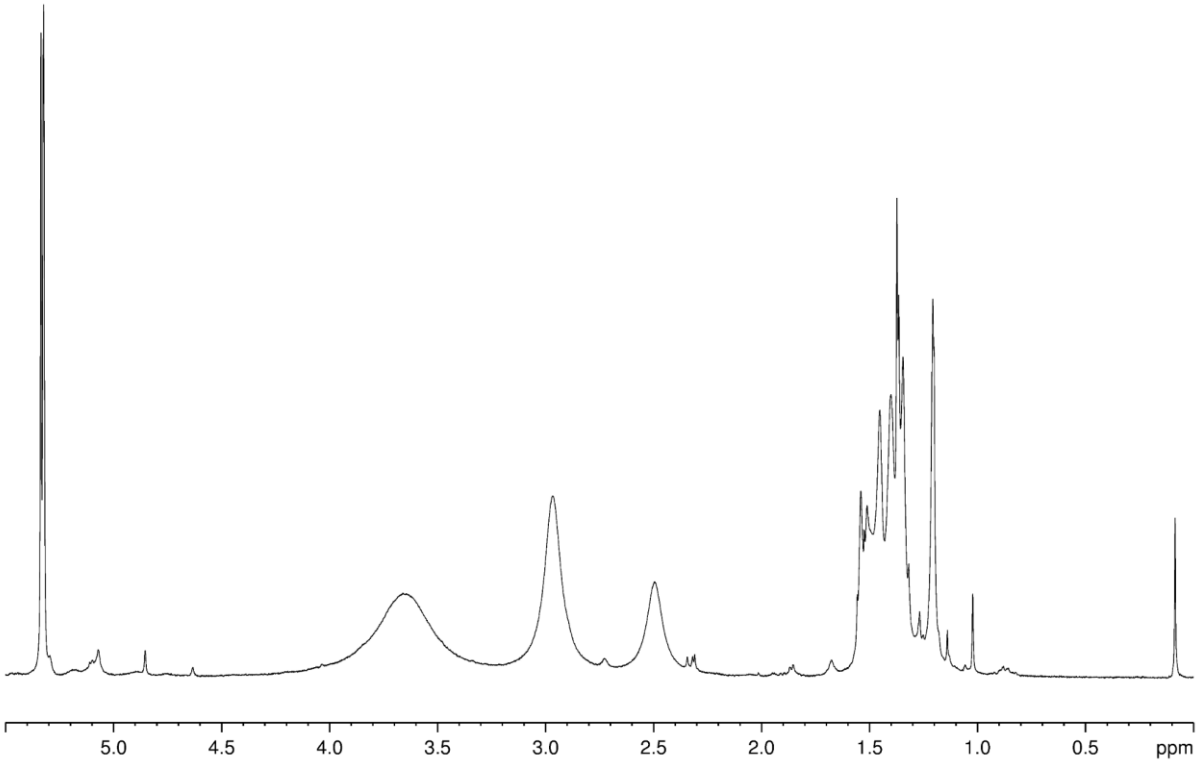


Figure S27: ^{1}H NMR of the reaction of **10** with Ag[FAl] in CD_2Cl_2 after one hour.

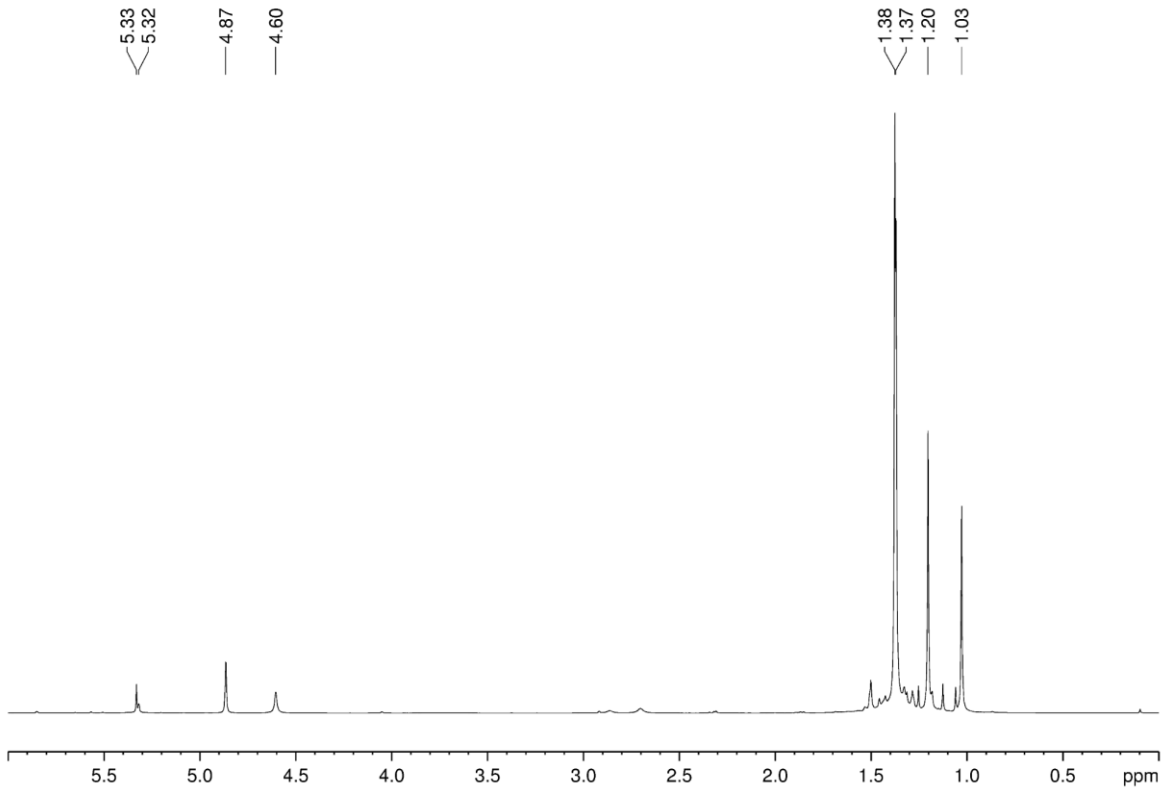


Figure S28: ^{1}H NMR of the reaction of **10** with Ag[FAl] in CD_2Cl_2 after one day.

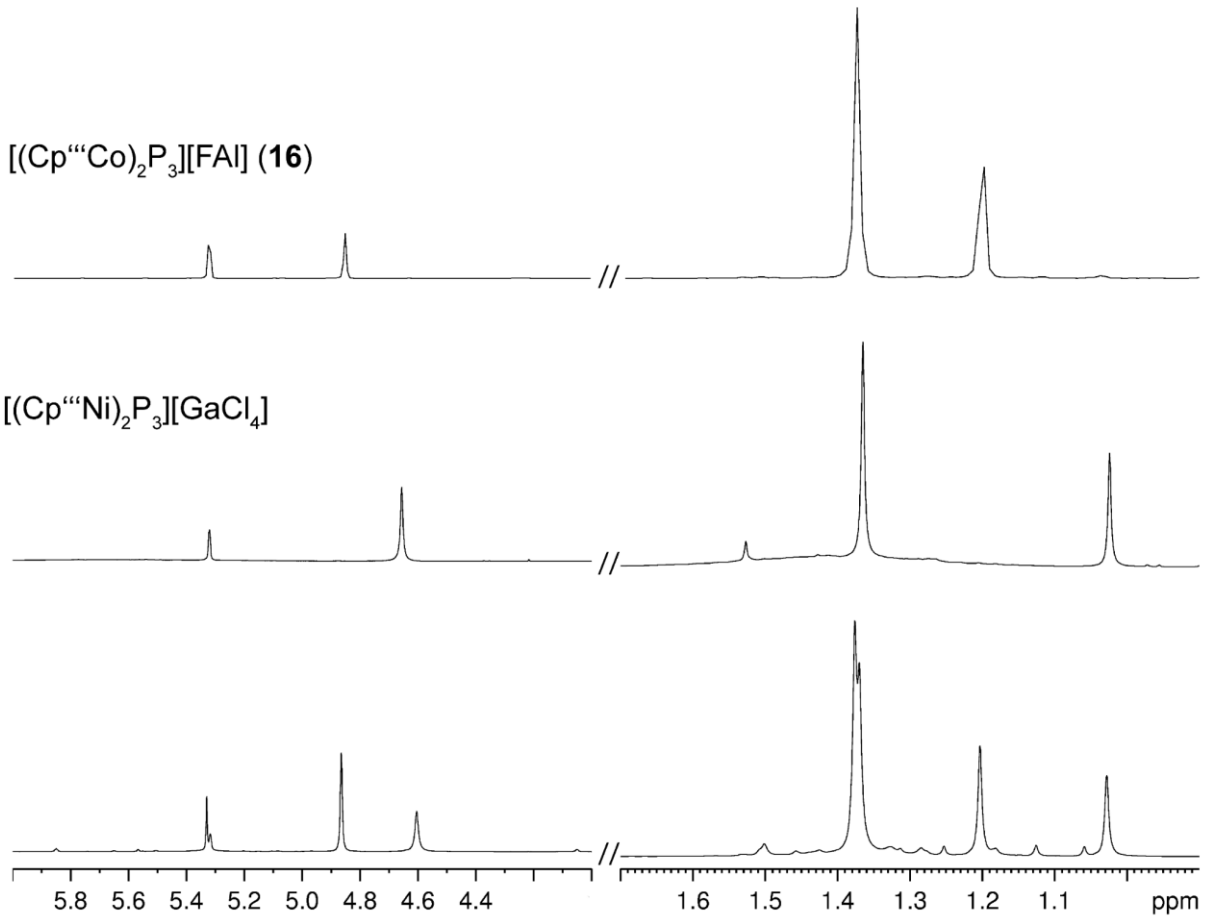


Figure S29: ^{1}H NMR of the reaction of **10** with Ag[FAl] in CD_2Cl_2 after one day and the spectra of isolated $[(Cp'''Co)_2P_3][FAl]$ (**16**) and $[(Cp'''Ni)_2P_3][GaCl_4]$ (as reference for **14**).[2]

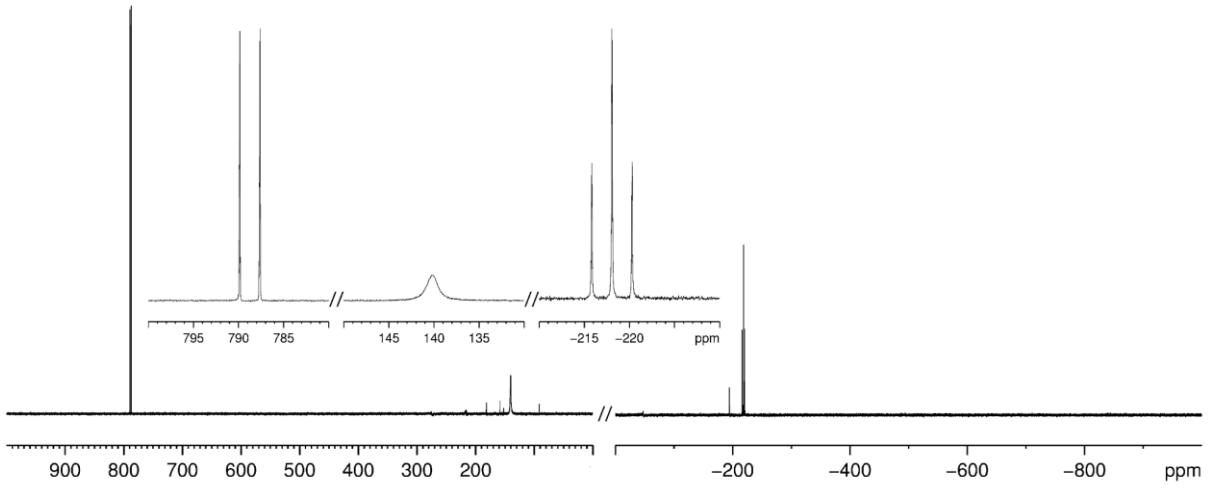


Figure S30: $^{31}P\{^{1}H\}$ NMR of the reaction of **10** with Ag[FAl] in CD_2Cl_2 after one day.

2.9 [(Cp’’’Co)$_2$(μ,η^3:η^3-P$_3$)][FAl] (16)

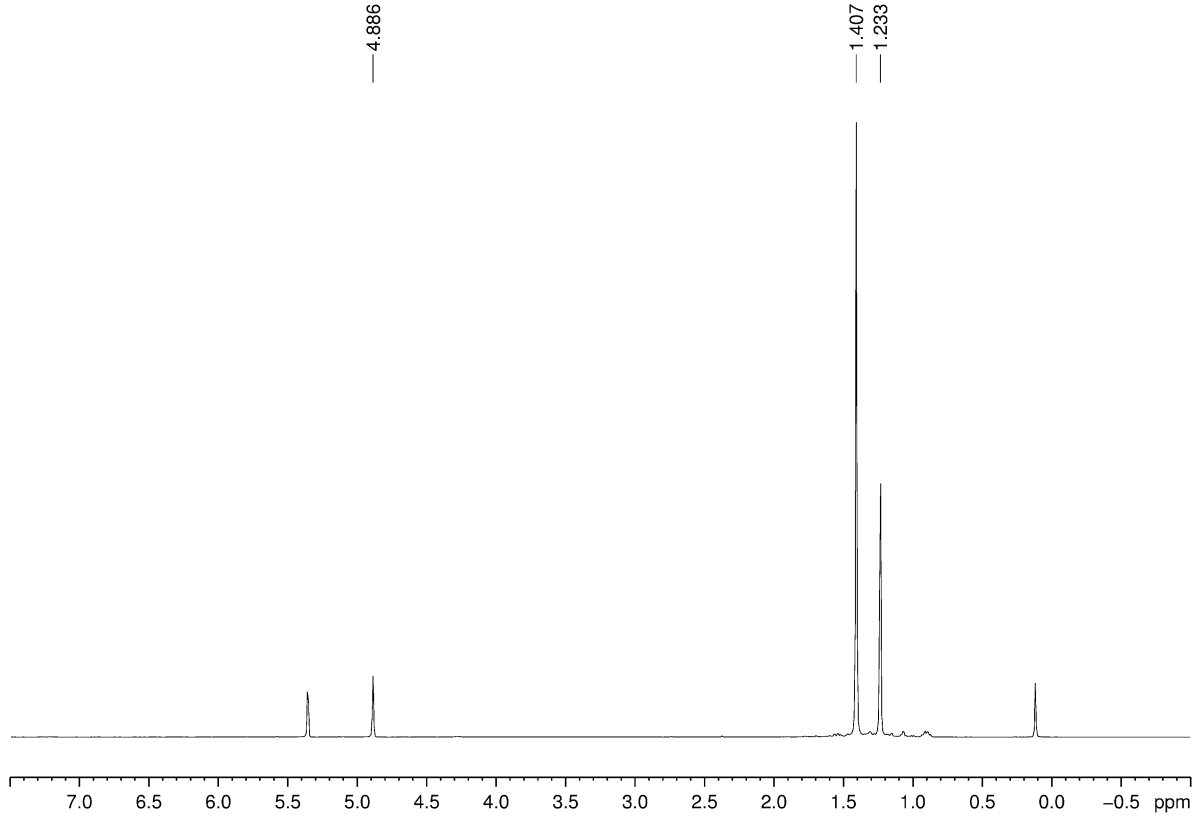


Figure S31: ^{1}H NMR of **16** in CD_2Cl_2.

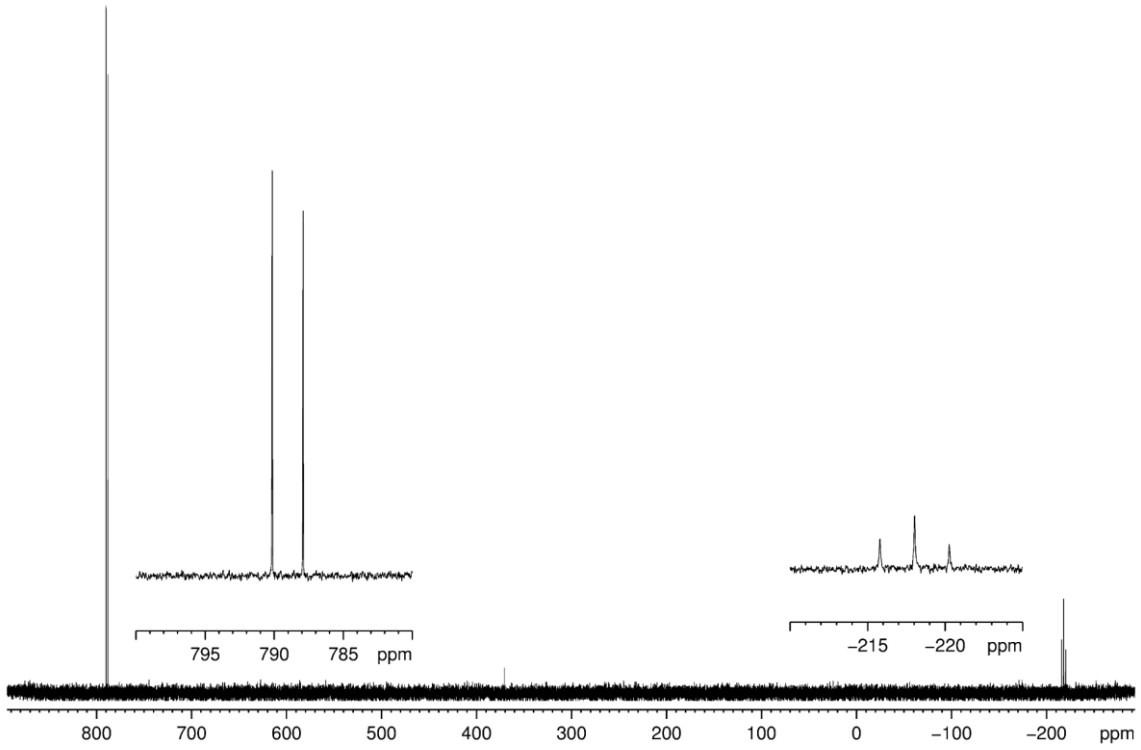


Figure S32: $^{31}P\{^1H\}$ NMR of **16** in CD_2Cl_2.

2.10 Reaction of [(Cp'''Co)(Cp'''Ni)(μ,η^3:η^3-As$_3$)] (11) with Ag[FAl]

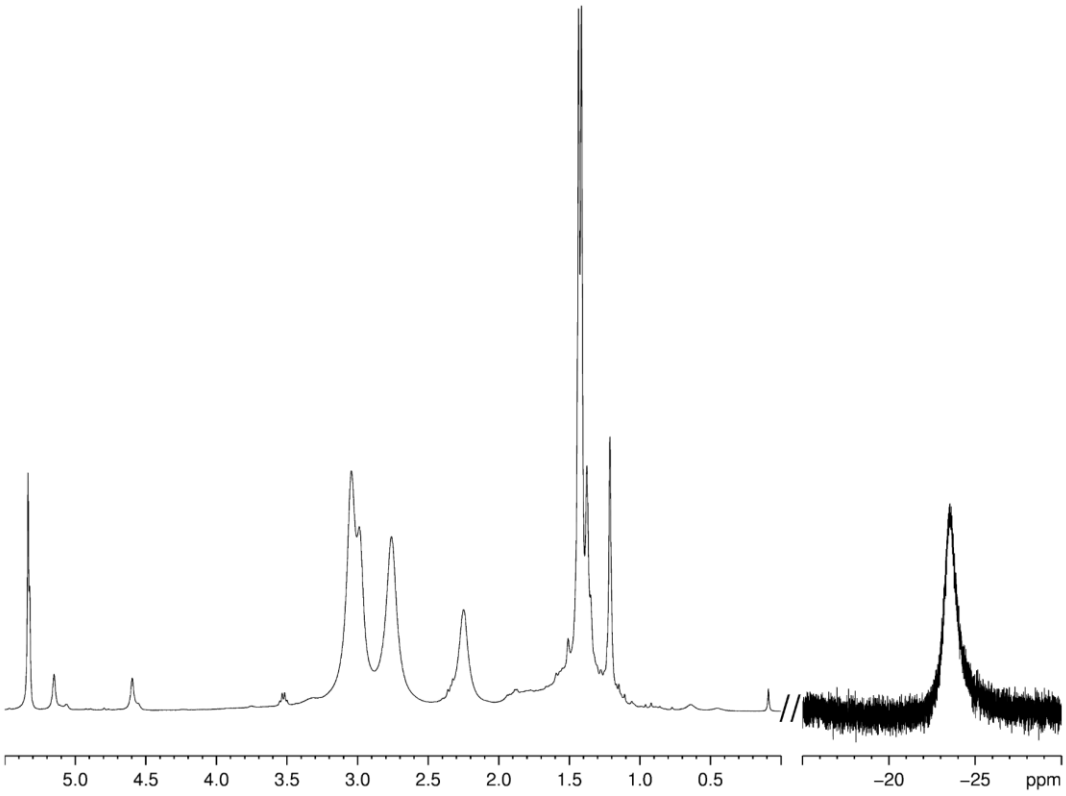


Figure S33: ^{1}H NMR of the reaction of **11** with Ag[FAl] in CD_2Cl_2 after one hour.

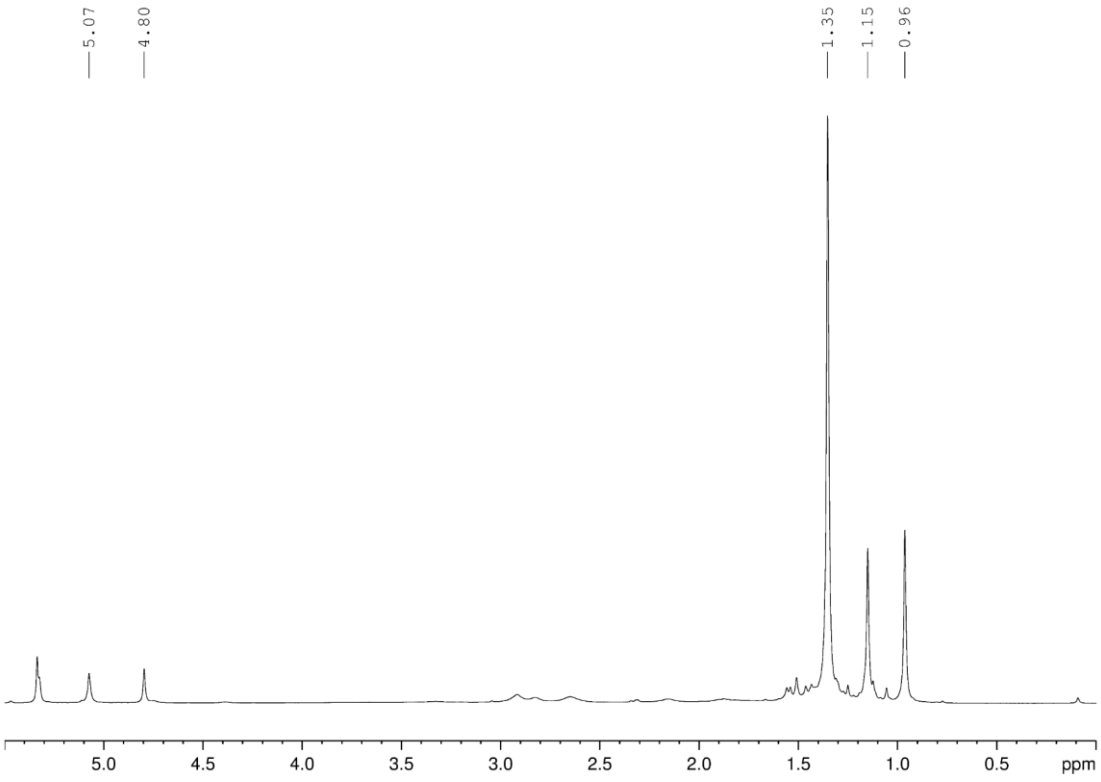


Figure S34: ^{1}H NMR of the reaction of **11** with Ag[FAl] in CD_2Cl_2 after one day.

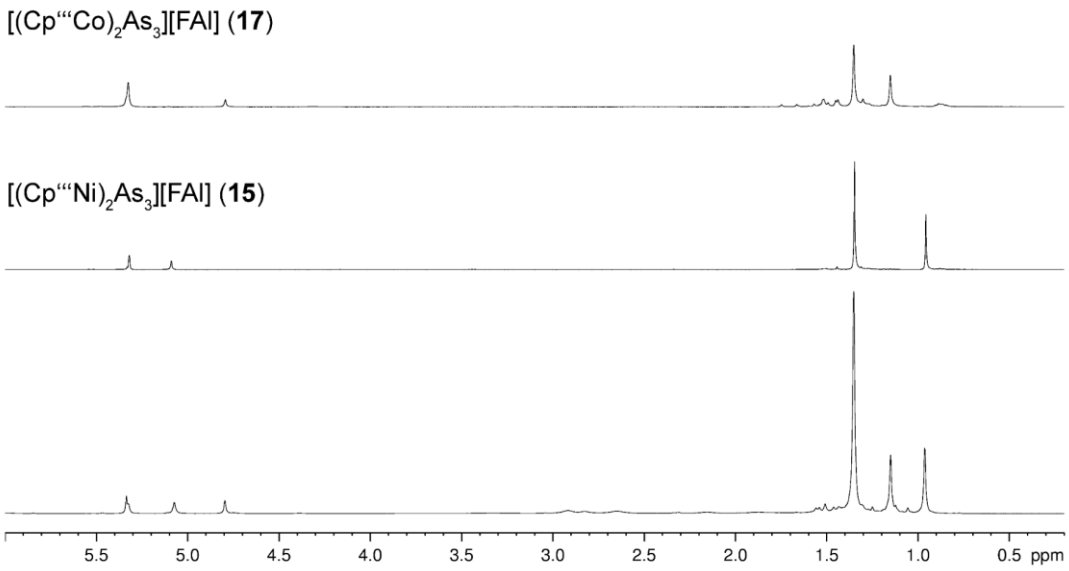


Figure S35: ^{1}H NMR of the reaction of **11** with Ag[FAl] in CD_2Cl_2 after one day and the spectra of isolated [(Cp’’’Co)$_2$As$_3$][FAl] (**17**) and [(Cp’’’Ni)$_2$As$_3$][FAl] (**15**).

2.11 $[(Cp'''Ni)_2(\mu,\eta^3:\eta^3\text{-}As_3)][FAl]$ (15)

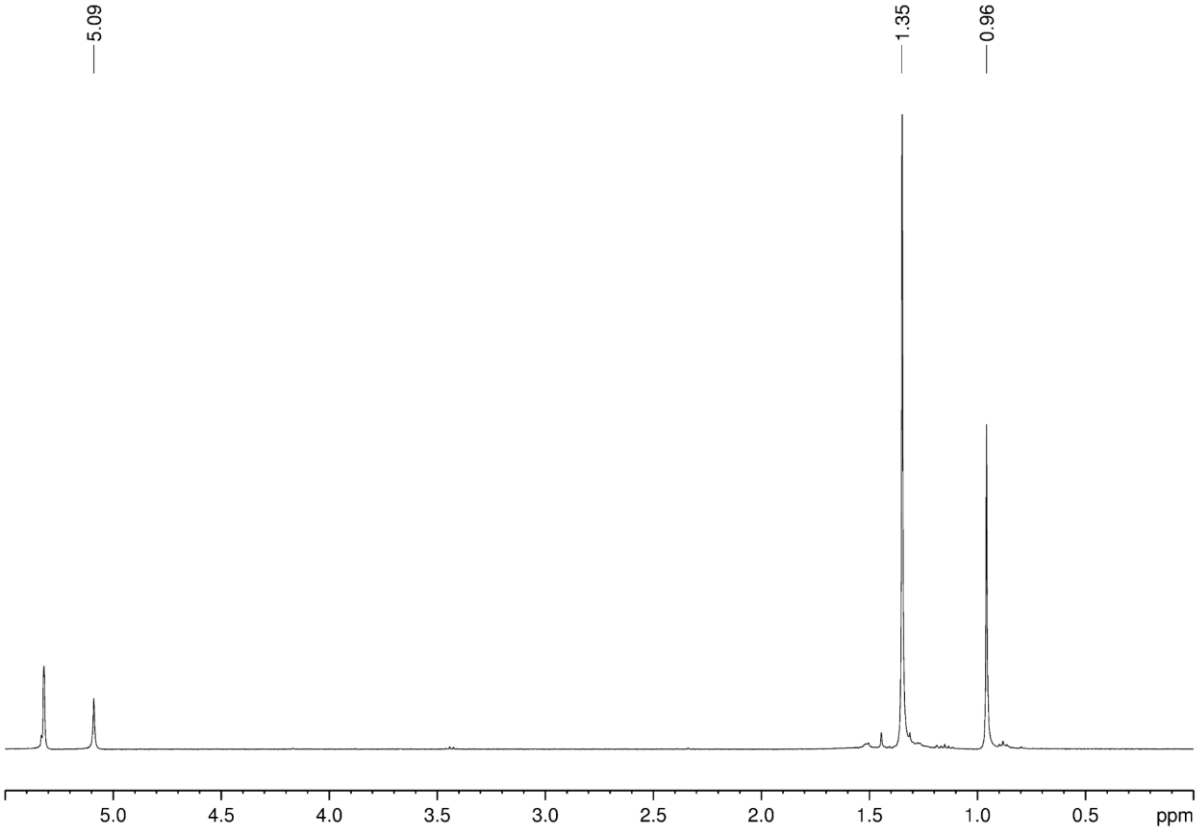


Figure S36: ^1H NMR of **15** in CD_2Cl_2.

2.12 $[(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}As_3)][FAl]$ (17)

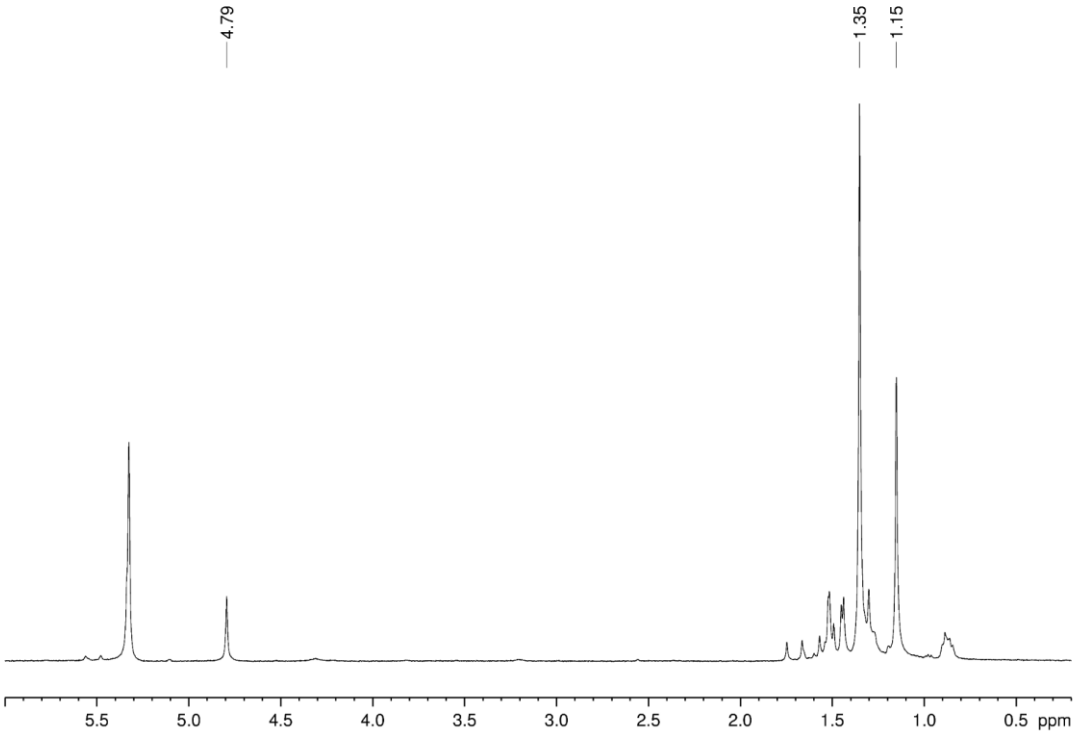


Figure S37: ^1H NMR of **17** in CD_2Cl_2.

2.13 [(Cp’’’Co)(Cp’’Ni)(μ,η^3:η^3-P$_3$)] (18)

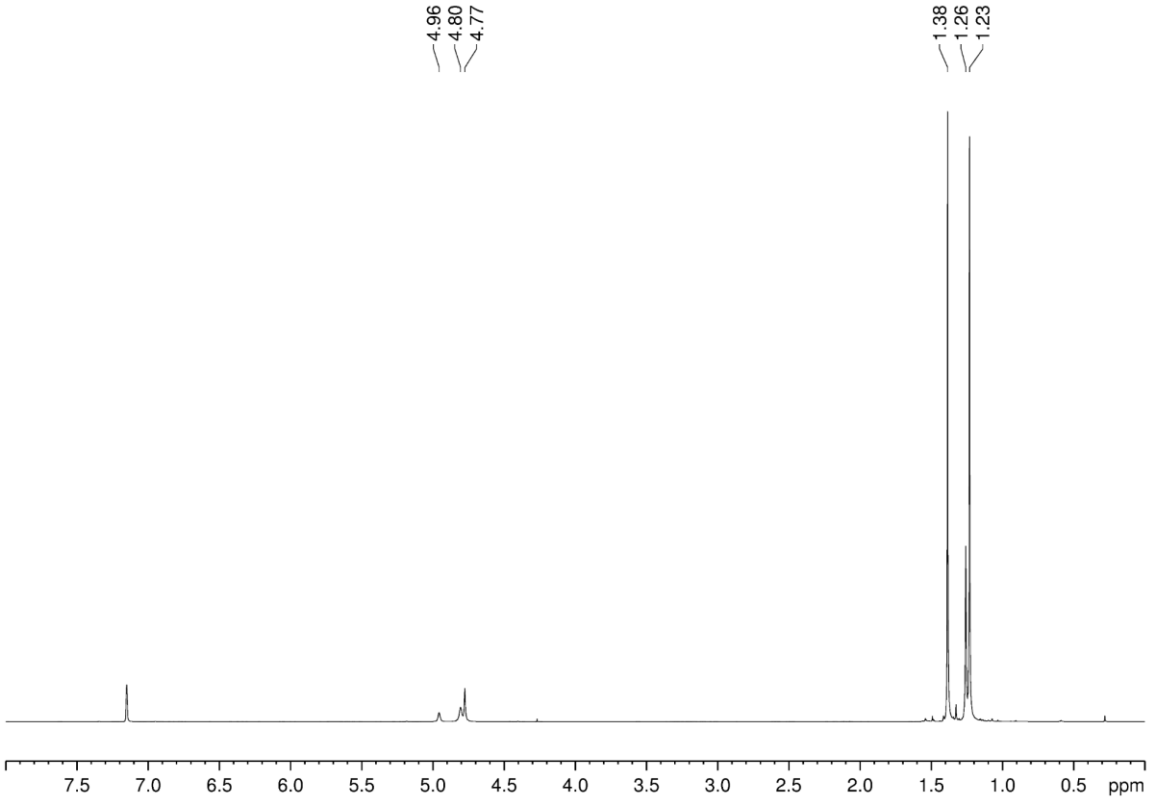


Figure S38: ^{1}H NMR of **18** in C_6D_6.

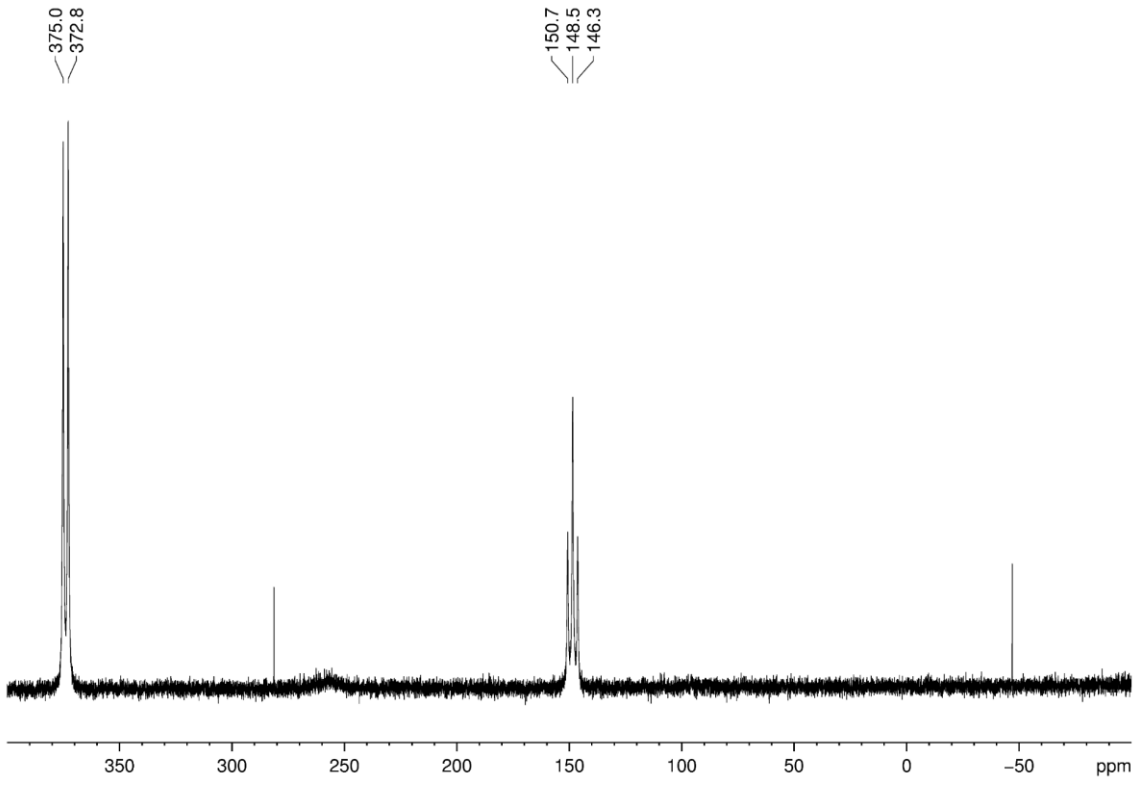


Figure S39: ^{31}P{^{1}H} NMR of **18** in C_6D_6.

2.14 [(Cp'''Co)(Cp''Ni)(μ$_4$,η^3:η^2:η^1:η^1-P$_3$)Ag(CH$_2$Cl$_2$)]$_2$[FAl]$_2$ (19)

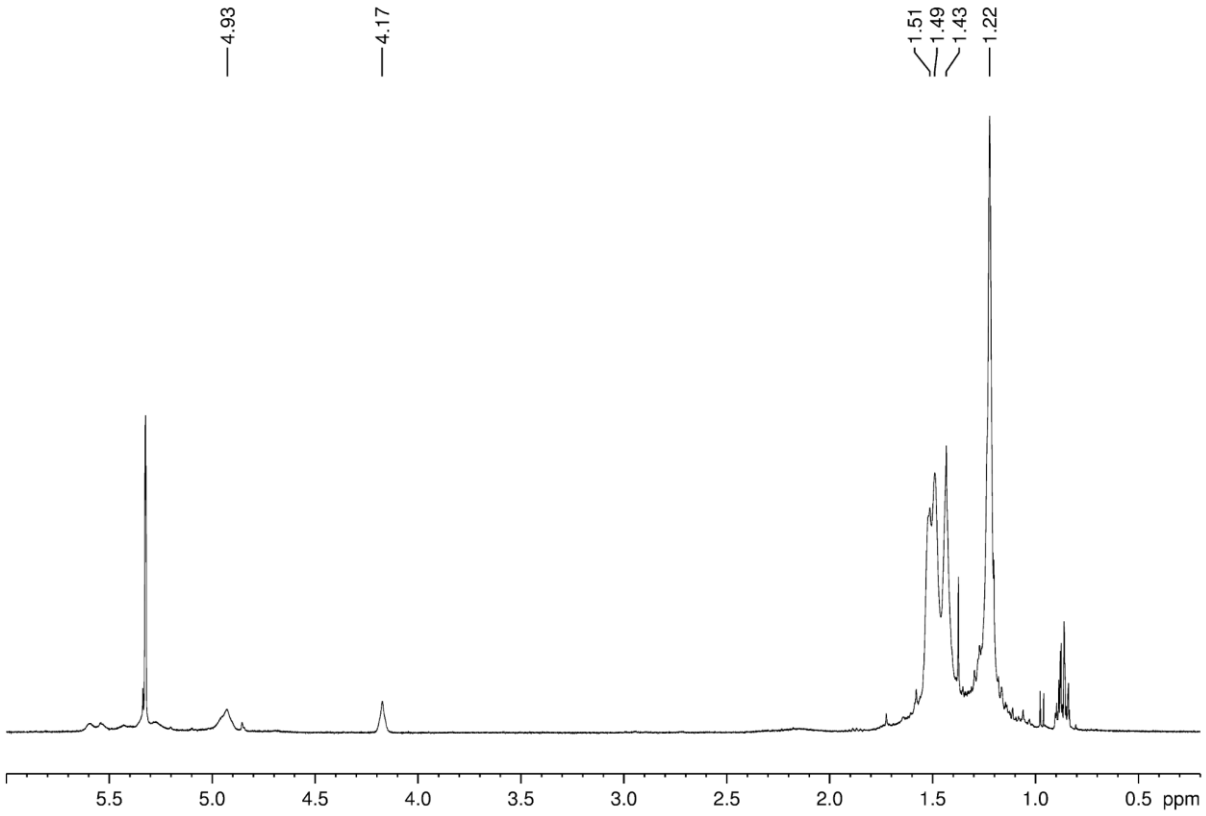


Figure S40: ^{1}H NMR of **19** in CD_2Cl_2.

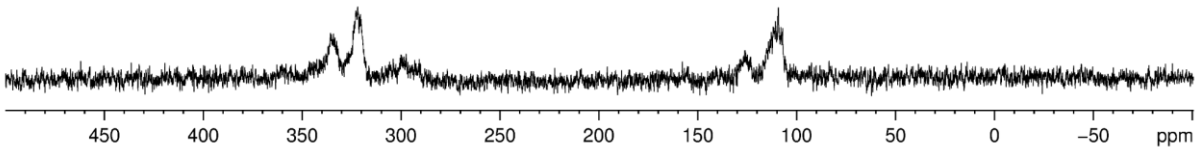


Figure S41: $^{31}P\{^1H\}$ NMR of **19** in CD_2Cl_2.

2.15 [(Cp’’’Co)(Cp’’’Ni)(μ,η^3:η^3:η^1-P$_3$){W(CO)$_5$}][FAl] (21)

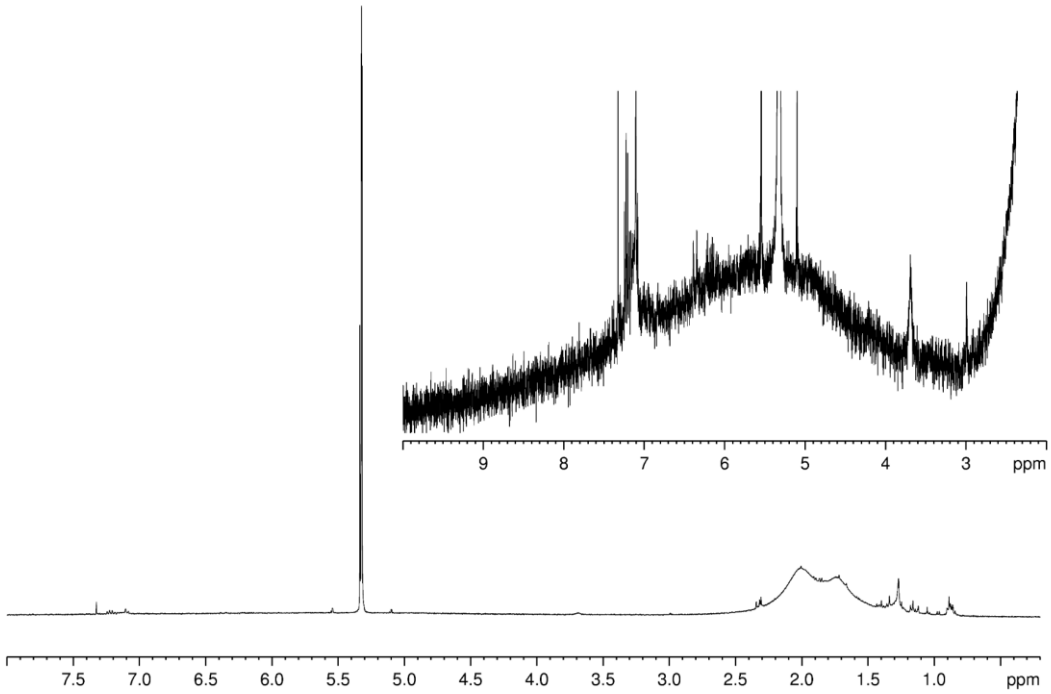


Figure S42: ^{1}H NMR of the reaction of **20** with Ag[FAl] in CD_2Cl_2 after 1 h.

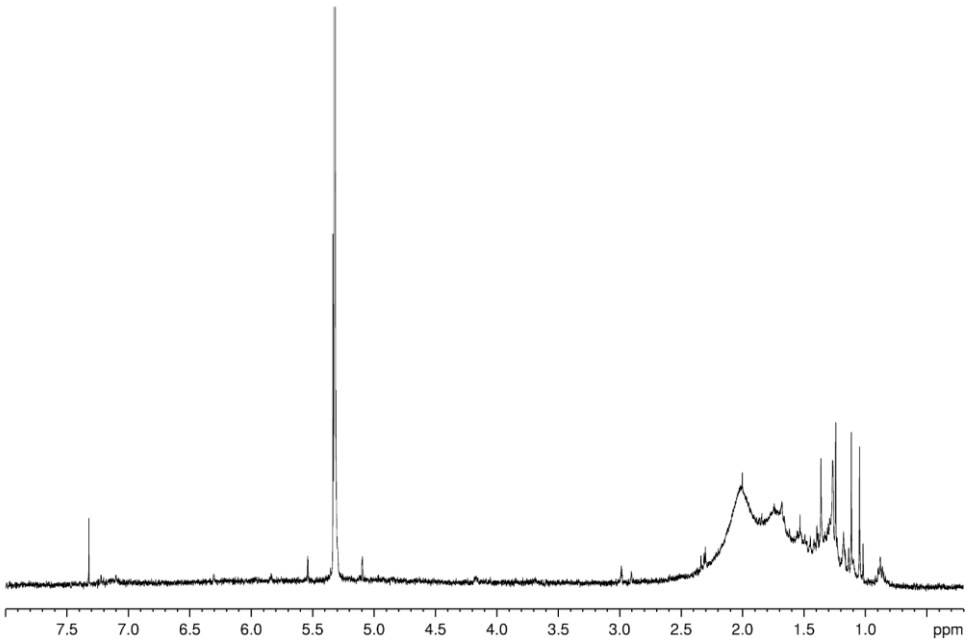


Figure S43: ^{1}H NMR of the reaction of **20** with Ag[FAl] in CD_2Cl_2 after 1 d.

2.16 [K(2,2,2-crypt)][(Cp’’’Co)(Cp’’Ni)(μ,η^3:η^3 -P_3)] (22)

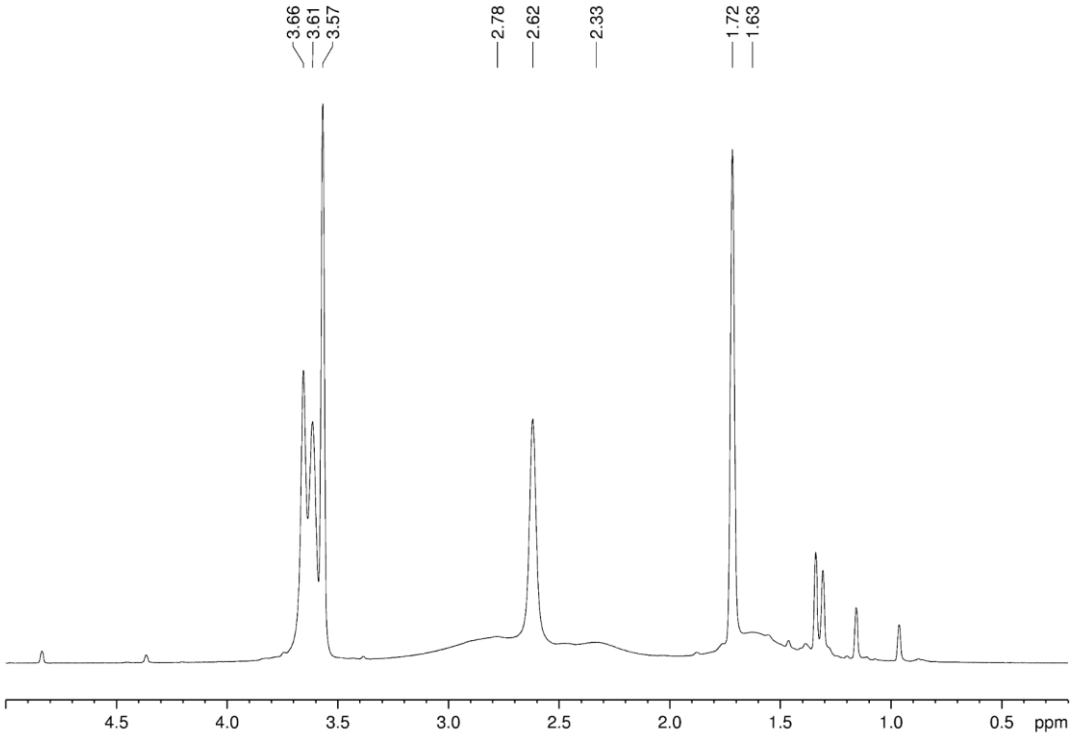


Figure S44: ^{1}H NMR of **22** in thf-d_8.

2.17 [K(2,2,2-crypt)][(Cp’’’Co)(Cp’’Ni)(μ,η^3:η^3-As$_3$)] (23)

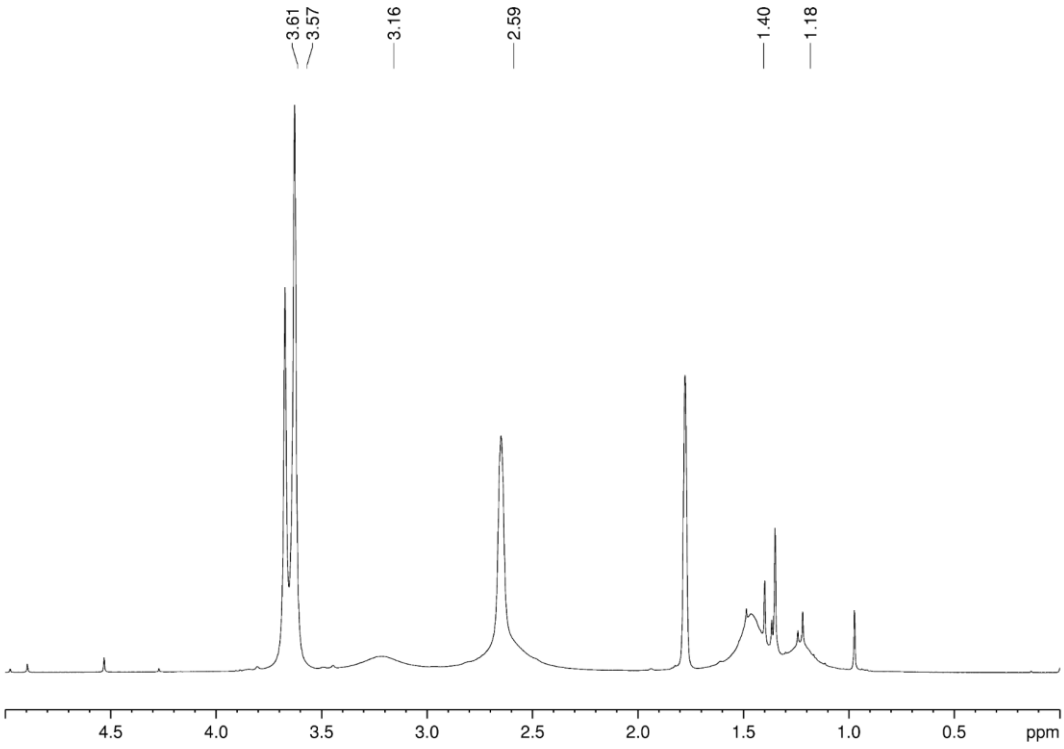


Figure S45: ^{1}H NMR of **23** in thf-d$_8$.

3. Cyclic voltametric measurements

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

The measurement was conducted in 5 ml thf with 500 mg conducting salt [^{n}Bu$_4$N][PF$_6$] and 0.01 mmol of **1** were used. A platinum working electrode, a platinum counter electrode and a silver wire as a reference electrode were used. Ferrocene was added as an in internal standard for referencing.

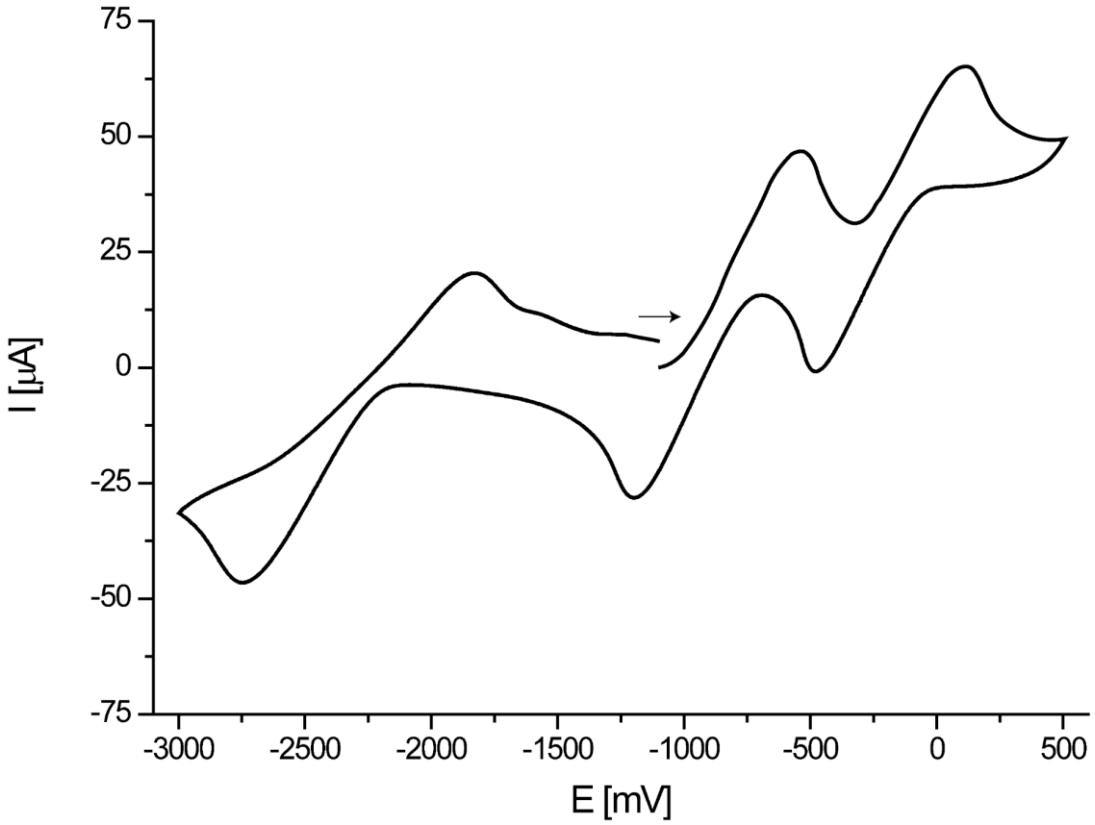


Figure S46. Cyclic voltammogram of **1** in thf against [Cp$_2$Fe]/[Cp$_2$Fe]$^+$ (electrolyte ^{n}Bu$_4$NPF$_6$, scan rate: 100 mV/s. temperature: r.t.).

3.2 [(Cp*Fe)(Cp’’’Co)(μ,η^5:η^5-As$_5$)] (2)

The measurement was conducted in 5 ml CH_2Cl_2 with 750 mg conducting salt [^{n}Bu$_4$N][PF_6] and 0.01 mmol of **2** were used. A platinum working electrode, a platinum counter electrode and a silver wire as a reference electrode were used. Ferrocene was added as an in internal standard for referencing.

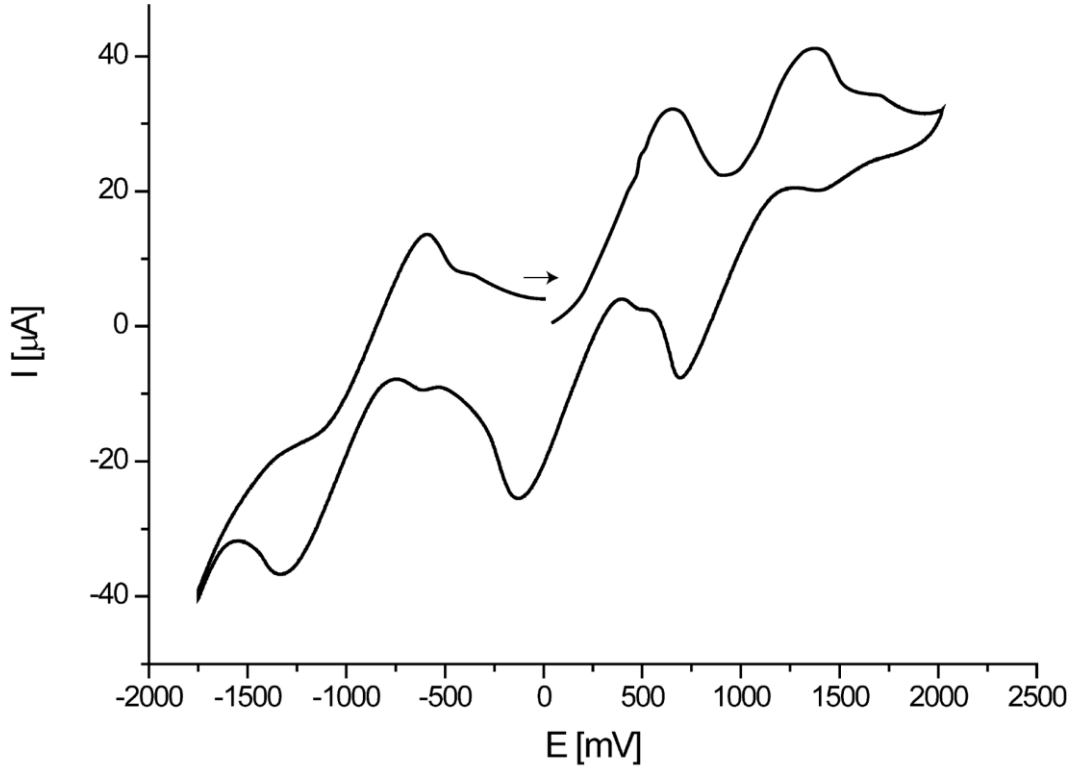


Figure S47. Cyclic voltammogram of **2** in CH_2Cl_2 against $[Cp_2Fe]/[Cp_2Fe]^+$ (electrolyte ^{n}Bu$_4$NPF$_6$, scan rate: 100 mV/s. temperature: r.t.).

3.3 [(Cp'''Co)(Cp'''Ni)(μ,η³:η³-P₃)] (10)

The measurement was conducted in 5 ml *o*-difluorobenzene with 750 mg conducting salt [^{n}Bu$_4$N][PF$_6$] and 0.01 mmol of **10** were used. A platinum working electrode, a platinum counter electrode and a silver wire as a reference electrode were used. Ferrocene was added as an in internal standard for referencing.

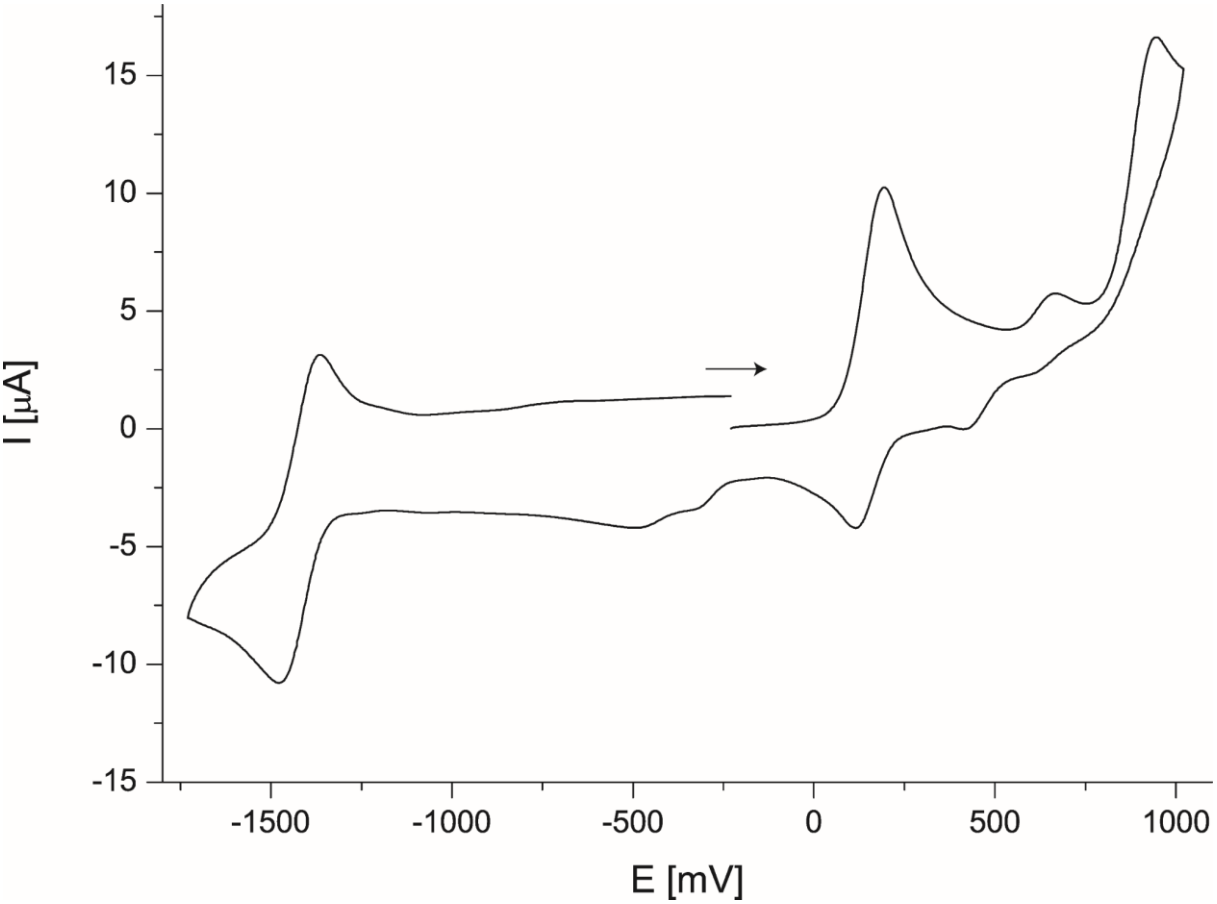


Figure S48. Cyclic voltammogram of **10** in *o*-$C_6H_4F_2$ against $[Cp_2Fe]/[Cp_2Fe]^+$ (electrolyte $^{n}Bu_4NPF_6$, scan rate: 100 mV/s. temperature: r.t.).

3.4 [(Cp'''Co)(Cp'''Ni)(μ,η³:η³-As₃)] (11)

The measurement was conducted in 5 ml dme with 500 mg conducting salt [^{n}Bu$_4$N][PF$_6$] and 0.01 mmol of **11** were used. A platinum working electrode, a platinum counter electrode and a silver wire as a reference electrode were used. Ferrocene was added as an in internal standard for referencing.

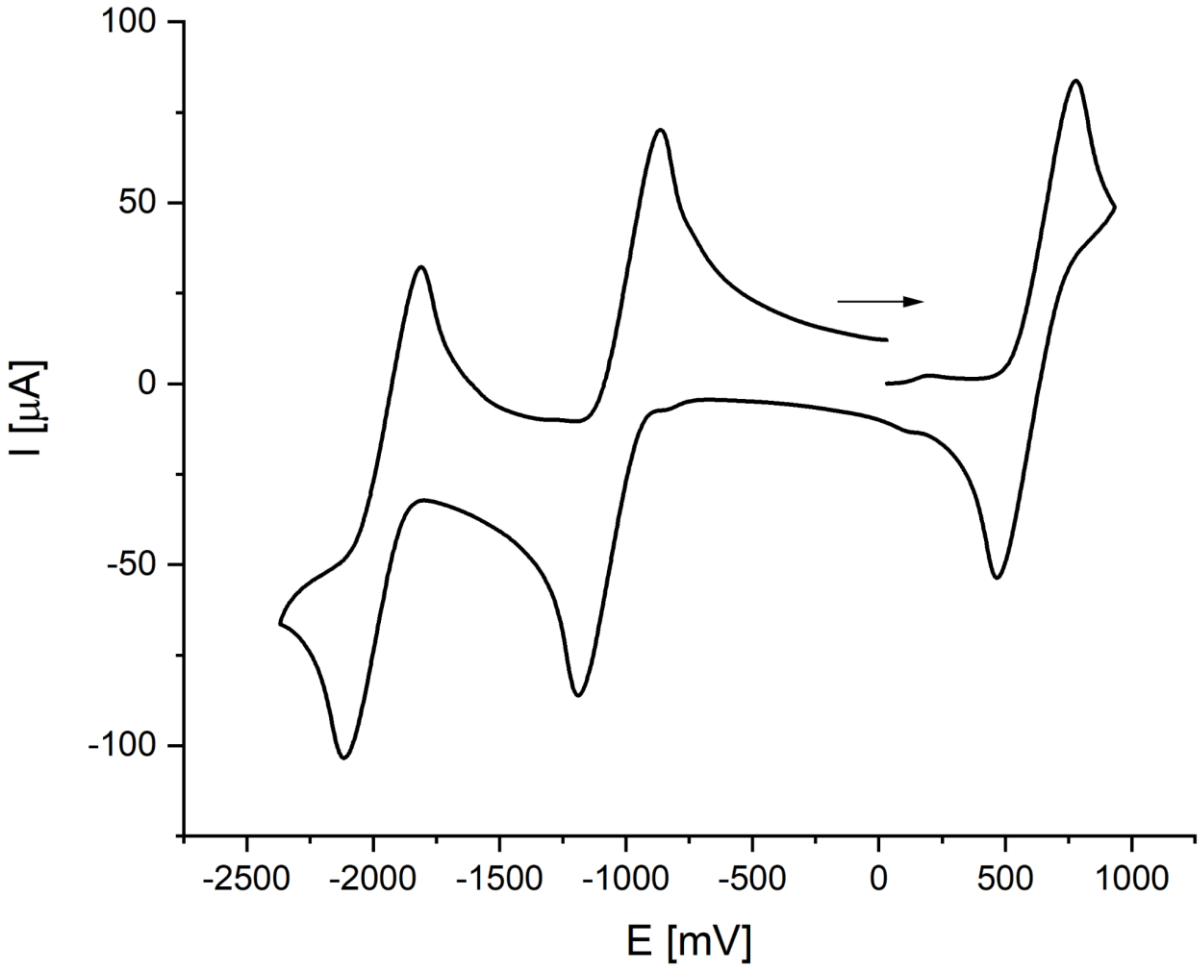


Figure S49. Cyclic voltammogram of **11** in dme against [Cp_2Fe]/[Cp_2Fe]$^{+}$ (electrolyte ^{n}Bu$_4$NPF$_6$, scan rate: 100 mV/s. temperature: r.t.).

4. Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on either an Gemini Ultra diffractometer (Oxford diffraction) with an AtlasS2 detector Mo radiation (λ = 0.71073 Å) (**6**, **9**, **19**, **20**) or Cu-K*α* radiation (λ = 1.54178 Å) (**4**, **15**), on a GV 50 diffractometer (Rigaku, formerly Agilent Technologies) with TitanS2 detector from applying Cu-K*α* radiation (λ = 1.54178 Å) (**3**, **11**, **16**, **18**, **21**, [Cp'''Ni(η^3-As_3)]) or Cu-K*β* radiation (λ = 1.39222 Å) (**7**) or on a SuperNova (Agilent Technologies) with an Atlas detector applying Cu-K*α* radiation (λ = 1.54178 Å) (**5**). All measurements were performed at 123 K. Data collection and reduction were performed with CrysAlispro (Version 171.37.34 (), 171.38.43, 2015 (**4, 7**), 171.40.14a, 2018 (**3**, **5**, **6**, **9**, **11**, **16**, **17**, **18**, **20**, **21**), 171.41.27a, 2019 (**15,** [Cp'''Ni(η^3-As_3)]), 171.41.76a, 2020 (**19**)). For the compounds (**4**, **7**, **15**, [Cp'''Ni(η^3-As_3)]) an analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C.Clark & J.S. Reid was applied.[3] For the compounds (**3**, **5**, **6**, **9**, **11**, **16**, **18**, **19**, **20**, **21**) a gaussian absorption correction based on gaussian integration over a multifaceted crystal model was applied. All structures were solved by direct methods with ShelXT[4] and Olex2[5] and refined by full-matrix least-squares method against F^2 in anisotropic approximation using ShelXL[4]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined in calculated positions using riding on pivot atom model.

CCDC-2064647 (**3**), CCDC-2064648 (**4**), CCDC-2064649 (**5**), CCDC-2064650 (**6**), CCDC-2064651 (**7**), CCDC-2064652 (**9**), CCDC-2064653 (**11**), CCDC-2064654 (**15**), CCDC-2064655 (**16**), CCDC-2064656 (**17**), CCDC-2064657 (**18**), CCDC-2064658 (**19**), CCDC-2064659 (**21**), CCDC-2064660 (**22**), CCDC-2064661 (23) and CCDC-2064662 ([Cp'''Ni(η^3-As_3)]) 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^5-P$_5$)][FAl] (3)

Compound **3** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at -30 °C in the triclinic space group $P\bar{1}$ as dark green blocks. The asymmetric unit contains one cation **3**, one [FAL] counterion and 2.5 molecules CH_2Cl_2. A solvent mask was calculated and 193 electrons were found in a volume of 820 Å^3 in two voids. This is consistent with the presence of 2.5 CH_2Cl_2 per asymmetric unit which account for 210 electrons per unit cell. The structure in solid state is depicted in Figure S50 and S51.

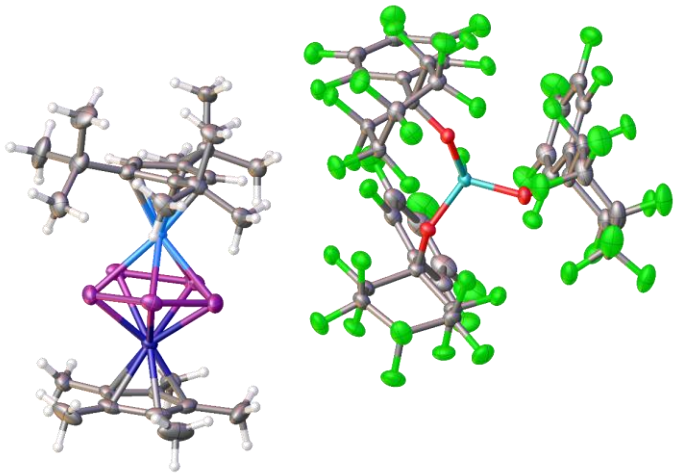


Figure S50: Molecular structure of **3** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

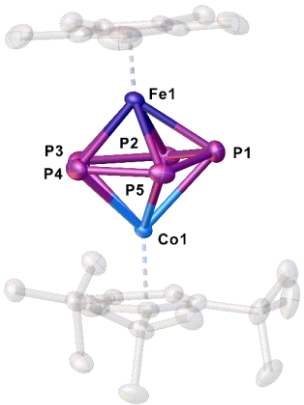


Figure S51: Molecular structure of the cation in **3** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Co1-Fe1 3.1539(4), P1-P2 2.1215(9), P2-P3 2.1601(9), P3-P4 2.1226(9), P4-P5 2.1518(9), P1-P5 2.1400(8), P2-P4-P5-P1 9.363, (Cp*-centroid)FeCo(Cp’’’-centroid) 176.043.

4.2 [(Cp*Fe)(Cp’’’Co)(μ,η^5:η^5-As$_5$)][FAl] (4)

Compound **4** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at -30 °C in the triclinic space group $P\bar{1}$ as dark brown plates. The asymmetric unit contains one cation **4**, one [FAL] counterion and 2.5 molecules CH_2Cl_2. A solvent mask was calculated and 206 electrons were found in a volume of 808 Å^3 in two voids. This is consistent with the presence of five CH_2Cl_2 per unit cell. The structure in solid state is depicted in Figure S52 and S53.

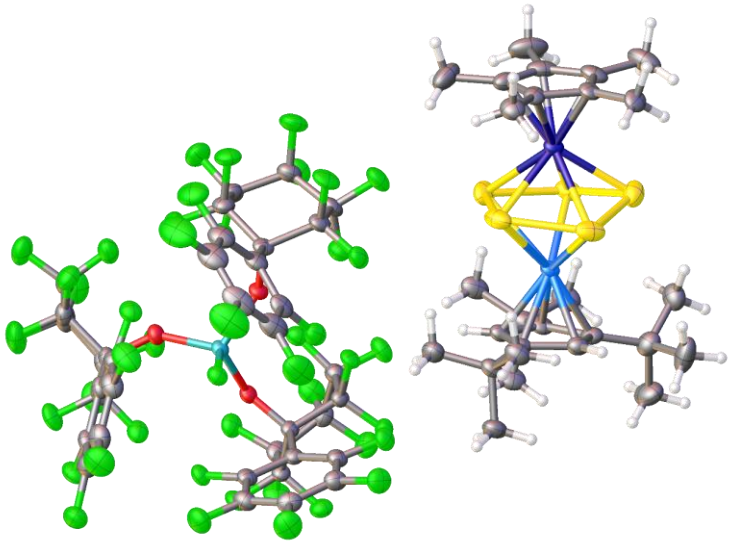


Figure S52: Molecular structure of **4** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

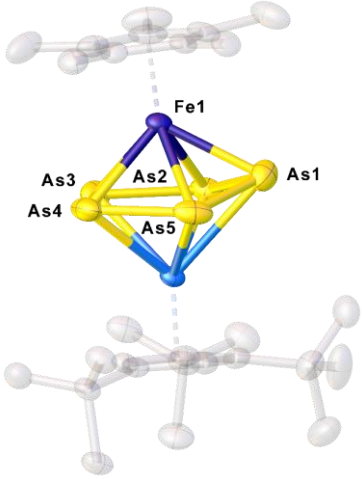


Figure S53: Molecular structure of the cation in **4** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Co1-Fe1 3.2188(6), As1-As2 2.3392(7), As2-As3 2.3596(7), As3-As4 2.3252(8), As4-As5 2.3619(8), As1-As5 2.3224(8), As2-As4-As5-As1 13.611, (Cp*-centroid)FeCo(Cp’’’-centroid) 174.958.

4.3 [(Cp*Fe)(Cp’’’Co)(μ,η^5:η^5-P$_5$)][FAl]$_2$ (5)

Compound **5** crystallizes from a concentrated solution in *o*-$C_6H_4F_2$ layered with toluene at -30 °C in the monoclinic space group *P2$_1$* as dark brown blocks. The asymmetric unit contains one dication **5**, two [FAL] counterions 3 molecules *o*-$C_6H_4F_2$ and 0.5 molecule toluene. The toluene molecule (0.5) share the position with 0.5 molecules *o*-$C_6H_4F_2$. The restraints SADI, SIMU, FLAT were applied to describe the solvent molecules appropriate. The structure in solid state is depicted in Figure S54 and S55.

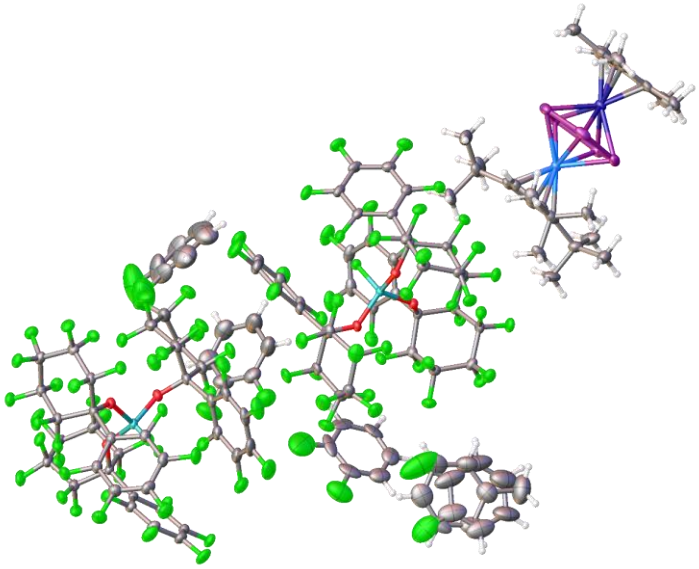


Figure S54: Molecular structure of **5** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

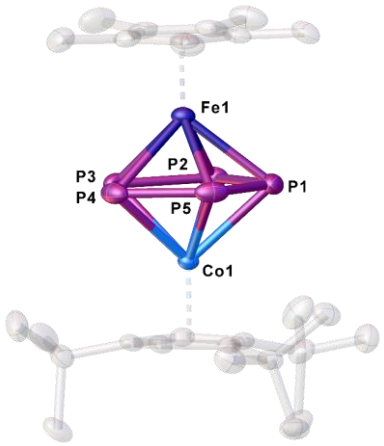


Figure S55: Molecular structure of the dication in **5** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Fe1-Co1 3.0637(8), P1-P2 2.1449(12), P2-P3 2.1440(12), P3-P4 2.1439(12), P4-P5 2.1422(13), P1-P5 2.1523(13), P2-P4-P5-P1 -0.841, (Cp*-centroid)FeCo(Cp’’’-centroid).

4.4 [(Cp*Fe)(Cp’’’Co)(μ,η^5:η^5-As$_5$)][FAl]$_2$ (6)

Compound **6** crystallizes from a concentrated solution in *o*-$C_6H_4F_2$ layered with toluene at -30 °C in the monoclinic space group *P2$_1$* as dark brown blocks. The asymmetric unit contains one dication of **6**, two [FAL] counterions 3.5 molecules *o*-$C_6H_4F_2$. A solvent mask was calculated and 298 electrons were found in a volume of 1198 Å^3 in one void. This is consistent with the presence of seven molecules *o*-$C_6H_4F_2$ per unit cell. A twin refinement (BASF of 0.216) was applied. The structure in solid state is depicted in Figure S56 and S57.

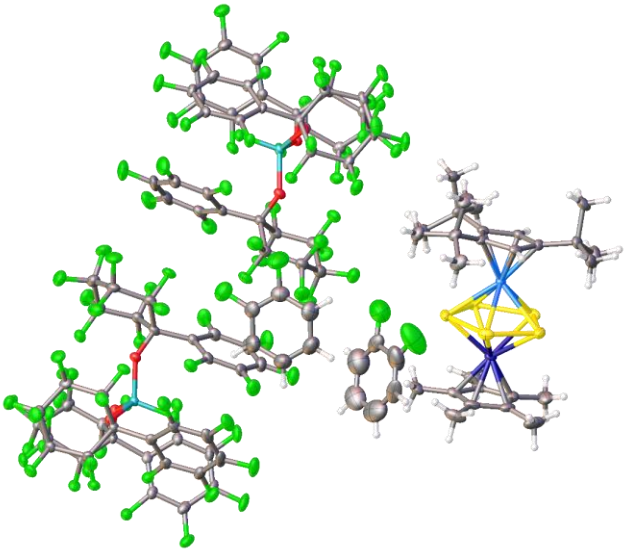


Figure S56: Molecular structure of **6** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

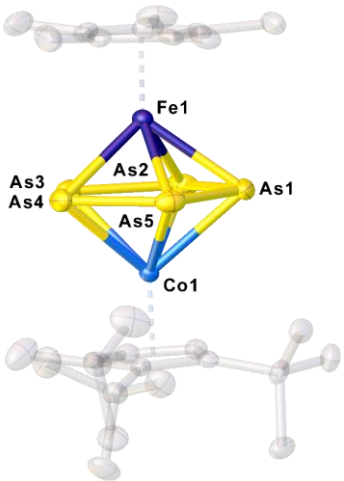


Figure S57: Molecular structure of the dication **6** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Fe1-Co1 3.0891(9), As1-As2 2.3518(6), As2-As3 2.3418(6), As3-As4 2.3380(6), As4-As5 2.3493(6), As1-As5 2.3410(7), As2-As4-As5-As1 1.419, (Cp*-centroid)FeCo(Cp’’’-centroid) 177.368.

4.5 [K(2,2,2-crypt)][(Cp*Fe)(Cp’’’Co)(μ,η^4:η^3-P$_5$)] (7)

Compound **7** crystallizes from a concentrated solution in dme layered with hexane at -30 °C in the triclinic space group $P\bar{1}$ as dark green blocks. The asymmetric unit contains two anions of **7**, two potassium counterions chelated by 2,2,2-cryptand and 0.45 molecules hexane. Both cations are disordered over two positions, one anion is disordered over two positions, the Cp* ligand of the other anion is disordered over three positions. The restraints SIMU, SADI and RIGU were applied to describe the disorder appropriate. A solvent mask was calculated and 44 electrons in a void of 152 Å^3 was found. This is consistent with the presence of 0.9 molecules hexane per unit cell. The structure in solid state is depicted in Figure S58 and S59.

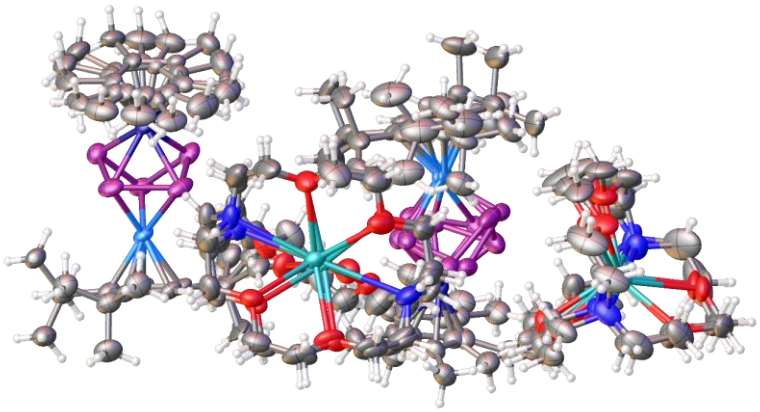


Figure S58: Molecular structure of **7** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

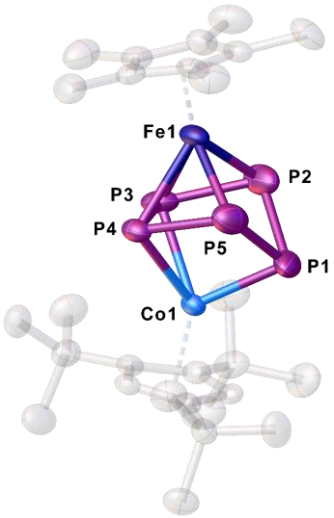


Figure S59: Molecular structure of the non-disordered anion (P$_5$ ligand) in **7** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Fe1-Co1 3.6620(6), P1-P2 2.1952(9), P2-P3 2.1741(12), P3-P4 2.2456(13), P4-P5 2.1770(12), P1-P5 2.2083(11), P2-P4-P5-P1 -44.456, (Cp*-centroid)FeCo(Cp’’’-centroid) 152.772.

4.6 [K(2,2,2-crypt)][(Cp*Fe)(Cp’’’Co)(μ,η^4:η^4-As$_6$)] (9)

Compound **9** crystallizes from a concentrated solution in dme layered with hexane at room temperature in the triclinic space group $P\bar{1}$ as dark brown plates. The asymmetric unit contains one anion of **9** and one potassium ion chelated by 2,2,2-cryptand. The structure in solid state is depicted in Figure S60 and S61.

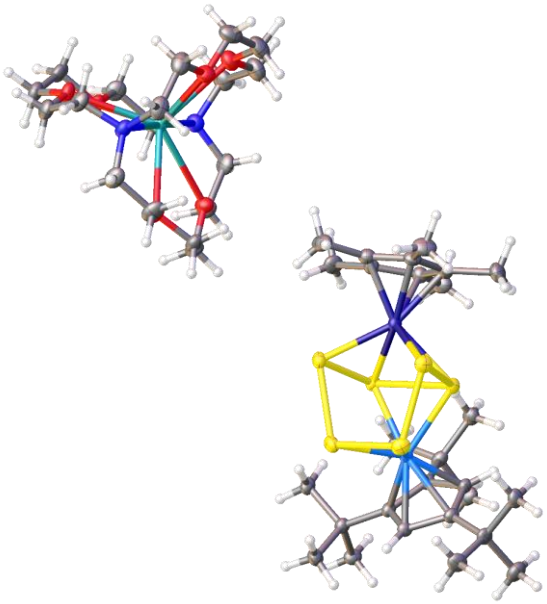


Figure S60: Molecular structure of **9** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

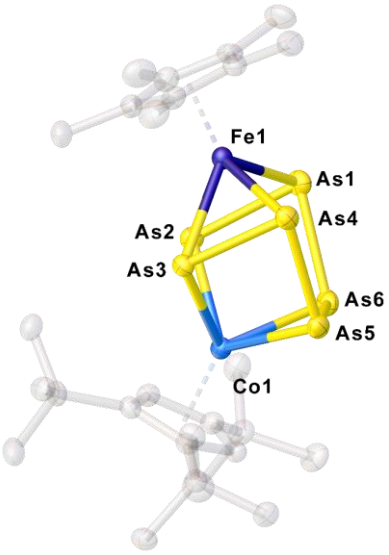


Figure S61: Molecular structure of the anion in **9** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Fe1-Co1 3.8385(6), As1-As2 2.3871(5), As2-As3 2.6901(7), As3-As4 2.3843(5), As4-As5 2.4420(5), As5-As6 2.3441(5), As1-As6 2.4406(6), (Cp*-centroid)FeCo(Cp’’’-centroid) 129.762.

4.7 [(Cp’’’Co)(Cp’’’Ni)(μ,η^3:η^3-As$_3$)] (11)

Compound **11** crystallizes from a concentrated solution in CH_2Cl_2 layered with MeCN at room temperature in the triclinic space group $P\bar{1}$ as dark green needles. The asymmetric unit contains one molecule of **11**. Since both {Cp’’’M} fragments contain the same Cp’’’ ligand and a mixed occupation could not be neglected both metal atoms are refined as 50 % Co and 50 % Ni. The structure in solid state is depicted in Figure S62 and S63.

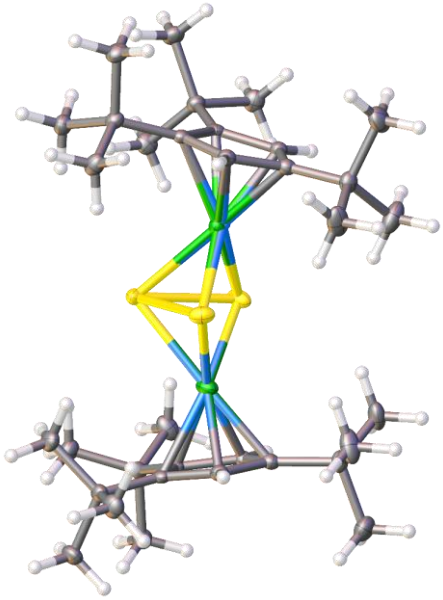


Figure S62: Molecular structure of **11** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

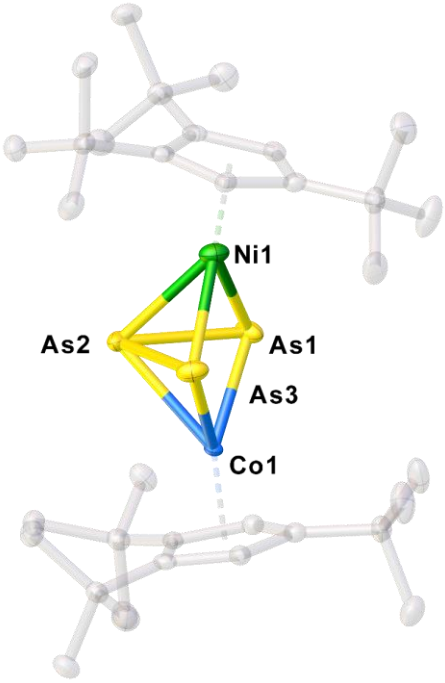


Figure S63: Molecular structure of one part of **11** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Co1-Ni1 3.495(5), As1-As2 2.4130(3), As2-As3 2.4155(3), As1-As3 2.9891(3), (Cp’’’-centroid)CoNi(Cp’’’-centroid) 162.947.

4.8 [(Cp’’’Ni)$_2$(μ,η^3:η^3-As$_3$)][FAl] (15)

Compound **15** crystallizes from a concentrated solution in CH_2Cl_2 layered with pentane at room temperature in the triclinic space group $P\bar{1}$ as dark brown blocks. The asymmetric unit contains one cation of **15** and one [FAl] counterion. The structure in solid state is depicted in Figure S64 and S65.

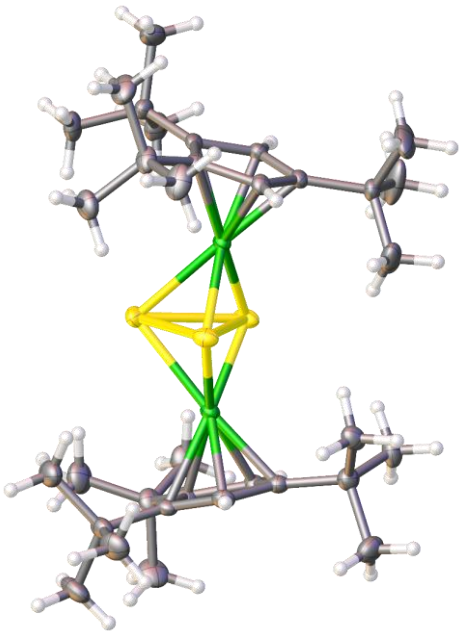


Figure S64: Molecular structure of **15** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

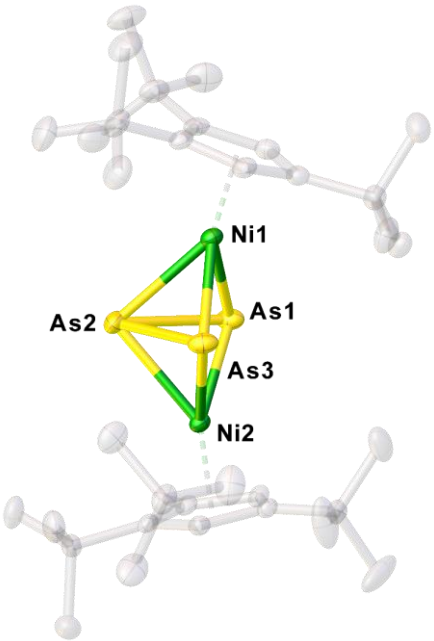


Figure S65: Molecular structure of the cation in **15** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ni1-Ni2 3.5434(5), As1-As2 2.4179(4), As2-As3 2.4294(3), As1-As3 2.8730(4), (Cp’’’-centroid)CoNi(Cp’’’-centroid) 156.046.

4.9 $[(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}P_3)][FAl]$ (16)

Compound **16** crystallizes from a concentrated solution in CH_2Cl_2 layered with toluene at -30 °C in the monoclinic space group *P2₁/c* as dark red rods. The asymmetric unit contains one cation of **16,** one [FAl] counterion 1.4 molecules CH_2Cl_2 and 0.9 molecules toluene. The toluene molecule is disordered over two positions with side occupancies of 0.55 and 0.35. The restraints SADI and SIMU were applied to describe the disorder. The structure in solid state is depicted in Figure S66 and S67.

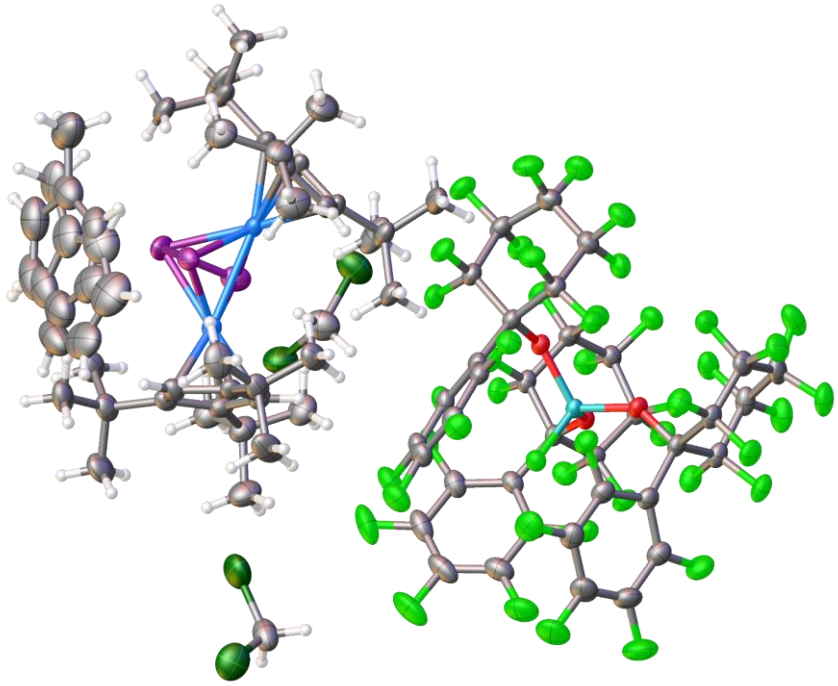


Figure S66: Molecular structure of **16** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

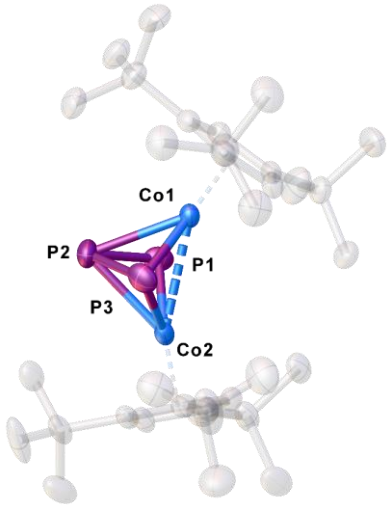


Figure S67: Molecular structure of the cation in **16** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Co1-Co2 2.6213(6), P1-P2 2.1532(12), P2-P3 2.1516(12), P1-P3 3.2571(11), (Cp'''-centroid)CoCo(Cp'''-centroid) 133.616.

4.10 [(Cp'''Co)$_2$(μ,η^3:η^3-As$_3$)][FAl] (17)

Compound **17** crystallizes from a concentrated solution in *o*-$C_6H_4F_2$ layered with pentane at -30 °C in the monoclinic space group *P2$_1$/c* as dark brown blocks. The asymmetric unit contains one cation of **17,** one [FAl] counterion and two molecules *o*-$C_6H_4F_2$. One *o*-$C_6H_4F_2$ molecule is disordered over three positions with side occupancies of 0.75, 0.125 and 0.125. The restraints SADI, SIMU, DFIX and DANG were applied to describe the disorder. The structure in solid state is depicted in Figure S68 and S69.

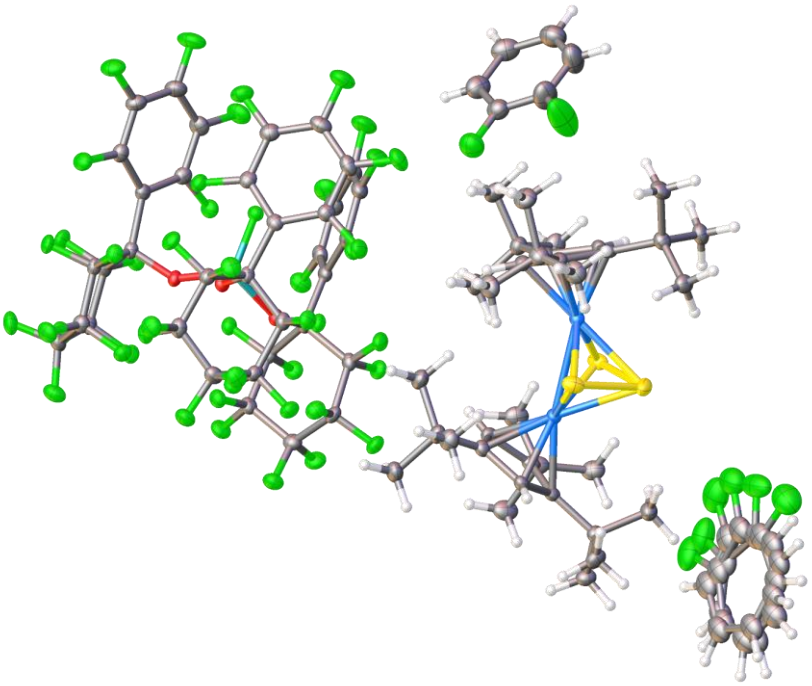


Figure S68: Molecular structure of **17** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

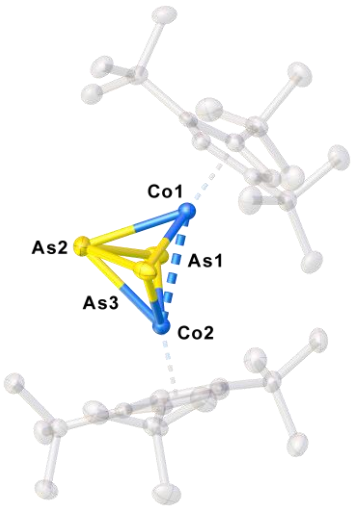


Figure S69: Molecular structure of the cation in **17** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Co1-Co2 2.6827(6), As1-As2 2.3770(5), As2-As3 2.3638(5), As1-As3 3.5176(6), (Cp'''-centroid)CoCo(Cp'''-centroid) 132.367.

4.11 [(Cp’’’Co)(Cp’’Ni)(μ,η^3:η^2-P$_3$)] (18)

Compound **18** crystallizes from a concentrated solution in CH_2Cl_2 layered with MeCN at room temperature in the monoclinic space group *P2$_1$/n* as dark brown needles. The asymmetric unit contains one molecule of **18**. The structure in solid state is depicted in Figure S70.

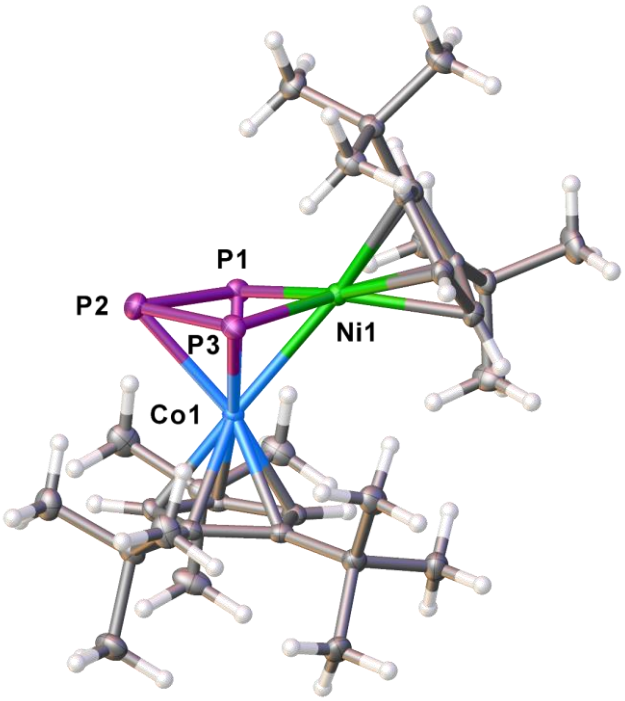


Figure S70: Molecular structure of **18** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Co1-Ni1 2.5588(4), P1-P2 2.1361(6), P2-P3 2.1514(6), P1-P3 2.8677(6), (Cp’’’-centroid)CoNi(Cp’’’-centroid) 118.650.

4.12 $[(Cp'''Co)(Cp''Ni)(\mu_4,\eta^3:\eta^2:\eta^1:\eta^1\text{-}P_3)Ag(CH_2Cl_2)]_2[FAl]_2$ (19)

Compound **19** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at room temperature in the monoclinic space group $C2_1/c$ as dark brown blocks. The asymmetric unit contains one cation of **19**, one [FAl] counterion and 1.4 molecules CH_2Cl_2. The silver atom is disordered over two positions with side occupancies of 0.97 and 0.03. The restraints SADI and SIMU were applied to describe the disorder. The structure in the solid state is depicted in Figure S71 and S72.

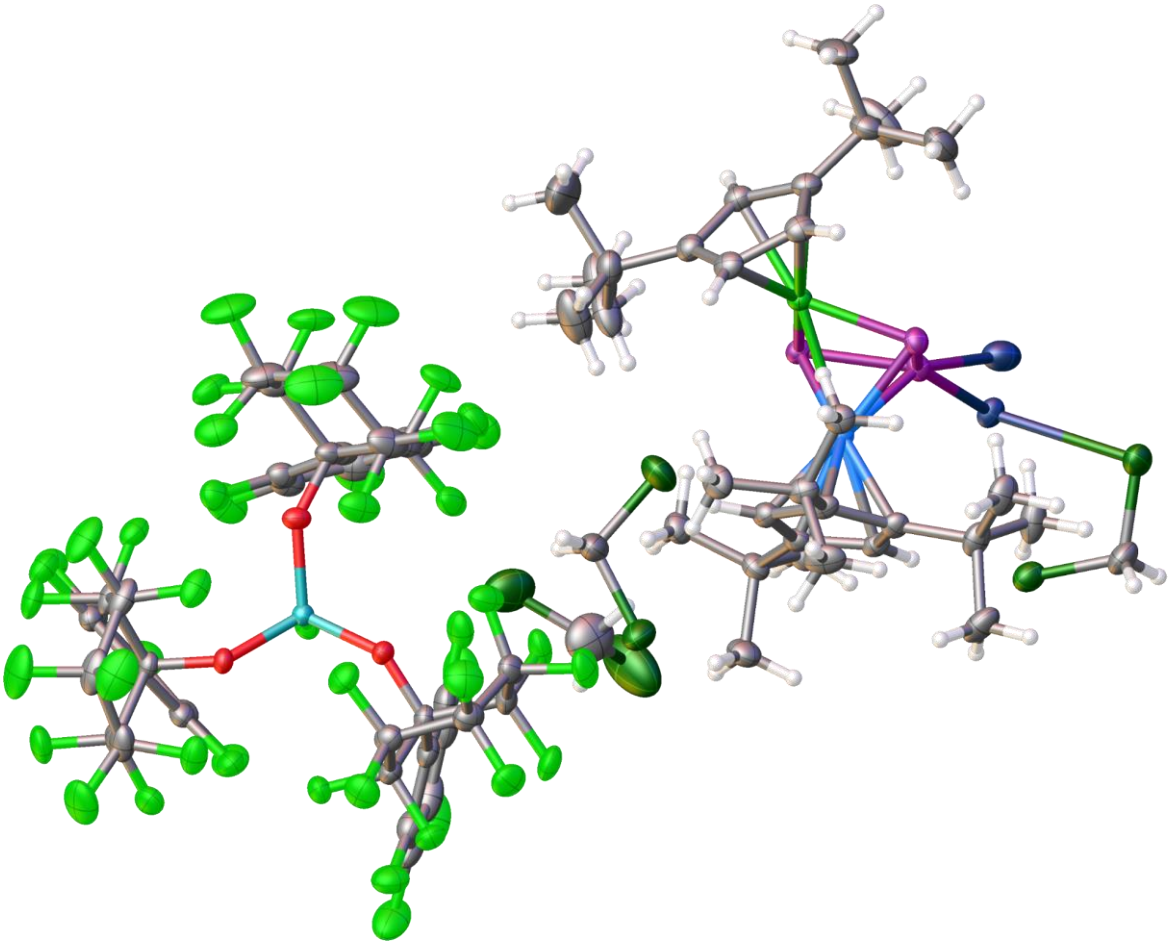


Figure S71: Molecular structure of **19** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

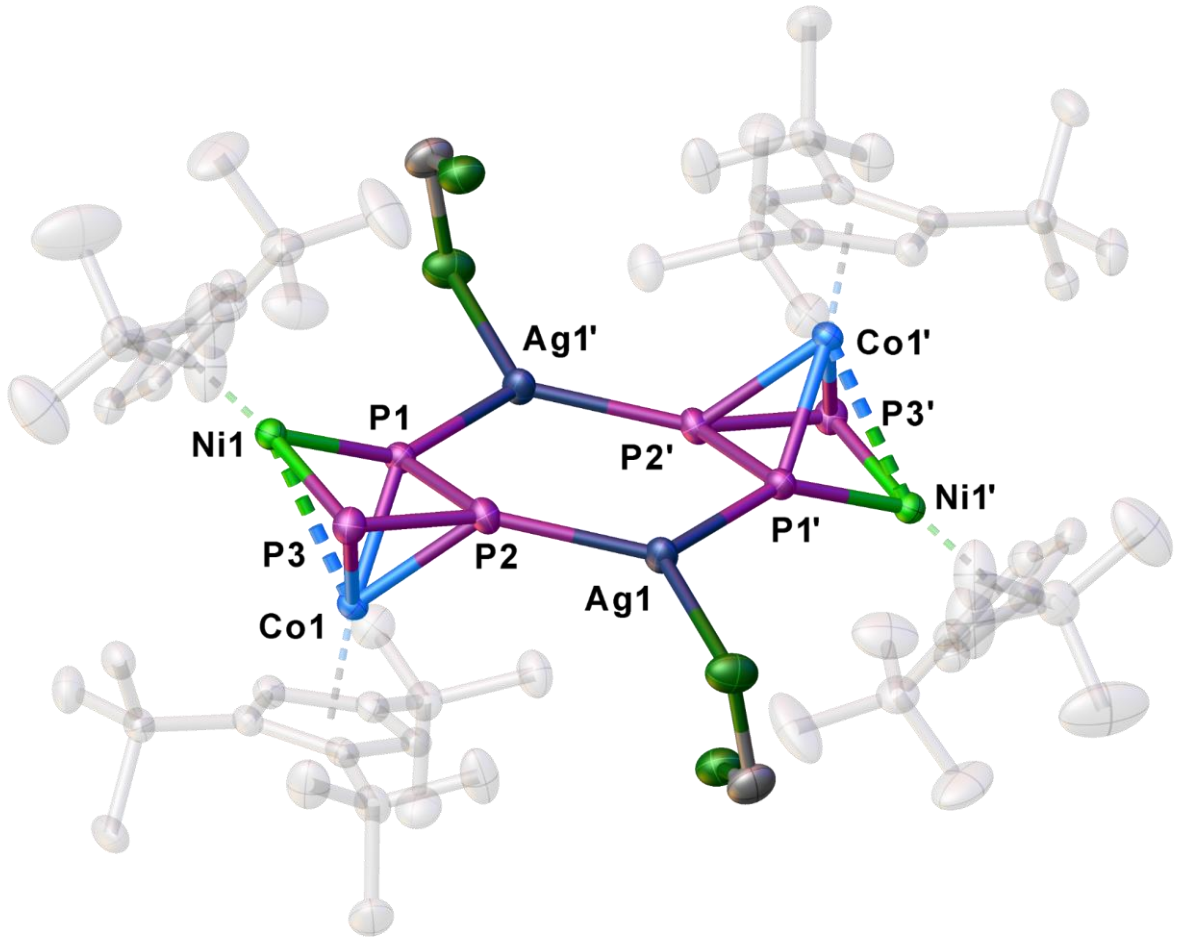


Figure S72: Molecular structure of the full cation in **19** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Co1-Ni1/Co1'-Ni1' 2.5846(4), P1-P2/P1'-P2' 2.1277(9), P2-P3/P2'-P3' 2.1407(9), P1-P3/P1'-P3' 2.9733(8), P1-Ag1/P1'-Ag1' 2.4404(7), P2'-Ag1/P2-Ag1' 2.4256(7), (Cp'''-centroid)CoNi(Cp'''-centroid) 121.947.

4.13 [(Cp’’’Co)(Cp’’’Ni)(μ,η^3:η^3:η^1-P$_3$){W(CO)$_5$}][FAl] (21)

Compound **21** crystallizes from a concentrated solution in CH_2Cl_2 layered with pentane at room temperature in the triclinic space group $P\bar{1}$ as dark brown blocks. The asymmetric unit contains one cation of **21**, one [FAl] counterion and one molecule CH_2Cl_2. The solvent molecule is disordered over two positions with side occupancies of 0.59 and 0.41. The structure in the solid state is depicted in Figure S73 and S74.

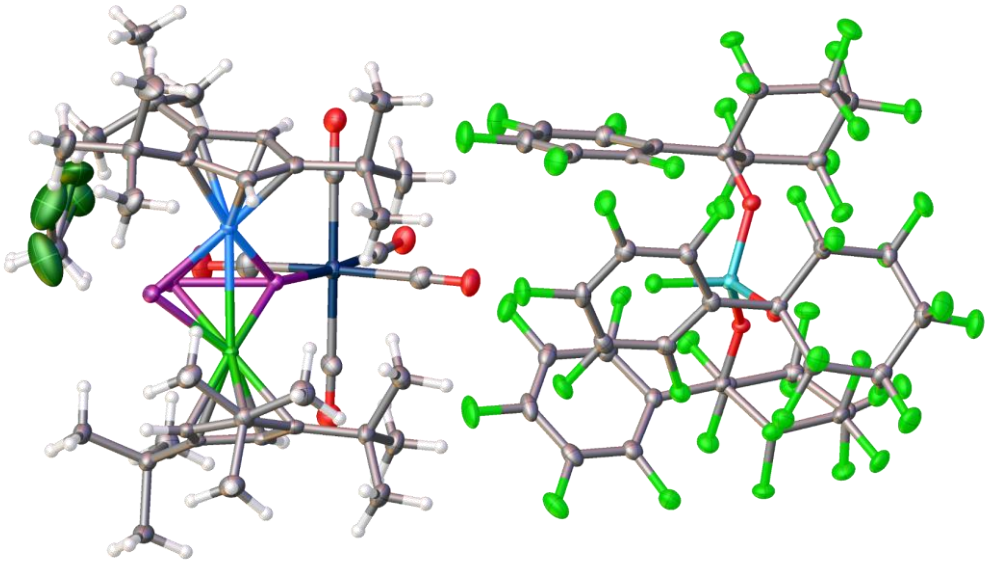


Figure S73: Molecular structure of **21** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

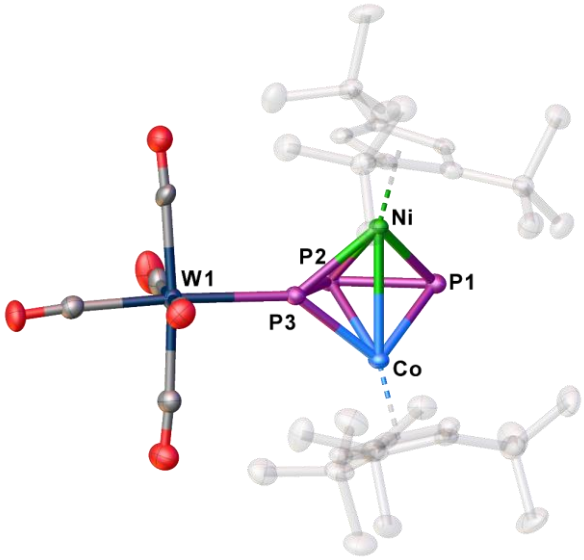


Figure S74: Molecular structure of the cation in **21** in the solid state. Hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Co1-Ni1 2.6783(7), P1-P2 2.1228(13), P2-P3 2.2180(12), P1-P3 3.2798(12), (Cp’’’-centroid)CoNi(Cp’’’-centroid) 142.990.

4.14 [K(2,2,2-crypt)][(Cp’’’Co)(Cp’’Ni)(μ,η^3:η^3-P$_3$)] (22)

Compound **22** crystallizes from a concentrated solution in thf layered with hexane at room temperature in the triclinic space group $P\bar{1}$ as dark brown plates. The asymmetric unit contains one anion of **22** and one [K(2,2,2-crypt)] counterion. Since both {Cp’’’M} fragments contain the same Cp’’’ ligand and a mixed occupation could not be neglected both metal atoms are refined as 50 % Co and 50 % Ni. The P_3 ligand is disordered over two positions with side occupancies of 70 and 30 %. The structure in the solid state is depicted in Figure S75 and S76.

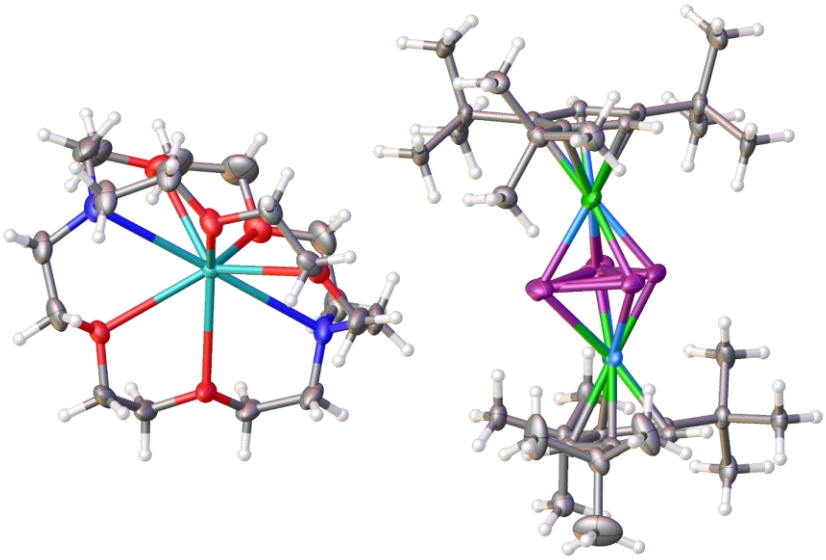


Figure S75: Molecular structure of **22** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

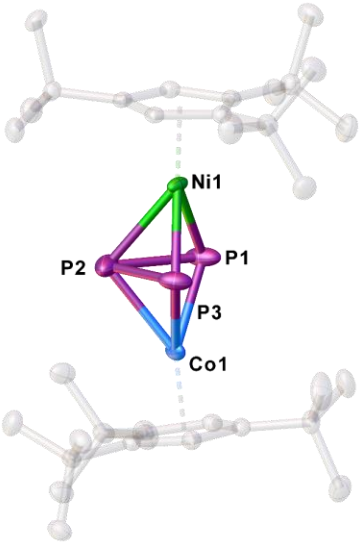


Figure S76: Molecular structure of the anion of **22** in the solid state. Hydrogen atoms are omitted for clarity. Depicted is only the part with higher occupancy (70 %). Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Co1-Ni1 3.588(4), P1-P2 2.1792(10), P2-P3 2.172(1), P1-P3 2.5537(11), (Cp’’’-centroid)CoNi(Cp’’’-centroid) 174.077.

4.15 [K(2,2,2-cryptand)][(Cp'''Co)(Cp''Ni)(μ,η³:η³-As₃)] (23)

Compound **23** crystallizes from a concentrated solution in thf layered with hexane at room temperature in the triclinic space group $P\bar{1}$ as dark brown blocks. The asymmetric unit contains one anion of **23**, one counterion. The As_3 ligand is disordered over two positions with side occupancies of 0.83 and 0.17. Since both {Cp'''M} fragments contain the same Cp''' ligand and a mixed occupation could not be neglected both metal atoms are refined as 50 % Co and 50 % Ni. The structure in the solid state is depicted in Figure S77 and S78.

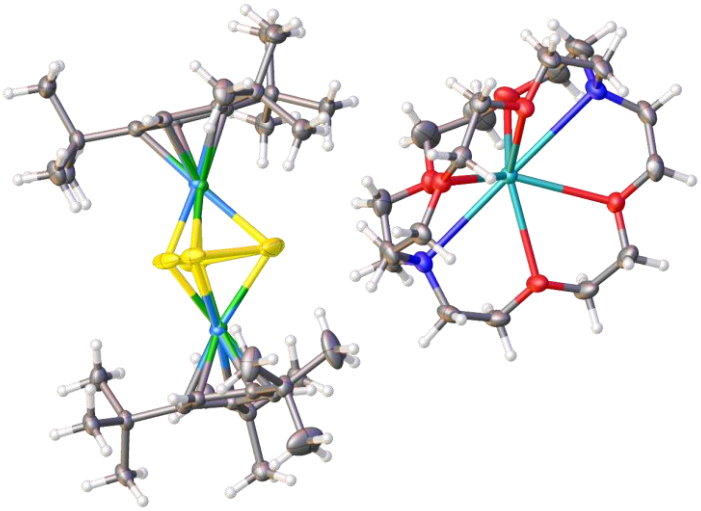


Figure S77: Molecular structure of **23** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

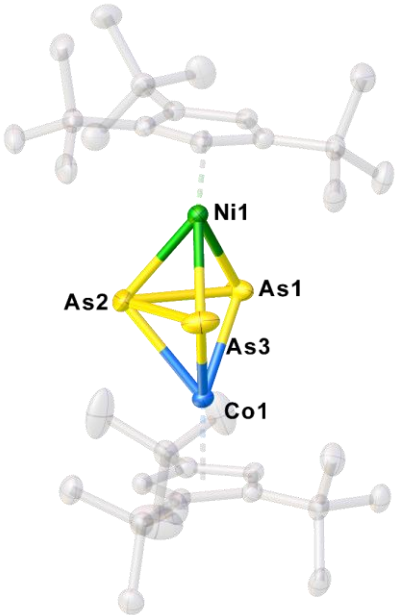


Figure S78: Molecular structure of the anion of **23** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Co1-Ni1 3.688(7), As1-As2 2.4323(7), As2-As3 2.3962(12), As1-As3 2.7799(10), (Cp'''-centroid)CoNi(Cp'''-centroid) 174.876.

4.16 [Cp‘‘‘Ni(η^3-As_3)]

[Cp‘‘‘Ni(η^3-As_3)] crystallizes from a concentrated solution in a mixture of toluene and CH_2Cl_2 (1:2) at -30 °C in the monoclinic space group *P2₁/c* as dark red blocks. The asymmetric unit contains one molecule of [Cp‘‘‘Ni(η^3-As_3)]. The structure in solid state is depicted in Figure S79.

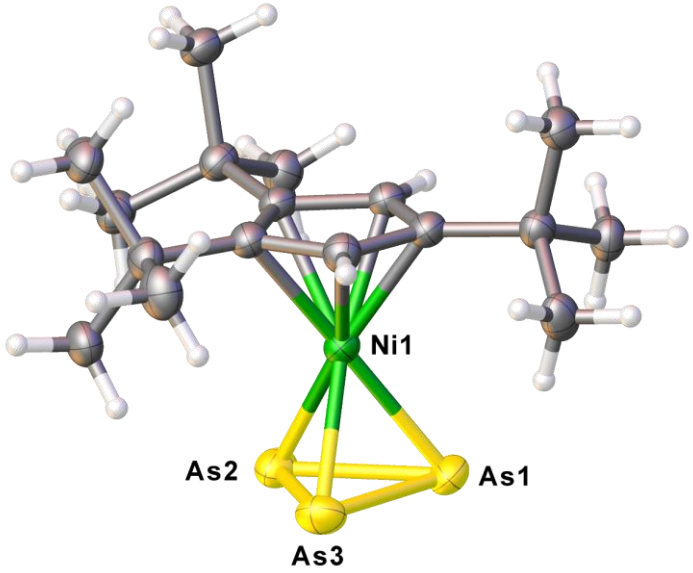


Figure S79: Molecular structure [Cp‘‘‘Ni(η^3-As_3)] in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: As1-As2 2.3700(5), As2-As3 2.3821(6), As1-As3 2.3700(6).

4.17 Crystallographic information

Table S1: Crystallographic data for **3** - **9**.

	3	**4**	**5**	**6**	**7**
CCDC	**2064647**	**2064648**	**2064649**	**2064650**	**2064651**
Formula	$AlC_{63}CoF_{46}FeH_{49}O_3P_5$ · 2.5 CH_2Cl_2	$AlAs_5C_{63}CoF_{46}FeH_{49}O_3$ · 2.5 CH_2Cl_2	$C_{99}H_{44}Al_2CoF_{92}FeO_6P_5$ · 3 $C_6H_4F_2$ + 0.5 C_7H_8	$Al_2As_5C_{99}CoF_{92}FeH_{44}O_6$ · 3.5 $C_6H_4F_2$	$C_{90}Co_2Fe_2H_{160}K_2N_4O_{12}P_{10}$ · 0.45 C_6H_{14}
$D_{calc.}$/ g cm^{-3}	1.781	1.934	1.834	1.941	1.291
μ/mm^{-1}	6.822	8.031	4.219	1.622 B	5.113
Formula Weight	2231.90	2451.65	3789.27	4020.00	2146.45
Colour	clear dark green	clear dark brown	clear dark brown	dark brown	clear dark green
Shape	block	plate	block	block	block
Size/mm^3	0.29×0.16×0.10	0.57×0.46×0.18	0.38×0.31×0.21	0.30×0.22×0.15	0.42×0.31×0.23
T/K	123.00(10)	123	123.01(10)	123(1)	123.0(3)
Crystal System	triclinic	triclinic	monoclinic	monoclinic	triclinic
Flack Parameter			0.0062(8)	0.216(4)	
Hooft Parameter			0.0020(6)	0.249(2)	
Space Group	*P*-1	*P*-1	$P2_1$	$P2_1$	*P*-1
a/Å	13.4750(3)	13.4946(4)	17.5277(2)	17.5971(2)	16.1521(6)
b/Å	18.3242(3)	18.4836(4)	19.54690(10)	19.5391(2)	17.2031(6)
c/Å	19.9317(5)	20.0500(3)	21.7863(2)	21.7687(3)	20.0003(6)
α/°	116.796(2)	117.102(2)	90	90	86.912(2)
β/°	104.727(2)	104.793(2)	113.1770(10)	113.2570(10)	84.332(3)
γ/°	93.3840(10)	93.649(2)	90	90	89.021(3)
V/Å^3	4161.88(17)	4209.21(18)	6861.84(12)	6876.57(15)	5521.8(3)
Z	2	2	2	2	2
Z'	1	1	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184	0.71073	1.39222
Radiation type	Cu K_α	CuK_α	Cu K_α	MoK_α	Cu K_β
θ_{min}/°	3.462	3.464	3.555	3.271	3.380
θ_{max}/°	73.479	72.918	73.712	32.428	74.590
Measured Refl.	46279	25697	78688	62619	50007
Independent Refl.	16041	16118	27038	39669	29142
Reflections with I > 2(I)	14851	14021	26513	34588	21916
R_{int}	0.0289	0.0361	0.0236	0.0255	0.0415
Parameters	1095	1095	2221	1942	2134
Restraints	0	0	297	1	527
Largest Peak	0.428	1.403	0.583	0.523	0.701
Deepest Hole	-0.312	-0.889	-0.326	-0.358	-0.668
GooF	1.018	1.038	1.053	0.995	1.021
wR_2 (all data)	0.0929	0.1439	0.0721	0.0830	0.1490
wR_2	0.0909	0.1382	0.0716	0.0790	0.1327
R_1 (all data)	0.0390	0.0577	0.0271	0.0477	0.0725
R_1	0.0360	0.0516	0.0265	0.0392	0.0541

Table S2: Crystallographic data for **9** - **19**.

	9	**11**	**15**	**16**	**17**	**18**
CCDC	**2064652**	**2064653**	**2064654**	**2064655**	**2064656**	**2064657**
Formula	$C_{45}H_{80}As_6CoFeKN_2O_6$	$C_{34}H_{58}As_3CoNi$	$C_{70}H_{58}O_3F_{46}AlNi_2As_3$	$C_{77.7}H_{68}AlCl_{2.8}Co_2F_{46}O_3P_3$	$C_{82}H_{66}AlAs_3Co_2F_{50}O_3$	$C_{30}H_{50}CoNiP_3$
$D_{calc.}$/ g cm^{-3}	1.633	1.500	1.850	1.672	1.824	1.311
μ/mm^{-1}	4.279	7.492	3.549	5.567	5.728	6.423
Formula Weight	1348.51	809.20	2190.32	2260.73	2418.94	621.25
Colour	clear dark brown	clear dark brown	clear dark orange	red	clear dark brown	clear dark brown
Shape	plate	block	block	block	block	plate
Size/mm^3	0.53×0.23×0.06	0.17×0.09×0.06	0.48×0.40×0.22	0.35×0.13×0.07	0.12×0.07×0.06	0.22×0.13×0.03
T/K	123(1)	122.99(10)	123	122.94(19)	100.00(10)	123.01(10)
Crystal System	triclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space Group	P-1	P-1	P-1	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	10.4742(2)	12.3686(4)	14.3245(4)	16.96980(10)	17.4140(4)	18.1357(2)
b/Å	13.8238(4)	12.8206(6)	17.2360(5)	19.9741(2)	20.5608(3)	9.64220(10)
c/Å	19.3001(4)	13.3202(5)	19.5299(5)	26.6848(3)	25.1613(6)	18.7312(3)
α/°	91.715(2)	66.380(4)	99.648(2)	90	90	90
β/°	100.138(2)	71.427(3)	109.149(2)	96.8420(10)	102.166(2)	106.1070(10)
γ/°	93.830(2)	71.715(4)	113.282(3)	90	90	90
V/Å^3	2742.27(11)	1791.86(14)	3931.0(2)	8980.57(15)	8806.6(3)	3146.91(7)
Z	2	2	2	4	4	4
Z'	1	1	1	1	1	1
Wavelength/Å	0.71073	1.54184	1.54184	1.54184	1.54184	1.54184
Radiation type	Mo K_α	Cu K_α	Cu K_α	Cu K_α	Cu K_α	Cu K_α
θ_{min}/°	3.437	3.714	3.469	3.432	2.596	3.991
θ_{max}/°	32.387	73.656	72.120	73.512	73.168	74.215
Measured Refl.	26611	11640	31525	75562	47673	11930
Independent Refl.	17246	6881	14915	17763	16761	6138
Reflections with I > 2(I)	13244	5709	13757	16418	14230	4997
R_{int}	0.0369	0.0163	0.0290	0.0439	0.0290	0.0235
Parameters	573	388	1144	1326	1432	331
Restraints	0	0	0	108	545	0
Largest Peak	1.535	0.274	1.017	0.734	0.689	0.470
Deepest Hole	-2.036	-0.293	-0.642	-0.450	-0.698	-0.261
GooF	1.031	0.881	1.045	1.086	1.062	0.920
wR_2 (all data)	0.1349	0.0395	0.0881	0.1147	0.0966	0.0551
wR_2	0.1207	0.0390	0.0856	0.1123	0.0929	0.0544
R_1 (all data)	0.0718	0.0226	0.0367	0.0482	0.0437	0.0317
R_1	0.0518	0.0180	0.0336	0.0446	0.0354	0.0252

Table S3: Crystallographic data for **20** and **21**.

	19	**21**	**22**	**23**	**[Cp'''Ni(η^3-As$_3$)]**
CCDC	**2064658**	**2064659**	**2064660**	**2064661**	**2064662**
Formula	$C_{68.4}H_{54.8}AgAlCl_{4.8}CoF_{46}NiO_3P_3$	$C_{76}H_{60}AlCl_2CoF_{46}NiO_8P_3W$	$C_{52}H_{94}CoKN_2NiO_6P_3$	$C_{52}H_{94}As_3CoKN_2NiO_6$	$C_{17}H_{29}As_3Ni$
$D_{calc.}$/ g cm^{-3}	1.819	1.880	1.241	1.383	1.771
μ/mm^{-1}	1.010	6.698	4.385	5.462	7.052
Formula Weight	2314.28	2467.52	1092.94	1224.79	516.87
Colour	dark brown	clear dark brown	clear light brown	clear dark brown	clear intense red
Shape	block	block	plate	block	plate
Size/mm^3	0.48×0.28×0.18	0.31×0.13×0.11	0.46×0.24×0.07	0.22×0.16×0.15	0.48×0.31×0.23
T/K	123(1)	100.00(10)	100.01(10)	122.97(11)	123.00(10)
Crystal System	monoclinic	triclinic	triclinic	triclinic	monoclinic
Space Group	*C*2/*c*	*P*-1	*P*-1	*P*-1	*P*2$_1$/*c*
a/Å	28.8667(4)	11.60730(10)	10.70820(10)	10.6876(3)	9.3497(2)
b/Å	19.18723(19)	17.9579(2)	13.4327(3)	13.4382(3)	14.6749(2)
c/Å	34.0000(5)	21.1425(2)	21.0766(4)	21.1997(4)	14.6948(2)
α/°	90	93.3120(10)	99.596(2)	99.356(2)	90
β/°	116.1848(17)	91.8540(10)	101.7700(10)	101.402(2)	105.950(2)
γ/°	90	97.3480(10)	90.2540(10)	90.819(2)	90
V/Å^3	16899.1(4)	4359.99(7)	2924.07(9)	2941.56(12)	1938.59(6)
Z	8	2	2	2	4
Z'	1	1	1	1	1
Wavelength/Å	0.71073	1.54184	1.54184	1.54184	1.54184
Radiation type	Mo K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$
θ_{min}/°	3.300	2.095	2.173	3.337	4.344
θ_{max}/°	29.130	73.327	74.145	73.859	73.918
Measured Refl.	78063	48178	31913	33005	10592
Independent Refl.	22718	16705	11046	11593	3859
Reflections with I > 2(I)	19528	16192	10007	9588	3810
R_{int}	0.0200	0.0341	0.0210	0.0262	0.0445
Parameters	1214	1288	640	646	199
Restraints	37	0	0	8	0
Largest Peak	2.363	1.354	0.693	0.474	1.370
Deepest Hole	-0.979	-1.757	-0.595	-0.483	-0.780
GooF	1.039	1.090	1.078	0.928	1.100
wR_2 (all data)	0.1285	0.1044	0.0987	0.0629	0.1387
wR_2	0.1230	0.1036	0.0967	0.0619	0.1380
R_1 (all data)	0.0527	0.0398	0.0410	0.0314	0.0474
R_1	0.0449	0.0387	0.0373	0.0255	0.0468

5. Computational Details

Gaussian 09 program[6] was used throughout. Density functional theory (DFT) in form of or BP86[7] (Becke's exchange and Perdew 86 correlation functional) with def2-TZVP all electron basis set was employed. For solvents effects has been accounted by using continuous polarizable continuum model (CPM).[8] The dielectric constant of dichloromethane (ε = 8.93) has been used in the calculations of the cations (**3**, **4**, **5**, **6**, **12-bent**, **12-linear**, **13-bent**, **13-linear**, **14**, **15**, **16**, **17**, **19**, **21**) and the dielectric constant of thf (ε = 7.4257) has been used in the calculations of the anions (**7**, **8**, **9**, **22**, **23**, **24**, **25**, **26**, **27**). The Natural Bond Orbital (NBO) analysis has been performed with the NBO6 program.[9] The long range dispersion correction GD3BJ was applied.[10] The figures for the supporting information concerning the DFT calculations were created with Chemcraft[11] and concerning the energetic schemata with OLEX2.[5]

Table S4: Total energies for all optimized geometries (BP86/def2-TZVP level of theory).

	total energy [Ha]
1 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-P_5)]	-5410.19002426
2 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-As_5)]	-14884.0016082
3 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-P_5)]$^+$	-5410.03741142
4 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-As_5)]$^+$	-14883.8485530
5 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-P_5)]$^{2+}$	-5409.85428357
6 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-As_5)]$^{2+}$	-14883.6731821
7 [(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-P_5)]$^-$	-5410.29374369
8 [(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-As_5)]$^-$	-14884.1104474
9 [(Cp*Fe)(Cp'''Co)(μ,η^4:η^4-As_6)]$^-$	-17120.3321848
10 [(Cp'''Co)(Cp'''Ni)(μ,η^3:η^3-P_3)]	-5247.23890479
10-I [(Cp'''Co)(Cp'''Ni)(μ,η^3:η^2-P_3)] (bent)	-5247.25107762
11 [(Cp'''Co)(Cp'''Ni)(μ,η^3:η^3-As_3)]	-10931.5360793
12-bent [(Cp'''Co)(Cp'''Ni)(μ,η^3:η^3-P_3)]$^+$	-5247.08120128
12-linear [(Cp'''Co)(Cp'''Ni)(μ,η^3:η^3-P_3)]$^+$	-5247.07345366
13-bent [(Cp'''Co)(Cp'''Ni)(μ,η^3:η^3-As_3)]$^+$	-10931.3763388
13-linear [(Cp'''Co)(Cp'''Ni)(μ,η^3:η^3-As_3)]$^+$	-10931.3750215
14 [(Cp'''Ni)$_2$(μ,η^3:η^3-P_3)]$^+$	-5372.64435099
15 [(Cp'''Ni)$_2$(μ,η^3:η^3-As_3)]$^+$	-11056.9475006
16 [(Cp'''Co)$_2$(μ,η^3:η^3-P_3)]$^+$	-5121.53892363
17 [(Cp'''Co)$_2$(μ,η^3:η^3-As_3)]$^+$	-10805.8307017
18 [(Cp'''Co)(Cp''Ni)(μ,η^3:η^2-P_3)]	-5089.93874216
18-I [(Cp'''Co)(Cp''Ni)(μ,η^3:η^3-P_3)] (linear)	-5089.92600098

19 $[(Cp'''Co)(Cp''Ni)(\mu_4,\eta^3:\eta^2:\eta^1:\eta^1\text{-}P_3)\{Ag(CH_2Cl_2)\}]_2^{2+}$	-12388.8868048
20 $[(Cp'''Co)(Cp'''Ni)(\mu_3,\eta^3:\eta^2:\eta^1\text{-}P_3)\{W(CO_5)\}]$	-5877.76924900
21 $[(Cp'''Co)(Cp'''Ni)(\mu_3,\eta^3:\eta^2:\eta^1\text{-}P_3)\{W(CO_5)\}]^+$	-5881.60679031
22 $[(Cp'''Co)(Cp'''Ni)(\mu,\eta^3:\eta^3\text{-}P_3)]^-$	-5247.34366753
23 $[(Cp'''Co)(Cp'''Ni)(\mu,\eta^3:\eta^3\text{-}As_3)]^-$	-10931.6388229
24 $[(Cp'''Ni)_2(\mu,\eta^3:\eta^3\text{-}P_3)]^-$	-5372.91636772
25 $[(Cp'''Ni)_2(\mu,\eta^3:\eta^3\text{-}As_3)]^-$	-11057.2109513
26 $[(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}P_3)]^-$	-5121.78815045
27 $[(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}As_3)]^-$	-10806.0801740

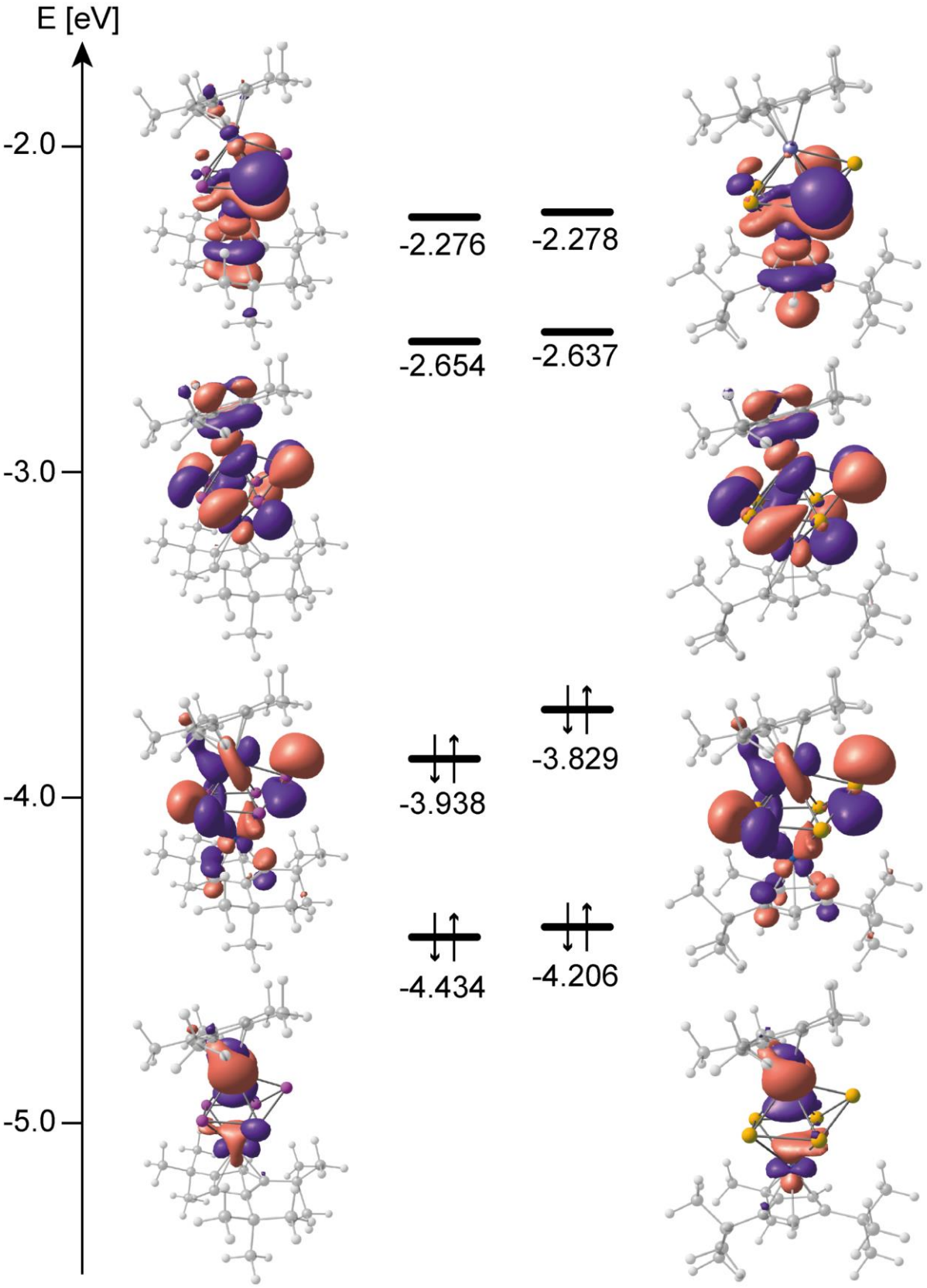


Figure S80. Frontier molecular orbitals of **1** (left) and **2** (right) at the BP86/def2-TZVP level of theory.

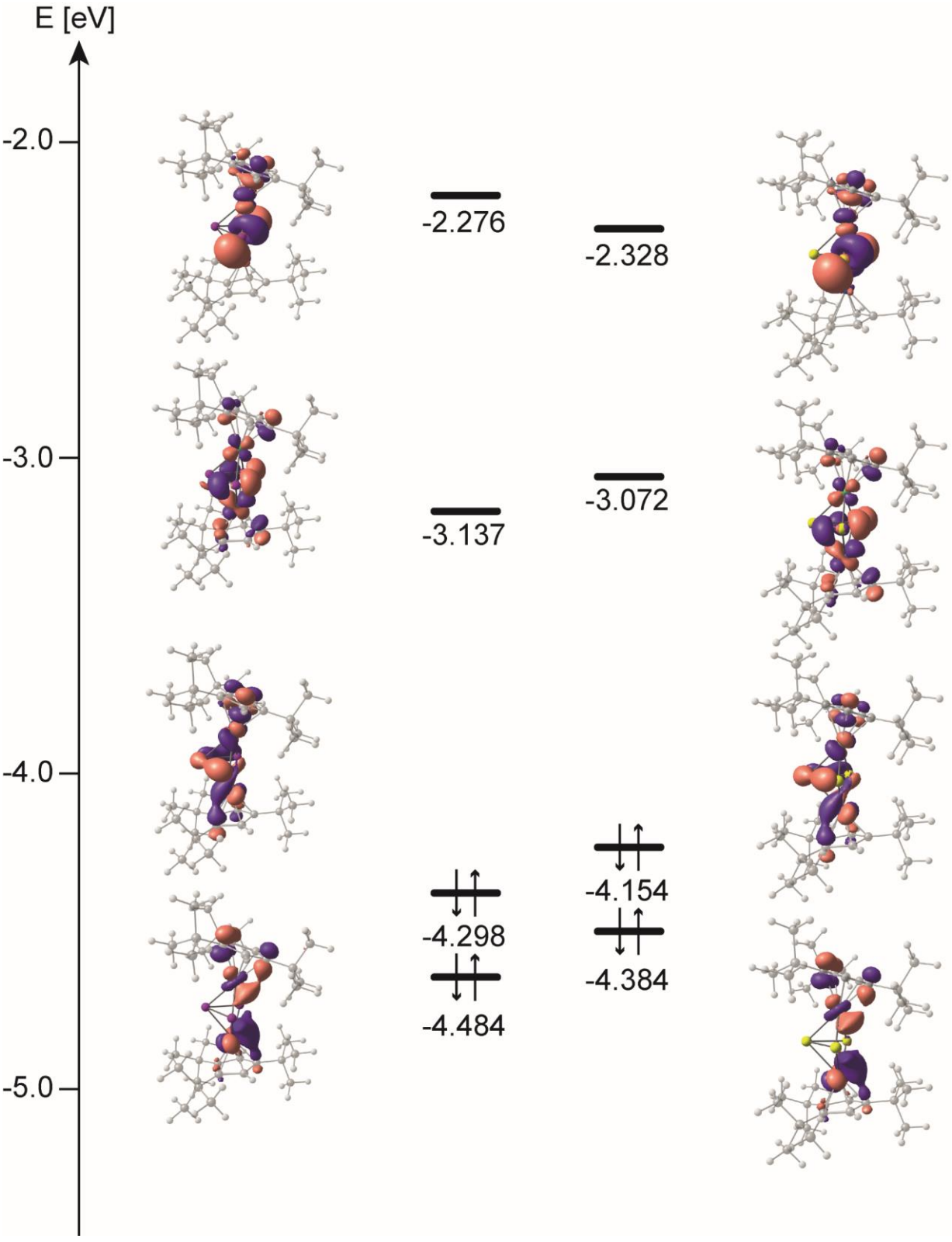


Figure S81. Frontier molecular orbitals of **10** (left) and **11** (right) at the BP86/def2-TZVP level of theory.

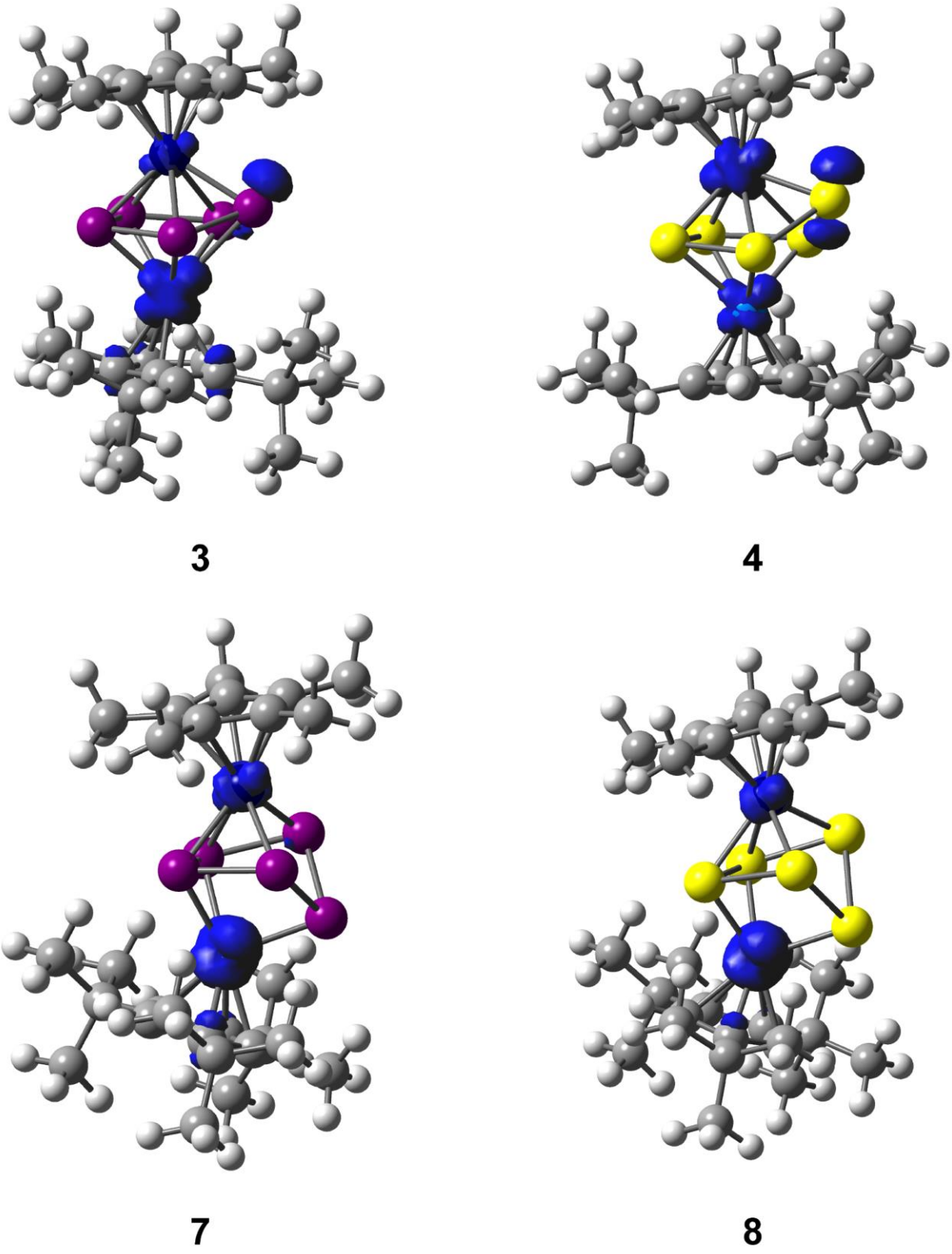


Figure S82: Isosurfaces of the calculated spin density in **3**, **4**, **7** and **8**, BP86/def2-TZVP level of theory.

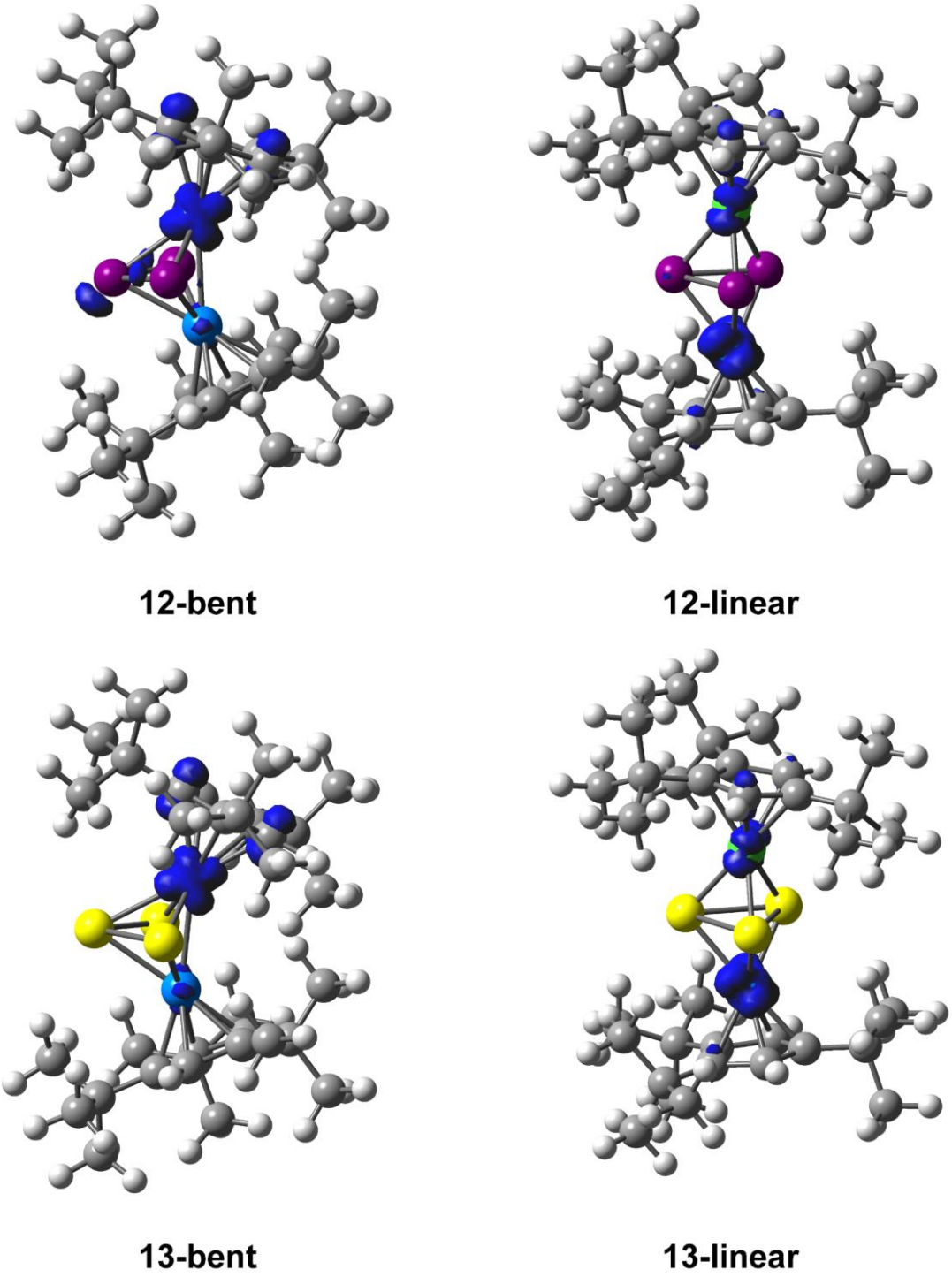
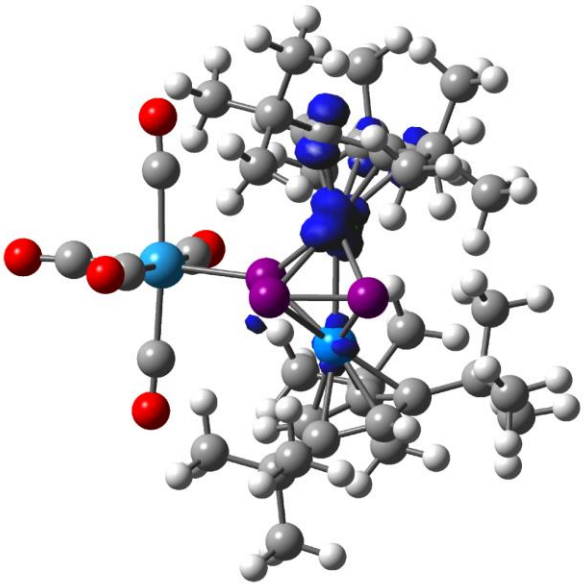
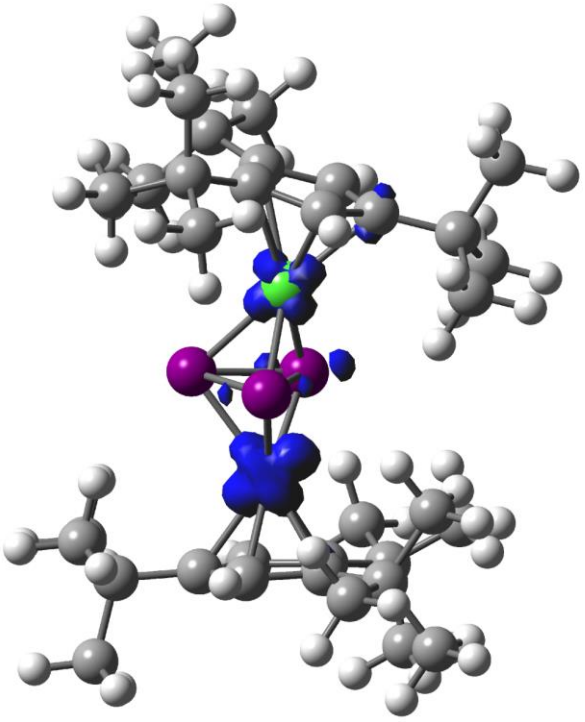


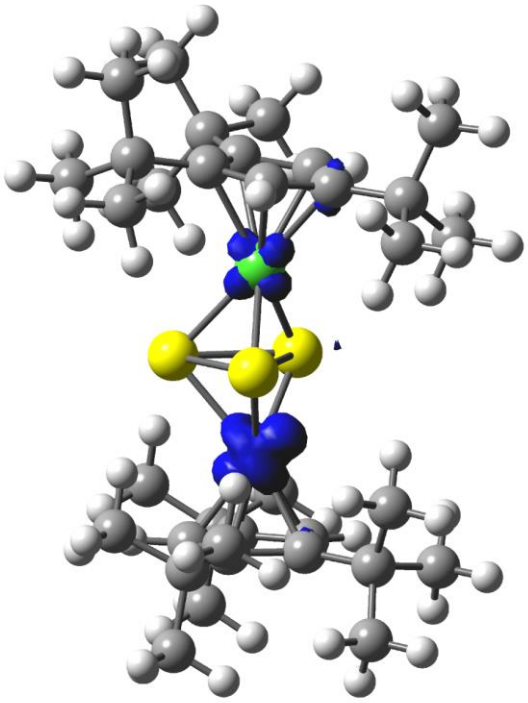
Figure S83: Isosurfaces of the calculated spin density in **12-bent**, **12-linear**, **13-bent** and **13-linear**, BP86/def2-TZVP level of theory.



21



22



23

Figure S84: Isosurfaces of the calculated spin density in **21**, **22** and **23**, BP86/def2-TZVP level of theory.

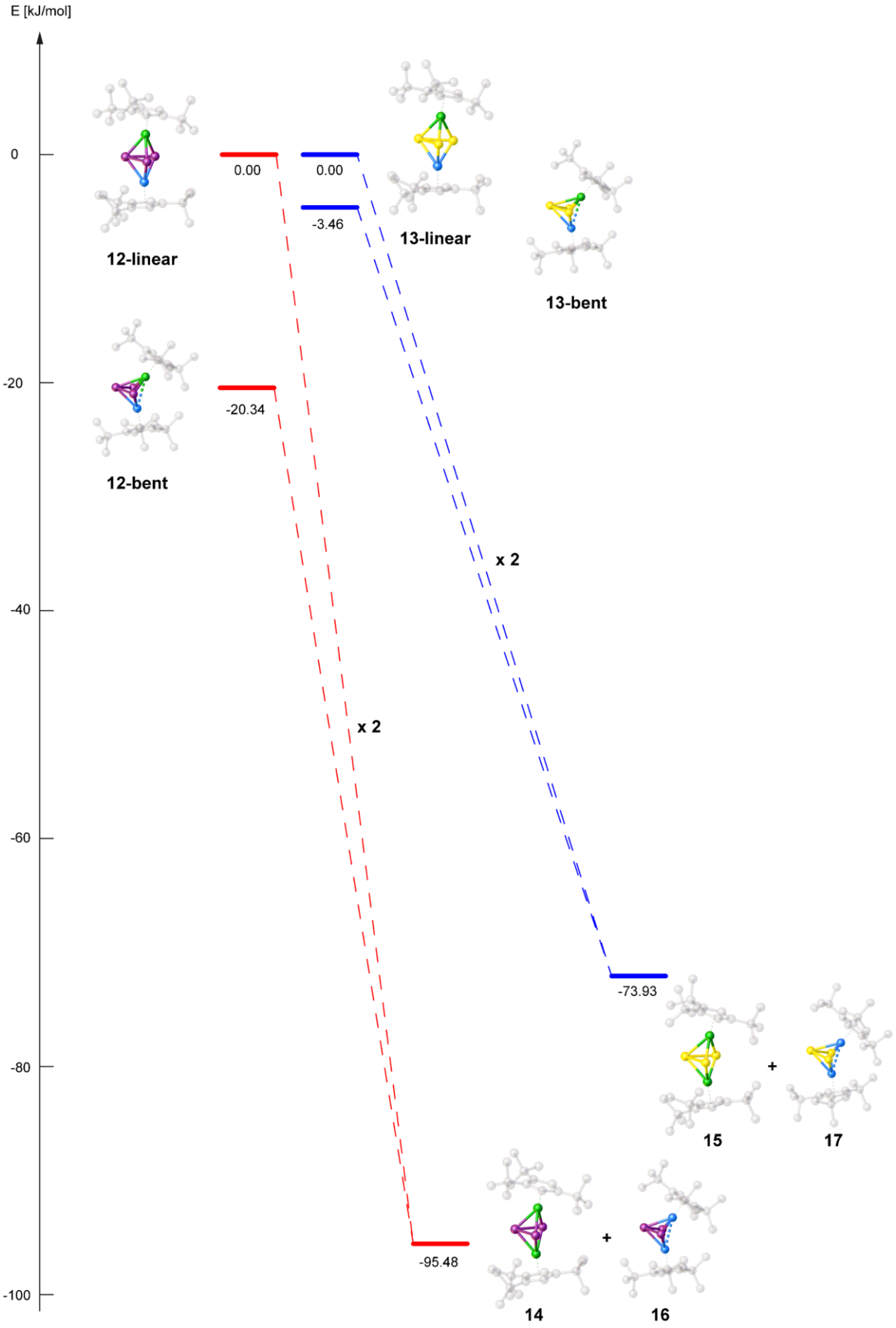


Figure S85. Energetic diagram of the conversion of the two isomer pairs **12-bent**/**12-linear** and **13-bent**/**13-linear** into **14**/**16** and **15**/**17**. The energetically less favored isomer (**12-linear**/**13-linear**) were chosen as reference.

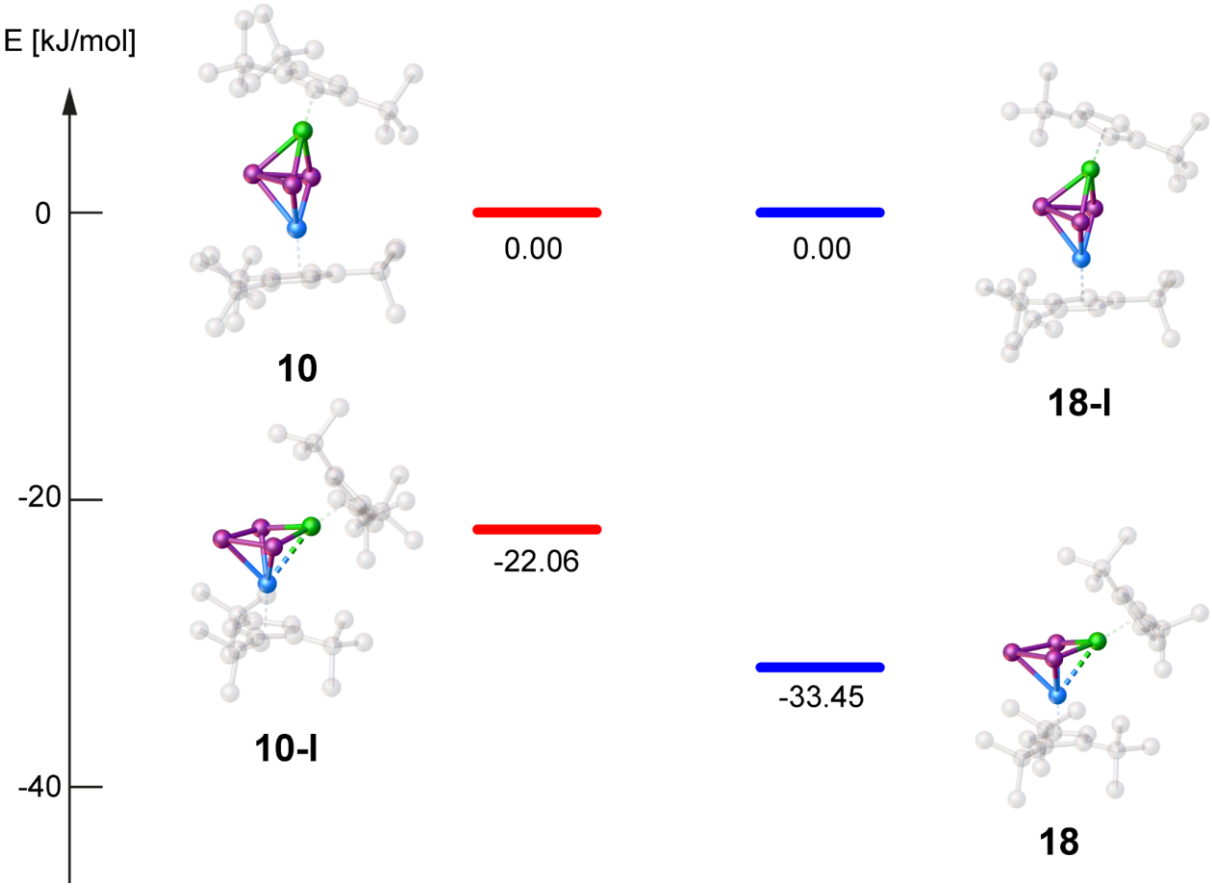


Figure S86. Energetic diagram of the isomer pairs **10**/**10-I** and **18**/**18-I**.

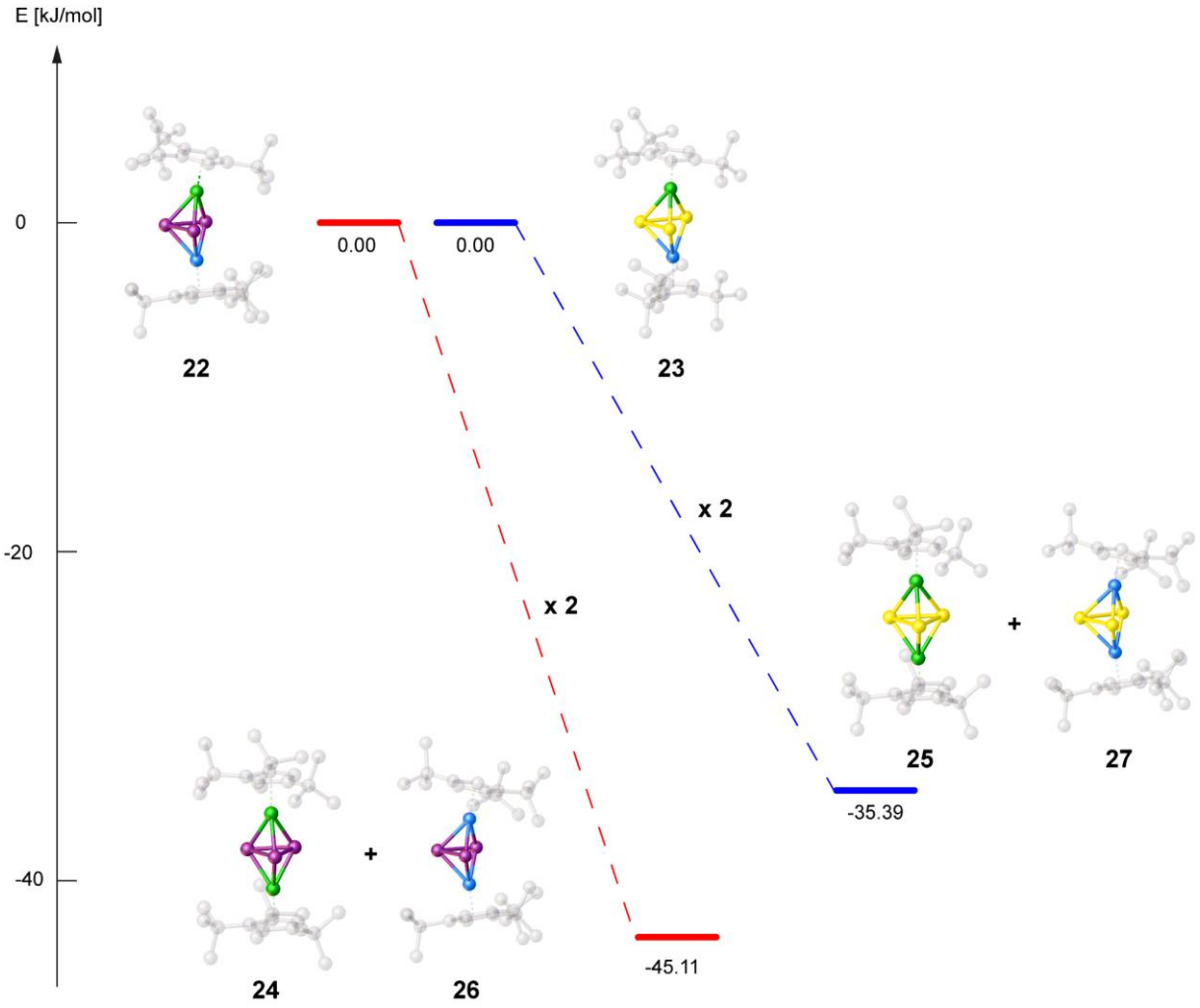
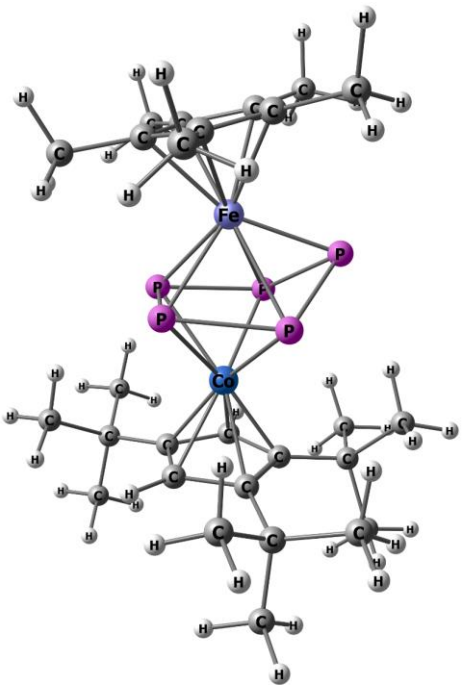


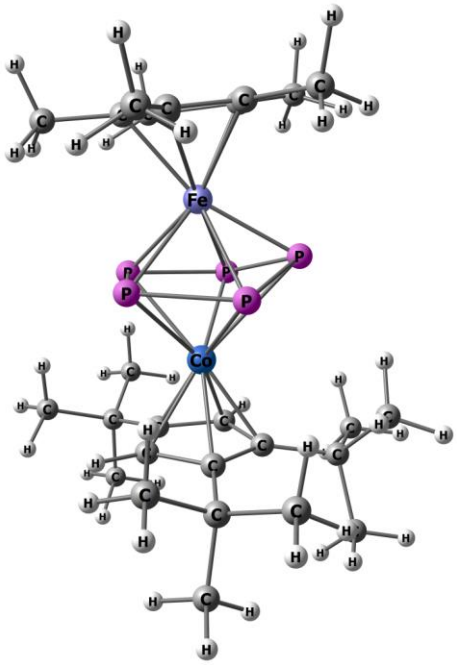
Figure S87. Energetic diagram of the conversion of **22** and **23** into **24**/**26** and **25**/**27**.

Table S5: Optimized geometries of **1** (left) and **2** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.



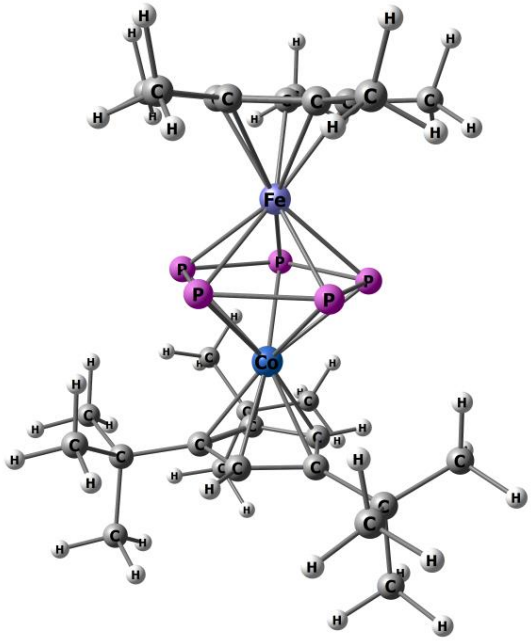
Co	-0.983296000	0.225091000	-0.031174000	H	3.070522000	3.035374000	1.166298000		As	0.218197000	-1.641108000	0.759689000	H	-4.177526000	4.760593000	-0.150567000
Fe	2.282592000	-0.126427000	-0.018176000	H	4.610793000	2.667568000	1.977758000		As	0.373061000	0.636106000	1.757517000	H	-4.459341000	3.368772000	0.928986000
P	0.813077000	1.679508000	-0.291484000	H	3.078717000	2.039979000	2.631379000		As	0.349524000	-1.072017000	-1.525797000	C	-2.651206000	-0.961381000	3.210191000
P	0.331130000	-1.493644000	0.731881000	C	-2.143537000	-2.932490000	-1.578560000		As	0.536610000	1.388256000	-1.333869000	H	-1.573971000	-1.131931000	3.072216000
P	0.664404000	0.590982000	1.548140000	H	-1.133499000	-2.632715000	-1.885458000		As	1.817854000	2.120171000	0.554794000	H	-2.992496000	-1.594425000	4.042867000
P	1.360171000	-1.879705000	-1.140956000	H	-2.484978000	-3.731146000	-2.255674000		Co	-1.170987000	0.200117000	-0.068434000	H	-2.794281000	0.082773000	3.516114000
P	0.484612000	0.001280000	-1.775707000	H	-2.068840000	-3.350080000	-0.572870000		Fe	2.152226000	-0.227617000	-0.002321000	C	-4.943733000	-1.042623000	2.211424000
C	-2.555449000	1.689454000	-0.108888000	C	3.996548000	2.169504000	-1.474625000		C	-3.059296000	-0.577745000	-0.692111000	H	-5.098919000	0.022547000	2.437289000
C	-2.652573000	0.913954000	1.073854000	H	3.556278000	1.926677000	-2.451563000		C	-2.791699000	0.733089000	-1.229309000	H	-5.291531000	-1.632005000	3.074426000
H	-2.606830000	1.315533000	2.080018000	H	5.034737000	2.501813000	-1.642332000		H	-2.710235000	0.962453000	-2.285441000	H	-5.570643000	-1.296897000	1.345868000
C	-2.795670000	-0.588706000	-0.702867000	H	3.433282000	3.017133000	-1.061693000		C	-3.036203000	-0.436688000	0.759963000	C	-2.642238000	3.207070000	-0.296528000
C	-2.617508000	0.759018000	-1.188397000	C	-4.566464000	-2.189031000	-1.457328000		C	3.312545000	-1.941421000	-0.325148000	C	-2.607740000	-3.006328000	-1.497998000
H	-2.532349000	1.030378000	-2.234236000	H	-4.714739000	-2.653055000	-0.474826000		C	-2.768705000	0.955718000	1.028110000	H	-1.584947000	-2.815335000	-1.850118000
C	3.956822000	0.990048000	-0.559084000	H	-4.847312000	-2.928279000	-2.223594000		H	-2.704112000	1.388471000	2.020604000	H	-3.041359000	-3.798510000	-2.128349000
C	-2.564140000	3.201767000	-0.202736000	H	-5.255479000	-1.334357000	-1.535269000		C	-2.645605000	1.695673000	-0.180689000	H	-2.535066000	-3.386145000	-0.478195000
C	-2.806005000	-0.485066000	0.759066000	C	4.424248000	-0.855469000	-2.336966000		C	-3.446529000	-1.331816000	1.938338000	C	4.681356000	1.462836000	-1.187625000
C	4.138707000	-0.380228000	-0.948578000	H	4.107918000	-1.896927000	-2.476533000		C	3.642883000	-0.918524000	-1.282624000	H	4.114774000	1.748633000	-2.085030000
C	3.825855000	-0.329126000	1.358544000	H	5.504390000	-0.793531000	-2.552583000		C	3.545261000	-1.410659000	0.992995000	H	5.728415000	1.293810000	-1.492301000
C	3.787480000	1.025446000	0.871005000	H	3.898489000	-0.243842000	-3.083042000		C	4.118068000	0.227160000	-0.560146000	H	4.660299000	2.313977000	-0.495273000
C	-3.164802000	-1.443491000	1.903449000	C	-1.807422000	3.833017000	0.978148000		C	-3.462912000	-1.731494000	-1.623106000	C	3.379906000	-2.143924000	2.284668000
C	-3.105693000	-1.734770000	-1.675567000	H	-2.248434000	3.540502000	1.942150000		C	4.061977000	-0.079319000	0.848275000	H	3.083342000	-1.463579000	3.094644000
C	-2.400349000	-1.059437000	3.190901000	H	-1.850566000	4.930688000	0.910174000		C	-3.254175000	-2.841298000	1.743950000	H	4.324055000	-2.631755000	2.581154000
H	-1.313610000	-1.137603000	3.046403000	H	-0.751453000	3.526896000	0.979633000		H	-3.894153000	-3.252333000	0.955608000	H	2.608685000	-2.922242000	2.208052000
H	-2.687244000	-1.750326000	3.997698000	C	4.287637000	-2.672055000	0.315377000		H	-3.516093000	-3.357681000	2.679890000	C	-3.341155000	-1.286679000	-3.096711000
H	-2.632194000	-0.043178000	3.534886000	H	3.669780000	-3.131519000	1.099350000		H	-2.205296000	-3.075738000	1.511722000	H	-4.021112000	-0.456247000	-3.335846000
C	4.065025000	-1.195477000	0.237492000	H	5.343472000	-2.886680000	0.552784000		C	-4.952649000	-2.057540000	-1.371850000	H	-3.603244000	-2.132168000	-3.749483000
C	-4.679370000	-1.255437000	2.167587000	H	4.043500000	-3.166570000	-0.633124000		H	-5.121894000	-2.476443000	-0.372749000	H	-2.311928000	-0.982715000	-3.339051000
H	-4.902344000	-0.211392000	2.431901000	C	-3.002729000	-1.230706000	-3.131498000		H	-5.305158000	-2.794605000	-2.110016000	C	4.564107000	0.769721000	1.972751000
H	-4.998836000	-1.899544000	3.001840000	H	-3.732425000	-0.436903000	-3.348535000		H	-5.569065000	-1.151027000	-1.467477000	H	4.604031000	1.830005000	1.693835000
H	-5.278171000	-1.514145000	1.283473000	H	-3.206599000	-2.068550000	-3.814303000		C	3.600170000	-1.048645000	-2.770961000	H	5.579626000	0.452386000	2.265809000
C	-1.950980000	3.684807000	-1.527262000	H	-1.992730000	-0.855527000	-3.356241000		H	2.858864000	-1.794221000	-3.088858000	H	3.918278000	0.682556000	2.857775000
H	-0.901275000	3.370807000	-1.617555000	C	-4.046880000	3.642638000	-0.147775000		H	4.582783000	-1.360507000	-3.163889000	C	-1.740527000	3.839511000	0.774826000
H	-1.988041000	4.783539000	-1.577704000	H	-4.617599000	3.202522000	-0.979082000		H	3.333795000	-0.094276000	-3.245717000	H	-2.059639000	3.557478000	1.788853000
H	-2.503837000	3.293583000	-2.394036000	H	-4.122275000	4.739147000	-0.218466000		C	2.880947000	-3.333696000	-0.647406000	H	-1.780244000	4.937134000	0.704675000
C	-2.882974000	-2.932985000	1.666229000	H	-4.516063000	3.323260000	0.794463000		H	2.271227000	-3.766329000	0.158016000	H	-0.698182000	3.516283000	0.648667000
H	-3.469742000	-3.349787000	0.840877000	C	3.697638000	-0.758436000	2.784171000		H	3.760318000	-3.983319000	-0.791429000	C	-2.195883000	3.672038000	-1.690259000
H	-3.152095000	-3.492964000	2.574792000	H	3.032826000	-0.087079000	3.344980000		H	2.280479000	-3.370837000	-1.567546000	H	-1.161093000	3.366464000	-1.903662000
H	-1.815603000	-3.106393000	1.470697000	H	4.679808000	-0.761211000	3.286056000		C	-4.104412000	3.664737000	-0.069195000	H	-2.246903000	4.769456000	-1.751896000
C	3.626419000	2.253887000	1.703568000	H	3.278337000	-1.771035000	2.855719000		H	-4.776777000	3.217193000	-0.816574000	H	-2.843444000	3.262073000	-2.479495000

Table S6: Optimized geometries of **3** (left) and **4** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.



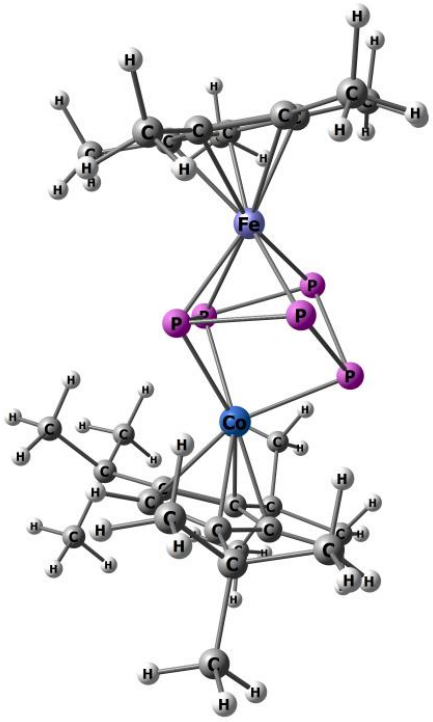
Fe	2.228631000	-0.103493000	-0.010914000	H	-3.164172000	-3.606241000	2.397351000	As	0.337492000	-0.434764000	1.875125000	C	-3.446975000	-1.654166000	-1.667212000
Co	-0.910362000	0.209971000	-0.006155000	H	-1.808083000	-3.203778000	1.328804000	As	0.292486000	-1.866791000	-0.066982000	C	-2.777673000	-1.459187000	-3.044573000
P	0.411708000	-1.627342000	0.637800000	C	-2.376695000	-1.224758000	3.146323000	As	0.484509000	-0.378940000	-1.912096000	H	-2.989527000	-0.478783000	-3.489398000
P	0.630542000	0.793386000	-1.674084000	H	-1.290709000	-1.345434000	3.029520000	As	0.629608000	1.796550000	-0.924031000	H	-3.161825000	-2.221767000	-3.736974000
P	0.885192000	1.780883000	0.263427000	H	-2.710898000	-1.935999000	3.914804000	As	1.324715000	1.659474000	1.346595000	H	-1.687788000	-1.583685000	-2.977655000
P	0.947022000	-1.324873000	-1.432516000	H	-2.574631000	-0.215949000	3.528957000	Co	-1.100400000	0.193222000	-0.049883000	C	-4.974646000	-1.467834000	-1.862024000
P	0.699841000	0.236270000	1.749090000	C	-2.182939000	-2.863134000	-1.736919000	Fe	2.118063000	-0.164277000	-0.031201000	H	-5.525840000	-1.588018000	-0.921087000
C	-2.586765000	0.864586000	1.125424000	H	-1.208839000	-2.599661000	-2.170434000	C	-3.004201000	-0.566356000	-0.682382000	H	-5.347695000	-2.214432000	-2.579156000
H	-2.535219000	1.215562000	2.149641000	H	-2.618411000	-3.661654000	-2.355925000	C	-2.927494000	-0.477303000	0.777516000	H	-5.194997000	-0.466591000	-2.259861000
C	-2.547581000	0.797886000	-1.145722000	H	-2.004091000	-3.265088000	-0.737699000	C	-2.677366000	0.914795000	1.094347000	C	-3.155961000	-3.101572000	-1.248609000
H	-2.482133000	1.121471000	-2.178263000	C	-3.996644000	3.574255000	-0.246725000	H	-2.581898000	1.308416000	2.099336000	H	-2.079922000	-3.258540000	-1.082120000
C	-2.751146000	-0.521812000	0.737810000	H	-4.392537000	3.166260000	-1.188115000	C	-2.617109000	1.692670000	-0.087744000	H	-3.467104000	-3.774023000	-2.061214000
C	-2.476057000	1.687379000	-0.013342000	H	-4.100636000	4.669215000	-0.273400000	C	-2.761236000	0.760039000	-1.169514000	H	-3.700512000	-3.406484000	-0.349351000
C	-2.777651000	-0.550809000	-0.730484000	H	-4.604649000	3.185606000	0.582728000	H	-2.726863000	1.035404000	-2.217773000	C	-3.287373000	-1.461765000	1.902766000
C	-2.503043000	3.198538000	-0.061013000	C	-3.119637000	-1.639866000	-1.753992000	C	3.592936000	-1.508869000	0.577848000	C	-4.775125000	-1.847919000	1.724398000
C	3.987265000	-0.397474000	-1.113584000	C	-4.640656000	-1.311918000	2.084017000	C	3.928573000	-0.183325000	1.021693000	H	-5.401311000	-0.951416000	1.607249000
C	3.993308000	0.902274000	-0.495017000	H	-4.839303000	-0.280478000	2.408527000	C	4.041913000	0.661242000	-0.141344000	H	-5.116943000	-2.391818000	2.617277000
C	4.117893000	2.206306000	-1.209517000	H	-4.977874000	-1.995564000	2.877293000	C	3.780065000	-0.144150000	-1.302331000	H	-4.937425000	-2.495756000	0.855953000
H	3.656409000	2.163138000	-2.204801000	H	-5.236733000	-1.506489000	1.183162000	C	3.517112000	-1.488541000	-0.859309000	C	-2.415644000	-2.729466000	1.989931000
H	5.180804000	2.464673000	-1.342737000	C	-4.585734000	-2.075420000	-1.523653000	C	3.437474000	-2.705218000	1.457201000	H	-2.266035000	-3.226247000	1.029295000
H	3.643890000	3.022666000	-0.648994000	H	-4.717877000	-2.614120000	-0.578455000	H	4.423955000	-3.145124000	1.676421000	H	-2.893231000	-3.446309000	2.674487000
C	3.887433000	-1.385283000	-0.070595000	H	-4.898937000	-2.745943000	-2.337755000	H	2.824120000	-3.481171000	0.980864000	H	-1.426594000	-2.491751000	2.404888000
C	-3.124920000	-1.529706000	1.829739000	H	-5.256454000	-1.203685000	-1.517812000	H	2.967148000	-2.441171000	2.414274000	C	-3.172972000	-0.766918000	3.277376000
C	3.914284000	0.716715000	0.929832000	C	-3.039430000	-1.060984000	-3.183097000	C	4.208399000	0.205164000	2.436349000	H	-2.152986000	-0.399914000	3.467070000
C	-1.990413000	3.810619000	1.251427000	H	-3.765264000	-0.251090000	-3.344725000	H	4.100721000	1.286433000	2.593514000	H	-3.411910000	-1.498642000	4.062060000
H	-2.600355000	3.494326000	2.109621000	H	-3.266267000	-1.861474000	-3.901371000	H	5.241797000	-0.071535000	2.701854000	H	-3.875303000	0.072762000	3.376842000
H	-2.038421000	4.907432000	1.193321000	H	-2.031055000	-0.685125000	-3.412294000	H	3.536312000	-0.310971000	3.135694000	C	-2.698186000	3.202808000	-0.168754000
H	-0.946112000	3.525223000	1.444953000	C	3.890210000	-2.867107000	-0.249258000	C	4.440072000	2.098942000	-0.156287000	C	-2.323724000	3.725570000	-1.563562000
C	-1.703709000	3.757092000	-1.250047000	H	3.258517000	-3.362987000	0.500046000	H	3.962062000	2.643655000	-0.979278000	H	-1.288548000	3.466502000	-1.831077000
H	-0.627016000	3.567182000	-1.138299000	H	4.914049000	-3.257548000	-0.133218000	H	5.534444000	2.183342000	-0.292578000	H	-2.412063000	4.821227000	-1.584159000
H	-1.847924000	4.845526000	-1.310106000	H	3.531593000	-3.158126000	-1.244865000	H	4.184038000	2.603195000	0.783779000	H	-2.990223000	3.320977000	-2.338657000
H	-2.032831000	3.323855000	-2.205138000	C	3.947681000	1.796482000	1.958721000	C	3.868495000	0.315592000	-2.720391000	C	-4.191481000	3.532624000	0.097029000
C	3.832740000	-0.696405000	1.191293000	H	3.544288000	2.740795000	1.569262000	H	3.226310000	-0.279473000	-3.383367000	H	-4.841337000	3.029634000	-0.633808000
C	4.119423000	-0.659446000	-2.576931000	H	4.986747000	1.981945000	2.274760000	H	4.904630000	0.214840000	-3.082708000	H	-4.349962000	4.618185000	0.014471000
H	3.697666000	-1.633599000	-2.855192000	H	3.372024000	1.521645000	2.852583000	H	3.580867000	1.370305000	-2.824245000	H	-4.492144000	3.212277000	1.104884000
H	5.183323000	-0.657735000	-2.863836000	C	3.777438000	-1.338878000	2.537214000	C	3.289458000	-2.669891000	-1.742071000	C	-1.841774000	3.892949000	0.904512000
H	3.613933000	0.114417000	-3.170312000	H	3.272624000	-0.698564000	3.272861000	H	2.670920000	-3.433227000	-1.251422000	H	-2.055904000	3.505190000	1.910533000
C	-2.873370000	-3.010859000	1.519687000	H	4.799142000	-1.527141000	2.905140000	H	4.254920000	-3.136411000	-1.996207000	H	-2.053742000	4.972106000	0.907786000
H	-3.457296000	-3.377643000	0.669714000	H	3.252802000	-2.302709000	2.505345000	H	2.799461000	-2.388028000	-2.683442000	H	-0.768986000	3.759080000	0.711732000

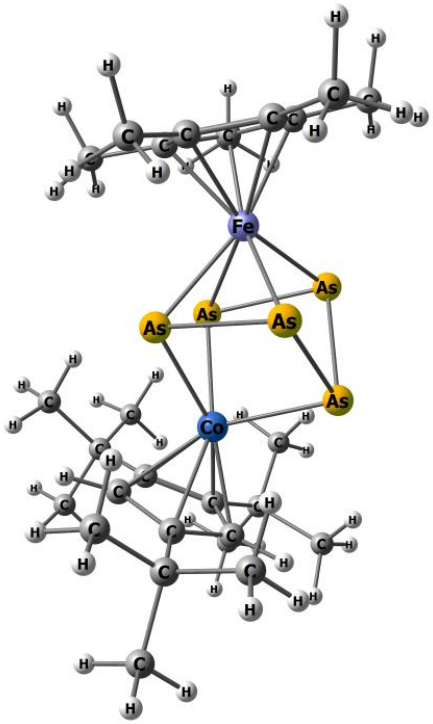
Table S7: Optimized geometries of **5** (left) and **6** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.



Co	-0.852881000	0.229224000	0.016424000	H	-4.305548000	3.114709000	1.213700000		As	-0.459866000	-1.124861000	1.636599000	C	3.301489000	-1.524260000	-1.785767000
Fe	2.143114000	-0.086706000	-0.002543000	C	-3.093359000	-1.553775000	-1.793196000		As	-0.685384000	1.234952000	1.649795000	C	4.806638000	-1.178745000	-1.988550000
P	0.661039000	0.086404000	-1.831984000	C	-2.896993000	-3.041712000	-1.479969000		As	-0.824200000	1.953285000	-0.608874000	H	4.933624000	-0.135912000	-2.310696000
P	0.905042000	1.811094000	-0.542054000	H	-1.837015000	-3.284005000	-1.318763000		As	-0.532773000	0.060390000	-2.016107000	H	5.213964000	-1.834875000	-2.770881000
P	0.488127000	-1.669329000	-0.572277000	H	-3.234342000	-3.621685000	-2.350097000		As	-0.301604000	-1.854316000	-0.623917000	H	5.389749000	-1.328982000	-1.072324000
P	0.788672000	1.139761000	1.511783000	H	-3.477711000	-3.383882000	-0.618163000		Co	0.994760000	0.226559000	0.012537000	C	3.165710000	-3.018963000	-1.471710000
P	0.599806000	-1.014777000	1.492317000	C	4.129881000	1.361030000	2.125677000		Fe	-2.029112000	-0.129262000	-0.010656000	H	3.749885000	-3.333423000	-0.601731000
C	-2.679714000	-0.550329000	0.753998000	H	3.797235000	2.386816000	1.922523000		C	2.842000000	-0.531291000	-0.715111000	H	3.538004000	-3.586533000	-2.335943000
C	-3.028755000	-1.618783000	1.789412000	H	5.202376000	1.405437000	2.375648000		C	2.829974000	-0.529800000	0.754491000	H	2.115900000	-3.309709000	-1.320726000
C	-2.391392000	1.682078000	0.022253000	H	3.600985000	0.992186000	3.014094000		C	2.586662000	0.834066000	1.153652000	C	2.588491000	-1.286513000	-3.134063000
C	3.936596000	0.468113000	0.946352000	C	-2.447282000	3.186947000	0.024926000		H	2.514460000	1.165205000	2.183310000	H	1.518733000	-1.528977000	-3.077528000
C	-2.689802000	-0.547492000	-0.716315000	C	-4.607911000	-1.268992000	-2.017221000		C	2.518777000	1.696854000	0.015683000	H	3.034410000	-1.954931000	-3.882670000
C	-2.468261000	0.820474000	-1.113016000	H	-5.197963000	-1.444015000	-1.109672000		C	2.600409000	0.832601000	-1.116416000	H	2.697237000	-0.263003000	-3.512986000
H	-2.398266000	1.157623000	-2.141113000	H	-4.975185000	-1.941176000	-2.805831000		H	2.545705000	1.168548000	-2.145647000	C	3.228723000	-1.578779000	1.794703000
C	-2.459430000	0.815701000	1.157695000	H	-4.772739000	-0.232078000	-2.341709000		C	-3.680578000	-0.761198000	1.123603000	C	2.447618000	-2.907327000	1.747429000
H	-2.381485000	1.143499000	2.188399000	C	-2.002082000	3.779456000	-1.320286000		C	-3.566653000	-1.561251000	-0.067598000	H	1.485693000	-2.809206000	2.268568000
C	-2.179526000	-2.905515000	1.735669000	H	-0.957760000	3.523944000	-1.552269000		C	-3.664839000	-0.684275000	-1.204482000	H	3.023299000	-3.680781000	2.275022000
H	-1.969460000	-3.254717000	0.723518000	H	-2.076047000	4.874396000	-1.277767000		C	-3.845969000	0.658123000	-0.716466000	H	2.247994000	-3.263459000	0.735704000
H	-2.710701000	-3.705739000	2.269819000	H	-2.636714000	3.434734000	-2.148525000		C	-3.849643000	0.611248000	0.722092000	C	4.743012000	-1.840521000	1.579173000
H	-1.221027000	-2.753988000	2.249035000	C	-1.646456000	3.808995000	1.179340000		C	-3.731847000	-1.276332000	2.523008000	H	4.940143000	-2.405127000	0.661612000
C	3.782166000	-0.963834000	0.983657000	H	-1.912872000	3.372212000	2.151491000		H	-4.779012000	-1.482014000	2.797749000	H	5.119308000	-2.431630000	2.425916000
C	3.708952000	-1.437849000	-0.374731000	H	-1.861182000	4.885325000	1.228145000		H	-3.338891000	-0.547663000	3.243981000	H	5.307525000	-0.897986000	1.539994000
C	3.963058000	0.877694000	-0.433687000	H	-0.564441000	3.693940000	1.029972000		H	-3.172853000	-2.215062000	2.635120000	C	3.066787000	-1.016234000	3.222463000
C	-2.887592000	-1.052060000	3.217817000	C	3.805692000	-1.814331000	2.208970000		C	-3.470578000	-3.049106000	-0.109703000	H	3.737009000	-0.167212000	3.415388000
H	-1.863318000	-0.709990000	3.428376000	H	3.450138000	-1.270504000	3.093269000		H	-3.013799000	-3.406361000	-1.041834000	H	3.323373000	-1.808904000	3.938225000
H	-3.117364000	-1.854076000	3.932043000	H	4.842881000	-2.128116000	2.410305000		H	-4.482392000	-3.481910000	-0.051825000	H	2.031903000	-0.708058000	3.432184000
H	-3.586840000	-0.226684000	3.411349000	H	3.205127000	-2.725708000	2.092722000		H	-2.894302000	-3.446118000	0.736177000	C	2.622974000	3.200861000	0.014461000
C	3.625531000	-2.864614000	-0.801618000	C	3.874776000	-0.339251000	-2.740433000		C	-3.698203000	-1.111886000	-2.633752000	C	1.822799000	3.861470000	1.147033000
H	3.110139000	-3.486781000	-0.059158000	H	3.348462000	-1.211206000	-3.148536000		H	-3.386778000	-0.306601000	-3.311429000	H	0.742270000	3.824005000	0.954764000
H	4.643616000	-3.268819000	-0.922565000	H	4.925985000	-0.405267000	-3.064535000		H	-4.729086000	-1.390455000	-2.906179000	H	2.107959000	4.919802000	1.222588000
H	3.110484000	-2.975114000	-1.764638000	H	3.448458000	0.567460000	-3.189381000		H	-3.061439000	-1.987530000	-2.816955000	H	2.019170000	3.393044000	2.121401000
C	-4.529279000	-1.950622000	1.572925000	C	-2.363202000	-1.279825000	-3.125754000		C	-4.102529000	1.863384000	-1.558117000	C	4.139031000	3.452121000	0.265184000
H	-5.139727000	-1.036805000	1.543991000	H	-2.524768000	-0.266616000	-3.513047000		H	-3.832674000	2.792826000	-1.040338000	H	4.444727000	3.076847000	1.251799000
H	-4.874394000	-2.567765000	2.414370000	H	-2.749055000	-1.977607000	-3.880718000		H	-5.177856000	1.919497000	-1.792861000	H	4.328048000	4.534454000	0.228672000
H	-4.700639000	-2.514531000	0.649763000	H	-1.282625000	-1.456525000	-3.038478000		H	-3.559976000	1.824934000	-2.512195000	H	4.756463000	2.963710000	-0.501504000
C	3.820591000	-0.300108000	-1.250547000	C	4.202582000	2.263542000	-0.931270000		C	-4.090146000	1.769213000	1.631578000	C	2.236114000	3.802264000	-1.344382000
C	-3.958147000	3.493130000	0.242100000	H	3.772307000	2.423307000	-1.927927000		H	-3.655619000	1.605287000	2.626202000	H	2.887073000	3.436021000	-2.150458000
H	-4.573197000	3.044677000	-0.549926000	H	5.288290000	2.435758000	-1.010457000		H	-5.174459000	1.913888000	1.764372000	H	2.338904000	4.895005000	-1.303074000
H	-4.100987000	4.582837000	0.219906000	H	3.799578000	3.024127000	-0.249794000		H	-3.679809000	2.702049000	1.223506000	H	1.193784000	3.574806000	-1.611916000

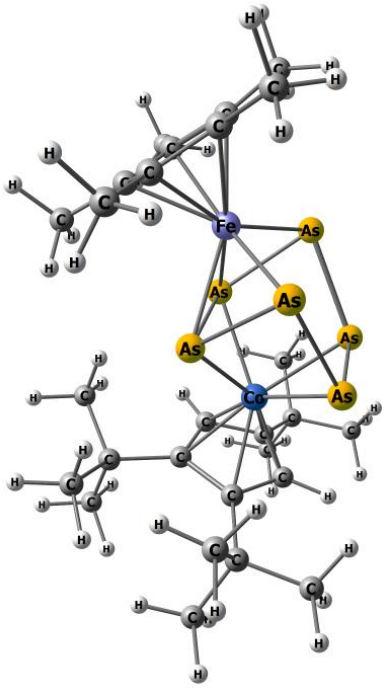
Table S8: Optimized geometries of **7** (left) and **8** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.





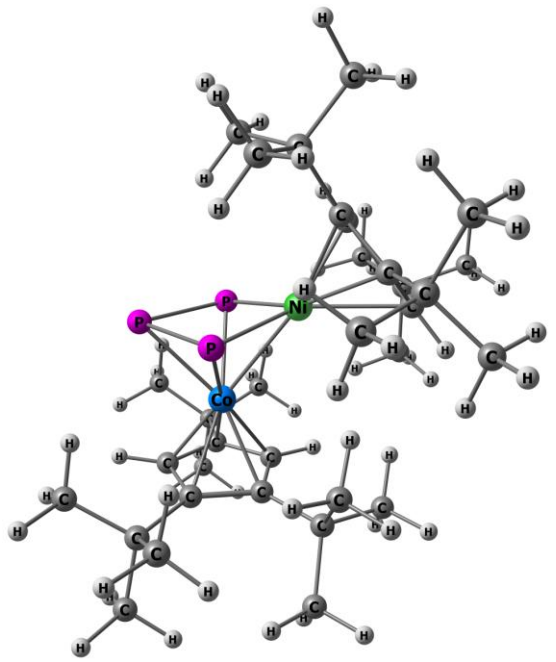
Co	1.137536000	0.260565000	-0.183374000	H	5.115071000	-2.981501000	-1.962093000	Co	1.368169000	0.263097000	-0.064031000	H	5.310019000	-3.040160000	-1.843706000
Fe	-2.438767000	-0.098311000	-0.072900000	H	4.697351000	-2.850605000	-0.242063000	Fe	-2.362083000	-0.104385000	0.118035000	H	4.906476000	-2.891867000	-0.120994000
P	0.066195000	0.483096000	-2.154432000	C	-4.364517000	-0.504566000	-0.783155000	As	0.306597000	0.545249000	-2.155128000	C	-4.299102000	-0.717327000	-0.390335000
P	-1.158461000	1.698368000	-0.743767000	C	-3.991625000	-1.425471000	0.260328000	As	-1.278655000	1.861591000	-0.765444000	C	-3.764442000	-1.518158000	0.680503000
P	-0.674799000	0.684867000	1.148684000	C	-3.707143000	-0.655796000	1.449603000	As	-0.489428000	0.906865000	1.304363000	C	-3.443783000	-0.633991000	1.777345000
P	-1.303977000	-1.192925000	-1.701617000	C	-3.922203000	0.735953000	1.138387000	As	-1.331023000	-1.256858000	-1.742225000	C	-3.800383000	0.709075000	1.381282000
P	-0.486168000	-1.417197000	0.316690000	C	-4.313094000	0.825892000	-0.243051000	As	-0.297479000	-1.494039000	0.407998000	C	-4.314059000	0.653671000	0.039224000
C	3.070049000	-0.535721000	-0.555607000	C	-4.808703000	-0.873996000	-2.163493000	C	3.282372000	-0.585704000	-0.432208000	C	-4.845233000	-1.238937000	-1.682362000
C	2.813443000	-0.580350000	0.877139000	H	-4.580348000	-0.075407000	-2.882965000	C	3.019677000	-0.636558000	1.001762000	H	-4.733490000	-0.504631000	-2.492147000
C	2.968975000	0.857607000	-0.934409000	H	-5.898357000	-1.053346000	-2.194859000	C	3.222820000	0.810960000	-0.800856000	H	-5.920034000	-1.476872000	-1.588139000
H	3.090210000	1.228827000	-1.944959000	H	-4.306248000	-1.786346000	-2.513123000	H	3.365968000	1.188675000	-1.806602000	H	-4.323184000	-2.154291000	-1.993981000
C	2.581869000	0.781055000	1.296962000	C	-3.932342000	-2.915087000	0.133038000	C	2.819623000	0.724062000	1.429908000	C	-3.599998000	-3.005330000	0.656539000
H	2.338185000	1.077432000	2.311326000	H	-3.595941000	-3.211454000	-0.871641000	H	2.583393000	1.020801000	2.445009000	H	-3.229179000	-3.345929000	-0.322946000
C	2.689266000	1.675728000	0.198950000	H	-4.917412000	-3.382596000	0.308138000	C	2.949399000	1.625124000	0.336660000	H	-4.553172000	-3.526858000	0.853360000
C	2.916916000	-1.674392000	1.948876000	H	-3.223022000	-3.343162000	0.855544000	C	3.103193000	-1.737218000	2.069880000	H	-2.872905000	-3.333139000	1.412484000
C	3.466823000	-1.600569000	-1.587559000	C	-3.326646000	-1.209163000	2.786988000	C	3.668145000	-1.650784000	-1.468097000	C	-2.917086000	-1.045465000	3.115974000
C	2.613256000	3.189180000	0.227269000	H	-2.784819000	-2.159512000	2.680956000	C	2.921205000	3.140703000	0.370943000	H	-2.260460000	-1.922553000	3.026559000
C	2.357233000	-2.642936000	-1.828578000	H	-4.213915000	-1.394332000	3.417444000	C	2.557414000	-2.692065000	-1.707379000	H	-3.733181000	-1.298488000	3.815339000
H	2.077678000	-3.184267000	-0.921312000	H	-2.667796000	-0.515784000	3.329351000	H	2.271847000	-3.228253000	-0.799074000	H	-2.320005000	-0.240020000	3.567238000
H	2.689395000	-3.375248000	-2.582966000	C	-3.784444000	1.894077000	2.074788000	H	2.892291000	-3.428941000	-2.456036000	C	-3.700737000	1.944781000	2.219048000
H	1.450848000	-2.140651000	-2.195754000	H	-3.154127000	1.636551000	2.937146000	H	1.653202000	-2.192034000	-2.082802000	H	-2.994478000	1.906823000	3.049328000
C	3.725476000	-0.933464000	-2.955956000	H	-4.765097000	2.224546000	2.459427000	C	3.921649000	-0.983761000	-2.837460000	H	-4.679004000	2.221459000	2.649594000
H	2.819782000	-0.434469000	-3.332013000	H	-3.317085000	2.755734000	1.573456000	H	3.017267000	-0.474892000	-3.204762000	H	-3.345289000	2.802077000	1.625818000
H	4.014183000	-1.706661000	-3.684086000	C	-4.692704000	2.085448000	-0.957074000	H	4.196279000	-1.758376000	-3.569519000	C	-4.866295000	1.812463000	-0.730426000
H	4.539675000	-0.195192000	-2.904260000	H	-4.106170000	2.941790000	-0.594917000	H	4.743298000	-0.253515000	-2.792179000	H	-4.330777000	2.741343000	-0.488374000
C	4.375036000	-1.673251000	2.467931000	H	-5.761139000	2.320697000	-0.803553000	C	4.551893000	-1.734144000	2.615642000	H	-5.934945000	1.969202000	-0.497549000
H	5.085867000	-1.923277000	1.668105000	H	-4.521850000	2.001739000	-2.039445000	H	5.276300000	-1.976062000	1.825128000	H	-4.779967000	1.653455000	-1.814232000
H	4.492963000	-2.410593000	3.278843000	C	1.707008000	3.670167000	1.372796000	H	4.659015000	-2.478004000	3.422073000	C	2.125588000	3.650979000	1.582696000
H	4.643199000	-0.681248000	2.861454000	H	0.687190000	3.277757000	1.247740000	H	4.810764000	-0.744511000	3.020707000	H	1.084267000	3.298220000	1.537065000
C	2.543044000	-3.095035000	1.498198000	H	1.664415000	4.770749000	1.383818000	C	2.749303000	-3.160433000	1.610927000	H	2.122696000	4.752130000	1.596323000
H	1.512868000	-3.118514000	1.114651000	H	2.086490000	3.339293000	2.351171000	H	1.722357000	-3.199230000	1.220124000	H	2.566026000	3.304511000	2.529700000
H	2.602412000	-3.772497000	2.364674000	C	4.044035000	3.733652000	0.448527000	H	2.810124000	-3.839094000	2.476333000	C	4.382148000	3.637975000	0.476829000
H	3.216045000	-3.489586000	0.729604000	H	4.460069000	3.363667000	1.398067000	H	3.432577000	-3.544954000	0.846428000	H	4.860825000	3.250038000	1.389042000
C	1.984749000	-1.344014000	3.136812000	H	4.038314000	4.835442000	0.480178000	C	2.145997000	-1.416875000	3.240449000	H	4.415271000	4.739118000	0.511023000
H	2.272886000	-0.416494000	3.649586000	H	4.713774000	3.415328000	-0.364962000	H	2.407624000	-0.482520000	3.754590000	H	4.973332000	3.301410000	-0.388318000
H	2.035981000	-2.158419000	3.875591000	C	2.066370000	3.731958000	-1.104312000	H	2.196283000	-2.227639000	3.983343000	C	2.288237000	3.702009000	-0.914461000
H	0.941787000	-1.246157000	2.800186000	H	2.698277000	3.432682000	-1.953505000	H	1.107050000	-1.338546000	2.885176000	H	2.836462000	3.374660000	-1.810104000
C	4.789231000	-2.282551000	-1.175074000	H	2.035328000	4.832586000	-1.078480000	C	4.992029000	-2.333403000	-1.060418000	H	2.302408000	4.803209000	-0.893472000
H	5.582193000	-1.531797000	-1.034526000	H	1.047343000	3.355860000	-1.281780000	H	5.787421000	-1.582866000	-0.933227000	H	1.244976000	3.364949000	-1.009964000

Table S9: Optimized geometries of **9** (left) and **10** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.

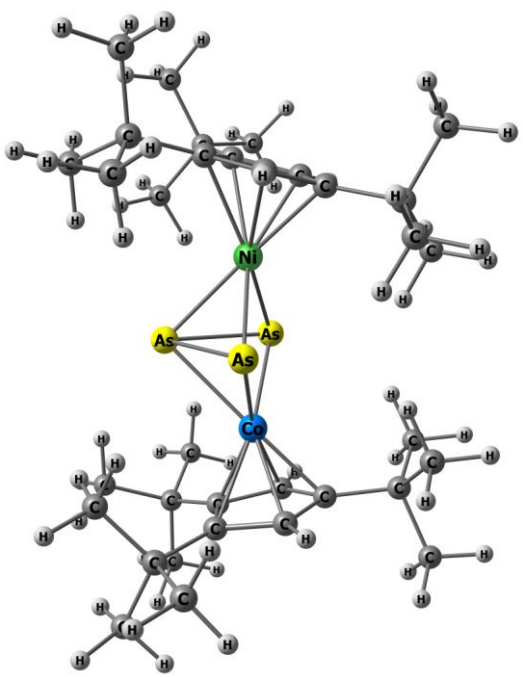


As	0.358698000	-1.468328000	0.009185000	H	-0.552835000	-1.651560000	2.690726000	Ni	-1.651672000	0.113190000	0.044805000	H	-1.013250000	2.686386000	1.998657000
As	0.490206000	0.806521000	1.356596000	H	-1.440023000	-2.677814000	3.846146000	Co	1.706472000	0.142741000	-0.059435000	C	-1.804785000	3.673717000	-0.474151000
As	1.618471000	-0.919904000	-1.967414000	H	-1.797272000	-0.944670000	3.747741000	P	0.011254000	0.305941000	-1.402610000	H	-0.860534000	3.115633000	-0.546210000
As	1.804138000	2.152200000	-0.154596000	C	-2.534584000	-2.907756000	-1.757324000	P	-0.017069000	-1.509491000	-0.144494000	H	4.983080000	3.262985000	-1.393922000
As	-0.589362000	0.132635000	-2.358037000	H	-1.743345000	-2.358906000	-2.287946000	P	0.110892000	0.108759000	1.380842000	C	2.118003000	3.671184000	0.547445000
As	-0.448670000	2.172597000	-1.166932000	H	-2.950230000	-3.668405000	-2.438220000	C	-3.651606000	-0.324806000	-0.743896000	H	1.137433000	3.180917000	0.615727000
Co	-1.417645000	0.215484000	-0.066910000	H	-2.067017000	-3.420871000	-0.914511000	C	-3.591963000	-0.615278000	0.693374000	H	1.963966000	4.743495000	0.354910000
Fe	2.412570000	-0.141952000	0.157814000	C	-4.750901000	2.723406000	1.779745000	C	-3.230048000	0.609994000	1.344012000	H	2.614731000	3.574536000	1.523704000
C	-2.745631000	-1.002916000	1.086558000	H	-5.571022000	2.216202000	1.249148000	H	-3.080743000	0.724352000	2.410981000	C	2.265677000	3.302052000	-1.928233000
C	-3.426969000	0.519675000	-0.534198000	H	-5.067271000	3.754864000	2.002593000	C	-3.004421000	1.644644000	0.381472000	H	2.864782000	2.923815000	-2.769496000
H	-3.760551000	0.942547000	-1.474672000	H	-4.583680000	2.199123000	2.732371000	C	-3.285494000	1.051286000	-0.893624000	H	2.121480000	4.382237000	-2.079824000
C	-2.684037000	0.335598000	1.603236000	C	3.559919000	-3.150248000	-0.100909000	H	-3.206923000	1.571145000	-1.841092000	H	1.283612000	2.808074000	-1.960349000
H	-2.373601000	0.594476000	2.610321000	H	2.626086000	-3.601282000	0.265623000	C	3.548638000	-0.479313000	0.767777000	H	-1.573425000	4.730970000	-0.275089000
C	-3.208442000	-0.887768000	-0.297456000	H	4.396274000	-3.783099000	0.244139000	C	3.507702000	-0.731861000	-0.684064000	H	-2.306471000	3.617904000	-1.450916000
C	-3.126060000	1.280964000	0.633401000	H	3.534194000	-3.192035000	-1.199127000	C	3.312070000	0.538393000	-1.321723000	C	-4.023301000	3.871407000	0.702093000
C	3.708880000	-1.745283000	0.389528000	C	-2.340098000	3.419408000	1.713478000	H	3.218500000	0.687095000	-2.391258000	H	-4.563701000	3.781459000	-0.251712000
C	3.279254000	-1.254976000	1.675517000	H	-2.114894000	2.875346000	2.642607000	C	3.146482000	1.563488000	-0.341966000	H	-3.844187000	4.939767000	0.899254000
C	3.705094000	0.115184000	1.788013000	H	-2.638755000	4.445033000	1.981997000	C	3.320805000	0.924382000	0.933654000	H	-4.670914000	3.476393000	1.498853000
C	4.388499000	0.471066000	0.571657000	H	-1.416307000	3.462744000	1.119465000	H	3.258829000	1.433361000	1.888083000	C	3.830168000	-1.380785000	1.977844000
C	-3.463185000	2.731400000	0.919868000	C	2.594404000	-2.060432000	2.732802000	C	-4.024422000	-1.169720000	-1.970740000	C	3.969337000	-0.517716000	3.251081000
C	4.388042000	-0.670819000	-0.295243000	H	2.004561000	-1.417482000	3.400571000	C	-2.926159000	-2.190481000	-2.338574000	H	4.784787000	0.215629000	3.164207000
C	-3.649756000	-1.934847000	-1.330820000	H	3.320708000	-2.616195000	3.351440000	H	-1.999756000	-1.664947000	-2.611177000	H	4.191704000	-1.173045000	4.106131000
C	-2.601595000	-2.164491000	2.084503000	H	1.901692000	-2.787376000	2.284262000	H	-3.249132000	-2.792039000	-3.203317000	H	3.035267000	0.015976000	3.478979000
C	-3.741457000	3.510421000	-0.374080000	C	3.531192000	1.011600000	2.972553000	H	-2.686353000	-2.872101000	-1.517583000	C	5.177515000	-2.112336000	1.793564000
H	-2.859745000	3.497668000	-1.031434000	H	3.287247000	2.038176000	2.658831000	C	-5.380557000	-1.874995000	-1.763856000	H	5.155804000	-2.841797000	0.976117000
H	-3.986864000	4.557300000	-0.137306000	H	4.450901000	1.053464000	3.581545000	H	-5.345907000	-2.637676000	-0.978181000	H	5.435928000	-2.655118000	2.715815000
H	-4.592692000	3.079644000	-0.922834000	H	2.713997000	0.664295000	3.619228000	H	-5.685214000	-2.374781000	-2.696222000	H	5.982574000	-1.392415000	1.582996000
C	-4.130389000	-1.238976000	-2.622315000	C	-3.968347000	-2.297006000	2.801290000	H	-6.160484000	-1.146421000	-1.496019000	C	2.692058000	-2.381344000	2.267278000
H	-5.008352000	-0.600836000	-2.443314000	H	-4.238030000	-1.353735000	3.298814000	C	-4.189360000	-0.253983000	-3.203904000	H	1.791614000	-1.840165000	2.592778000
H	-4.416344000	-2.007429000	-3.356605000	H	-3.920942000	-3.091360000	3.563753000	H	-4.951512000	0.522031000	-3.038236000	H	2.994308000	-3.065296000	3.076212000
H	-3.329276000	-0.627790000	-3.063396000	H	-4.770671000	-2.546932000	2.093137000	H	-4.503940000	-0.862005000	-4.064805000	H	2.414259000	-2.980009000	1.396453000
C	-2.213136000	-3.534815000	1.508923000	C	5.077933000	-0.767193000	-1.619158000	H	-3.242017000	0.234275000	-3.474068000	C	3.723242000	-1.978586000	-1.549260000
H	-2.961544000	-3.933062000	0.815756000	H	4.550640000	-1.455316000	-2.295228000	C	-3.873371000	-1.866061000	1.533434000	C	5.237033000	-2.086556000	-1.851326000
H	-2.121181000	-4.251924000	2.339682000	H	6.112664000	-1.135136000	-1.502329000	C	-3.140288000	-1.761540000	2.890494000	H	5.594486000	-1.178935000	-2.359520000
H	-1.242902000	-3.482781000	0.995050000	H	5.122539000	0.212625000	-2.114249000	H	-2.060173000	-1.607076000	2.747835000	H	5.430283000	-2.948970000	-2.508342000
C	-4.865418000	-2.709555000	-0.771715000	C	5.092359000	1.766611000	0.320110000	H	-3.285269000	-2.696285000	3.451685000	H	5.827077000	-2.213549000	-0.934386000
H	-4.608719000	-3.322457000	0.100238000	H	5.157412000	1.987447000	-0.754179000	H	-3.530009000	-0.945028000	3.513983000	C	3.220284000	-3.295511000	-0.937510000
H	-5.270777000	-3.379813000	-1.546273000	H	6.120107000	1.734194000	0.722409000	C	-3.390383000	-3.178869000	0.894885000	H	3.744098000	-3.572154000	-0.017380000
H	-5.661377000	-2.010735000	-0.471696000	H	4.570527000	2.607671000	0.799171000	H	-3.919924000	-3.428195000	-0.030162000	H	3.377441000	-4.109685000	-1.661288000
C	-1.535346000	-1.829007000	3.151953000					H	-3.556034000	-4.007880000	1.599746000	H	2.142736000	-3.239345000	-0.723759000
								H	-2.313433000	-3.128913000	0.674712000	C	2.975788000	-1.825534000	-2.893329000
								C	-5.391050000	-1.940871000	1.822778000	H	1.902178000	-1.651911000	-2.727824000
								H	-5.727365000	-1.030091000	2.339941000	H	3.091867000	-2.749809000	-3.478020000
								H	-5.610424000	-2.804756000	2.469875000	H	3.371066000	-1.002893000	-3.504376000
								H	-5.980907000	-2.042659000	0.903260000	C	2.956531000	3.045299000	-0.580229000
								C	-2.683313000	3.099116000	0.649978000	C	4.362594000	3.691996000	-0.593232000
								C	-1.951840000	3.260439000	1.992209000	H	4.879655000	3.528193000	0.363829000
								H	-2.568225000	2.913247000	2.834293000	H	4.282259000	4.777088000	-0.760916000
								H	-1.713073000	4.320019000	2.168063000				

Table S10: Optimized geometries of **10-I** (left) and **11** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.

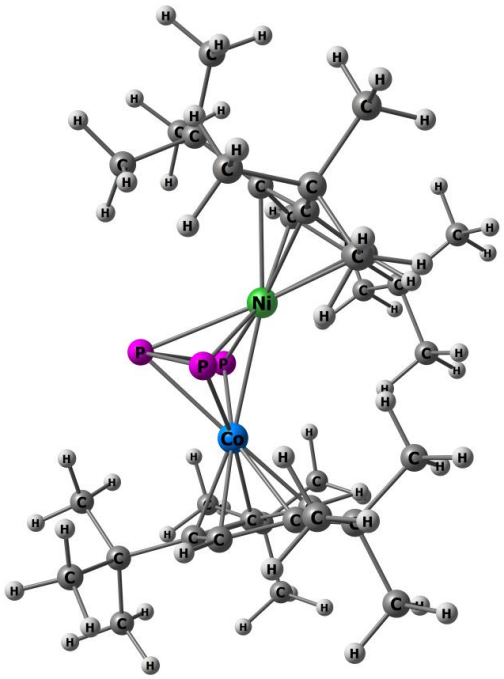


Ni	1.162776000	-0.242990000	-0.282251000
Co	-1.393534000	-0.066096000	-0.522504000
P	-0.060906000	-1.524185000	-1.541061000
P	0.114646000	1.363525000	-1.312923000
P	-0.830501000	0.068911000	-2.784050000
C	-2.345922000	-0.785314000	1.148420000
H	-1.895500000	-1.410887000	1.909379000
C	-3.047753000	1.095283000	-0.034972000
C	-2.349959000	0.662456000	1.175145000
C	-3.431911000	-0.111937000	-0.727927000
H	-3.937692000	-0.135075000	-1.686419000
C	-3.025956000	-1.272570000	-0.004235000
C	2.878451000	-1.430400000	-0.342153000
H	2.979792000	-2.231564000	-1.064975000
C	2.967971000	0.669804000	0.663535000
C	2.383642000	-1.587709000	0.980515000
C	2.013868000	-2.889120000	1.662298000
C	2.428687000	-0.292816000	1.573881000
H	2.112065000	-0.069401000	2.587517000
C	-3.385692000	-2.706318000	-0.329625000
C	3.217345000	-0.046391000	-0.597980000
C	-3.544114000	2.443965000	-0.566367000
C	3.891624000	0.316672000	-1.926706000
C	-1.315513000	0.420572000	3.458602000
H	-2.110216000	-0.252841000	3.810636000
H	-0.935490000	0.979778000	4.325676000
H	-0.489478000	-0.183055000	3.058996000
C	3.340931000	-0.578963000	-3.060743000
H	3.550575000	-1.644222000	-2.895986000
H	3.819794000	-0.293430000	-4.009150000
H	2.254289000	-0.451860000	-3.164949000
C	5.406342000	0.021715000	-1.791994000
H	5.875736000	0.633899000	-1.011381000
H	5.916708000	0.228849000	-2.745412000
H	5.569717000	-1.036057000	-1.537676000
C	-2.662726000	3.654475000	-0.231327000
H	-2.619156000	3.868306000	0.841610000
H	-3.077106000	4.545999000	-0.725319000
H	-1.639327000	3.500311000	-0.605579000
C	-1.826200000	1.420876000	2.401298000
C	3.678931000	1.763465000	-2.392443000
H	2.604411000	1.990737000	-2.462509000
H	4.120258000	1.889421000	-3.392760000
H	4.147936000	2.501437000	-1.733563000
C	-2.403675000	-3.690897000	0.322262000
H	-1.385545000	-3.534031000	-0.063240000
H	-2.703378000	-4.724802000	0.095160000
H	-2.381953000	-3.580561000	1.416021000
C	-3.406863000	-2.942564000	-1.848868000
H	-4.110935000	-2.268965000	-2.357982000
H	-3.716318000	-3.976555000	-2.062497000
H	-2.406003000	-2.782211000	-2.276937000
C	1.815895000	-4.007052000	0.626455000
H	1.038101000	-3.733765000	-0.102701000
H	1.507923000	-4.935884000	1.129096000
H	2.744580000	-4.214460000	0.074512000
C	-0.635360000	2.339129000	2.084981000
H	0.202461000	1.727934000	1.724557000
H	-0.319541000	2.866950000	2.998395000
H	-0.856963000	3.084685000	1.318323000
C	3.165836000	-3.275514000	2.618126000
H	4.109148000	-3.396220000	2.064748000
H	2.939134000	-4.225997000	3.126592000
H	3.316423000	-2.501478000	3.385476000
C	-2.980635000	2.214256000	3.051156000
H	-3.337377000	3.033598000	2.416693000
H	-2.637451000	2.652765000	4.000659000
H	-3.833912000	1.553997000	3.266796000
C	0.718437000	-2.720820000	2.471331000
H	0.828483000	-1.955031000	3.252394000
H	0.443132000	-3.666830000	2.962129000
H	-0.098563000	-2.418890000	1.803214000
C	-3.654180000	2.409166000	-2.107515000
H	-2.681290000	2.183809000	-2.567652000
H	-3.987222000	3.394344000	-2.465169000
H	-4.382929000	1.669479000	-2.464202000
C	-4.967474000	2.658256000	0.005223000
H	-5.632654000	1.835576000	-0.296298000
H	-5.387856000	3.600520000	-0.378600000
H	-4.804325000	-2.945906000	0.242903000
H	-4.818588000	-2.789378000	1.331812000
H	-5.126486000	-3.977999000	0.036524000
H	-5.532588000	-2.258389000	-0.212314000
C	3.343528000	2.083735000	1.134711000
C	4.859417000	2.306621000	0.932644000
C	3.094613000	2.218262000	2.652843000
H	2.037673000	2.075424000	2.912925000
H	3.696117000	1.497963000	3.226664000
H	3.381722000	3.230839000	2.972570000
H	5.436742000	1.499778000	1.408634000
H	5.156491000	3.260342000	1.395688000
H	5.143645000	2.348846000	-0.124293000
C	2.544663000	3.209706000	0.450894000
H	2.614478000	3.178365000	-0.639320000
H	1.481778000	3.144162000	0.713080000
H	2.921103000	4.186578000	0.793424000

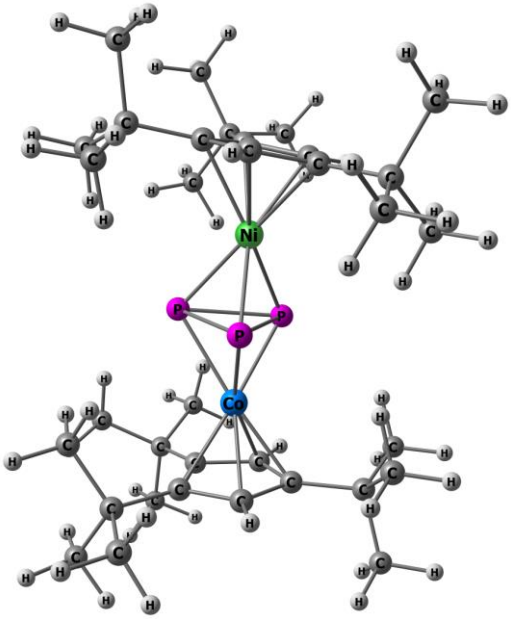


As	0.003440000	0.358955000	-1.513059000
As	-0.024659000	-1.600295000	-0.049887000
As	0.111031000	0.284845000	1.522355000
Co	1.747170000	0.190658000	-0.045664000
C	-3.047776000	1.696113000	0.347182000
C	3.532601000	-0.687055000	-0.690412000
C	-3.304040000	1.078431000	-0.921443000
H	-3.215824000	1.582986000	-1.876358000
C	3.582357000	-0.446589000	0.763656000
C	3.332703000	0.590049000	-1.314192000
H	3.240306000	0.750396000	-2.382373000
C	3.184050000	1.609319000	-0.323592000
C	-3.291410000	0.679489000	1.324218000
H	-3.169582000	0.815215000	2.392374000
C	3.880380000	-1.355733000	1.964579000
C	-3.646104000	-0.557948000	0.689864000
C	-3.677345000	-0.295153000	-0.752636000
C	-3.969052000	-1.782944000	1.552625000
C	3.014563000	3.096058000	-0.546879000
C	-2.744004000	3.159221000	0.588062000
C	-4.045141000	-1.157420000	-1.968803000
C	3.766052000	-1.920690000	-1.569835000
C	4.000941000	-0.504636000	3.247676000
H	4.807770000	0.239504000	3.174094000
H	4.226222000	-1.166224000	4.097109000
H	3.058678000	0.015335000	3.474971000
C	2.768269000	-2.386274000	2.245897000
H	1.853211000	-1.871132000	2.570674000
H	3.086626000	-3.066180000	3.052107000
H	2.508830000	-2.988772000	1.372063000
C	3.366487000	0.958679000	0.943334000
H	3.321361000	1.460776000	1.902450000
C	-2.975239000	-2.222347000	-2.289329000
H	-3.305417000	-2.840980000	-3.139192000
H	-2.767019000	-2.883949000	-1.443960000
H	-2.029597000	-1.734153000	-2.565023000
C	5.281228000	-1.997018000	-1.876966000
H	5.876014000	-2.121208000	-0.962677000
H	5.619951000	-1.077960000	-2.377300000
H	5.489376000	-2.849421000	-2.542497000
C	3.292898000	-3.254096000	-0.971209000
H	3.458907000	-4.056763000	-1.705771000
H	2.216271000	-3.220287000	-0.748126000
H	3.828733000	-3.531872000	-0.058232000
C	5.242776000	-2.056631000	1.770304000
H	5.231227000	-2.780420000	0.947456000
H	5.516658000	-2.600780000	2.687318000
H	6.031681000	-1.318773000	1.561029000
C	-3.237550000	-1.676715000	2.910495000
H	-3.415939000	-2.594907000	3.489264000
H	-3.600089000	-0.835634000	3.517248000
H	-2.152374000	-1.561866000	2.768329000
C	-3.534010000	-3.126764000	0.946173000
H	-2.453497000	-3.126285000	0.739710000
H	-4.062126000	-3.373673000	0.019750000
H	-3.742100000	-3.933163000	1.665834000
C	-5.490535000	-1.798391000	1.833263000
H	-5.744836000	-2.639302000	2.497581000
H	-6.076330000	-1.900512000	0.910816000
H	-5.798770000	-0.864817000	2.326634000
C	-4.151434000	-0.266855000	-3.226872000
H	-3.184348000	0.191832000	-3.479251000
H	-4.899464000	0.530242000	-3.102255000
H	-4.455459000	-0.887772000	-4.082343000
C	-5.429648000	-1.810192000	-1.774639000
H	-5.735138000	-2.319043000	-2.701881000
H	-6.187561000	-1.048895000	-1.536300000
H	-5.436043000	-2.555931000	-0.972061000
C	3.014317000	-1.770392000	-2.911458000
H	3.381050000	-0.925163000	-3.509177000
H	1.935082000	-1.636731000	-2.745249000
H	3.161737000	-2.680711000	-3.510998000
C	-2.114773000	3.372710000	1.972823000
H	-1.175631000	2.806443000	2.066056000
H	-2.789079000	3.050729000	2.779747000
H	-1.893607000	4.439363000	2.127260000
C	-1.785031000	3.697802000	-0.487547000
H	-1.594989000	4.769984000	-0.327543000
H	-2.198318000	3.575773000	-1.499009000
H	-0.826393000	3.161312000	-0.448290000
C	4.430253000	3.721884000	-0.537884000
H	5.053860000	3.289273000	-1.334210000
H	4.933026000	3.542646000	0.423987000
H	4.368438000	4.809260000	-0.698161000
C	2.342082000	3.380501000	-1.898069000
H	2.222869000	4.464933000	-2.040802000
H	1.348533000	2.910690000	-1.940659000
H	2.938632000	2.996070000	-2.738269000
C	-4.084813000	3.929167000	0.512637000
H	-4.790931000	3.557341000	1.269948000
H	-4.551518000	3.808056000	-0.476028000
H	-3.922651000	5.003877000	0.688926000
C	2.172462000	3.723368000	0.577117000
H	2.643216000	3.588879000	1.561655000
H	1.175944000	3.262182000	0.612061000
H	2.056233000	4.804052000	0.405401000
Ni	-1.700440000	0.152463000	0.058776000

Table S11: Optimized geometries of **12-bent** (left) and **12-linear** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.

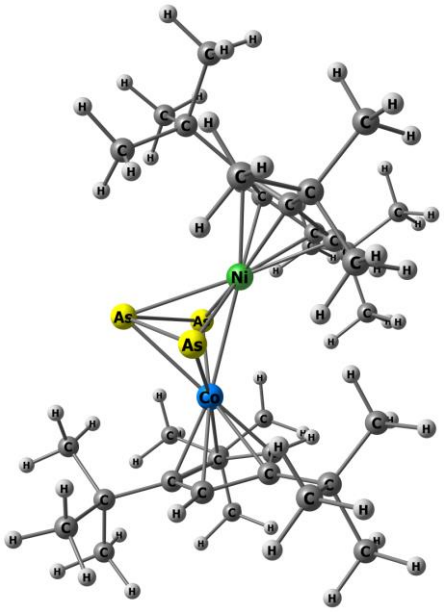


Ni	1.250582000	-0.201812000	-0.273831000	C	-3.882711000	-2.536493000	-1.366794000
Co	-1.302062000	0.338576000	-0.197879000	H	-4.585400000	-1.950369000	-1.966998000
P	-0.381971000	-1.369635000	-1.195475000	H	-4.269197000	-3.564897000	-1.323392000
P	0.305849000	1.773444000	-0.532124000	H	-2.913058000	-2.566198000	-1.885685000
P	-0.089746000	0.503371000	-2.247550000	C	5.504522000	0.132995000	-1.938493000
C	-2.767589000	1.704996000	0.309937000	H	5.671144000	1.103925000	-1.459484000
H	-2.743807000	2.754885000	0.044689000	H	6.005077000	0.152804000	-2.917849000
C	-2.430029000	-0.262127000	1.405285000	H	5.986242000	-0.640700000	-1.322726000
H	-2.104330000	-0.978318000	2.151050000	C	-2.837662000	1.978392000	3.706562000
C	-3.334021000	0.663704000	-0.516826000	H	-3.688162000	2.526702000	3.276330000
C	2.761611000	-1.663047000	-0.432159000	H	-2.504683000	2.508172000	4.611334000
H	2.701207000	-2.516398000	-1.096507000	H	-3.183141000	0.976445000	3.999049000
C	2.548613000	-0.364976000	1.426221000	C	3.823892000	2.868217000	-0.307280000
H	2.309589000	-0.026641000	2.427414000	H	4.498657000	2.576408000	-1.117624000
C	-3.157434000	-0.598172000	0.215131000	H	4.208426000	3.806817000	0.117211000
C	2.290489000	-1.663115000	0.927597000	H	2.831490000	3.077440000	-0.733442000
C	3.174231000	0.454981000	0.410175000	C	-2.848004000	-3.031023000	0.821104000
C	3.342834000	-0.400890000	-0.774836000	H	-1.815689000	-3.023560000	0.443689000
C	-2.209499000	1.153040000	1.495607000	H	-3.255840000	-4.039133000	0.665547000
C	1.763389000	-2.844237000	1.709482000	H	-2.826469000	-2.852854000	1.903927000
C	-0.502749000	1.114962000	3.333380000	C	5.152216000	1.550726000	1.385555000
H	-0.823377000	0.127026000	3.691435000	H	5.100884000	0.854324000	2.234935000
H	-0.107428000	1.672500000	4.194069000	H	5.589681000	2.496379000	1.739034000
H	0.307838000	0.967419000	2.608005000	H	5.822942000	1.121054000	0.631159000
C	-3.728415000	-2.011166000	0.066748000	C	1.287945000	-3.967919000	0.776579000
C	-1.665614000	1.891089000	2.695520000	H	0.483280000	-3.625139000	0.108622000
C	-4.047501000	1.012011000	-1.826310000	H	0.898420000	-4.804724000	1.373302000
C	4.005111000	-0.184817000	-2.138655000	H	2.107365000	-4.353301000	0.153237000
C	-3.448174000	0.318979000	-3.066237000	C	2.938530000	-3.367614000	2.572586000
H	-2.474181000	0.764998000	-3.315902000	H	3.785131000	-3.673478000	1.940926000
H	-4.115987000	0.473328000	-3.926551000	H	2.609109000	-4.239983000	3.156630000
H	-3.298020000	-0.754556000	-2.935454000	H	3.289494000	-2.594289000	3.270836000
C	0.609448000	-2.410184000	2.627294000	C	-1.213915000	3.312065000	2.329219000
H	0.928626000	-1.645175000	3.347897000	H	-0.397635000	3.300365000	1.591423000
H	0.231855000	-3.272963000	3.194300000	H	-0.849428000	3.828353000	3.228473000
H	-0.213246000	-1.994962000	2.030472000	H	-2.039868000	3.906395000	1.912932000
C	3.929358000	-1.483521000	-2.970174000	C	-5.547024000	0.660291000	-1.677011000
H	4.465247000	-2.314004000	-2.488077000	H	-5.722089000	-0.419822000	-1.624125000
H	4.396804000	-1.304093000	-3.948547000	H	-6.094590000	1.046255000	-2.549151000
H	2.887534000	-1.787407000	-3.149720000	H	-5.969775000	1.124158000	-0.773889000
C	3.321466000	0.908245000	-2.986843000	C	-3.965196000	2.530386000	-2.091621000
H	2.349555000	0.546861000	-3.353672000	H	-4.472847000	3.114406000	-1.310618000
H	3.944138000	1.134746000	-3.865238000	H	-4.462793000	2.747693000	-3.047096000
H	3.144424000	1.837623000	-2.440809000	H	-2.924047000	2.875030000	-2.173952000
C	3.736426000	1.821115000	0.812114000	C	-5.113046000	-1.984213000	0.764990000
C	2.886514000	2.448410000	1.938427000	H	-5.010579000	-1.680302000	1.816867000
H	1.840760000	2.582165000	1.625078000	H	-5.553727000	-2.991812000	0.737215000
H	3.291802000	3.440333000	2.181714000	H	-5.807765000	-1.290631000	0.275440000
H	2.899775000	1.855673000	2.861869000				

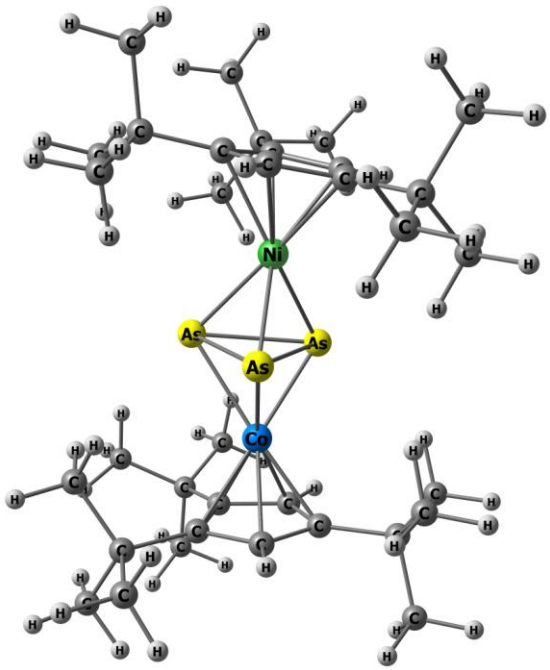


Ni	-1.756184000	0.193318000	0.057162000	H	-1.625526000	2.838666000	2.205558000
Co	1.790613000	0.199400000	-0.050108000	C	-2.245697000	3.723478000	-0.355592000
P	0.001171000	0.661922000	-1.204349000	H	-1.222258000	3.325723000	-0.284513000
P	0.007135000	-1.259339000	0.010727000	H	-2.211056000	4.804628000	-0.159593000
P	0.081266000	0.650139000	1.226980000	H	-2.597663000	3.578696000	-1.386367000
C	-3.600793000	-0.456078000	-0.801436000	C	-4.595102000	3.634505000	0.550771000
C	-3.544253000	-0.763467000	0.645402000	H	-4.998508000	3.494641000	-0.462357000
C	-3.398457000	0.494549000	1.323373000	H	-4.561871000	4.712558000	0.765461000
H	-3.311361000	0.611121000	2.396928000	H	-5.279961000	3.157856000	1.266536000
C	-3.295512000	1.563156000	0.380307000	C	3.803336000	-1.362515000	2.032454000
C	-3.440791000	0.960230000	-0.916739000	C	3.980696000	-0.472096000	3.281261000
H	-3.405264000	1.504057000	-1.853423000	H	4.838740000	0.208453000	3.182954000
C	3.594079000	-0.488330000	0.792972000	H	4.159577000	-1.117360000	4.152919000
C	3.512730000	-0.792984000	0.646048000	H	3.078376000	0.120862000	3.499923000
C	3.388242000	0.472573000	-1.326592000	C	5.109228000	-2.174019000	1.874916000
H	3.294125000	0.590499000	-2.399556000	H	5.059594000	-2.913172000	1.068244000
C	3.327028000	1.539246000	-0.383903000	H	5.316073000	-2.714174000	2.810334000
C	3.453960000	0.932497000	0.912757000	H	5.957282000	-1.503940000	1.671485000
H	3.434667000	1.475805000	1.850077000	C	2.603099000	-2.287395000	2.330218000
C	-3.818195000	-1.324959000	-2.042270000	H	1.728038000	-1.685374000	2.614738000
C	-2.624288000	-2.260570000	-2.332594000	H	2.853993000	-2.946707000	3.174600000
H	-1.736526000	-1.664170000	-2.588874000	H	2.318783000	-2.913055000	1.480767000
H	-2.866123000	-2.902353000	-3.192815000	C	3.644256000	-2.071027000	-1.476315000
H	-2.364856000	-2.903278000	-1.487977000	C	5.151686000	-2.242900000	-1.792441000
C	-5.132903000	-2.123684000	-1.896142000	H	5.539153000	-1.362237000	-2.324779000
H	-5.097350000	-2.863324000	-1.089249000	H	5.294692000	-3.125411000	-2.433707000
H	-5.335954000	-2.662319000	-2.833183000	H	5.746055000	-2.378778000	-0.879847000
H	-5.976504000	-1.445752000	-1.700755000	C	3.099273000	-3.349929000	-0.823800000
C	-3.975896000	-0.429046000	-3.289761000	H	3.621116000	-3.623072000	0.098009000
H	-4.822206000	0.265237000	-3.193957000	H	3.222513000	-4.184673000	-1.528898000
H	-4.161093000	-1.069471000	-4.163502000	H	2.025443000	-3.253991000	-0.605231000
H	-3.062672000	0.149262000	-3.492518000	C	2.887571000	-1.914252000	-2.815760000
C	-3.704471000	-2.040671000	1.470317000	H	1.826386000	-1.678510000	-2.646549000
C	-2.960221000	-1.894912000	2.817970000	H	2.945152000	-2.861606000	-3.369457000
H	-1.894291000	-1.672820000	2.658716000	H	3.319848000	-1.136116000	-3.458327000
H	-3.035664000	-2.842147000	3.369586000	C	3.222277000	3.018036000	-0.669002000
H	-3.388901000	-1.112227000	3.457404000	C	4.670614000	3.570662000	-0.615332000
C	-3.164446000	-3.323014000	0.820012000	H	5.115429000	3.415708000	0.378066000
H	-3.681406000	-3.591106000	-0.106000000	H	4.660111000	4.650051000	-0.826121000
H	-3.300035000	-4.157578000	1.522915000	H	5.307823000	3.076405000	-1.362585000
H	-2.088435000	-3.233718000	0.609677000	C	2.368457000	3.730868000	0.394402000
C	-5.217544000	-2.197414000	1.768510000	H	1.333348000	3.359784000	0.377031000
H	-5.600687000	-1.316162000	2.302809000	H	2.352484000	4.811407000	0.191972000
H	-5.376126000	-3.082714000	2.402048000	H	2.768619000	3.584544000	1.407367000
H	-5.803442000	-2.321033000	0.848830000	C	2.626569000	3.279719000	-2.060220000
C	-3.167734000	3.038711000	0.669055000	H	3.235584000	2.831265000	-2.857902000
C	-2.625805000	3.281963000	2.085451000	H	2.577993000	4.362284000	-2.244646000
H	-3.287333000	2.858401000	2.854550000	H	1.605797000	2.874990000	-2.133350000
H	-2.545675000	4.362320000	2.271317000				

Table S12: Optimized geometries of **13-bent** (left) and **13-linear** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.

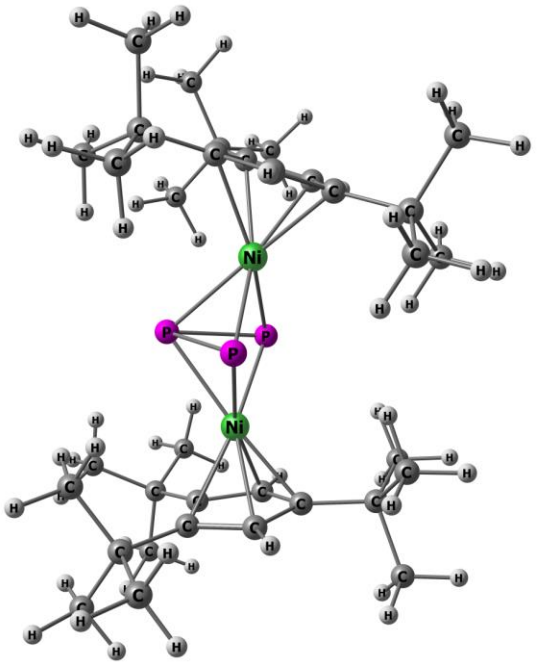


Ni	1.283474000	-0.214423000	-0.192371000	C	-4.046294000	-2.079289000	-1.776675000
Co	-1.332584000	0.290059000	0.064361000	H	-4.733527000	-1.326666000	-2.176114000
As	-0.430442000	-1.293972000	-1.321486000	H	-4.470101000	-3.066422000	-2.010513000
As	0.336872000	1.870328000	0.117841000	H	-3.085700000	-1.995594000	-2.307451000
As	-0.131185000	0.970227000	-2.059720000	C	5.557930000	0.586168000	-1.670233000
C	-2.741768000	1.500700000	0.964213000	H	5.725489000	1.382998000	-0.937218000
H	-2.700806000	2.582311000	1.008297000	H	6.069575000	0.876205000	-2.599874000
C	-2.443036000	-0.702035000	1.462083000	H	6.027964000	-0.333255000	-1.291462000
H	-2.131589000	-1.604566000	1.973889000	C	-2.716092000	0.724437000	4.317658000
C	-3.355959000	0.745501000	-0.103036000	H	-3.597589000	1.346410000	4.104925000
C	2.815212000	-1.550162000	-0.751595000	H	-2.351273000	0.972567000	5.325390000
H	2.768721000	-2.185096000	-1.628056000	H	-3.026308000	-0.330315000	4.311934000
C	2.583921000	-0.829241000	1.397257000	C	3.881208000	2.758953000	0.661757000
H	2.344477000	-0.792201000	2.453508000	H	4.560292000	2.706704000	-0.194277000
C	-3.207481000	-0.675158000	0.246727000	H	4.263790000	3.536095000	1.338917000
C	2.343611000	-1.937738000	0.553445000	H	2.891883000	3.084474000	0.306397000
C	3.205090000	0.248033000	0.656171000	C	-3.034520000	-3.203084000	0.182547000
C	3.382733000	-0.237957000	-0.722489000	H	-2.009588000	-3.178208000	-0.216854000
C	-2.177132000	0.625583000	1.934046000	H	-3.519166000	-4.108689000	-0.207489000
C	1.868003000	-3.307195000	0.985971000	H	-2.981330000	-3.307556000	1.273977000
C	-0.389559000	0.081940000	3.604618000	C	5.186997000	0.995857000	1.911403000
H	-0.678420000	-0.977090000	3.651449000	H	5.118143000	0.087669000	2.527409000
H	0.036272000	0.358646000	4.579515000	H	5.632864000	1.795569000	2.521313000
H	0.386690000	0.187271000	2.835808000	H	5.858755000	0.78874200	1.069408000
C	-3.853310000	-1.969936000	-0.258230000	C	1.490465000	-4.182249000	-0.217870000
C	-1.592541000	0.980992000	3.280830000	H	0.664972000	-3.739772000	-0.796013000
C	-4.093864000	1.464845000	-1.236832000	H	1.162890000	-5.171767000	0.131062000
C	4.058145000	0.354217000	-1.963901000	H	2.343030000	-4.329241000	-0.896135000
C	-3.568294000	1.125474000	-2.645995000	C	3.054757000	-3.966721000	1.733297000
H	-2.602488000	1.622231000	-2.818903000	H	3.935540000	-4.046650000	1.079541000
H	-4.275117000	1.503586000	-3.399497000	H	2.772199000	-4.979253000	2.058222000
H	-3.425265000	0.056057000	-2.813866000	H	3.335779000	-3.382320000	2.621091000
C	0.668793000	-3.192261000	1.941778000	C	-1.182605000	2.458227000	3.345936000
H	0.916582000	-2.600492000	2.833610000	H	-0.402939000	2.694590000	2.605964000
H	0.354474000	-4.191812000	2.275084000	H	-0.781807000	2.689918000	4.342715000
H	-0.179538000	-2.709074000	1.437956000	H	-2.037680000	3.124767000	3.163062000
C	3.978715000	-0.652197000	-3.132024000	C	-5.601806000	1.135960000	-1.129454000
H	4.507941000	-1.589514000	-2.907687000	H	-5.822927000	0.096794000	-1.396250000
H	4.450153000	-0.204602000	-4.018482000	H	-6.160569000	1.784884000	-1.819276000
H	2.935203000	-0.885299000	-3.390568000	H	-5.971824000	1.319487000	-0.110189000
C	3.399986000	1.652663000	-2.474694000	C	-3.953691000	2.994302000	-1.078405000
H	2.424440000	1.427382000	-2.929081000	H	-4.418024000	3.358685000	-0.150902000
H	4.034981000	2.101390000	-3.253080000	H	-4.463646000	3.482720000	-1.920757000
H	3.235936000	2.396987000	-1.692309000	H	-2.900628000	3.311346000	-1.098898000
C	3.778624000	1.436600000	1.433217000	C	-5.229840000	-2.058578000	0.451815000
C	2.930403000	1.725856000	2.690225000	H	-5.102093000	-2.060009000	1.544008000
H	1.892212000	1.973347000	2.424076000	H	-5.730910000	-2.993612000	0.160599000
C	3.355693000	2.591533000	3.216430000	H	-5.883792000	-1.219602000	0.186247000
H	2.916295000	0.887281000	3.397706000				



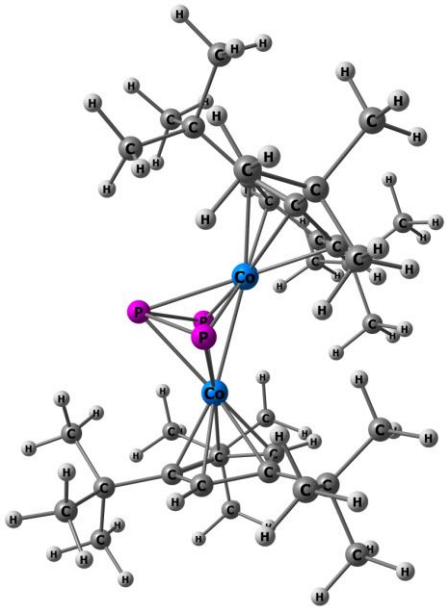
Ni	-1.782770000	0.183361000	0.059168000	H	-1.694578000	2.844278000	2.259393000
Co	1.809014000	0.187767000	-0.059373000	C	-2.230876000	3.720727000	-0.322785000
As	-0.010568000	0.707086000	-1.352333000	H	-1.210074000	3.325443000	-0.208156000
As	0.002305000	-1.413401000	0.013787000	H	-2.205748000	4.803959000	-0.136652000
As	0.084974000	0.708615000	1.359084000	H	-2.541841000	3.563456000	-1.364951000
C	-3.633487000	-0.450866000	-0.800797000	C	-4.607621000	3.642425000	0.509277000
C	-3.581415000	-0.761150000	0.643622000	H	-4.979428000	3.501274000	-0.515657000
C	-3.421430000	0.494644000	1.324452000	H	-4.578735000	4.720755000	0.723295000
H	-3.341182000	0.609140000	2.398831000	H	-5.316168000	3.168398000	1.203524000
C	-3.310926000	1.564522000	0.384270000	C	3.839057000	-1.357402000	2.033184000
C	-3.459588000	0.964928000	-0.913376000	C	3.986897000	-0.465291000	3.284548000
H	-3.426977000	1.510993000	-1.849002000	H	4.831210000	0.233378000	3.195046000
C	3.613850000	-0.487054000	0.793218000	H	4.171255000	-1.107690000	4.157203000
C	3.543799000	-0.792694000	-0.645297000	H	3.070609000	0.108771000	3.486114000
C	3.411511000	0.471792000	-1.326609000	C	5.167248000	-2.133177000	1.879722000
H	3.330906000	0.589943000	-2.400755000	H	5.137129000	-2.876145000	1.075442000
C	3.337796000	1.538770000	-0.384915000	H	5.388833000	-2.664605000	2.816842000
C	3.463051000	0.933397000	0.911828000	H	5.996680000	-1.441104000	1.673560000
H	3.441406000	1.476931000	1.849252000	C	2.665916000	-2.316567000	2.325834000
C	-3.870826000	-1.312859000	-2.043557000	H	1.776960000	-1.740649000	2.620353000
C	-2.703062000	-2.279268000	-2.335652000	H	2.936549000	-2.980387000	3.160566000
H	-1.801230000	-1.706065000	-2.595619000	H	2.393782000	-2.937884000	1.469144000
H	-2.962824000	-2.918273000	-3.192815000	C	3.709693000	-2.066695000	-1.477000000
H	-2.457520000	-2.925144000	-1.489116000	H	5.220854000	-2.200457000	-1.789459000
C	-5.205610000	-2.078266000	-1.899938000	H	5.587309000	-1.310208000	-2.320597000
H	-5.187129000	-2.822546000	-1.096648000	H	5.388304000	-3.079093000	-2.430112000
H	-5.424640000	-2.607048000	-2.839096000	H	5.815611000	-2.320753000	-0.874917000
H	-6.031157000	-1.380049000	-1.699025000	C	3.197360000	-3.361542000	-0.829540000
C	-4.005323000	-0.412436000	-3.290637000	H	3.721894000	-3.623068000	0.094167000
H	-4.838781000	0.298772000	-3.197467000	H	3.345577000	-4.191184000	-1.535919000
H	-4.199923000	-1.047769000	-4.166100000	H	2.120152000	-3.296991000	-0.615048000
H	-3.080131000	0.148152000	-3.489305000	C	2.952188000	-1.928985000	-2.818371000
C	-3.773089000	-2.034941000	1.468229000	H	1.882940000	-1.731710000	-2.650801000
C	-3.024379000	-1.910728000	2.815349000	H	3.044868000	-2.870664000	-3.377167000
H	-1.951621000	-1.725510000	2.654525000	H	3.358322000	-1.132344000	-3.455157000
H	-3.131571000	-2.853199000	3.370121000	C	3.240325000	3.018736000	-0.670201000
H	-3.425285000	-1.111786000	3.452593000	C	4.678428000	3.582003000	-0.527606000
C	-3.269777000	-3.331990000	0.818530000	H	5.061338000	3.430805000	0.491841000
H	-3.793697000	-3.586988000	-0.107337000	H	4.674975000	4.660945000	-0.741016000
H	-3.426969000	-4.162438000	1.521889000	H	5.364230000	3.089992000	-1.232161000
H	-2.191865000	-3.273424000	0.606735000	C	2.318601000	3.723354000	0.340932000
C	-5.289416000	-2.153366000	1.767708000	H	1.285609000	3.358603000	0.242085000
H	-5.649671000	-1.262850000	2.302500000	H	2.322973000	4.807103000	0.155556000
H	-5.471205000	-3.034760000	2.400502000	H	2.642129000	3.556555000	1.377774000
H	-5.878271000	-2.260715000	0.847809000	C	2.727897000	3.282022000	-2.093600000
C	-3.187262000	3.041011000	0.673489000	H	3.387059000	2.840223000	-2.854313000
C	-2.690310000	3.288165000	2.105231000	H	2.681441000	4.364788000	-2.277684000
H	-3.375891000	2.866710000	2.854134000	H	1.715976000	2.870576000	-2.231127000
H	-2.613683000	4.368834000	2.291027000				

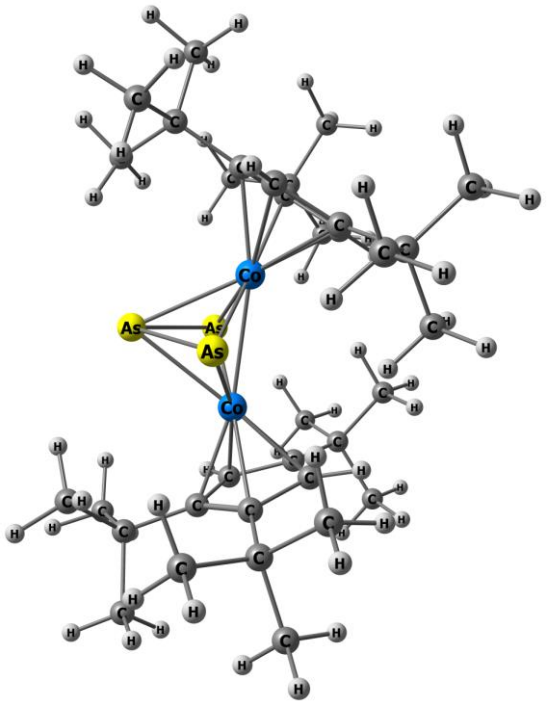
Table S13: Optimized geometries of **14** (left) and **15** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.



Ni	-1.714762000	0.126347000	0.045996000	H	-1.160886000	2.849532000	1.825393000	As	-0.021717000	0.187213000	1.521157000	C	2.910303000	-2.774484000	1.723849000
Ni	1.720626000	0.129803000	-0.048310000	C	-2.122429000	3.690227000	-0.645466000	As	0.020496000	0.438863000	-1.463787000	H	1.981001000	-2.374068000	2.154248000
P	-0.037075000	0.290038000	-1.334118000	H	-1.133086000	3.221868000	-0.748223000	As	-0.007361000	-1.628223000	-0.142633000	H	3.248043000	-3.608116000	2.357651000
P	0.004884000	-1.501320000	-0.017271000	H	-1.977616000	4.765470000	-0.469292000	Ni	-1.733297000	0.144864000	-0.007857000	H	2.676779000	-3.173046000	0.732872000
P	0.042774000	0.260024000	1.337281000	H	-2.657432000	3.576189000	-1.598629000	Ni	1.730071000	0.140404000	0.040649000	C	-4.079571000	-0.725898000	3.232677000
C	-3.635480000	-0.438065000	-0.765019000	C	-4.310062000	3.724750000	0.604531000	C	-3.109271000	1.674186000	-0.118026000	H	-4.351158000	-1.458221000	4.006145000
C	-3.585685000	-0.673586000	0.700010000	H	-4.872058000	3.561179000	-0.326000000	C	3.636650000	-0.439973000	-0.745205000	H	-4.844830000	0.063800000	3.230689000
C	-3.320629000	0.591542000	1.309924000	H	-4.204471000	4.808274000	0.761060000	C	-3.333038000	0.911828000	1.083289000	H	-3.114729000	-0.284423000	3.521352000
H	-3.215341000	0.758318000	2.375141000	H	-4.891003000	3.307044000	1.439184000	H	-3.257960000	1.314713000	2.086514000	C	5.378665000	-2.279205000	1.360598000
C	-3.134535000	1.599442000	0.308120000	C	3.948854000	-1.326110000	1.962871000	C	3.097594000	1.674869000	0.142358000	H	5.393378000	-2.802933000	0.399247000
C	-3.359000000	0.945381000	-0.956978000	C	4.105592000	-0.471299000	3.239730000	C	-3.635043000	-0.542762000	-0.709248000	H	5.655971000	-3.005797000	2.138311000
H	-3.299690000	1.439619000	-1.918946000	H	4.909352000	0.272592000	3.139147000	C	3.340469000	0.763857000	1.226667000	H	6.148912000	-1.494364000	1.335956000
C	3.644815000	-0.417819000	0.766528000	H	4.359368000	-1.133219000	4.079594000	H	3.261999000	1.026902000	2.274368000	C	3.493095000	-2.866342000	-1.619035000
C	3.598276000	-0.657384000	-0.697522000	H	3.171873000	0.047409000	3.500739000	C	3.316123000	0.918724000	-1.059394000	H	4.001641000	-3.342395000	-0.775465000
C	3.325586000	0.604772000	-1.311817000	C	5.289360000	-2.063593000	1.756705000	H	3.221942000	1.317812000	-2.062304000	H	3.704937000	-3.471117000	-2.512538000
H	3.218698000	0.767388000	-2.377368000	H	5.255701000	-2.792839000	0.940585000	C	-3.332941000	0.767082000	-1.203192000	H	2.408010000	-2.902207000	-1.438850000
C	3.126614000	1.612299000	-0.314181000	H	5.547267000	-2.608630000	2.676446000	H	-3.241647000	1.029639000	-2.250409000	C	4.092703000	-1.132030000	3.139732000
C	3.354891000	0.963555000	0.954450000	H	6.097852000	-1.348702000	1.545053000	C	3.997062000	-1.677360000	1.697688000	H	4.870102000	-0.360181000	3.235574000
H	3.294498000	1.461714000	1.914813000	C	2.804762000	-2.323375000	2.246743000	C	3.956129000	-1.423174000	-1.872374000	H	4.352020000	-1.959902000	3.814565000
C	-3.933315000	-1.350497000	-1.959765000	H	1.900476000	-1.779219000	2.555922000	C	-2.839154000	3.156392000	-0.198789000	H	3.134676000	-0.715111000	3.482292000
C	-2.782287000	-2.339666000	-2.243446000	H	3.097903000	-2.993384000	3.068804000	C	3.663927000	-0.535284000	0.731296000	C	3.270627000	-0.973877000	-3.182598000
H	-1.882477000	-1.788497000	-2.553162000	H	2.546023000	-2.938574000	1.380653000	C	2.189954000	3.508588000	1.598894000	H	2.178721000	-0.905687000	-3.061213000
H	-3.071020000	-3.012034000	-3.065114000	C	3.844833000	-1.886076000	-1.573527000	H	1.982423000	4.587030000	1.642918000	H	3.478244000	-1.716774000	-3.965346000
H	-2.518619000	-2.952643000	-1.377259000	C	5.368923000	-1.968333000	-1.841437000	H	2.850633000	3.260079000	2.441224000	H	3.642700000	-0.006723000	-3.546215000
C	-5.268579000	-2.097109000	-1.752070000	H	5.723714000	-1.052191000	-2.335215000	H	1.239930000	2.970758000	1.735659000	C	4.210895000	3.854747000	0.136378000
H	-5.230161000	-2.824487000	-0.934534000	H	5.577595000	-2.821343000	-2.504239000	C	-3.659241000	-0.442288000	0.765986000	H	4.682898000	3.642413000	-0.833536000
H	-5.522314000	-2.645638000	-2.670884000	H	5.942744000	-2.101791000	-0.916454000	C	-3.939972000	-1.665392000	-1.703235000	H	4.887287000	3.514595000	0.933602000
H	-6.082066000	-1.387419000	-1.542164000	C	3.338997000	-3.213519000	-0.986466000	C	5.487221000	-1.384919000	-2.107252000	H	4.082497000	4.942985000	0.230184000
C	-4.096983000	-0.498993000	-3.238099000	H	3.845343000	-3.498449000	-0.059796000	H	5.810997000	-0.365762000	-2.363696000	C	-5.387139000	-2.068789000	1.612167000
H	-4.906568000	0.238711000	-3.138761000	H	3.517775000	-4.015497000	-1.717173000	H	5.748267000	-2.051194000	-2.943074000	H	-5.414322000	-2.691396000	0.711806000
H	-4.345632000	-1.164407000	-4.076736000	H	2.256110000	-3.170966000	-0.794852000	H	6.047782000	-1.707685000	-1.221800000	H	-6.148658000	-1.282147000	1.506976000
H	-3.167410000	0.026612000	-3.500177000	C	3.133085000	-1.717044000	-2.935128000	C	2.829663000	3.155558000	0.247315000	H	-5.666746000	-2.704055000	2.465361000
C	-3.823855000	-1.902450000	1.577888000	H	2.053358000	-1.550475000	-2.802941000	C	-3.996344000	-1.448775000	1.871181000	C	-3.519539000	-3.072196000	-1.252617000
C	-3.113489000	-1.726426000	2.939168000	H	3.267972000	-2.635720000	-3.522561000	C	1.921877000	3.644349000	-0.893058000	H	-3.742180000	-3.784208000	-2.060276000
H	-2.034647000	-1.554365000	2.806743000	H	3.545435000	-0.889274000	-3.526910000	H	1.797572000	4.734867000	-0.830603000	H	-4.048539000	-3.415570000	-0.358925000
H	-3.243446000	-2.644381000	3.528850000	C	2.864164000	3.081183000	-0.530702000	H	0.926621000	3.181192000	-0.820394000	H	-2.437103000	-3.114840000	-1.059281000
H	-3.530327000	-0.899330000	3.528760000	C	4.234875000	3.795498000	-0.397006000	H	2.338886000	3.408619000	-1.882204000	C	-4.194634000	3.866730000	0.054432000
C	-3.308738000	-3.227034000	0.992263000	H	4.661185000	3.645298000	0.605167000	C	-3.205141000	-1.404962000	-3.038348000	H	-4.942843000	3.562270000	-0.691489000
H	-3.813548000	-3.516292000	0.066115000	H	4.104818000	4.875241000	-0.560622000	H	-3.399996000	-2.242922000	-3.722234000	H	-4.059251000	4.956053000	-0.013724000
H	-3.481654000	-4.029517000	1.723830000	H	4.950379000	3.414571000	-1.139707000	H	-2.117755000	-1.335061000	-2.883496000	H	-4.584236000	3.626716000	1.053993000
H	-2.226289000	-3.177252000	0.799950000	C	1.899337000	3.629355000	0.535113000	H	-3.547899000	-0.490204000	-3.538712000	C	-1.827962000	3.589104000	0.876832000
C	-5.347327000	-1.995160000	1.845586000	H	0.917400000	3.142009000	0.452741000	C	-5.463570000	-1.633004000	-1.985063000	H	-2.167317000	3.327391000	1.888683000
H	-5.708366000	-1.081545000	2.339538000	H	1.762873000	4.710959000	0.394144000	H	-5.761619000	-0.651849000	-2.382094000	H	-1.682261000	4.678203000	0.839123000
H	-5.550506000	-2.849774000	2.508034000	H	2.277106000	3.465979000	1.553913000	H	-6.052711000	-1.828579000	-1.080472000	H	-0.856868000	3.102388000	0.706111000
H	-5.920095000	-2.132130000	0.920470000	C	2.284205000	3.339856000	-1.928892000	H	-5.715281000	-2.399485000	-2.733361000	C	-2.309238000	3.548632000	-1.585514000
C	-2.903335000	3.073009000	0.526776000	H	2.978995000	3.031584000	-2.723142000	C	-2.921901000	-2.547212000	2.029430000	H	-1.375518000	3.013095000	-1.816583000
C	-2.150160000	3.330726000	1.840865000	H	2.085203000	4.413253000	-2.056361000	H	-1.982371000	-2.104672000	2.390795000	H	-2.099448000	4.627138000	-1.613925000
H	-2.702058000	2.950340000	2.711815000	H	1.337433000	2.795709000	-2.068332000	H	-2.706393000	-3.078603000	1.098536000	H	-3.037306000	3.326636000	-2.378589000
H	-2.006269000	4.411462000	1.980853000					H	-3.259818000	-3.282945000	2.774652000				

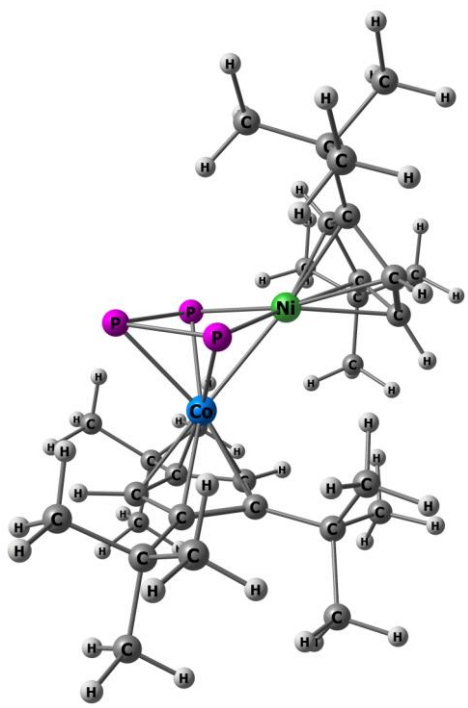
Table S14: Optimized geometries of **16** (left) and **17** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.



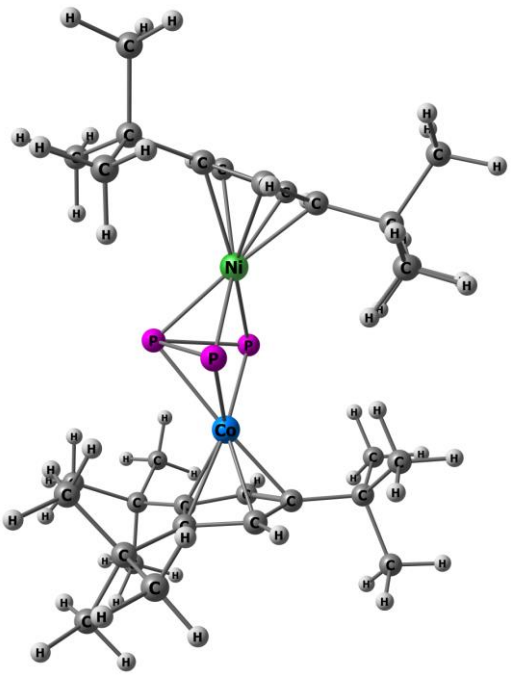


Co	1.264962000	-0.289011000	-0.234506000	C	-3.866677000	-2.740358000	-0.859184000	As	0.411299000	-1.735590000	-0.617885000	C	3.781918000	2.095327000	-2.483231000
Co	-1.264841000	0.288854000	-0.234654000	H	-4.542033000	-2.278578000	-1.585812000	As	-0.411390000	1.738208000	-0.612126000	H	4.239159000	2.117858000	-3.482412000
P	-0.367408000	-1.603422000	-0.811890000	H	-4.275695000	-3.731495000	-0.615872000	As	-0.000165000	0.003796000	-2.228069000	H	4.266744000	2.873457000	-1.876866000
P	0.367515000	1.602789000	-0.813081000	H	-2.886830000	-2.893038000	-1.335198000	Co	-1.287532000	-0.302261000	-0.074397000	H	2.716306000	2.343839000	-2.597489000
P	-0.000067000	-0.000844000	-2.236202000	C	5.466591000	-0.333863000	-1.870135000	Co	1.287548000	0.303326000	-0.073776000	C	0.520521000	1.819662000	3.215840000
C	-2.722664000	1.741372000	-0.078516000	H	5.661396000	0.707319000	-1.591399000	C	-2.717936000	-1.772336000	0.091406000	H	-0.314081000	1.606736000	2.535455000
H	-2.674684000	2.710568000	-0.559818000	H	5.990170000	-0.531361000	-2.816802000	H	-2.667400000	-2.745805000	-0.381187000	H	0.175535000	2.521225000	3.988648000
C	-2.450320000	0.053938000	1.425562000	H	5.899883000	-0.984470000	-1.096368000	C	-3.291793000	-0.594530000	-0.516892000	H	0.803139000	0.881630000	3.712486000
H	-2.167965000	-0.486874000	2.321533000	C	-2.876231000	2.732330000	3.194222000	C	3.292134000	0.595565000	-0.515139000	C	-5.209835000	1.600174000	1.272681000
C	-3.281529000	0.554264000	-0.681652000	H	-3.724573000	3.161051000	2.641278000	C	-2.209585000	-1.469573000	1.388311000	H	-5.852393000	0.983461000	0.632218000
C	2.722750000	-1.741501000	-0.076555000	H	-2.560315000	3.455545000	3.960274000	C	-3.173047000	0.487253000	0.469802000	H	-5.719445000	2.558453000	1.452831000
H	2.674766000	-2.711155000	-0.556929000	H	-3.218640000	1.818440000	3.700805000	C	2.718911000	1.771811000	0.096763000	H	-5.092016000	1.084385000	2.236642000
C	2.450098000	-0.052498000	1.425703000	C	3.866903000	2.739277000	-0.861854000	H	2.669037000	2.746771000	-0.372848000	C	3.420110000	-0.303584000	-2.930608000
H	2.167724000	0.489224000	2.321116000	H	4.542377000	2.276652000	-1.587837000	C	3.172643000	-0.489253000	0.468138000	H	2.447173000	0.048083000	-3.303058000
C	-3.143160000	-0.523612000	0.306639000	H	4.275889000	3.730684000	-0.619593000	C	2.210134000	1.465248000	1.392599000	H	3.279432000	-1.315003000	-2.545057000
C	2.210846000	-1.450554000	1.219622000	H	2.887145000	2.891418000	-1.338216000	C	-2.463645000	-0.074849000	1.587929000	H	4.107356000	-0.349678000	-3.788431000
C	3.143191000	0.523860000	0.306308000	C	-2.889259000	-2.789415000	1.406826000	H	-2.190340000	0.473009000	2.482423000	C	-4.015951000	2.682156000	-0.664055000
C	3.281767000	-0.555056000	-0.680809000	H	-1.857446000	-2.907540000	1.044948000	C	2.463307000	0.069741000	1.587863000	H	-3.052796000	2.899258000	-1.153064000
C	-2.211037000	1.451782000	1.218080000	H	-3.333717000	-3.792011000	1.473215000	H	2.189308000	-0.480709000	2.480549000	H	-4.471055000	3.648752000	-0.403822000
C	1.689353000	-2.427560000	2.246883000	H	-2.859110000	-2.379482000	2.424420000	C	-3.971498000	-0.680669000	-1.886575000	H	-4.677005000	2.194277000	-1.387174000
C	-0.538669000	1.812311000	3.052742000	C	5.132153000	1.744943000	1.079945000	C	1.700236000	2.426802000	2.441788000	C	-1.283696000	-3.774203000	1.813782000
H	-0.859302000	0.908007000	3.587597000	H	5.049429000	1.232333000	2.049348000	C	3.971825000	0.685643000	-1.884593000	H	-0.935290000	-4.457351000	2.601388000
H	-0.172521000	2.533483000	3.797148000	H	5.591548000	2.730162000	1.248339000	C	-1.699654000	-2.434226000	2.434643000	H	-0.461860000	-3.646922000	1.092556000
H	0.290895000	1.541197000	2.387759000	H	5.801967000	1.157598000	0.439627000	C	-2.881249000	-2.674439000	3.408436000	H	-2.121036000	-4.259791000	1.292723000
C	-3.733289000	-1.932122000	0.439123000	C	1.222876000	-3.734708000	1.591069000	H	-2.578205000	-3.388593000	4.188129000	C	3.022948000	-2.756917000	1.591040000
C	-1.689818000	2.429794000	2.244530000	H	0.403474000	-3.555948000	0.877893000	H	-3.750903000	-3.088523000	2.878006000	H	2.968315000	-2.336212000	2.603199000
C	-3.958375000	0.624404000	-2.053814000	H	0.855568000	-4.426742000	2.362071000	H	-3.187551000	-1.738017000	3.896539000	H	3.516949000	-3.735076000	1.670666000
C	3.958821000	-0.626625000	-2.052783000	H	2.040312000	-4.234696000	1.052242000	C	-3.826742000	1.866294000	0.622182000	H	1.998693000	-2.932930000	1.230509000
C	-3.339254000	-0.320560000	-3.103058000	C	2.875520000	-2.729099000	3.197220000	C	-3.781228000	-2.088448000	-2.489658000	C	-3.023818000	2.751826000	1.599066000
H	-2.366843000	0.071339000	-3.434688000	H	3.723989000	-3.158465000	2.644972000	H	-4.238620000	-2.108006000	-3.488837000	H	-2.969459000	2.328592000	2.610177000
H	-3.996191000	-0.368293000	-3.984113000	H	2.559369000	-3.451451000	3.963986000	H	-4.265708000	-2.868618000	-1.885641000	H	-3.517720000	3.729841000	1.681014000
H	-3.179653000	-1.336042000	-2.735170000	H	3.217832000	-1.814669000	3.702885000	H	-2.715569000	-2.336300000	-2.604897000	H	-1.999429000	2.928623000	1.239273000
C	0.537937000	-1.809321000	3.054127000	C	-1.223080000	3.736286000	1.587561000	C	-3.420385000	0.312064000	-2.929619000	C	2.881861000	2.664200000	3.416251000
H	0.858331000	-0.904361000	3.589023000	H	-0.403371000	3.556834000	0.874911000	H	-2.447170000	-0.037740000	-3.303107000	H	3.188230000	1.726341000	3.901563000
H	0.171704000	-2.529702000	3.799258000	H	-0.856118000	4.429121000	2.358008000	H	-3.280450000	1.322465000	-2.541120000	H	2.578808000	3.376017000	4.198073000
H	-0.291500000	-1.539082000	2.388623000	H	-2.040307000	4.235705000	1.047890000	H	-4.107605000	0.360232000	-3.787358000	H	3.751479000	3.079910000	2.887027000
C	3.843451000	-2.052650000	-2.631835000	C	-5.466189000	0.332016000	-1.871005000	C	1.284203000	3.768546000	1.824828000	C	5.209116000	-1.604813000	1.267951000
H	4.358837000	-2.796522000	-2.007741000	H	-5.661121000	-0.708852000	-1.591168000	H	2.121218000	4.255141000	1.304186000	H	5.851805000	-0.986263000	0.629413000
H	4.313182000	-2.066576000	-3.625375000	H	-5.989650000	0.528546000	-2.817940000	H	0.936864000	4.449777000	2.614558000	H	5.718616000	-2.563668000	1.445341000
H	2.793704000	-2.356584000	-2.755885000	H	-5.899506000	0.983487000	-1.097979000	H	0.461597000	3.643491000	1.104075000	H	5.091172000	-1.091847000	2.233400000
C	3.339655000	0.317123000	-3.103095000	C	-3.842736000	2.049771000	-2.634418000	C	-0.519860000	-1.829399000	3.210335000	C	4.015059000	-2.681325000	-0.671903000
H	2.367421000	-0.075365000	-3.434529000	H	-4.358148000	2.794395000	-2.011250000	H	-0.802190000	-0.892461000	3.709212000	H	3.051864000	-2.987807000	-1.161516000
H	3.996743000	0.364183000	-3.984075000	H	-4.312270000	2.062671000	-3.628064000	H	0.314914000	-1.615086000	2.530576000	H	4.469820000	-3.648780000	-0.414255000
H	3.179679000	1.332912000	-2.736216000	H	-2.792923000	2.353424000	-2.758576000	H	-0.175147000	-2.532941000	3.981467000	H	4.676301000	-2.191839000	-1.393757000
C	3.733259000	1.932518000	0.437356000	C	-5.132306000	-1.743794000	1.081221000	C	3.826050000	-1.868882000	0.616555000	C	5.491891000	0.475100000	-1.686556000
C	2.888995000	2.790860000	1.403913000	H	-5.049749000	-1.230120000	2.050074000	C	-5.491639000	-0.471269000	-1.687660000	H	6.012907000	0.689920000	-2.630884000
H	1.857221000	2.908546000	1.041727000	H	-5.591758000	-2.728819000	1.250606000	H	-6.012684000	-0.683382000	-2.632577000	H	5.736398000	-0.552474000	-1.395409000
H	3.333383000	3.793563000	1.469234000	H	-5.801976000	-1.157141000	0.440121000	H	-5.736429000	0.555344000	-1.393351000	H	5.883074000	1.154289000	-0.914980000
H	2.858677000	2.382099000	2.421971000					H	-5.882491000	-1.152939000	-0.918107000				

Table S15: Optimized geometries of **18** (left) and **18-I** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.

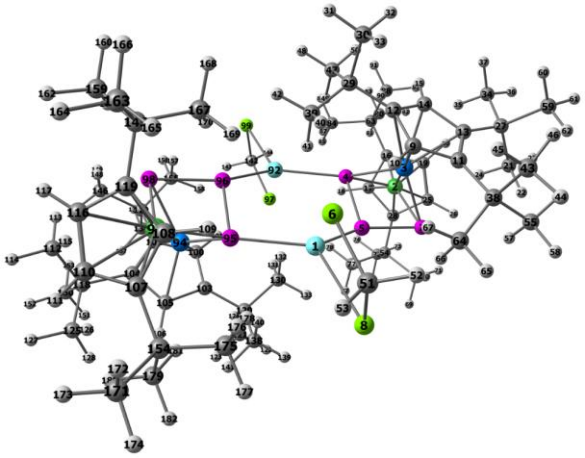


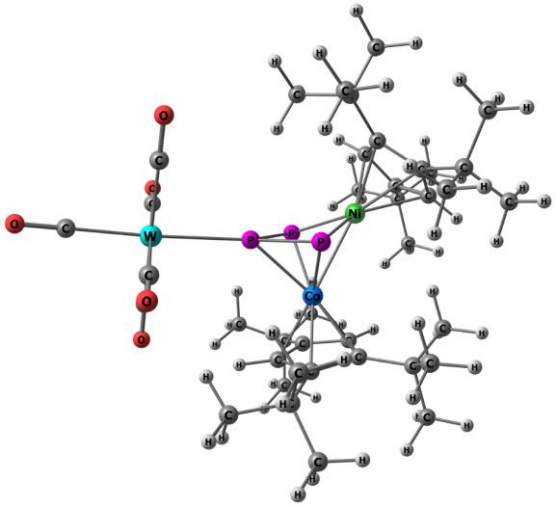
Ni	-1.441337000	-0.220666000	-0.082360000	H	-3.969135000	-4.262437000	-0.816817000
Co	1.052200000	-0.070713000	-0.516914000	H	-3.702762000	-3.654042000	0.831935000
P	-0.559088000	0.798336000	-1.782606000	C	1.464939000	3.768027000	-0.798795000
P	-0.191913000	-1.887688000	-0.729023000	H	0.473014000	3.353134000	-1.031230000
P	0.428363000	-0.950617000	-2.589921000	H	1.579626000	4.715603000	-1.345676000
C	1.866755000	1.250341000	0.814758000	H	1.504415000	3.994589000	0.276495000
H	1.311495000	1.990415000	1.378350000	C	2.510355000	2.567776000	-2.734229000
C	2.882105000	-0.755472000	0.198665000	H	3.286795000	1.870253000	-3.078764000
C	2.117384000	-0.105724000	1.262789000	H	2.660965000	3.524566000	-3.256263000
C	3.053172000	0.237546000	-0.834967000	H	1.530128000	2.164048000	-3.028433000
H	3.553363000	0.059248000	-1.780196000	C	-2.947491000	3.355949000	-0.419766000
C	2.457143000	1.478489000	-0.461558000	H	-2.153788000	3.008012000	-1.097886000
C	-3.432023000	0.428334000	-0.212130000	H	-2.870740000	4.449649000	-0.328974000
H	-3.851417000	0.839147000	-1.125049000	H	-3.918093000	3.125026000	-0.882861000
C	-2.770949000	-1.058719000	1.419418000	C	0.732053000	-1.713106000	2.719826000
H	-2.567023000	-1.975172000	1.965444000	H	-0.217473000	-1.399055000	2.268529000
C	-2.864948000	1.193362000	0.859638000	H	0.546506000	-2.003871000	3.765670000
C	-2.817204000	2.704662000	0.966670000	H	1.080165000	-2.592862000	2.174603000
C	-2.459262000	0.256342000	1.861320000	C	-3.999821000	3.157586000	1.853615000
H	-1.978177000	0.501258000	2.803899000	H	-4.958705000	2.842446000	1.415691000
C	2.571752000	2.787796000	-1.213228000	H	-4.007989000	4.254805000	1.949945000
C	-3.379261000	-0.974370000	0.117802000	H	-3.923710000	2.722162000	2.861079000
C	3.611431000	-2.095974000	0.058441000	C	3.017571000	-0.892510000	3.468216000
C	-4.019648000	-2.094404000	-0.677495000	H	3.518457000	-1.786317000	3.079813000
C	1.059738000	0.627577000	3.425714000	H	2.764446000	-1.081790000	4.522515000
H	1.736870000	1.485923000	3.545231000	H	3.733368000	-0.057634000	3.432067000
H	0.760049000	0.291187000	4.428824000	C	-1.496747000	3.156626000	1.613635000
H	0.156891000	0.962051000	2.897719000	H	-1.378970000	2.742999000	2.625672000
C	-3.755871000	-1.914100000	-2.183032000	H	-1.465674000	4.253853000	1.693960000
H	-4.125344000	-0.943854000	-2.545700000	H	-0.643331000	2.828486000	1.005708000
H	-4.266365000	-2.705162000	-2.753196000	C	3.686297000	-2.510766000	-1.428248000
H	-2.677869000	-1.964979000	-2.394110000	H	2.678883000	-2.604118000	-1.858308000
C	-5.544077000	-2.032078000	-0.416297000	H	4.189667000	-3.485492000	-1.504202000
H	-5.761924000	-2.144685000	0.656268000	H	4.257082000	-1.800034000	-2.039985000
H	-6.057353000	-2.840007000	-0.960392000	C	5.057109000	-1.872509000	0.568118000
H	-5.960718000	-1.070813000	-0.751664000	H	5.554339000	-1.079283000	-0.009385000
C	2.983059000	-3.284375000	0.798299000	H	5.639886000	-2.799408000	0.455274000
H	2.980115000	-3.161521000	1.886075000	H	5.071496000	-1.581759000	1.626862000
H	3.564359000	-4.191081000	0.573375000	C	3.950530000	3.386357000	-0.840981000
H	1.949986000	-3.448852000	0.458196000	H	4.024987000	3.551807000	0.244142000
C	1.733936000	-0.544029000	2.681519000	H	4.095302000	4.351907000	-1.349302000
C	-3.488618000	-3.465024000	-0.230414000	H	4.765180000	2.710954000	-1.141726000
H	-2.400128000	-3.533526000	-0.381024000				



Ni	1.994227000	-0.188161000	0.479678000	H	-2.316380000	-2.966582000	1.316996000
Co	-1.309352000	0.153727000	0.085019000	H	-3.838820000	-3.277265000	0.441328000
P	0.205690000	0.512604000	1.587781000	H	-3.777569000	-3.471528000	2.197112000
P	0.169200000	-1.568668000	0.838947000	H	-1.282646000	-2.385814000	-2.039660000
P	0.418446000	-0.432258000	-1.054354000	H	-2.569363000	-3.524658000	-2.519050000
C	-3.285367000	-0.395599000	0.559416000	H	-2.278096000	-3.160326000	-0.802265000
C	-3.076320000	-0.451068000	-0.898220000	H	-4.975927000	-2.573814000	-0.936707000
C	-2.647843000	0.859756000	-1.288614000	H	-4.938057000	-2.764793000	-2.699539000
C	-2.589959000	1.732578000	-0.146469000	H	-5.454950000	-1.218227000	-1.979269000
C	-3.022627000	0.954626000	0.966863000	H	-3.775642000	-0.156545000	-3.576144000
C	-3.805214000	-1.395657000	1.598527000	H	-3.263934000	-1.779324000	-4.096943000
C	-5.348196000	-1.272046000	1.634826000	H	-2.051718000	-0.626709000	-3.501110000
C	-3.267448000	-1.034400000	3.002180000	H	-2.700218000	3.572413000	1.952566000
C	-3.410519000	-2.860708000	1.358602000	H	-1.643845000	4.784782000	1.194910000
C	-3.293151000	-1.554672000	-1.941449000	H	-0.997090000	3.174289000	1.611288000
C	-2.301129000	-2.729319000	-1.805884000	H	-0.207366000	2.939963000	-0.824812000
C	-4.751259000	-2.057961000	-1.876756000	H	-0.873618000	4.567102000	-1.151768000
C	-3.082664000	-0.982977000	-3.360071000	H	-1.348937000	3.184395000	-2.165290000
C	-2.262819000	3.209316000	-0.167320000	H	-3.824412000	3.619358000	-1.655807000
C	-1.880002000	3.711003000	1.233193000	H	-3.347310000	5.036543000	-0.682844000
C	-1.104033000	3.491136000	-1.138140000	H	-4.376410000	3.766351000	0.032350000
C	-3.532478000	3.951950000	-0.648728000	H	3.718365000	-0.018896000	-1.777911000
C	3.862768000	-0.671403000	1.504241000	H	3.493806000	1.357739000	2.369046000
C	3.927530000	-1.141526000	0.148982000	H	5.946508000	-3.784232000	-0.755808000
C	3.736892000	-0.001782000	-0.692973000	H	6.204246000	-2.599908000	0.554392000
C	3.525271000	1.170784000	0.120265000	H	6.151237000	-2.053844000	-1.140840000
C	3.619357000	0.730440000	1.491248000	H	2.528907000	-3.441426000	0.813274000
C	4.187183000	-2.563357000	-0.308047000	H	4.076681000	-3.456829000	1.696373000
C	5.716876000	-2.761195000	-0.418695000	H	3.811136000	-4.599596000	0.361860000
C	3.616141000	-3.572123000	0.704440000	H	3.718439000	-3.853264000	-1.996214000
C	3.539173000	-2.814506000	-1.680633000	H	3.956968000	-2.153551000	-2.453912000
C	3.389518000	2.595256000	-0.372995000	H	2.452723000	-2.644614000	-1.635998000
C	2.718702000	2.628769000	-1.756374000	H	1.722129000	2.165599000	-1.713795000
C	2.562153000	3.440700000	0.609312000	H	3.313827000	2.091135000	-2.508502000
C	4.814414000	3.190163000	-0.481919000	H	2.605769000	3.668828000	-2.096833000
H	-2.387222000	1.154886000	-2.298364000	H	1.550963000	3.024073000	0.723088000
H	-3.070184000	1.315687000	1.987455000	H	2.472996000	4.471960000	0.236337000
H	-5.800752000	-1.542031000	0.671672000	H	3.029091000	3.482034000	1.603897000
H	-5.648213000	-0.241292000	1.874405000	H	4.767392000	4.228539000	-0.844865000
H	-5.758949000	-1.940655000	2.407294000	H	5.429083000	2.606086000	-1.182810000
H	-3.606773000	-1.793415000	3.722181000	H	5.314267000	3.187695000	0.497992000
H	-3.634257000	-0.062182000	3.357559000	H	3.936242000	-1.286890000	2.396533000
H	-2.167734000	-1.015603000	3.012191000				

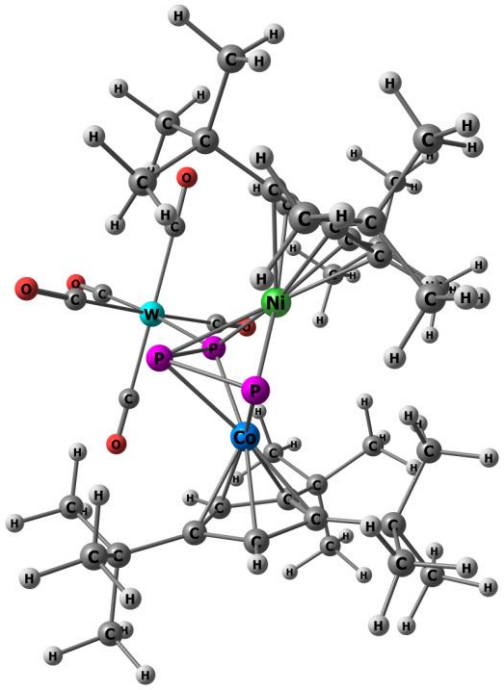
Table S16: Optimized geometries of **19** (left) and **20** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.





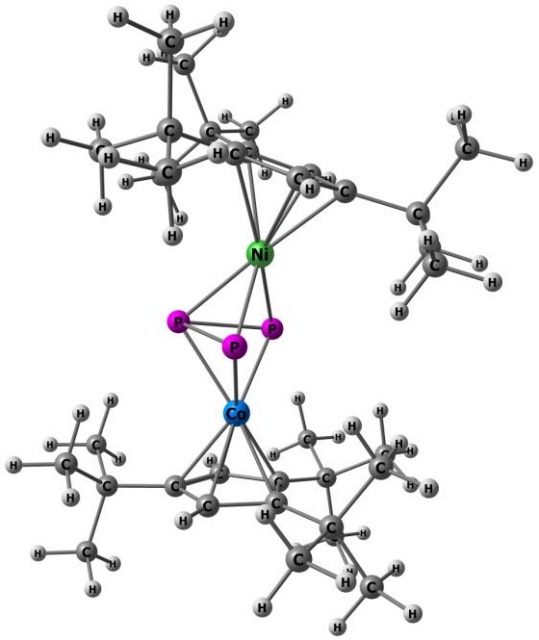
Ag	0.328520000	-1.702611000	1.085868000	Ag	-0.328782000	1.702935000	-1.086648000	W	-3.644157000	-1.115057000	0.041510000	H	4.524833000	2.982502000	-1.618595000
Ni	-4.380764000	0.989930000	0.593127000	Ni	4.380799000	-0.989807000	-0.593503000	Ni	1.922514000	-0.698152000	0.233997000	H	3.544370000	1.724477000	-0.818878000
Co	-3.478604000	-1.198104000	-0.265995000	Co	3.478406000	1.198065000	0.266121000	Co	0.314404000	1.356561000	0.087465000	C	-0.278928000	3.302559000	2.807283000
P	-2.420039000	0.750051000	-0.284046000	P	2.420285000	-0.750244000	0.284216000	P	0.303938000	-0.257863000	1.656502000	C	-0.496398000	4.830995000	2.954995000
P	-1.825887000	-0.633682000	1.267698000	P	1.825692000	0.633633000	-1.267388000	P	-1.128460000	-0.529977000	0.077283000	H	0.400284000	5.393045000	2.649165000
Cl	0.837504000	-4.352330000	-0.134078000	Cl	-0.836982000	4.352659000	0.134978000	P	0.455334000	-0.364364000	-1.373870000	H	-0.717840000	5.085387000	4.004278000
P	-3.931161000	-0.764064000	1.870335000	P	3.930860000	0.764396000	-1.870330000	O	-2.791320000	-4.042699000	-1.039347000	H	-1.339501000	5.176290000	2.336397000
Cl	0.568523000	-4.062607000	2.828584000	Cl	-0.567792000	4.063328000	-2.827583000	O	-3.364911000	-2.147565000	3.090745000	C	-1.559078000	2.573470000	3.257043000
C	-2.744835000	-2.950985000	-1.006120000	C	2.744722000	2.950911000	1.006327000	O	-4.441697000	1.812145000	1.123335000	H	-2.438402000	2.872002000	2.667560000
H	-1.770828000	-3.374505000	-0.743632000	H	1.770801000	3.374520000	0.743659000	O	-3.942421000	-0.105302000	-3.007699000	H	-1.774891000	2.813142000	4.310405000
C	-3.974860000	-3.203212000	-0.280225000	C	3.974941000	3.203119000	0.280729000	O	-6.702088000	-1.997441000	0.034676000	H	-1.447119000	1.481716000	3.175800000
C	-2.966770000	-2.055337000	-2.099491000	C	2.966361000	2.055074000	2.099610000	C	-3.092226000	-3.002572000	-0.656524000	C	0.890324000	2.880133000	3.712900000
C	-5.012328000	-2.404351000	-0.948382000	C	5.012173000	2.404055000	0.948928000	C	-3.457211000	-1.778997000	2.007130000	H	1.084768000	1.800543000	3.636507000
C	-4.352246000	-1.701297000	-2.036153000	C	4.351813000	1.700904000	2.036489000	C	-4.160967000	0.762777000	0.738733000	H	0.651301000	3.106384000	4.764000000
H	-4.848041000	-1.006827000	-2.718899000	H	4.847413000	1.006326000	2.719273000	C	-3.826894000	-0.462590000	-1.920561000	H	1.818544000	3.418413000	3.465931000
C	-5.385077000	2.648411000	-0.401061000	C	5.385395000	-2.648348000	0.400478000	C	-5.593329000	-1.679250000	0.037501000	C	4.270638000	-1.703307000	-2.203194000
C	-4.506585000	3.057119000	0.674407000	C	4.506720000	-3.057029000	-0.674857000	C	-0.285192000	3.092747000	-1.015994000	C	5.233844000	-1.374835000	-3.297350000
H	-3.640225000	3.718937000	0.565422000	H	3.640416000	-3.718902000	-0.565759000	C	1.148146000	3.119009000	-0.749940000	H	2.380052000	-2.059451000	-3.307877000
C	-6.376849000	1.793403000	0.178820000	C	6.376968000	-1.793206000	-0.179514000	C	1.295585000	3.075764000	0.688653000	H	3.712717000	-1.417784000	-4.289437000
H	-7.196801000	1.300789000	-0.356259000	H	7.196985000	-1.300578000	0.355444000	H	2.249418000	3.091381000	1.205971000	H	2.838776000	-0.357932000	-3.161664000
C	-7.013114000	-1.863598000	0.589411000	C	7.013077000	1.863434000	-0.588750000	C	0.028660000	3.060711000	1.332065000	C	5.381013000	-0.632614000	-2.328883000
H	-6.689343000	-2.512480000	1.417069000	H	6.689982000	2.512860000	-1.416246000	C	-0.922955000	3.006797000	0.273334000	H	5.001785000	0.382093000	-2.142273000
H	-8.120854000	-1.811254000	0.609698000	H	8.120794000	1.810451000	-0.608712000	H	-1.994953000	2.943850000	0.424507000	H	5.783706000	-0.648230000	-3.353414000
H	-6.610431000	-0.850608000	0.775561000	H	6.609858000	0.850751000	-0.775410000	C	3.690087000	-1.710687000	-0.764324000	H	6.219467000	-0.822164000	-1.641641000
C	-6.119998000	1.674205000	1.582204000	C	6.119851000	-1.673943000	-1.582853000	C	2.775701000	-2.630628000	-0.062529000	C	4.954335000	-3.057980000	-2.506280000
H	-6.712948000	1.082872000	2.289531000	H	6.712639000	-1.082494000	-2.290223000	C	2.821078000	-2.244197000	1.323049000	H	5.698732000	-3.305512000	-1.732987000
C	-6.540079000	-2.358065000	-0.793615500	C	6.539934000	2.357614000	0.794344000	H	2.294223000	-2.756286000	2.121712000	H	5.479457000	-3.002344000	-3.473685000
C	-4.957485000	2.473719000	1.914599000	C	4.957544000	-2.473536000	-1.915098000	C	3.702359000	-1.136957000	1.512281000	H	4.243086000	-3.889478000	-2.569312000
C	-1.955535000	-1.677251000	-3.164043000	C	1.954919000	1.676852000	3.163920000	C	4.210307000	-0.824727000	0.228832000	C	2.061212000	-3.949464000	-0.443672000
C	-2.070736000	-2.753882000	-4.275996000	C	2.070057000	2.753222000	4.276143000	H	4.919674000	-0.028085000	0.031159000	C	1.519451000	-4.014836000	-1.883132000
H	-1.338052000	-2.547970000	-5.083545000	H	1.337266000	2.547175000	5.083562000	C	-1.141498000	3.295945000	-2.294429000	H	0.816845000	-3.191258000	-2.080764000
H	-3.086787000	-2.759258000	-4.720389000	H	3.086054000	2.758421000	4.720661000	C	-0.811049000	4.674647000	-2.917588000	H	0.972287000	-4.960011000	-2.024653000
H	-1.866098000	-3.766002000	-3.871240000	H	1.865541000	3.765451000	3.871600000	H	-0.890437000	5.478894000	-2.168981000	H	2.308701000	-3.985223000	-2.643021000
C	-7.141953000	-1.390506000	-1.837718000	C	7.141573000	1.389745000	1.838293000	H	-1.527053000	4.896147000	-3.724857000	C	0.843140000	-4.187140000	0.483197000
H	-6.742899000	-0.366616000	-1.711728000	H	6.742343000	0.365964000	1.712032000	H	0.194175000	4.715670000	-3.354255000	H	1.130335000	-4.331714000	1.534649000
H	-8.240998000	-1.343597000	-1.704500000	H	8.240621000	1.342702000	1.705161000	C	-2.643339000	3.341508000	-1.927173000	H	0.314306000	-5.099537000	0.167843000
H	-6.944782000	-1.717784000	-2.878077000	H	6.944368000	1.716821000	2.878704000	H	-2.983769000	2.406773000	-1.461859000	H	0.131073000	-3.351197000	0.434357000
C	-3.967293000	-4.294829000	0.803529000	C	3.967755000	4.294897000	-0.802829000	H	-3.234824000	3.481094000	-2.844463000	C	3.051362000	-5.119977000	-0.209183000
C	-0.533407000	-1.701590000	-2.576226000	C	0.532850000	1.701452000	2.575921000	H	-2.882406000	4.174635000	-1.248941000	H	3.943904000	-5.043943000	-0.844530000
H	-0.230001000	-2.720190000	-2.264014000	H	0.229539000	2.720192000	2.264095000	C	-0.990898000	2.184174000	-3.353975000	H	2.560674000	-6.082849000	-0.427656000
H	-0.462428000	-1.040430000	-1.689891000	H	0.461941000	1.040668000	1.689310000	H	0.044427000	2.016494000	-3.663156000	H	3.389089000	-5.143135000	0.838668000
H	0.203799000	-1.349533000	-3.324105000	H	-0.204476000	1.349132000	3.323563000	H	-1.574594000	2.448571000	-4.250575000	C	4.191464000	-0.559041000	2.837576000
C	-3.989580000	-5.644431000	0.034004000	C	3.989517000	5.644386000	-0.033076000	H	-1.380377000	1.229190000	-2.976142000	C	4.320913000	0.974321000	2.754399000
H	-3.961563000	-6.490482000	0.751245000	H	3.961845000	6.490531000	-0.750215000	C	2.392954000	3.413571000	-1.614644000	H	5.029261000	1.281867000	1.969171000
H	-3.114725000	-5.733579000	-0.642134000	H	3.114278000	5.733364000	0.642584000	C	2.340037000	2.873300000	-3.053840000	H	4.688914000	1.382911000	3.709495000
H	-4.905806000	-5.743231000	-0.581050000	H	4.905393000	5.743146000	0.582506000	H	2.160191000	1.788457000	-3.065314000	H	3.348690000	1.437573000	2.533785000
C	-2.259430000	-0.291221000	-3.763475000	C	2.258669000	0.290672000	3.763037000	H	3.305415000	3.060063000	-3.549877000	C	5.586809000	-1.165629000	3.127057000
H	-1.515885000	-0.042691000	-4.547474000	H	1.515014000	0.041980000	4.546884000	H	1.569016000	3.355645000	-3.664573000	H	5.536344000	-2.264458000	3.183006000
H	-2.215950000	0.498919000	-2.985817000	H	2.215283000	-0.499292000	2.985186000	C	2.580987000	4.953019000	-1.644414000	H	5.980439000	-0.793399000	4.087843000
H	-3.264107000	-0.256140000	-4.230534000	H	3.263281000	0.255452000	4.230227000	H	1.729252000	5.466620000	-2.109502000	H	6.308552000	-0.902322000	2.338087000
C	0.799600000	-5.199882000	1.459831000	C	-0.799704000	5.200444000	-1.458720000	H	3.487677000	5.212413000	-2.215338000	C	3.245746000	-0.928646000	3.995377000
H	-0.050903000	-5.902125000	1.448056000	H	0.050247000	5.903373000	-1.446948000	H	2.697705000	5.354466000	-0.625590000	H	2.222018000	-0.565059000	3.819543000
H	1.768045000	-5.710044000	1.592018000	H	-1.768539000	5.709832000	-1.590975000	C	3.657002000	2.807076000	-0.964440000	H	3.607215000	-0.485278000	4.936865000
C	-4.390484000	2.771838000	3.292404000	C	4.390151000	-2.771601000	-3.292832000	H	3.895659000	3.261466000	0.007730000	H	3.195235000	-2.018408000	4.145779000
C	-5.110362000	-4.267971000	1.830114000	C	5.111378000	4.268350000	-1.828815000								
H	-6.105816000	-4.430149000	1.381311000	H	6.106552000	4.430660000	-1.379427000								
H	-5.117125000	-3.308975000	2.386056000	H	5.118622000	3.309405000	-2.384836000								
H	-4.947715000	-5.080888000	2.566447000	H	4.948981000	5.081321000	-2.565142000								
C	-7.093418000	-3.770968000	-1.111913000	C	7.093371000	3.770399000	1.112995000								
H	-6.757480000	-4.108235000	-2.114651000	H	6.757445000	4.105422000	2.115819000								
H	-8.202563000	-3.748607000	-1.110612000	H	8.202515000	3.747980000	1.111684000								
H	-6.771724000	-4.530742000	-0.376067000	H	6.771692000	4.530376000	0.377347000								
C	-5.329543000	3.130381000	-1.840660000	C	5.330210000	-3.130805000	1.839916000								
C	-2.659774000	-4.214221000	1.622676000	C	2.660668000	4.214258000	-1.622641000								
H	-2.606720000	-5.067224000	2.328237000	H	2.607767000	5.067410000	-2.328037000								
H	-2.617754000	-3.279005000	2.218006000	H	2.619124000	3.279169000	-2.218218000								
H	-1.758408000	-4.248037000	0.986518000	H	1.758952000	4.247771000	-0.986955000								
C	-4.918465000	1.769024000	4.334284000	C	4.917920000	-1.768704000	-4.334742000								
H	-4.483694000	1.988250000	5.330521000	H	4.482935000	-1.987849000	-5.330904000								
H	-4.644228000	0.727999000	4.061257000	H	4.643731000	-0.727707000	-4.061563000								
H	-6.021995000	1.820673000	4.431235000	H	6.021429000	-1.820347000	-4.431939000								
C	-4.852978000	4.203357000	3.672401000	C	4.852618000	-4.203075000	-3.672997000								
H	-5.959899000	4.275446000	3.676981000	H	5.959540000	-4.275133000	-3.677752000								
H	-4.462586000	4.953612000	2.954695000	H	4.462356000	-4.953386000	-2.955279000								
H	-4.484199000	4.468352000	4.684976000	H	4.483689000	-4.468008000	-4.685533000								
C	-2.849604000	2.716642000	3.256355000	C	2.849274000	-2.716404000	-3.256507000								
H	-2.427682000	2.993342000	4.244173000	H	2.427156000	-2.993110000	-4.244239000								
H	-2.430227000	3.414496000	2.503787000	H	2.430030000	-3.414243000	-2.503848000								
H	-2.502503000	1.696242000	2.998587000	H	2.502248000	-1.695994000	-2.998681000								
C	-6.448946000	4.185797000	-2.023244000	C	6.449006000	-4.187084000	2.021443000								
H	-6.312106000	5.033622000	-1.321002000	H	6.311190000	-5.034566000	1.318973000								
H	-7.448833000	3.743252000	-1.837215000	H	7.449089000	-3.745163000	1.834981000								
H	-6.434377000	4.586009000	-3.058510000	H	6.434774000	-4.587652000	3.056576000								
C	-3.962334000	3.770421000	-2.128412000	C	3.962748000	-3.770141000	2.128104000								
H	-3.804930000	4.672235000	-1.502825000	H	3.804464000	-4.671588000	1.502217000								
H	-3.889314000	4.076607000	-3.190823000	H	3.890193000	-4.076754000	3.190421000								
H	-3.143070000	3.053409000	-1.922027000	H	3.143765000	-3.052577000	1.922524000								
C	-5.551744000	1.960538000	-2.818667000	C	5.553713000	-1.961567000	2.818311000								
H	-6.544577000	1.489510000	-2.677606000	H	6.546890000	-1.491303000	2.677116000								
H	-4.773850000	1.185197000	-2.673980000	H	4.776372000	-1.185545000	2.674264000								
H	-5.498011000	2.318069000	-3.867148000	H	5.500067000	-2.319506000	3.866658000								

Table S17: Optimized geometries of **21**. XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.

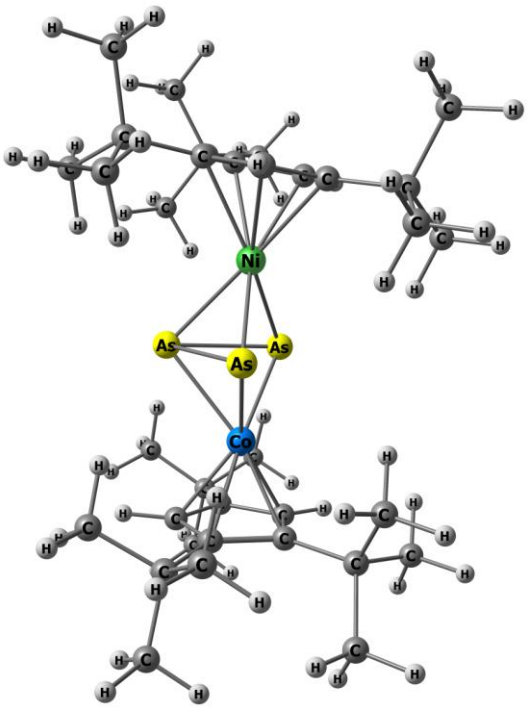


W	-3.526305000	-1.077269000	0.065947000	H	0.204559000	5.291788000	2.649262000
Ni	1.966729000	-0.630076000	0.237276000	H	-0.897983000	4.885407000	3.992467000
Co	0.285094000	1.312704000	0.062146000	H	-1.521656000	4.993237000	2.325415000
P	0.334449000	-0.260112000	1.638987000	C	-1.601509000	2.357917000	3.158068000
P	-1.094756000	-0.521728000	0.070589000	H	-2.492426000	2.640757000	2.582337000
P	0.498873000	-0.395211000	-1.361091000	H	-1.822710000	2.531005000	4.221650000
O	-2.604030000	-4.008621000	-0.894813000	H	-1.426836000	1.280891000	3.016524000
O	-3.079500000	-1.900821000	3.141664000	C	0.826196000	2.775528000	3.624063000
O	-4.445620000	1.843234000	1.029597000	H	1.060993000	1.708751000	3.502460000
O	-3.900053000	-0.284575000	-3.026777000	H	0.584625000	2.953326000	4.682367000
O	-6.553724000	-2.056314000	0.175134000	H	1.726125000	3.360321000	3.384500000
C	-2.936549000	-2.956949000	-0.546054000	C	4.211651000	-1.695261000	-2.173579000
C	-3.251946000	-1.608256000	2.035826000	C	3.149336000	-1.383350000	-3.242055000
C	-4.102231000	0.792572000	0.675969000	H	2.276094000	-2.038012000	-3.187829000
C	-3.751471000	-0.553751000	-1.910034000	H	3.592793000	-1.482209000	-4.245150000
C	-5.450068000	-1.697900000	0.132728000	H	2.794171000	-0.350210000	-3.129799000
C	-0.385373000	2.936567000	-1.072521000	C	5.329221000	-0.645675000	-2.362019000
C	1.052868000	3.022508000	-0.817887000	H	4.955728000	0.377014000	-2.211464000
C	1.212539000	3.055206000	0.622683000	H	5.710352000	-0.711242000	-3.391552000
H	2.167312000	3.105017000	1.133476000	H	6.172995000	-0.817864000	-1.677975000
C	-0.053788000	2.992081000	1.271373000	C	4.857471000	-3.073153000	-2.435097000
C	-1.016081000	2.888400000	0.222534000	H	5.614733000	-3.298936000	-1.669518000
H	-2.081218000	2.775772000	0.381752000	H	5.353729000	-3.070010000	-3.417797000
C	3.681180000	-1.644783000	-0.731738000	H	4.123678000	-3.886280000	-2.436225000
C	2.780921000	-2.532885000	0.026938000	C	2.005462000	-3.814967000	-0.299225000
C	2.866421000	-2.096047000	1.403155000	C	1.441608000	-3.896426000	-1.724466000
H	2.343722000	-2.563541000	2.229396000	H	0.778585000	-3.042198000	-1.928591000
C	3.731632000	-0.968533000	1.518218000	H	0.844406000	-4.814697000	-1.824213000
C	4.214242000	-0.709486000	0.208531000	H	2.218818000	-3.926651000	-2.495567000
H	4.900411000	0.090369000	-0.045569000	C	0.790509000	-3.952500000	0.647039000
C	-1.243429000	3.024380000	-2.344154000	H	1.084083000	-4.054513000	1.700231000
C	-0.952302000	4.365393000	-3.054054000	H	0.220091000	-4.852871000	0.378057000
H	-1.080815000	5.209993000	-2.360797000	H	0.122901000	-3.084653000	0.557708000
H	-1.655214000	4.498978000	-3.889995000	C	2.945956000	-5.016938000	-0.036406000
H	0.063621000	4.412901000	-3.462126000	H	3.828715000	-4.999311000	-0.688639000
C	-2.739462000	3.037002000	-1.964231000	H	2.407353000	-5.960711000	-0.212422000
H	-3.029594000	2.110610000	-1.451209000	H	3.297074000	-5.011720000	1.006002000
H	-3.341150000	3.106894000	-2.881336000	C	4.162176000	-0.260542000	2.785847000
H	-2.999577000	3.891131000	-1.322573000	C	4.137726000	1.263135000	2.573243000
C	-1.066989000	1.845623000	-3.317908000	H	4.812182000	1.565732000	1.759190000
H	-0.034170000	1.700442000	-3.641053000	H	4.454746000	1.785341000	3.488814000
H	-1.689956000	2.010589000	-4.210113000	H	3.122610000	1.590813000	2.314234000
H	-1.400601000	0.912728000	-2.844891000	C	5.605100000	-0.707154000	3.114398000
C	2.274302000	3.256634000	-1.707671000	H	5.654054000	-1.796957000	3.255458000
C	2.193250000	2.625743000	-3.102785000	H	5.956020000	-0.222503000	4.038988000
H	1.986001000	1.549637000	-3.026263000	H	6.295111000	-0.438163000	2.301072000
H	3.158286000	2.752292000	-3.615793000	C	3.240238000	-0.628616000	3.958809000
H	1.425252000	3.081893000	-3.735876000	H	2.190903000	-0.382731000	3.737838000
C	2.469417000	4.787317000	-1.830810000	H	3.539083000	-0.076416000	4.861969000
H	1.607733000	5.270107000	-2.309997000	H	3.295557000	-1.702701000	4.190398000
H	3.365565000	5.005654000	-2.431873000	H	4.392664000	2.781354000	-1.707771000
H	2.602350000	5.241140000	-0.837662000	H	3.377050000	1.593910000	-0.832934000
C	3.529250000	2.663066000	-1.036655000	C	-0.365165000	3.172363000	2.742278000
H	3.781182000	3.161964000	-0.091486000	C	-0.663071000	4.679550000	2.937154000

Table S18: Optimized geometries of **22** (left) and **23** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.

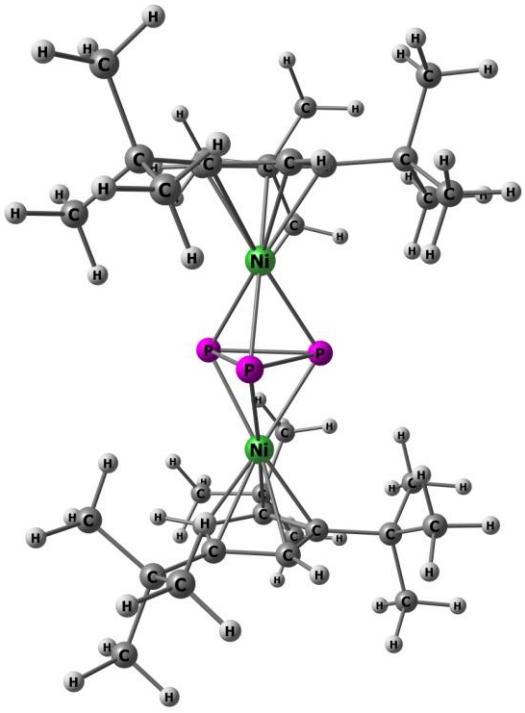


Co	-1.754708000	-0.408020000	0.050965000	C	5.582188000	-1.205563000	-2.069134000
Ni	1.662236000	0.147785000	0.036794000	H	5.798419000	-0.199829000	-2.460564000
P	-0.045690000	-0.254447000	-1.328202000	H	5.872525000	-1.942976000	-2.835905000
P	-0.124792000	0.284062000	1.345000000	H	6.213132000	-1.365377000	-1.185187000
P	0.192713000	-1.671346000	0.336296000	C	3.763307000	-2.769535000	-1.277591000
C	-3.385218000	-0.889632000	-1.176876000	H	4.365942000	-3.078988000	-0.416820000
H	-3.295093000	-1.204812000	-2.210643000	H	3.975229000	-3.473819000	-2.097718000
C	3.765871000	-0.149518000	0.727248000	H	2.700722000	-2.860624000	-1.006322000
C	-3.389435000	-1.775506000	-0.061915000	C	-3.108938000	2.855218000	1.561255000
C	-3.461782000	0.485126000	-0.736725000	H	-2.024133000	2.725188000	1.432381000
C	-3.489249000	-0.956548000	1.099407000	H	-3.277464000	3.512680000	2.428888000
H	-3.509487000	-1.328109000	2.118115000	H	-3.507022000	3.368634000	0.679435000
C	3.277425000	1.158915000	1.067995000	C	-3.563515000	1.059961000	-3.188126000
H	3.178614000	1.537802000	2.079155000	H	-2.647898000	0.487848000	-3.398247000
C	3.679659000	-0.253528000	-0.725208000	H	-3.617818000	1.889674000	-3.909565000
C	-3.520155000	0.440465000	0.729968000	H	-4.433446000	0.406878000	-3.353413000
C	3.170639000	1.010682000	-1.195446000	C	3.337117000	-2.299829000	2.066621000
H	2.976581000	1.249085000	-2.235532000	H	2.341638000	-1.940672000	2.364775000
C	2.917598000	1.890115000	-0.103305000	H	3.740389000	-2.933673000	2.874183000
C	4.076845000	-1.335589000	-1.737723000	H	3.201498000	-2.922319000	1.177483000
C	-3.394434000	-3.291151000	-0.115378000	C	3.704661000	4.238412000	-0.313185000
C	4.279566000	-1.101454000	1.819404000	H	4.378029000	4.107263000	0.547690000
C	2.458126000	3.333223000	-0.175621000	H	3.413191000	5.300543000	-0.365199000
C	-3.539281000	1.634316000	-1.755043000	H	4.267503000	3.990129000	-1.226044000
C	-2.870421000	-3.886947000	1.201469000	C	-4.848072000	2.433658000	-1.576711000
H	-1.842986000	-3.544593000	1.394569000	H	-5.719183000	1.761000000	-1.605477000
H	-2.870221000	-4.986959000	1.146710000	H	-4.955151000	3.169928000	-2.389580000
H	-3.499068000	-3.593054000	2.055272000	H	-4.876787000	2.981542000	-0.627536000
C	-3.782580000	1.496799000	1.810663000	C	4.374457000	-0.352544000	3.167470000
C	3.294994000	-1.133661000	-3.055771000	H	5.034479000	0.525132000	3.099520000
H	2.210065000	-1.120586000	-2.869408000	H	4.784107000	-1.031891000	3.930716000
H	3.524684000	-1.959936000	-3.746091000	H	3.385540000	-0.019141000	3.513691000
H	3.571162000	-0.197410000	-3.560954000	C	-5.312006000	1.689525000	1.944968000
C	-2.518397000	-3.797725000	-1.274344000	H	-5.761288000	2.053918000	1.011879000
H	-2.867269000	-3.410336000	-2.242986000	H	-5.539347000	2.414306000	2.743899000
H	-2.546303000	-4.898066000	-1.320973000	H	-5.794051000	0.733512000	2.200262000
H	-1.475777000	-3.475902000	-1.133782000	C	1.689530000	3.723354000	1.098599000
C	-4.852126000	-3.758247000	-0.337377000	H	0.815089000	3.069118000	1.233669000
H	-5.501666000	-3.403748000	0.477584000	H	1.346742000	4.767907000	1.031538000
H	-4.909620000	-4.858536000	-0.371903000	H	2.322022000	3.634282000	1.994442000
H	-5.248328000	-3.362464000	-1.284860000	C	-2.319709000	2.578460000	-1.707274000
C	5.704599000	-1.598853000	1.498775000	H	-2.136865000	2.994605000	-0.713335000
H	5.737268000	-2.227177000	0.601729000	H	-2.463383000	3.412551000	-2.414202000
H	6.092363000	-2.196790000	2.339179000	H	-1.417385000	2.020410000	-1.993754000
H	6.384737000	-0.747806000	1.340251000	C	1.541837000	3.551416000	-1.391895000
C	-3.254954000	1.004392000	3.177075000	H	2.059783000	3.317049000	-2.333782000
H	-3.783615000	0.107521000	3.527989000	H	1.215330000	4.602388000	-1.439951000
H	-3.406679000	1.792455000	3.931010000	H	0.652382000	2.909600000	-1.324492000
H	-2.179668000	0.777949000	3.117870000				

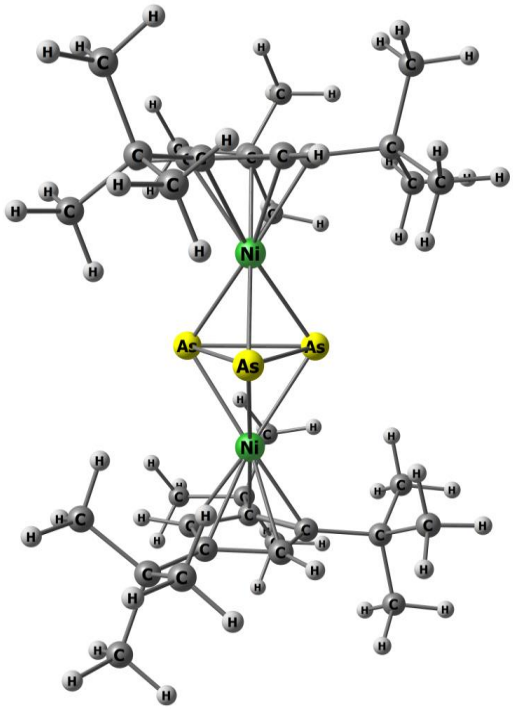


Co	1.812021000	-0.239801000	-0.139104000	H	2.298173000	2.274487000	2.296689000
Ni	-1.747351000	0.246683000	-0.131671000	C	5.338400000	2.583672000	-0.418321000
C	3.484583000	-0.414694000	-1.326747000	H	5.337263000	2.733952000	0.667737000
H	3.484101000	-0.337426000	-2.407729000	H	5.611234000	3.542263000	-0.888284000
C	-3.310278000	1.526315000	0.564930000	H	6.123917000	1.849859000	-0.655985000
H	-3.136245000	2.309153000	1.294718000	C	-5.438101000	0.049967000	2.672187000
C	-3.465238000	0.412790000	-1.410292000	H	-5.700055000	1.100459000	2.474449000
H	-3.431594000	0.189727000	-2.470772000	H	-5.644857000	-0.162342000	3.734203000
C	-3.166498000	1.688068000	-0.845098000	H	-6.097830000	-0.582113000	2.062161000
C	3.313434000	-1.636567000	-0.604833000	C	-4.215765000	3.619377000	-2.005205000
C	3.801409000	0.697330000	2.344252000	H	-4.797932000	2.942868000	-2.649248000
C	-3.945638000	-0.202773000	2.350856000	H	-4.045114000	4.559100000	-2.556049000
C	3.383119000	-1.286160000	0.775691000	H	-4.821146000	3.845542000	-1.114098000
H	3.258887000	-1.988102000	1.593914000	C	-5.615233000	-2.281901000	-0.150049000
C	-3.676901000	0.173162000	0.888126000	H	-5.606030000	-2.284813000	0.945870000
C	3.576412000	0.131616000	0.936074000	H	-5.956811000	-3.275049000	-0.484365000
C	-2.871991000	2.969161000	-1.600945000	H	-6.355312000	-1.535595000	-0.478199000
C	-3.793188000	-0.538370000	-0.383417000	C	2.871438000	3.139378000	-0.644003000
C	3.651993000	0.696301000	-0.417542000	H	1.924337000	2.813939000	-1.095779000
C	4.091681000	2.063050000	-2.490703000	H	3.151996000	4.119698000	-1.064783000
H	4.893267000	1.385589000	-2.820264000	H	2.689657000	3.263195000	0.426754000
H	4.324934000	3.072855000	-2.861392000	C	-2.082961000	3.952969000	-0.720663000
H	3.148653000	1.743037000	-2.957206000	H	-2.653179000	4.237731000	0.176477000
C	3.970939000	2.102541000	-0.951223000	H	-1.861013000	4.873188000	-1.283794000
C	5.304314000	0.562848000	2.685623000	H	-1.134261000	3.501450000	-0.393027000
H	5.617723000	-0.490373000	2.627353000	C	-4.377544000	-2.095276000	-2.282279000
H	5.503166000	0.928441000	3.706609000	H	-5.104823000	-1.375076000	-2.685888000
H	5.927269000	1.138379000	1.986756000	H	-4.729789000	-3.109621000	-2.524927000
C	-4.229317000	-1.965504000	-0.750047000	H	-3.415109000	-1.944844000	-2.792615000
C	-3.100841000	0.697401000	3.282090000	C	-2.052776000	2.674718000	-2.870679000
H	-2.033938000	0.629335000	3.020062000	H	-1.096177000	2.197124000	-2.610912000
H	-3.231354000	0.370014000	4.325205000	H	-1.848478000	3.609073000	-3.417346000
H	-3.403538000	1.752248000	3.229211000	H	-2.593532000	1.998820000	-3.549687000
C	2.996481000	-0.127826000	3.374705000	C	2.643041000	-3.000917000	-2.607997000
H	1.926861000	-0.123370000	3.116068000	H	2.579555000	-4.021741000	-3.016891000
H	3.119638000	0.314743000	4.375411000	H	3.274196000	-2.406228000	-3.285251000
H	3.335992000	-1.170931000	3.432549000	H	1.634008000	-2.559578000	-2.603613000
C	3.220625000	-3.035083000	-1.183501000	C	2.328454000	-3.931842000	-0.307820000
C	-3.197896000	-3.037192000	-0.338651000	H	1.308640000	-3.523147000	-0.253650000
H	-2.234640000	-2.833720000	-0.829182000	H	2.718288000	-4.007120000	0.718205000
H	-3.549907000	-4.035440000	-0.648503000	H	2.282494000	-4.949810000	-0.726733000
H	-3.014144000	-3.056962000	0.738999000	C	4.646685000	-3.632265000	-1.230206000
C	-3.579239000	-1.647876000	2.725095000	H	4.630251000	-4.649926000	-1.654016000
H	-4.199673000	-2.391436000	2.213369000	H	5.078892000	-3.685085000	-0.219343000
H	-3.722079000	-1.791072000	3.807883000	H	5.308971000	-3.009933000	-1.851414000
H	-2.524112000	-1.848139000	2.486050000	As	-0.034419000	-0.580308000	-1.491990000
C	3.363889000	2.155739000	2.544152000	As	-0.146201000	-1.285181000	0.884085000
H	3.944145000	2.860994000	1.939912000	As	0.204799000	1.130689000	0.840480000
H	3.504592000	2.434665000	3.600615000				

Table S19: Optimized geometries of **24** (left) and **25** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.

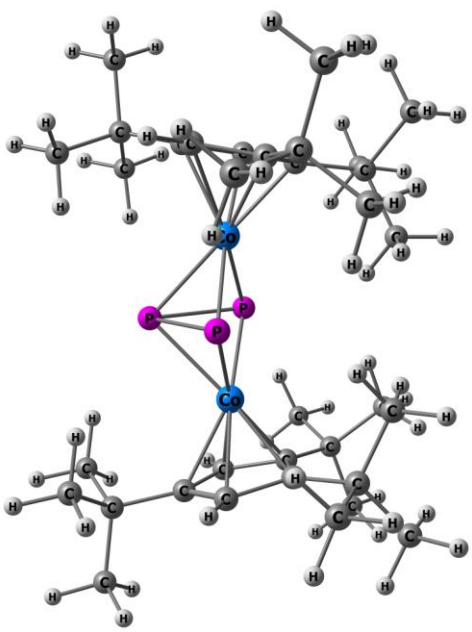


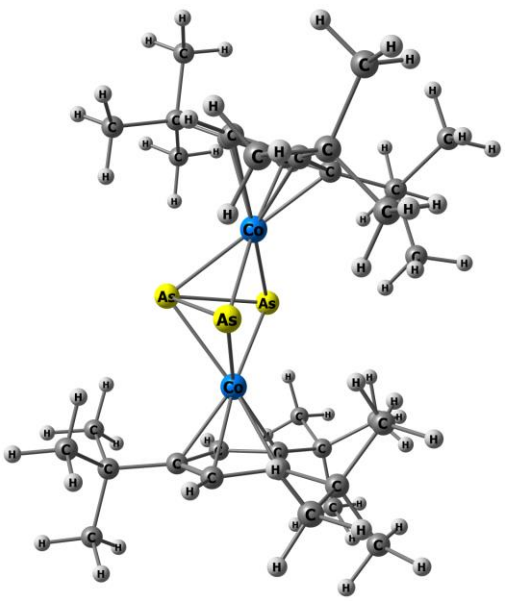
Ni	1.846889000	0.278863000	0.018786000	H	1.675540000	3.244567000	-1.060493000	H
Ni	-1.848805000	0.278390000	0.028666000		5.378976000	-2.774704000	2.885070000	
P	0.000502000	-0.913087000	0.548811000	H	5.758006000	-1.099574000	2.399142000	
P	0.001447000	1.338691000	0.784477000	H	5.761240000	-2.397249000	1.184734000	
P	-0.003851000	0.416511000	-1.272503000	H	2.069061000	-0.972092000	2.978932000	
C	3.599925000	0.664352000	-1.161216000	H	3.654371000	-0.384325000	3.549339000	
C	3.592099000	1.544872000	-0.041973000	H	3.161700000	-2.052156000	3.892722000	
C	3.625054000	0.709869000	1.115055000	H	3.113146000	-3.754363000	2.370239000	
C	3.628662000	-0.680008000	0.734281000	H	3.486378000	-3.607588000	0.647038000	
C	3.624811000	-0.710922000	-0.729602000	H	1.978843000	-2.903263000	1.286327000	
C	3.617947000	3.060721000	-0.087549000	H	5.852985000	-2.121659000	-1.528476000	
C	5.069873000	3.526350000	-0.342905000	H	5.023936000	-3.498393000	-2.304169000	
C	3.125688000	3.652257000	1.243546000	H	4.901964000	-3.256199000	-0.550429000	
C	2.712734000	3.574458000	-1.222110000	H	4.753795000	-0.658471000	-3.277160000	
C	3.752748000	-1.757168000	1.820364000	H	2.976847000	-0.657469000	-3.456117000	
C	5.253337000	-2.025970000	2.085361000	H	3.914679000	-2.100639000	-3.901700000	
C	3.121209000	-1.252097000	3.137412000	H	2.512302000	-3.508859000	-2.541927000	
C	3.043018000	-3.082516000	1.499785000	H	1.550107000	-2.081559000	-2.051614000	
C	4.938507000	-2.734800000	-1.513854000	H	2.188810000	-3.174328000	-0.823106000	
C	3.695205000	-1.852412000	-1.756045000	H	-3.593907000	1.076843000	-2.141453000	
C	3.845874000	-1.272334000	-3.179840000	H	-3.613856000	0.965179000	2.192493000	
C	2.412490000	-2.710634000	-1.787501000	H	-2.166829000	-3.116742000	-0.955246000	
C	-3.615534000	0.707884000	-1.121486000	H	-1.551898000	-1.975088000	-2.149091000	
C	-3.628487000	-0.685188000	-0.752347000	H	-2.501521000	-3.396084000	-2.682186000	
C	-3.620434000	-0.721819000	0.710681000	H	-5.016623000	-3.410160000	-2.441139000	
C	-3.621398000	0.650000000	1.154816000	H	-5.849136000	-2.078289000	-1.593938000	
C	-3.603293000	1.536626000	0.036560000	H	-4.882108000	-3.250858000	-0.678934000	
C	-3.695899000	-1.781531000	-1.826914000	H	-3.927901000	-1.941152000	-3.979620000	
C	-2.404823000	-2.623535000	-1.901049000	H	-2.998541000	-0.510810000	-3.480729000	
C	-4.930214000	-2.684454000	-1.616072000	H	-4.774408000	-0.533442000	-3.289953000	
C	-3.860932000	-1.143235000	-3.224078000	H	-1.955140000	-2.962039000	1.159479000	
C	-3.730343000	-1.847092000	1.748901000	H	-3.461113000	-3.647782000	0.496391000	
C	-3.017713000	-3.155117000	1.368407000	H	-3.081487000	-3.862225000	2.210859000	
C	-5.227451000	-2.132593000	2.014774000	H	-5.740586000	-2.470936000	1.104109000	
C	-3.087128000	-1.395858000	3.079547000	H	-5.732952000	-1.220957000	2.367761000	
C	-3.637576000	3.053070000	0.057509000	H	-5.344046000	-2.912594000	2.785420000	
C	-3.182971000	3.589856000	1.424697000	H	-3.111284000	-2.228428000	3.799629000	
C	-2.706084000	3.621091000	-1.029113000	H	-3.620846000	-0.551121000	3.536308000	
C	-5.085420000	3.521998000	-0.214282000	H	-2.039497000	-1.100881000	2.917909000	
H	3.567226000	0.986796000	-2.196218000	H	-3.850028000	3.252230000	2.232243000	
H	3.623907000	1.072282000	2.137454000	H	-3.190485000	4.691207000	1.420798000	
H	5.738973000	3.165728000	0.453542000	H	-2.162423000	3.246965000	1.652576000	
H	5.130416000	4.626965000	-0.373206000	H	-1.671860000	3.290072000	-0.851230000	
H	5.441788000	3.134524000	-1.301879000	H	-2.735885000	4.722569000	-1.025085000	
H	2.101722000	3.311561000	1.459259000	H	-3.002594000	3.276956000	-2.030958000	
H	3.128009000	4.752585000	1.194724000	H	-5.431154000	3.169236000	-1.197898000	
H	3.773107000	3.351541000	2.081044000	H	-5.151586000	4.622610000	-0.199943000	
H	3.039982000	3.192166000	-2.200354000	H	-5.772063000	3.125020000	0.549286000	
H	2.735243000	4.675345000	-1.263582000					



Ni	1.876425000	0.225868000	0.029234000	H	1.666090000	3.223404000	-1.001175000	
Ni	-1.878323000	0.223675000	0.034121000	H	5.527800000	-2.768068000	2.823279000	
As	0.001180000	-1.123203000	0.579341000	H	5.843264000	-1.079439000	2.336722000	
As	-0.000704000	1.370860000	0.931415000	H	5.868181000	-2.372492000	1.118186000	
As	-0.003232000	0.442410000	-1.399599000	H	2.161029000	-1.088077000	2.988465000	
C	3.611927000	0.645577000	-1.160269000	H	3.734280000	-0.450885000	3.537538000	
C	3.600566000	1.514841000	-0.031854000	H	3.306792000	-2.138628000	3.870052000	
C	3.650911000	0.668113000	1.115977000	H	3.294253000	-3.826647000	2.329262000	
C	3.675235000	-0.717754000	0.719961000	H	3.626108000	-3.647002000	0.600598000	
C	3.661145000	-0.733034000	-0.744259000	H	2.108101000	-3.006351000	1.278491000	
C	3.625561000	3.030986000	-0.065534000	H	5.921557000	-2.061559000	-1.578012000	
C	5.073576000	3.495284000	-0.345874000	H	5.131429000	-3.454466000	-2.366047000	
C	3.163569000	3.614069000	1.279671000	H	5.017446000	-3.240685000	-0.608225000	
C	2.699958000	3.555495000	-1.178300000	H	4.760934000	-0.624448000	-3.306186000	
C	3.850637000	-1.801324000	1.791518000	H	2.982497000	-0.671699000	-3.465494000	
C	5.364069000	-2.021157000	2.028831000	H	3.955156000	-2.083901000	-3.933476000	
C	3.225165000	-1.332475000	3.124532000	H	2.623376000	-3.553675000	-2.566594000	
C	3.182748000	-3.147759000	1.468680000	H	1.616973000	-2.158585000	-2.069859000	
C	5.028230000	-2.705126000	-1.564308000	H	2.295305000	-3.231714000	-0.846074000	
C	3.754162000	-1.861153000	-1.783707000	H	-3.579208000	1.019207000	-2.166809000	
C	3.871453000	-1.263893000	-3.203676000	H	-3.652272000	0.965283000	2.167240000	
C	2.500380000	-2.759936000	-1.810770000	H	-2.245528000	-3.168646000	-0.903341000	
C	-3.619488000	0.663841000	-1.142573000	H	-1.611299000	-2.093131000	-2.146630000	
C	-3.660811000	-0.723529000	-0.756575000	H	-2.601936000	-3.508957000	-2.616521000	
C	-3.670200000	-0.741197000	0.707506000	H	-5.108857000	-3.423792000	-2.432769000	
C	-3.650437000	0.636200000	1.133802000	H	-5.908721000	-2.064893000	-1.596792000	
C	-3.608230000	1.508126000	0.004554000	H	-4.980334000	-3.260288000	-0.670951000	
C	-3.746046000	-1.830664000	-1.818428000	H	-3.954836000	-2.013493000	-3.971205000	
C	-2.478690000	-2.708890000	-1.867409000	H	-2.999890000	-0.597540000	-3.480031000	
C	-5.007176000	-2.696846000	-1.610539000	H	-4.778154000	-0.578309000	-3.311013000	
C	-3.879211000	-1.207040000	-3.225539000	H	-2.081287000	-3.030470000	1.232451000	
C	-3.837503000	-1.848910000	1.755829000	H	-3.586927000	-3.667788000	0.526167000	
C	-3.156653000	-3.183173000	1.409022000	H	-3.270955000	-3.880934000	2.253993000	
C	-5.349309000	-2.086835000	1.985823000	H	-5.848595000	-2.425164000	1.067752000	
C	-3.219346000	-1.400016000	3.099183000	H	-5.837154000	-1.155307000	2.310626000	
C	-3.642614000	3.024531000	0.003858000	H	-5.507825000	-2.850164000	2.765584000	
C	-3.187851000	3.582602000	1.362178000	H	-3.287010000	-2.223527000	3.826921000	
C	-2.718058000	3.579734000	-1.094794000	H	-3.743492000	-0.536488000	3.531254000	
C	-5.093288000	3.484700000	-0.269597000	H	-2.159676000	-1.133999000	2.968530000	
H	3.567001000	0.978711000	-2.191605000	H	-3.851438000	3.252783000	2.175710000	
H	3.654619000	1.019920000	2.142029000	H	-3.199956000	4.683729000	1.343242000	
H	5.757716000	3.127407000	0.434374000	H	-2.165331000	3.247411000	1.593385000	
H	5.135405000	4.596003000	-0.369206000	H	-1.682210000	3.251654000	-0.921361000	
H	5.425358000	3.109982000	-1.315021000	H	-2.749314000	4.681136000	-1.103641000	
H	2.142660000	3.276496000	1.514665000	H	-3.021209000	3.223687000	-2.090574000	
H	3.168684000	4.714662000	1.238847000	H	-5.440755000	3.117281000	-1.247198000	
H	3.826908000	3.304535000	2.101331000	H	-5.162875000	4.585207000	-0.269968000	
H	3.008767000	3.180581000	-2.165441000	H	-5.775965000	3.095689000	0.501606000	
H	2.723093000	4.656693000	-1.210755000					

Table S20: Optimized geometries of **26** (left) and **27** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.





P	-0.030728000	0.304248000	-1.404969000	H	-3.607903000	4.791523000	0.020833000		As	0.030293000	-0.143947000	-1.531031000	H	3.704208000	-4.679814000	0.099602000			
P	0.000884000	2.047341000	-0.031010000	C	-5.323923000	2.932359000	1.139849000		As	-0.000968000	-2.065628000	-0.013590000	C	5.380436000	-2.767241000	1.192531000			
P	0.032283000	0.353151000	1.398869000	H	-5.629972000	2.264974000	1.959716000		As	-0.030868000	-0.164080000	1.527958000	H	5.669483000	-2.082889000	2.004490000			
Co	-1.685261000	0.402607000	0.024912000	H	-5.917340000	2.673005000	0.249761000		Co	1.734811000	-0.282317000	0.026754000	H	5.969996000	-2.506001000	0.300519000			
Co	1.686127000	0.399528000	-0.034371000	H	-5.567276000	3.968044000	1.428047000		Co	-1.735204000	-0.280847000	-0.030531000	H	5.645545000	-3.793584000	1.494537000			
C	-3.106305000	-0.959604000	0.590155000	C	-3.015329000	3.157793000	2.114972000		C	3.143886000	1.083202000	0.582062000	C	3.078831000	-3.029953000	2.168491000			
C	-3.267568000	-0.601351000	-0.833103000	H	-3.205679000	4.207014000	2.390953000		C	3.317802000	0.704688000	-0.834955000	H	3.306243000	-4.065558000	2.467079000			
C	-3.548785000	0.810534000	-0.867657000	H	-1.937268000	3.024349000	1.940271000		C	3.589123000	-0.710496000	-0.848606000	H	1.996596000	-2.939887000	1.991913000			
H	-3.694599000	1.392752000	-1.770727000	H	-3.301400000	2.527694000	2.970247000		H	3.742042000	-1.304653000	-1.742769000	H	3.340578000	-2.371662000	3.010209000			
C	-3.541456000	1.349703000	0.453945000	C	3.370380000	-1.418360000	2.133610000		C	3.572323000	-1.231986000	0.480406000	C	-3.460404000	1.511719000	2.137961000			
C	-3.309186000	0.261127000	1.336627000	C	4.836061000	-1.890275000	2.287226000		C	3.334364000	-0.130067000	1.346445000	C	-4.932151000	1.976102000	2.255920000			
H	-3.209987000	0.351840000	2.412042000	H	5.141825000	-2.552338000	1.466610000		H	3.231838000	-0.205104000	2.423068000	H	-5.221358000	2.639345000	1.430732000			
C	3.259181000	-0.603397000	0.837460000	H	4.964431000	-2.436649000	3.235971000		C	-3.311777000	0.708074000	0.838728000	H	-5.086737000	2.517809000	3.203377000			
C	3.108926000	-0.964160000	-0.586576000	H	5.515674000	-1.024645000	2.293369000		C	-3.143460000	1.087625000	-0.578777000	H	-5.606800000	1.106710000	2.242232000			
C	3.320801000	0.253996000	-1.334503000	C	3.040592000	-0.524316000	3.350977000		C	-3.340708000	-0.124205000	-1.343752000	C	-3.164699000	0.613159000	3.360016000			
H	3.231089000	0.342022000	-2.411035000	H	3.761004000	0.296708000	3.471182000		H	-3.243907000	-0.197990000	-2.421014000	H	-3.881551000	-0.214814000	3.450417000			
C	3.546543000	1.344326000	-0.451540000	H	3.078673000	-1.132106000	4.268472000		C	-3.576978000	-1.226545000	-0.477503000	H	-3.239960000	1.215582000	4.278717000			
C	3.542948000	0.808268000	0.870741000	H	2.031331000	-0.095331000	3.254348000		C	-3.586331000	-0.706540000	0.851971000	H	-2.149506000	0.192141000	3.299927000			
H	3.681297000	1.392677000	1.773516000	C	2.425596000	-2.624190000	2.227757000		H	-3.736124000	-1.301389000	1.746166000	C	-2.522357000	2.720302000	2.260005000			
C	-2.901714000	-2.299561000	1.313623000	H	1.383725000	-2.299703000	2.091662000		C	2.946770000	2.435152000	1.287116000	H	-1.478580000	2.398806000	2.128313000			
C	-1.540038000	-2.957091000	1.014273000	H	2.516734000	-3.082824000	3.224966000		C	1.600510000	3.114983000	0.964564000	H	-2.624700000	3.166498000	3.261696000			
H	-1.354243000	-3.089381000	-0.053831000	H	2.650908000	-3.401129000	1.488899000		H	1.412788000	3.206918000	-0.107415000	H	-2.742160000	3.504922000	1.527617000			
H	-1.483080000	-3.943279000	1.504341000	C	2.904162000	-2.305509000	-1.306710000		H	1.572563000	4.121812000	1.413445000	C	-2.945491000	2.440233000	-1.282094000			
H	-0.732017000	-2.321136000	1.401340000	C	4.050138000	-3.281208000	-0.961984000		H	0.775853000	2.519847000	1.381599000	C	-4.110344000	3.396070000	-0.943309000			
C	-4.052124000	-3.272896000	0.977360000	H	5.028180000	-2.814154000	-1.154821000		C	4.114991000	3.388801000	0.954022000	H	-5.079491000	2.912068000	-1.138901000			
H	-5.027698000	-2.804163000	1.178478000	H	3.973964000	-4.188319000	-1.582582000		H	5.082225000	2.903233000	1.155245000	H	-4.047168000	4.303572000	-1.564760000			
H	-3.972710000	-4.180642000	1.596643000	H	4.026379000	-3.594240000	0.088585000		H	4.050089000	4.296798000	1.574587000	H	-4.095007000	3.711464000	0.106695000			
H	-4.037567000	-3.585043000	-0.073628000	C	1.539450000	-2.957482000	-1.009124000		H	4.106014000	3.703493000	-0.096254000	C	-1.596726000	3.116446000	-0.961766000			
C	-2.933400000	-2.079010000	2.841012000	H	1.343264000	-3.069629000	0.059121000		C	2.957374000	2.233294000	2.817351000	H	-1.401299000	3.195491000	0.109719000			
H	-2.130537000	-1.395907000	3.155654000	H	1.486832000	-3.952495000	-1.481725000		H	2.145772000	1.559154000	3.129691000	H	-1.571838000	4.128445000	-1.399142000			
H	-2.778236000	-3.043346000	3.348833000	H	0.735220000	-2.329178000	-1.416034000		H	2.801477000	3.204826000	3.311127000	H	-0.774800000	2.526814000	-1.391860000			
H	-3.897389000	-1.668572000	3.176931000	C	2.942989000	-2.090270000	-2.834628000		H	3.914209000	1.821211000	3.171275000	C	-2.961271000	2.241219000	-2.812562000			
C	-3.385226000	-1.418791000	-2.127057000	H	2.144746000	-1.404356000	-3.154867000		C	3.472337000	1.509451000	-2.132732000	H	-2.153119000	1.564449000	-3.128092000			
C	-2.445605000	-2.628791000	-2.220171000	H	2.785254000	-3.055557000	-3.339903000		C	2.538666000	2.721380000	-2.255380000	H	-2.802911000	3.213000000	-3.305102000			
H	-1.402316000	-2.309026000	-2.084238000	H	3.910393000	-1.685717000	-3.168026000		H	1.493531000	2.403598000	-2.125763000	H	-3.920715000	1.833533000	-3.164590000			
H	-2.538851000	-3.087881000	-3.216977000	C	3.821355000	2.782275000	-0.846701000		H	2.644397000	3.168097000	-3.256494000	C	-3.876249000	-2.653415000	-0.894796000			
H	-2.674699000	-3.404090000	-1.480731000	C	5.335787000	2.924838000	-1.124360000		H	2.760199000	3.504601000	-1.521996000	C	-5.392763000	-2.755911000	-1.182306000			
C	-3.053759000	-0.528117000	-3.346460000	H	5.922342000	2.663871000	-0.230229000		C	3.176210000	0.613134000	-3.356310000	H	-5.977919000	-2.492001000	-0.288196000			
H	-3.770708000	0.295948000	-3.466468000	H	5.582397000	3.960520000	-1.409725000		H	3.890649000	-0.216963000	-3.446230000	H	-5.662548000	-3.781540000	-1.482576000			
H	-3.095841000	-1.136860000	-4.263150000	H	5.646883000	2.257959000	-1.942726000		H	3.254863000	1.216174000	-4.274320000	H	-5.682586000	-2.071144000	-1.993640000			
H	-2.042318000	-0.103841000	-3.251330000	C	3.424486000	3.743970000	0.286270000		H	2.159614000	0.195269000	-3.298192000	C	-3.510766000	-3.640847000	0.226351000			
C	-4.852896000	-1.885636000	-2.276486000	H	2.356903000	3.633694000	0.528176000		C	4.945810000	1.969308000	-2.246560000	H	-2.443611000	-3.557593000	0.480986000			
H	-5.159391000	-2.543938000	-1.453008000	H	3.610680000	4.785955000	-0.018109000		H	5.235133000	2.630216000	-1.419472000	H	-3.715858000	-4.673858000	-0.095871000			
H	-4.985096000	-2.434700000	-3.223164000	H	4.006824000	3.551915000	1.199780000		H	5.104315000	2.512228000	-3.192676000	H	-4.097099000	-3.450481000	1.137680000			
H	-5.529440000	-1.017620000	-2.284142000	C	3.034843000	3.154517000	-2.116009000		H	5.617734000	1.097818000	-2.232834000	C	-3.096198000	-3.027634000	-2.167076000			
C	-3.811727000	2.787902000	0.851049000	H	3.321878000	2.521051000	-2.968434000		C	3.865429000	-2.659706000	0.899894000	H	-3.354564000	-2.365757000	-3.006996000			
C	-3.421822000	3.749678000	-0.284140000	H	3.233202000	4.202117000	-2.392564000		C	3.501408000	-3.646514000	-0.223153000	H	-3.332837000	-4.060850000	-2.466787000			
H	-4.008405000	3.556441000	-1.194695000	H	1.955073000	3.028581000	-1.946672000		H	4.090511000	-3.456889000	-1.132869000	H	-2.012871000	-2.947288000	-1.992912000			
H	-2.355324000	3.640752000	-0.531345000						H	2.435099000	-3.561896000	-0.480812000							

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