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Teaching Old Tricks to New Dogs – Rational Synthesis of Multi-Decker Complexes Bearing *cyclo*-P_5 Decks

Christoph Riesinger, David Röhner, Ingo Krossing, Manfred Scheer*

Supporting Information

Author Contributions

Christoph Riesinger – performing experimental work, writing of original draft.

David Röhner – performing experimental work (synthesis of **2-Co**).

Ingo Krossing – project administration, funding acquisition, co-writing final manuscript.

Manfred Scheer – project administration, funding acquisition, co-writing final manuscript.

All authors contributed in preparing the manuscript.

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Synthesis and Analytical Data

1.1. General Considerations

All manipulations were carried out using standard Schlenk techniques at a Stock apparatus under N_2 as an inert gas or in a glove box with Ar atmosphere. All glassware was dried with a heat gun (600 °C) for at least 30 min prior to use. *o*-DFB (1,2-difluorobenzene) was distilled from P_2O_5, CD_2Cl_2 was distilled from CaH_2 and other solvents were directly taken from an MBraun SPS-800 solvent purification system and degassed at room temperature. Solution ^{1}H (400.130 MHz), ^{11}B (128.432 MHz), ^{19}F (376.498 MHz)a and ^{31}P (161.976 MHz) NMR spectra were recorded at an Avance400 (Bruker) spectrometer using $(H_3C)_4Si$ (^{1}H, ^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B) $CFCl_3$ (^{19}F) or 85% phosphoric acid (^{31}P), respectively, as external standards. Chemical shifts (δ) are provided in parts per million (ppm) and coupling constants (*J*) are reported in Hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, t = triplet, td = triplet of doublets br = broad and m = multiplet. Mass spectra were recorded at the internal mass spectrometry department using a ThermoQuest Finnigan TSQ 7000 (ESI) or Finnigan MAT 95 (LIFDI) mass spectrometer or by the first author on a Waters Micromass LCT ESI-TOF mass-spectrometer and peak assignment was performed using the Molecular weight calculator 6.50. Elemental analysis of the products was conducted by the elemental analysis department at the University of Regensburg using an Elementar Vario EL. The starting materials [Cp*Fe(η^5-P_5)],[1] [Cp*Fe(η^5-As_5)],[2] [Cp‴M(μ-X)]$_2$ (M = Cr,[3] Mn,[4] Fe,[5] Co,[6] Ni,[7] X = Cl, Br), K[BAr^F],[8] Tl[*pf*][9] and [Co(*o*-dfb)$_2$][*pf*][10] were synthesized according to literature procedures. All other chemicals were purchased from commercial vendors and used without further purification.

1.2. 1-Cr

A dark blue solution of [Cp‴Cr(μ-Cl)]$_2$ (64 mg, 0.1 mmol, 1 eq.) in 6 mL of *o*-DFB was added to a dark green solution of [Cp*Fe(η^5-P_5)] (70 mg, 0.2 mmol, 2 eq.) and K[BAr^F] (144 mg, 0.2 mmol, 2 eq.) in 6 mL of *o*-DFB. A rapid colour change to red and formation of a colourless solid was observed and the reaction was completed by stirring the solution at room temperature for 1 h. Afterwards the solution was filtered, constricted to 3 mL and layered with 15 mL of *n*-hexane. Storage of this mixture at room temperature for 4 days yielded dark red plate shaped crystals of [Cp*Fe(μ;$\eta^{5:5}$-P_5)CrCp‴][BAr^F] (**1-Cr**), which were isolated by decanting the solvent and drying under reduced pressure (10^{-3} mbar).

Yield:	140 mg (0.12 mmol, 60%)
Elemental Analysis:	calculated (%) for [Cp*Fe(μ;$\eta^{5:5}$-P_5)CrCp‴][BAr^F]: C: 46.72 H: 3.38, found: C: 47.17 H: 3.24
ESI(+)-MS (*o*-DFB):	m/z (%) = 631.3 (100, [**1-Cr**]$^+$)
^{1}H-NMR (CD_2Cl_2, 300 K):	δ/ ppm = 1.10 (s, 9 H, ^{t}Bu$_3$C$_5$H$_2$), 1.26 (s, 18 H, ^{t}Bu$_3$C$_5$H$_2$), 1.53 (s, 15 H, Cp*), 4.41 (s, 2 H, ^{t}Bu$_3$C$_5$H$_2$)
$^{31}P\{^{1}H\}$-NMR (CD_2Cl_2, 300 K):	δ/ ppm = 14.2 ppm (s, *cyclo*-P_5)
^{31}P-NMR (CD_2Cl_2, 300 K):	δ/ ppm = 14.2 ppm (s, *cyclo*-P_5)
$^{19}F\{^{1}H\}$-NMR (CD_2Cl_2, 300 K):	δ/ ppm = - 167.3 (br, 8 F, [BAr^F]$^-$), - 163.4 (br, 4 F, [BAr^F]$^-$), - 133.0 (br, 8 F, [BAr^F]$^-$)
$^{11}B\{^{1}H\}$-NMR (CD_2Cl_2, 300 K):	δ/ ppm = - 16.9 ppm (s, [BAr^F]$^-$)

1.3. 1-Mn

[Cp‴Mn(thf)(μ-Cl)]$_2$ (79 mg, 0.1 mmol, 1 eq.), [Cp*Fe(η^5-P$_5$)] (70 mg, 0.2 mmol, 2 eq.) and Tl[*pf*] (234 mg, 0.2 mmol, 2 eq.) were suspended in 4 mL of *o*-DFB to afford a clear green solution and formation of a colourless precipitate. The solution was stirred for 17 h and the solvent was removed under reduced pressure (10^{-3} mbar). 3 mL of CH_2Cl_2 were added to the mixture and the solution was then filtered. The now green solution was layered with 20 mL of *n*-hexane. Storage of this mixture for 2 weeks yielded dark green block shaped crystals of [Cp*Fe(μ;$\eta^{5:5}$-P$_5$)MnCp‴][*pf*] (**1-Mn**). As the formation of a polymeric coordination compound of [Cp*Fe(η^5-P$_5$)] and Tl[*pf*] during this reaction cannot be suppressed, the product has to be isolated by mechanical separation of the crystals of **1-Mn**, which results in decreased yields.

Yield:	65 mg (0.04 mmol, 20%)
Elemental Analysis:	calculated (%) for [Cp*Fe(μ;$\eta^{5:5}$-P$_5$)MnCp‴][*pf*]: C: 32.25 H: 2.77, found: C: 32.21 H: 2.97
ESI(+)-MS (*o*-DFB):	m/z (%) = 634.0 (100, [**1-Mn**]$^+$)
^{1}H-NMR (CD_2Cl_2, 300 K):	δ/ ppm = broad signal between 1 – 3 ppm
^{31}P{^{1}H}-NMR (CD_2Cl_2, 300 K):	δ/ ppm = no signal observed between +/-500 ppm
^{19}F{^{1}H}-NMR (CD_2Cl_2, 300 K):	δ/ ppm = - 75.7 (s, [*pf*]$^-$)

1.4. 1-Fe

[Cp‴Fe(μ-Br)]$_2$ (74 mg, 0.1 mmol, 1 eq.), [Cp*Fe(η^5-P$_5$)] (70 mg, 0.2 mmol, 2 eq.) and Tl[BAr^F] (277 mg, 0.2 mmol, 2 eq.) were suspended in 4 mL of *o*-DFB to afford a rapid colour change to greenish blue and formation of a colourless solid. The reaction was completed by stirring the solution at room temperature for 2 h and then the solvent was constrained to 2 mL. Afterwards the solution was filtered, the solvent removed, the residue dissolved in 3 mL of CH_2Cl_2 and layered with 30 mL of *n*-hexane. Storage of this mixture for 7 days yielded dark brownish blue block shaped crystals of [Cp*Fe(μ;$\eta^{5:5}$-P$_5$)FeCp‴][BAr^F] (**1-Fe**), which were isolated by decanting the solvent and drying under reduced pressure (10^{-3} mbar).

Yield:	185 mg (0.14 mmol, 70%)
Elemental Analysis:	calculated (%) for [Cp*Fe(μ;$\eta^{5:5}$-P$_5$)FeCp‴][BAr^F]: C: 46.61 H: 3.37, found: C: 46.27 H: 3.50
ESI(+)-MS (*o*-DFB):	m/z (%) = 635.1 (100, [**1-Fe**]$^+$)
^{1}H-NMR (CD_2Cl_2, 300 K):	δ/ ppm = 1.10 (s, 15 H, Cp*), 1.19 (s, 9 H, ^{t}Bu$_3$C$_5$H$_2$), 1.31 (s, 18 H, ^{t}Bu$_3$C$_5$H$_2$), 3.36 (s, 2 H, ^{t}Bu$_3$C$_5$H$_2$)
^{31}P{^{1}H}-NMR (CD_2Cl_2, 300 K):	δ/ ppm = - 12.5 ppm (s, *cyclo*-P$_5$)
^{31}P-NMR (CD_2Cl_2, 300 K):	δ/ ppm = - 12.5 ppm (s, *cyclo*-P$_5$)
^{19}F{^{1}H}-NMR (CD_2Cl_2, 300 K):	δ/ ppm = - 167.4 (br, 8 F, [BAr^F]$^-$), - 163.6 (br, 4 F, [BAr^F]$^-$), - 132.9 (br, 8 F, [BAr^F]$^-$)
^{11}B{^{1}H}-NMR (CD_2Cl_2, 300 K):	δ/ ppm = - 16.8 (s, [BAr^F]$^-$)

1.5. 1-Co

1-Co has already been prepared on a different route, we reported previously.[11]

[Cp‴Co(μ-Cl)]$_2$ (33 mg, 0.05 mmol, 1 eq.), [Cp*Fe(η^5-P$_5$)] (35 mg, 0.1 mmol, 2 eq.) and Tl[*pf*] (134 mg, 0.1 mmol, 2 eq.) were suspended in 4 mL of *o*-DFB to afford arapid colour change to dark olive green and formation of a colourless solid. The reaction was completed by stirring the solution at room temperature for 4 h. The solution was filtered and 40 mL of *n*-hexane were added to precipitate [Cp*Fe(μ;$\eta^{5:5}$-P$_5$)CoCp‴][*pf*] (**1-Co**) as an olive green powder, which could be isolated in 53% yield (85 mg, 0.085 mmol). Spectroscopic data of this product matches that reported earlier.

1.6. 1-Ni

[Cp‴Ni(μ-Br)]$_2$ (74 mg, 0.1 mmol, 1 eq.), [Cp*Fe(η^5-P$_5$)] (70 mg, 0.2 mmol, 2 eq.) and K[BAr^F] (144 mg, 0.2 mmol, 2 eq.) were suspended in 6 mL of *o*-DFB to afford a rapid colour change to brown and formation of a colourless solid. The reaction was completed by stirring the solution at 90 °C for 4 h. Afterwards the solution was filtered, the solvent removed, and the residue washed two times with 15 mL of *n*-hexane, each. The residue was dissolved in 2 mL of *o*-DFB and layered with 10 mL of *n*-hexane. Storage of this mixture at room temperature for 4 days yielded dark brownish block shaped crystals of [Cp*Fe(μ;$\eta^{5:5}$-P$_5$)NiCp‴][BAr^F] (**1-Ni**), which were isolated by decanting the solvent and drying under reduced pressure (10^{-3} mbar).

Yield:	108 mg (0.1 mmol, 50%)
Elemental Analysis:	calculated (%) for [Cp*Fe(μ;$\eta^{5:5}$-P$_5$)NiCp‴][BAr^F]: C: 46.50 H: 3.37, found: C: 46.62 H: 3.26
ESI(+)-MS (*o*-DFB):	m/z (%) = 637.1 (70, [**1-Ni**]$^+$), 332.2 (100, [**A**]$^+$)
^{1}H-NMR (CD_2Cl_2, 300 K):	δ/ ppm = 15.83 (br, 9 H, ^{t}Bu$_3$C$_5$H$_2$), 12.19 (br, 18 H, ^{t}Bu$_3$C$_5$H$_2$), 9.21 (br, 15 H, Cp*), signals for the ^{t}Bu$_3$C$_5$H$_2$ could not be found within the ^{1}H NMR spectrum of **1-Ni**
^{31}P{^{1}H}-NMR (CD_2Cl_2, 300 K):	δ/ ppm = no signals observed within +/- 500 ppm
^{31}P-NMR (CD_2Cl_2, 300 K):	δ/ ppm = no signals observed within +/- 500 ppm
^{19}F{^{1}H}-NMR (CD_2Cl_2, 300 K):	δ/ ppm = - 166.3 (br, 8 F, [BAr^F]$^-$), - 162.7 (br, 4 F, [BAr^F]$^-$), - 132.3 (br, 8 F, [BAr^F]$^-$)
^{11}B{^{1}H}-NMR (CD_2Cl_2, 300 K):	δ/ ppm = - 16.8 (s, [BAr^F]$^-$)

1.7. 2-Fe

$[Fe(tol)_2][pf]_2$ (217 mg, 0.1 mmol, 1 eq.) and $[Cp^*Fe(\eta^5\text{-}P_5)]$ (70 mg, 0.2 mmol, 2 eq.) were dissolved in 3 mL of *o*-DFB affording a dark green solution, which was stirred for 10 min. Afterwards the solution was layered with 20 mL of *n*-hexane and stored at 4 °C for three days, yielding dark green plate shaped crystals of $[\{Cp^*Fe(\eta^5\text{-}P_5)\}_2Fe][pf]_2$ (**2-Fe**).

As crystal quality of **2-Fe** could not be improved to a level suitable for single crystal X-ray diffractometry, its´ $[BAr^F]^-$ salt was prepared by sonication of $[Cp^*Fe(\eta^5\text{-}P_5)]$, $K[BAr^F]$ and $FeBr_2$•dme in *o*-DFB and crystallized from a CH_2Cl_2/*n*-hexane layering (3mL/20mL). Notably, the turnover and yield of **2-Fe** in this reaction is drastically decreased compared to the procedure using $[Fe(tol)_2][pf]_2$. Spectroscopic data for both compounds matches.

Yield:	240 mg (0.09 mmol, 90%)
Elemental Analysis:	calculated (%) for $[\{Cp^*Fe(\eta^5\text{-}P_5)\}_2Fe][pf]_2$•$(C_6H_4F_2)_{0.7}$: C: 24.42 H: 1.20, found: C: 24.46 H: 1.30
ESI(+)-MS (*o*-DFB):	m/z (%) = 373.8 (100, $[\mathbf{2\text{-}Fe}]^{2+}$), 747.7 (20, $[\{Cp^*Fe(\eta^5\text{-}P_5)\}_2Fe]^+$)
^{1}H-NMR (CD_2Cl_2, 300 K):	δ/ ppm = 0.70 (s, Cp*)
$^{31}P\{^1H\}$-NMR (CD_2Cl_2, 300 K):	δ/ ppm = 12.9 (s, *cyclo*-P_5)
^{31}P-NMR (CD_2Cl_2, 300 K):	δ/ ppm = 12.9 (s, *cyclo*-P_5)
$^{19}F\{^1H\}$-NMR (CD_2Cl_2, 300 K):	δ/ ppm = - 75.4 (s, $[pf]^-$)

1.8. 2-Co

$[Co(dfb)_2][pf]$ (125 mg, 0.1 mmol, 1 eq.) dissolved in 2 mL of *o*-DFB was slowly added to $[Cp^*Fe(\eta^5\text{-}P_5)]$ (70 mg, 0.2 mmol, 2 eq.) dissolved in 2 mL of *o*-DFB at -30 °C. A rapid colour change to dark green was observed, the solution stirred for 1 h at room temperature and then constrained to 1 mL. 30 mL of *n*-hexane were added to precipitate a dark green powder, which was dried under reduced pressure (10^{-3} mbar). 3 mL of *o*-DFB were added, and the solution was layered with 30 mL of *n*-hexane. Storage at room temperature for two days yielded dark green plate shaped crystals of $[\{Cp^*Fe(\eta^5\text{-}P_5)\}_2Co][pf]$ (**2-Co**).

Yield:	154 mg (0.09 mmol, 90%)
Elemental Analysis:	calculated (%) for $[\{Cp^*Fe(\eta^5\text{-}P_5)\}_2Fe][pf]_2$•$(C_6H_4F_2)$: C: 27.54 H: 1.87, found: C: 27.59 H: 1.98
ESI(+)-MS (*o*-DFB):	m/z (%) = 750.8 (100, $[\mathbf{2\text{-}Co}]^+$)
^{1}H-NMR (*o*-DFB/C_6D_6, 300 K):	δ/ ppm = 11.81 (br, Cp*)
$^{31}P\{^1H\}$-NMR (*o*-DFB/C_6D_6, 300 K):	δ/ ppm = no signals observed within +/- 500 ppm
^{31}P-NMR (*o*-DFB/C_6D_6, 300 K):	δ/ ppm = no signals observed within +/- 500 ppm
$^{19}F\{^1H\}$-NMR (*o*-DFB/C_6D_6, 300 K):	δ/ ppm = - 74.1 (s, $[pf]^-$)

1.9.3

$[Fe(tol)_2][pf]_2$ (24 mg, 0.01 mmol, 1 eq.) and $[Cp^*Fe(\eta^5\text{-}As_5)]$ (11 mg, 0.02 mmol, 2 eq.) were dissolved in 3 mL of *o*-DFB affording a dark brown solution, which was stirred for 2 h. Afterwards the solution was layered with 50 mL of *n*-hexane and stored at room temperature for three days, yielding dark brownish green plate shaped crystals of $[\{Cp^*Fe(\eta^5\text{-}As_5)\}_2Fe][TEF]_2$ (**3**).

Yield:	30 mg (0.0096 mmol, 96%)
Elemental Analysis:	calculated (%) for $[\{Cp^*Fe(\eta^5\text{-}As_5)\}_2Fe][pf]_2 \bullet (C_6H_4F_2)$: C: 21.51 H: 1.06, found: C: 21.30 H: 1.24
ESI(+)-MS (*o*-DFB):	m/z (%) = 593.6 (100, $[\mathbf{2\text{-}Fe}]^{2+}$), 1187.2 (20, $[\{Cp^*Fe(\eta^5\text{-}As_5)\}_2Fe]^+$)
^{1}H-NMR (*o*-DFB/C_6D_6, 300 K):	δ/ ppm = 0.36 (s, Cp*)
$^{19}F\{^1H\}$-NMR (*o*-DFB/C_6D_6, 300 K):	δ/ ppm = - 75.4 (s, $[pf]^-$)

1.10. $[Fe(tol)_2][pf]_2$

$Fe(CO)_5$ in 1.3 mL of toluene (1.96 mmol, 384 mg, 1 eq.) was added to a purple suspension of $[Ag(CH_2Cl_2)_2][pf]$ (3.92 mmol, 4.88 g, 2 eq.) and I_2 (497 mg, 1.96 mmol, 1 eq.) in 20 mL of *o*-DFB, which resulted in a rapid colour change to dark red and precipitation of colourless solid. Stirring at 90 °C for 16 hours completed the reaction, after which an orange solution with colourless precipitate was obtained. Filtration and precipitation with *n*-hexane afforded $[Fe(tol)_2][pf]_2$ as analytically pure compound. Crystals suitable for X-ray diffraction studies could be obtained by layering a concentrated solution in *o*-DFB with *n*-hexane and storage at room temperature for two days.

Yield:	3.45 g (1.6 mmol, 82%)
Elemental Analysis:	calculated (%) for $[Fe(tol)_2][pf]_2$: C: 25.39 H: 0.76, found: C: 25.77 H: 0.93
ESI(+)-MS (*o*-DFB):	m/z (%) = 239.0 (10, $[Fe(tol)_2]\text{-}H^+$), 240.1 (10, $[\mathbf{Fe(tol)_2}]^+$)
^{1}H-NMR (*o*-DFB/C_6D_6, 300 K):	δ/ ppm = 7.49 (m, 3 H, Ph<u>Me</u>), 7.41 (m, 2 H, <u>Ph</u>Me), 3.21 (s, 3 H, Ph<u>Me</u>)
$^{19}F\{^1H\}$-NMR (*o*-DFB/C_6D_6, 300 K):	δ/ ppm = -75.5 (s, $[pf]^-$)

2. Crystallographic Data

2.1. General Consideration

The crystallographic data for all described compounds were collected on a GV50 diffractometer (Rigaku) with a Titan^{S2} detector using Cu–K$_\alpha$ radiation (**1-Cr**, **1-Mn**, **1-Ni, 2-Co**) or an XtaLAB Synergy R, DW System with a HyPix-Arc 150 detector using Cu-K$_\alpha$ radiation from a rotating anode (**1-Fe**, **2-Fe**[BAr^F], **3)**. Data reduction and absorption correction were performed with the CrysAlisPro software package.[12] Structure solution and refinement was conducted in Olex2 (1.5-alpha)[13] with ShelXT[14] (solution) and ShelXL-2018/3[15] (least squares refinement (F^2)). All non-H atoms were refined with anisotropic displacement parameters and H atoms were treated as riding models with isotropic displacement parameters and fixed C–H bond lengths (sp^3: 0.96 (CH_3), 0.97 (CH_2); sp^2: 0.93 (CH)). Visualisation of the crystal structures was performed with Olex2 (1.5-alpha).[13]

CIF files with comprehensive information on the details of the diffraction experiments and full tables of bond lengths and angles for **1-Cr**, **1-Mn**, **1-Fe**, **1-Ni**, **2-Fe**, **2-Co**, **3 and [Fe(tol)$_2$][*pf*]$_2$** are deposited in Cambridge Crystallographic Data Centre under the deposition codes CCDC 2242844-2242851.

*Table S 1: Crystallographic and refinement data for compounds **1-Cr** – **1 -Ni, 2-Fe, 2-Co** and **3**.*

Compound	**1-Cr**	**1-Mn**	**1-Fe**	**1-Ni**
CCDC	2242844	2242845	2242846	2242847
Empirical formula	$C_{54}H_{46}BCrF_{21}FeP_5$	$C_{43}H_{44}AlF_{36}FeMnO_4P_5$	$C_{51.5}H_{45}BClF_{20}Fe_2P_5$	$C_{102}H_{88}B_2F_{40}Fe_2Ni_2P_{10}$
Formula weight	1367.42	1601.40	1356.68	2634.16
Temperature/K	122.99(10)	123.00(10)	123.00(10)	122.99(10)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1$
a/Å	15.7984(2)	11.95740(10)	15.6478(3)	15.8271(2)
b/Å	19.8256(2)	21.6035(2)	19.8608(3)	19.95370(10)
c/Å	18.1573(2)	23.2630(2)	18.1588(2)	17.9342(2)
α/°	90	90	90	90
β/°	104.2570(10)	93.7580(10)	104.7420(10)	105.1610(10)
γ/°	90	90	90	90
Volume/Å3	5511.94(11)	5996.42(9)	5457.58(15)	5466.65(10)
Z	4	4	4	2
ρcalcg/cm3	1.648	1.774	1.651	1.600
μ/mm-1	6.102	6.488	7.058	4.886
F(000)	2756.0	3188.0	2732.0	2656.0
Crystal size/mm3	0.38 × 0.22 × 0.04	0.259 × 0.2 × 0.163	0.29 × 0.23 × 0.06	0.293 × 0.248 × 0.219
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.294 to 133.46	7.41 to 133.506	5.84 to 144.244	7.288 to 133.626
Index ranges	-18 ≤ h ≤ 18, -23 ≤ k ≤ 23, -20 ≤ l ≤ 21	-13 ≤ h ≤ 14, -25 ≤ k ≤ 25, -27 ≤ l ≤ 27	-19 ≤ h ≤ 17, -24 ≤ k ≤ 23, -21 ≤ l ≤ 22	-18 ≤ h ≤ 18, -20 ≤ k ≤ 23, -21 ≤ l ≤ 20
Reflections collected	57435	63995	52174	52429
Independent reflections	9708 [Rint = 0.0577, Rsigma = 0.0324]	10585 [Rint = 0.0488, Rsigma = 0.0256]	10344 [Rint = 0.0479, Rsigma = 0.0331]	15560 [Rint = 0.0533, Rsigma = 0.0411]
Data/restraints/parameters	9708/200/906	10585/1041/1179	10344/18/803	15560/0/1449
Goodness-of-fit on F2	1.046	1.019	1.099	1.018
Final R indexes [I>=2σ (I)]	R1 = 0.0384, wR2 = 0.1067	R1 = 0.0370, wR2 = 0.0943	R1 = 0.0446, wR2 = 0.1226	R1 = 0.0363, wR2 = 0.0914
Final R indexes [all data]	R1 = 0.0427, wR2 = 0.1114	R1 = 0.0389, wR2 = 0.0961	R1 = 0.0541, wR2 = 0.1286	R1 = 0.0377, wR2 = 0.0928
Largest diff. peak/hole / e Å-3	0.45/-0.62	0.71/-0.37	0.67/-0.72	0.57/-0.44
Flack parameter	/	/	/	0.488(5)

Compound	**2-Fe**	**2-Co**	**3**	**$[Fe(tol)_2][pf]_2$**
CCDC	2242848	2242849	2242850	2242851
Empirical formula	$C_{69}H_{32}B_2Cl_2F_{40}Fe_3P_{10}$	$C_{39}H_{32}AlCoF_{37}Fe_2O_4P_{10}$	$C_{70}H_{42}Al_2As_{10}F_{78}Fe3O8$	$C_{92}H_{32}Al_4F_{144}Fe_2O_{16}$
Formula weight	2190.71	1774.95	3463.74	4348.79
Temperature/K	123.02(10)	123.00(10)	123.01(10)	123.00(10)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a/Å	19.4743(2)	10.87740(10)	33.7409(2)	15.9325(4)
b/Å	20.2790(2)	28.6587(3)	14.01600(10)	16.1088(4)
c/Å	20.0413(2)	20.0246(2)	22.6687(2)	26.3304(6)
α/°	90	90	90	92.872(2)
β/°	91.7850(10)	96.7550(10)	102.8080(10)	91.023(2)
γ/°	90	90	90	94.758(2)
Volume/Å3	7910.86(14)	6198.98(11)	10453.57(14)	6724.4(3)
Z	4	4	4	2
ρcalcg/cm3	1.839	1.902	2.201	2.148
μ/mm-1	8.166	9.782	8.760	4.454
F(000)	4312.0	3492.0	6648.0	4224.0
Crystal size/mm3	0.22 × 0.14 × 0.03	0.29 × 0.23 × 0.09	0.19 × 0.17 × 0.07	0.251 × 0.166 × 0.112
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.202 to 150.304	7.604 to 133.968	5.372 to 143.816	7.502 to 134.246
Index ranges	-23 ≤ h ≤ 24, -24 ≤ k ≤ 17, -24 ≤ l ≤ 24	-12 ≤ h ≤ 12, -34 ≤ k ≤ 33, -18 ≤ l ≤ 23	-39 ≤ h ≤ 41, -17 ≤ k ≤ 15, -26 ≤ l ≤ 27	-18 ≤ h ≤ 18, -19 ≤ k ≤ 19, -31 ≤ l ≤ 31
Reflections collected	85089	66406	103420	42141
Independent reflections	15714 [Rint = 0.0379, Rsigma = 0.0302]	10977 [Rint = 0.0698, Rsigma = 0.0392]	20045 [Rint = 0.0521, Rsigma = 0.0336]	42141 [Rint = ?, Rsigma = 0.0374]
Data/restraints/parameters	15714/280/1236	10977/1392/1244	20045/1584/2363	42141/2636/2870
Goodness-of-fit on F2	1.044	1.028	1.069	0.997
Final R indexes [I>=2σ (I)]	R1 = 0.0543, wR2 = 0.1477	R1 = 0.0470, wR2 = 0.1154	R1 = 0.0411, wR2 = 0.1087	R1 = 0.0579, wR2 = 0.1540
Final R indexes [all data]	R1 = 0.0708, wR2 = 0.1582	R1 = 0.0570, wR2 = 0.1235	R1 = 0.0534, wR2 = 0.1155	R1 = 0.0795, wR2 = 0.1642
Largest diff. peak/hole / e Å-3	0.91/-0.92	0.93/-0.70	0.99/-0.58	1.52/-0.68
Flack parameter	/	/	/	/

2.2. 1-Cr

Compound **1-Cr** crystallizes in the monoclinic space group $P2_1/c$ forming dark red plates from *o*-DFB/*n*-hexane mixtures at room temperature. The asymmetric unit contains the cation, one anion and one *o*-DFB molecule. All non-hydrogen atoms were refined anisotropically and the H atoms were treated as riding models.

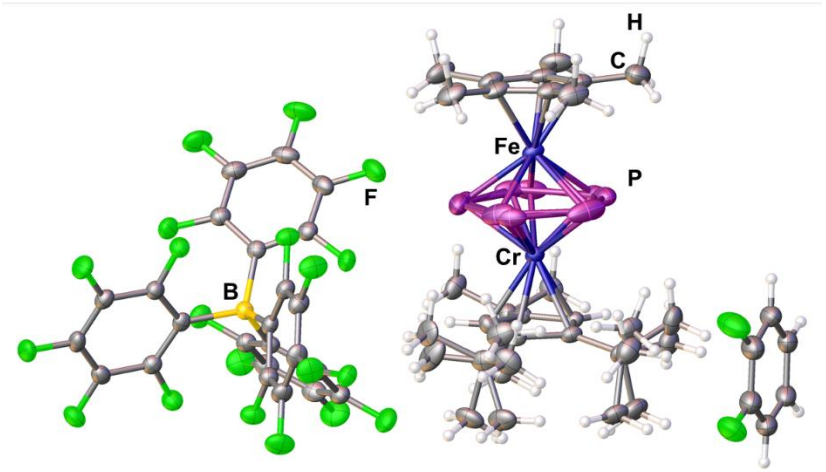


*Figure S 1: Solid state structure of **1-Cr**; Shown is the asymmetric unit containing one cation, one anion as well as one o-DFB molecule; thermal ellipsoids are drawn at the 50% probability level.*

2.3. 1-Mn

Compound **1-Mn** crystallizes in the monoclinic space group $P2_1/c$ forming dark green blocks from CH_2Cl_2/*n*-hexane mixtures at room temperature. The asymmetric unit contains the cation and one anion. All non-hydrogen atoms were refined anisotropically and the H atoms were treated as riding models. Disorder within the anion was treated with appropriate restraints.

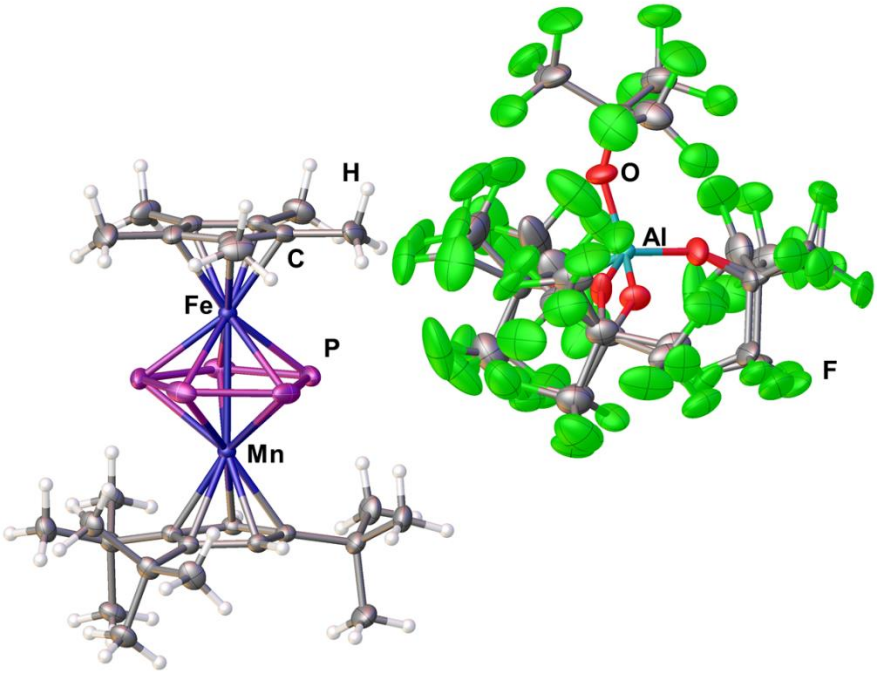


*Figure S 2: Solid state structure of **1-Mn**; Shown is the asymmetric unit containing one cation and one anion; thermal ellipsoids are drawn at the 50% probability level.*

2.4. 1-Fe

Compound **1-Fe** crystallizes in the monoclinic space group $P2_1/c$ forming dark brownish-blue blocks from CH_2Cl_2/*n*-hexane mixtures at room temperature. The asymmetric unit contains the cation and one anion. All non-hydrogen atoms were refined anisotropically and the H atoms were treated as riding models. Disorder within on ^{t}Bu group was treated with appropriate restraints.

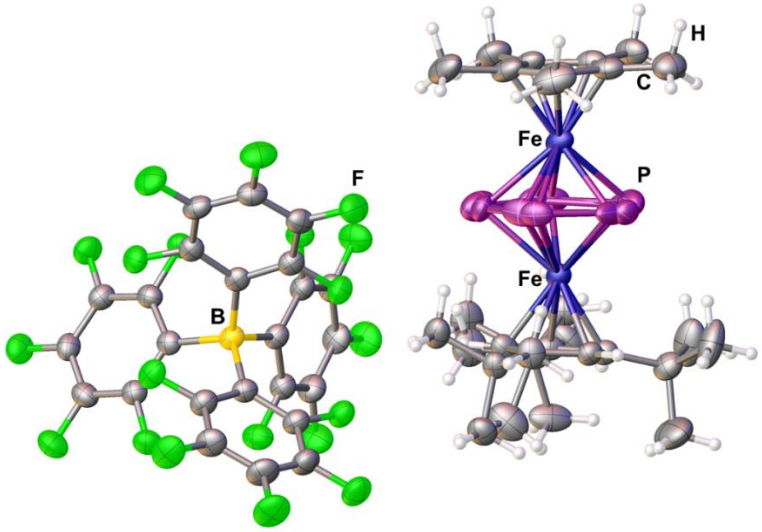


*Figure S 3: Solid state structure of **1-Fe**; Shown is the asymmetric unit containing one cation and one anion; thermal ellipsoids are drawn at the 50% probability level.*

2.5. 1-Ni

Compound **1-Ni** crystallizes in the monoclinic space group $P2_1$ forming dark brown blocks from *o*-DFB/*n*-hexane mixtures at room temperature. The asymmetric unit contains two distinct cations and two anions. All non-hydrogen atoms were refined anisotropically and the H atoms were treated as riding models.

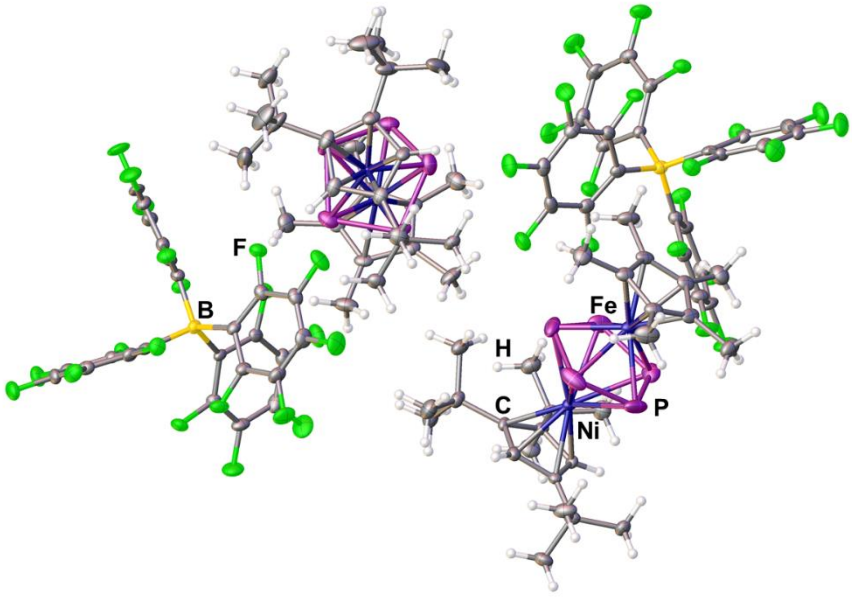


*Figure S 4: Solid state structure of **1-Ni**; Shown is the asymmetric unit containing two distinct cations and two anions; thermal ellipsoids are drawn at the 50% probability level.*

2.6. 2-Fe

Compound **2-Fe** crystallizes in the monoclinic space group $P2_1/c$ forming dark green plates from CH_2Cl_2/*n*-hexane mixtures at room temperature. The asymmetric unit contains one cation and two anions, as well 0.9 CH_2Cl_2 molecules. All non-hydrogen atoms were refined anisotropically and the H atoms were treated as riding models. Disorder within the *cyclo*-P_5 ligands was treated with appropriate restraints.

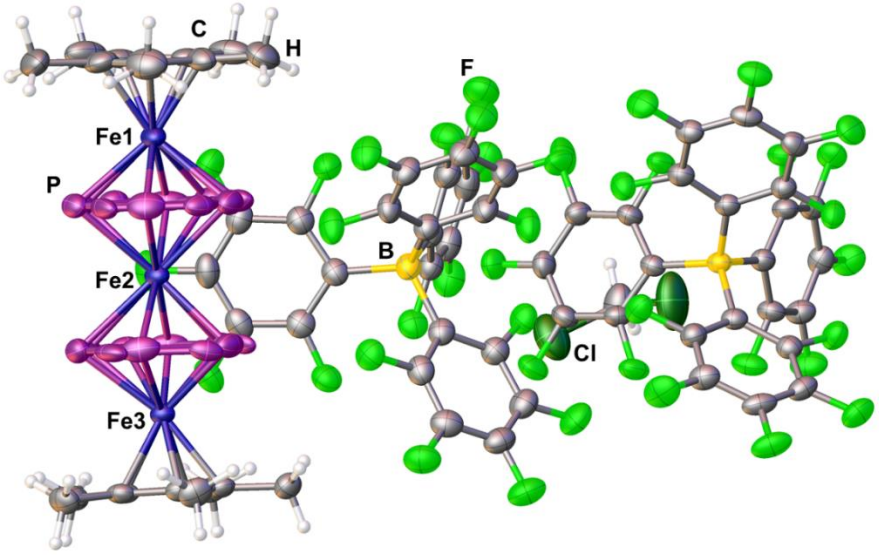


*Figure S 5: Solid state structure of **2-Fe**; Shown is the asymmetric unit containing one dication, two anions as well as one CH_2Cl_2 molecule; thermal ellipsoids are drawn at the 50% probability level.*

2.7. 2-Co

Compound **2-Co** crystallizes in the monoclinic space group $P2_1/c$ forming dark green plates from *o*-DFB/*n*-hexane mixtures at room temperature. The asymmetric unit contains one cation and one anion and an *o*-DFB molecule. All non-hydrogen atoms were refined anisotropically and the H atoms were treated as riding models. Disorder within the anion was treated with appropriate restraints.

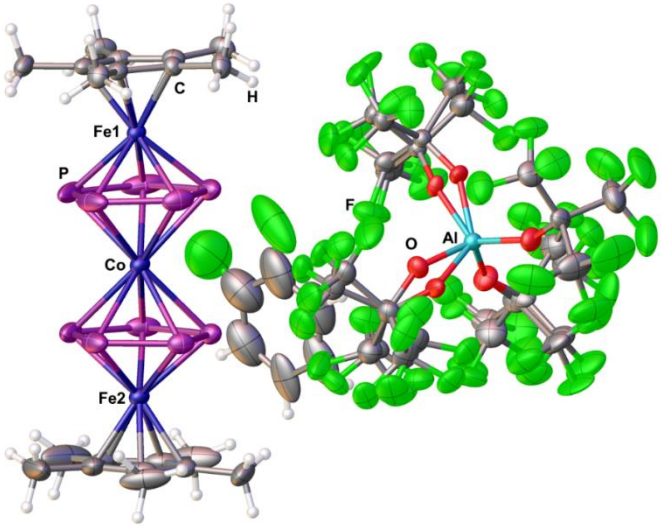


*Figure S 6: Solid state structure of **2-Co**; Shown is the asymmetric unit containing one cation, one anion as well as one o-DFB molecule; thermal ellipsoids are drawn at the 50% probability level.*

2.8.3

Compound **3** crystallizes in the monoclinic space group $P2_1/c$ forming dark brownish green plates from *o*-DFB/*n*-hexane mixtures at room temperature. The asymmetric unit contains one cation, two anions and three *o*-DFB molecules. All non-hydrogen atoms were refined anisotropically and the H atoms were treated as riding models. Disorder within the anions and solvent molecules was treated with appropriate restraints.

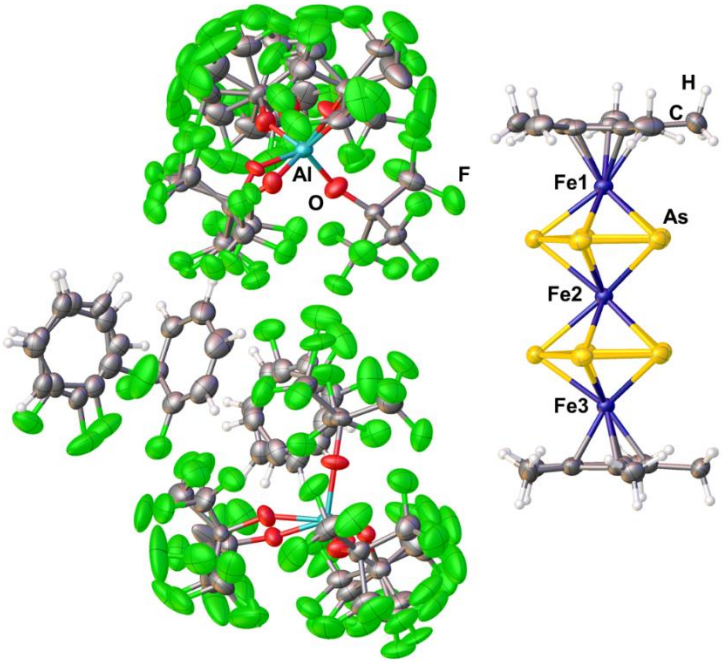


*Figure S 7: Solid state structure of **3**; Shown is the asymmetric unit containing one dication, two anions as well as three o-DFB molecules; thermal ellipsoids are drawn at the 50% probability level.*

2.9. [Fe(tol)$_2$][*pf*]$_2$

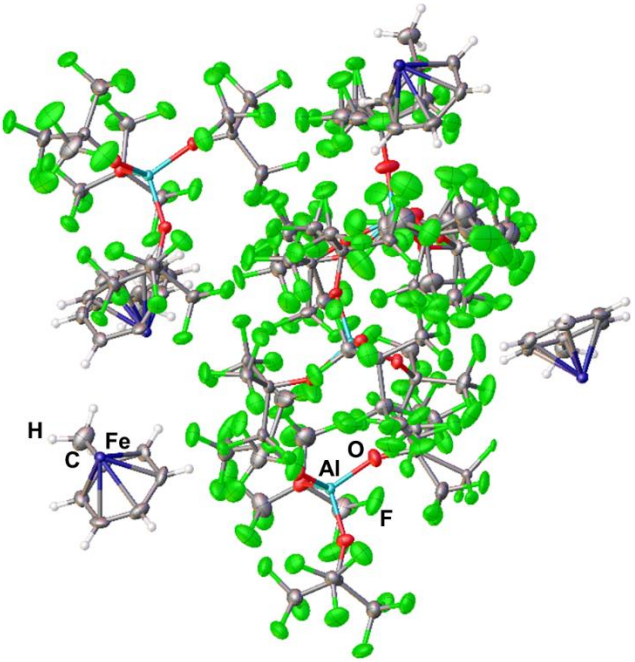


*Figure S 8: Solid state structure of **[Fe(tol)$_2$][pf]$_2$**; Shown is the asymmetric unit containing four half dications and four anions; thermal ellipsoids are drawn at the 50% probability level.*

3. Spectroscopic Data

3.1. 1-Cr

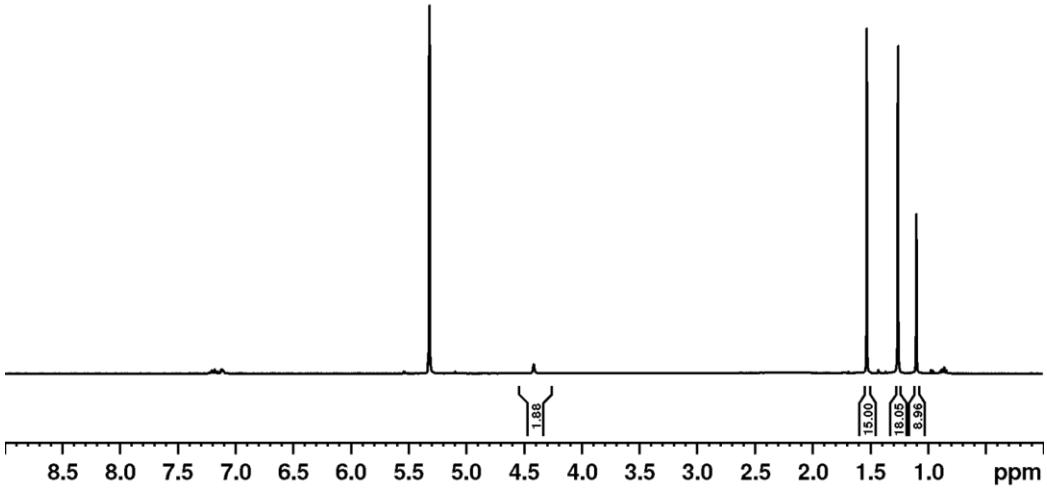


*Figure S 9: ^{1}H NMR spectrum of **1-Cr** in CD_2Cl_2 recorded at room temperature.*

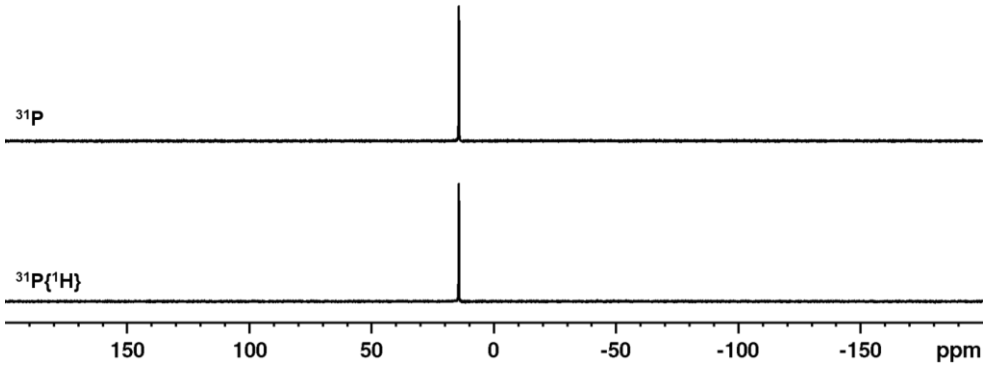


*Figure S 10: ^{31}P (top) and $^{31}P\{^{1}H\}$ (bottom) NMR spectrum of **1-Cr** in CD_2Cl_2 recorded at room temperature.*

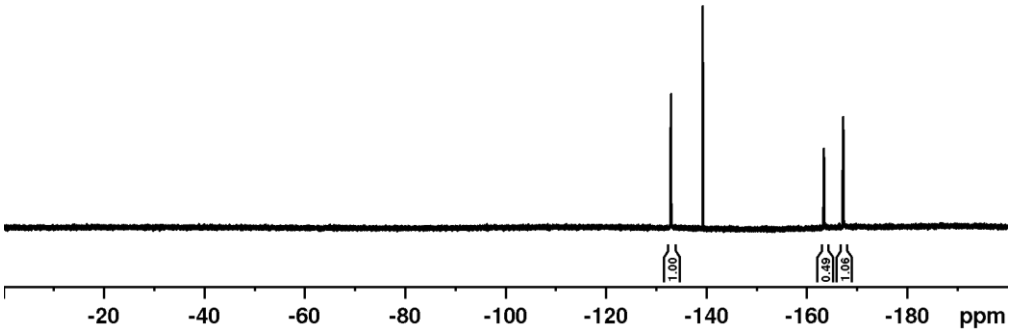


*Figure S 11: $^{19}F\{^{1}H\}$ NMR spectrum of **1-Cr** in CD_2Cl_2 recorded at room temperature.*

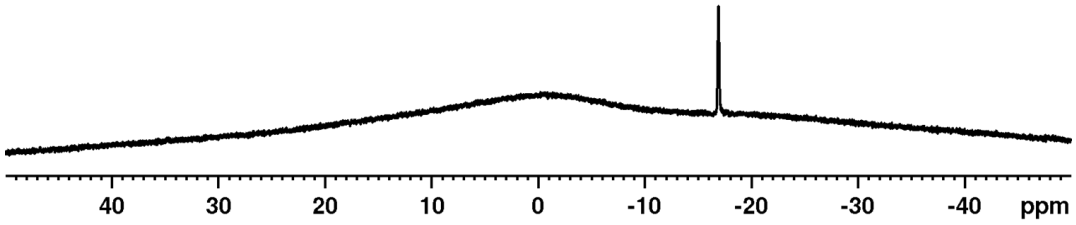


*Figure S 12: $^{11}B\{^{1}H\}$ NMR spectrum of **1-Cr** in CD_2Cl_2 recorded at room temperature.*

3.2. 1-Mn

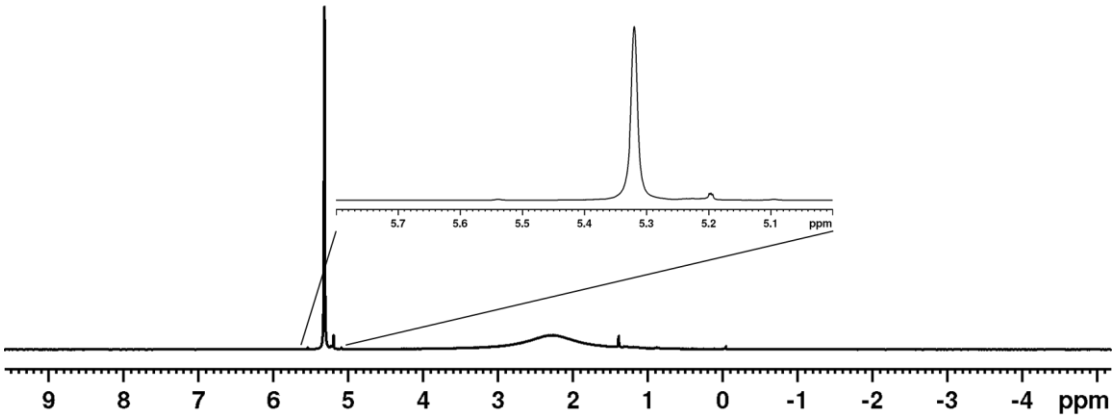


*Figure S 13: ^{1}H NMR spectrum of **1-Mn** in CD_2Cl_2 recorded at room temperature; 32 mg of substance were dissolved in 0.6 mL of CD_2Cl_2 inside the NMR tube and a coaxial capillary filled with CD_2Cl_2 was added to determine the number of unpaired electrons in **1-Mn** via the Evans method.*

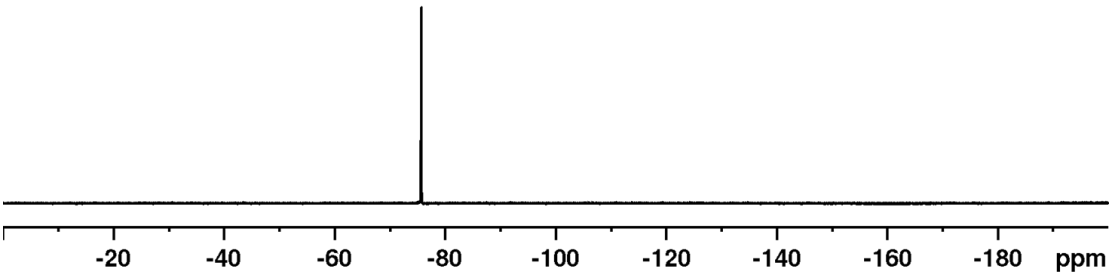


*Figure S 14: $^{19}F\{^{1}H\}$ NMR spectrum of **1-Mn** in CD_2Cl_2 recorded at room temperature.*

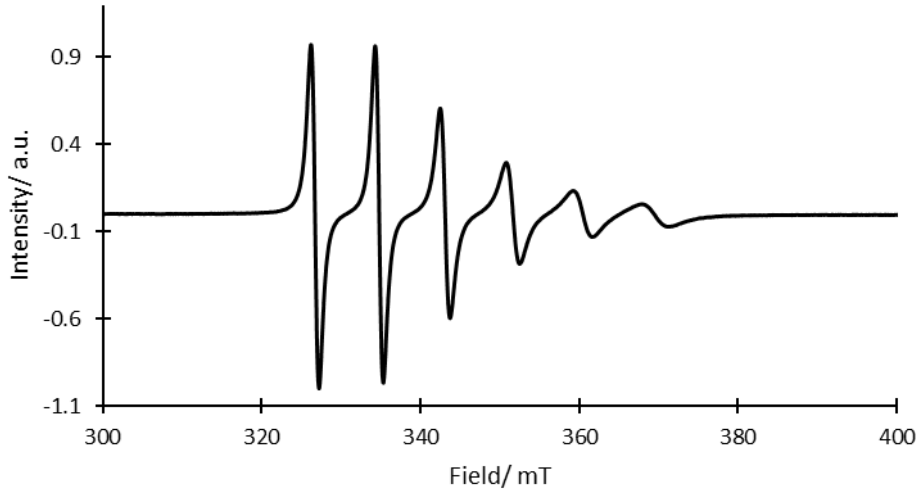


*Figure S 15: X-band EPR spectrum of **1-Mn** in o-DFB recorded at room temperature.*

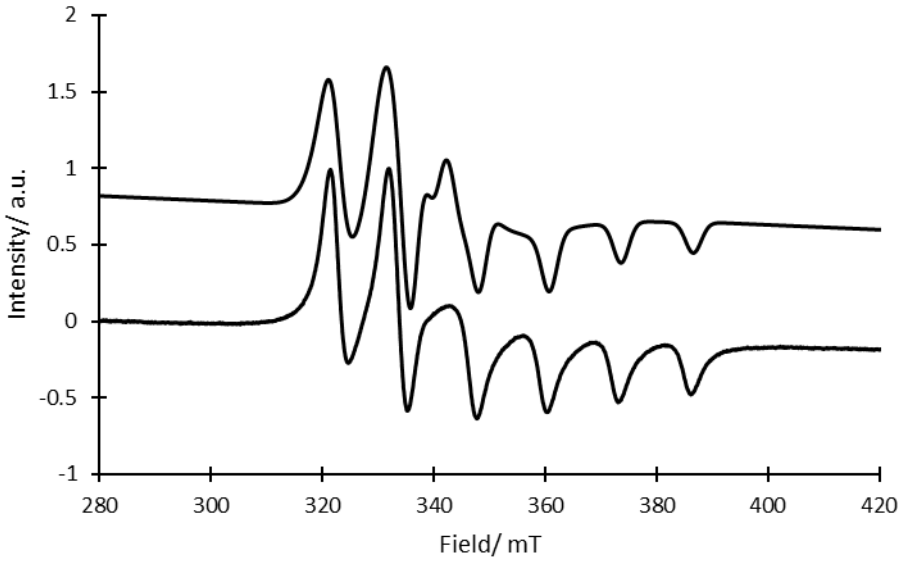


*Figure S 16: Experimental (bottom) and simulated (top) X-band EPR spectrum of **1-Mn** in frozen o-DFB solution recorded at 77 K; Simulation: $g_{\parallel}$ = 1.977, $g_{\perp}$ = 1.903, $A_{\parallel}$ = 125.26 MHz, $A_{\perp}$ = 337.72 MHz, lw = 3.2 mT.*

3.3.1-Fe

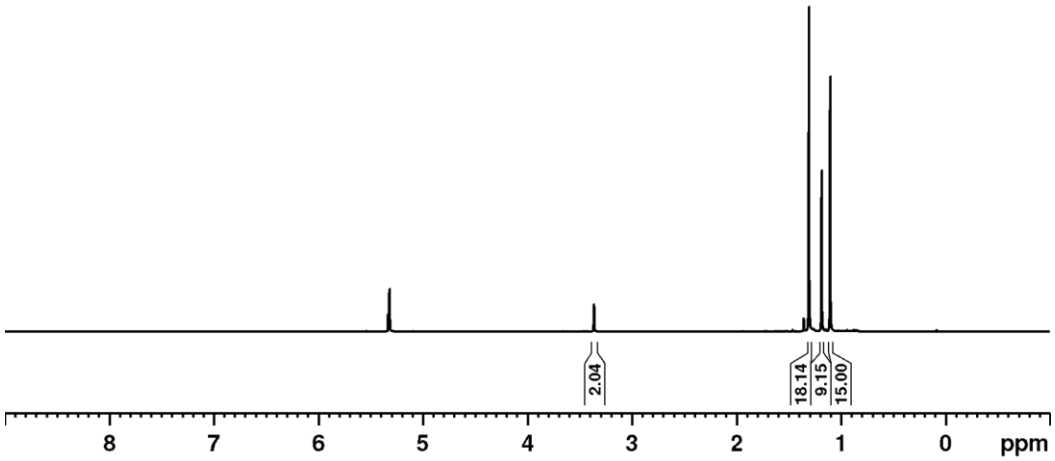


*Figure S 17: ^{1}H NMR spectrum of **1-Fe** in CD_2Cl_2 recorded at room temperature.*

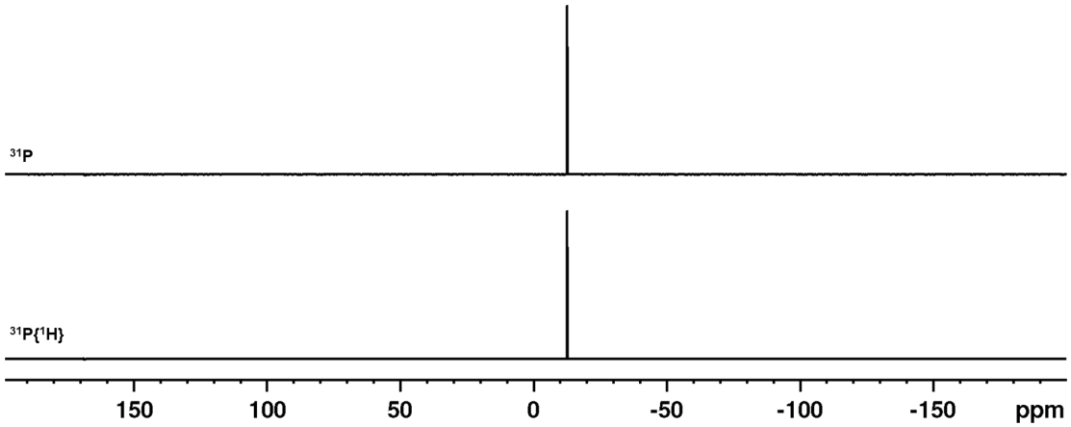


*Figure S 18: ^{31}P (top) and ^{31}P{^{1}H} (bottom) NMR spectrum of **1-Fe** in CD_2Cl_2 recorded at room temperature.*

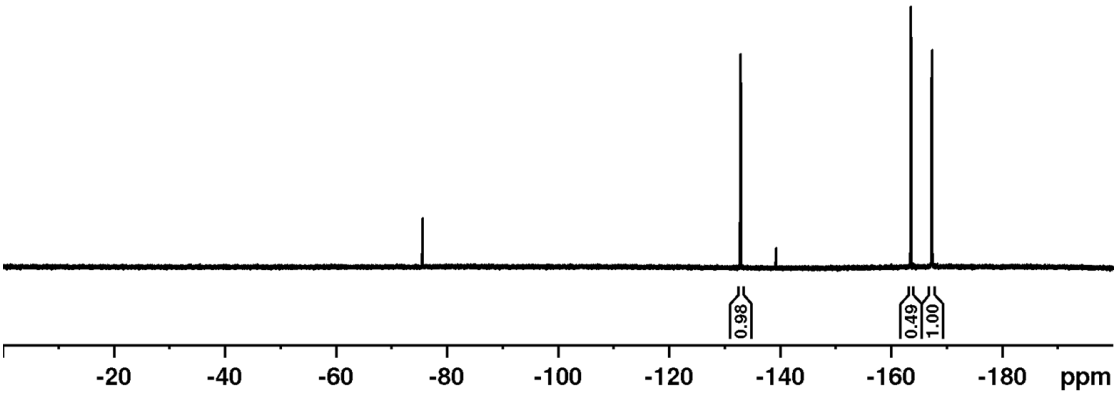


*Figure S 19: $^{19}F\{^{1}H\}$ NMR spectrum of **1-Fe** in CD_2Cl_2 recorded at room temperature.*

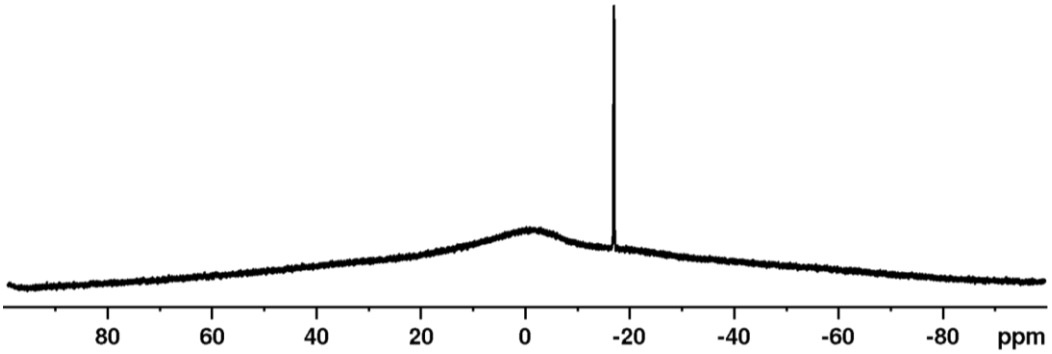


*Figure S 20: $^{11}B\{^{1}H\}$ NMR spectrum of **1-Fe** in CD_2Cl_2 recorded at room temperature.*

3.4. 1-Co

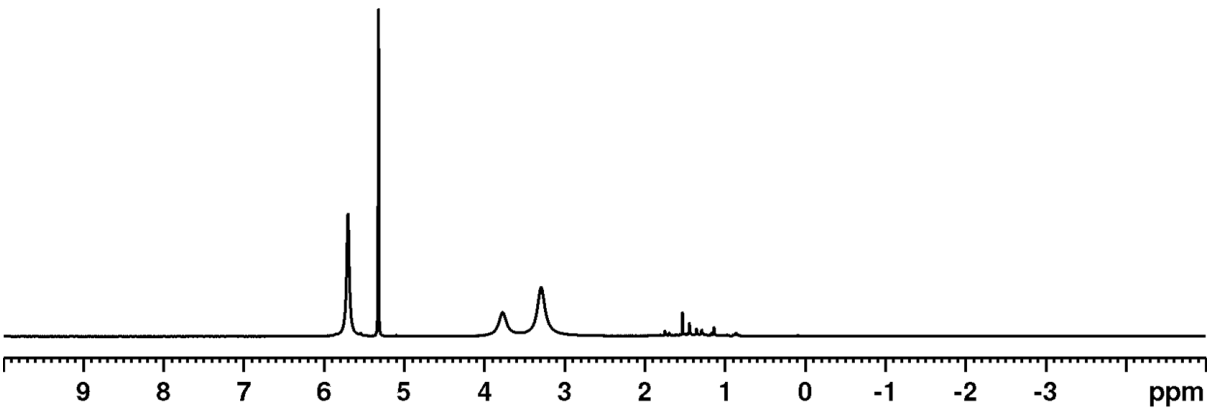


*Figure S 21: ^{1}H NMR spectrum of **1-Co** in CD_2Cl_2 recorded at room temperature.*

3.5. 1-Ni

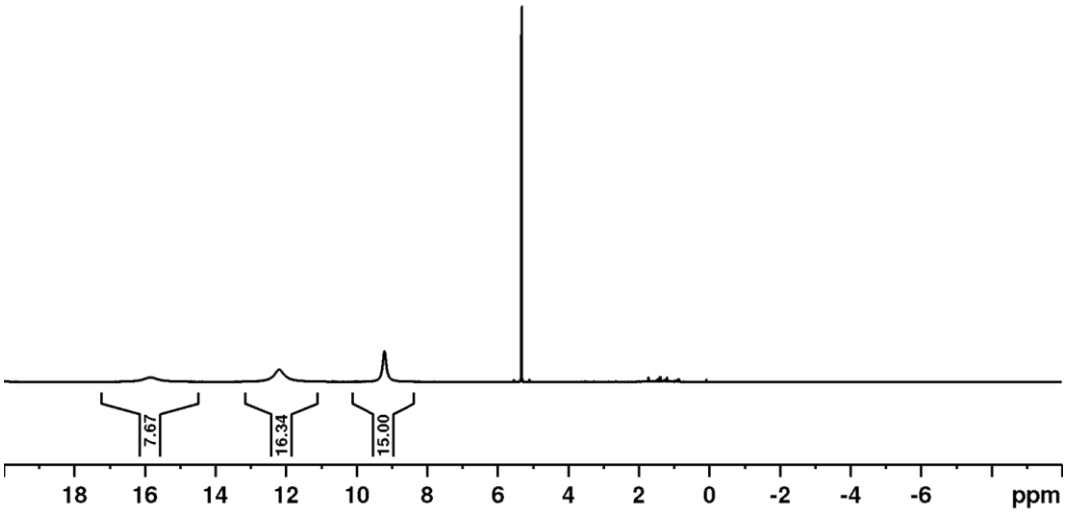


*Figure S 22: ^{1}H NMR spectrum of **1-Ni** in CD_2Cl_2 recorded at room temperature.*

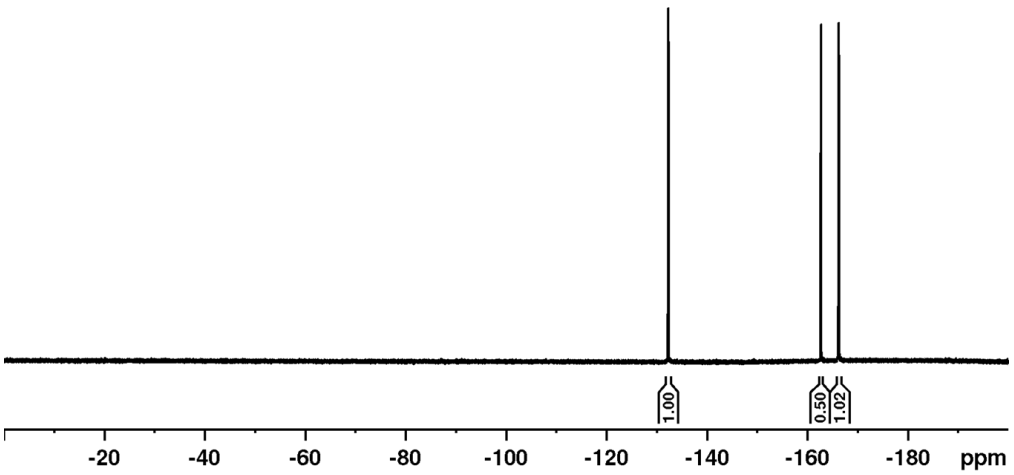


*Figure S 23: $^{19}F\{^{1}H\}$ NMR spectrum of **1-Ni** in CD_2Cl_2 recorded at room temperature.*

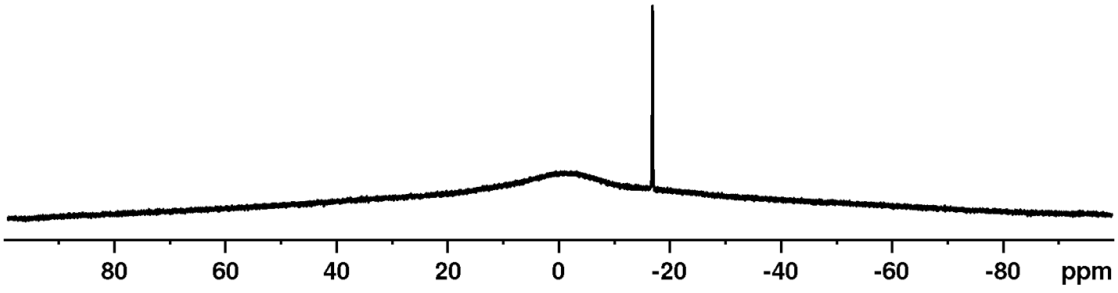


*Figure S 24: $^{11}B\{^{1}H\}$ NMR spectrum of **1-Ni** in CD_2Cl_2 recorded at room temperature.*

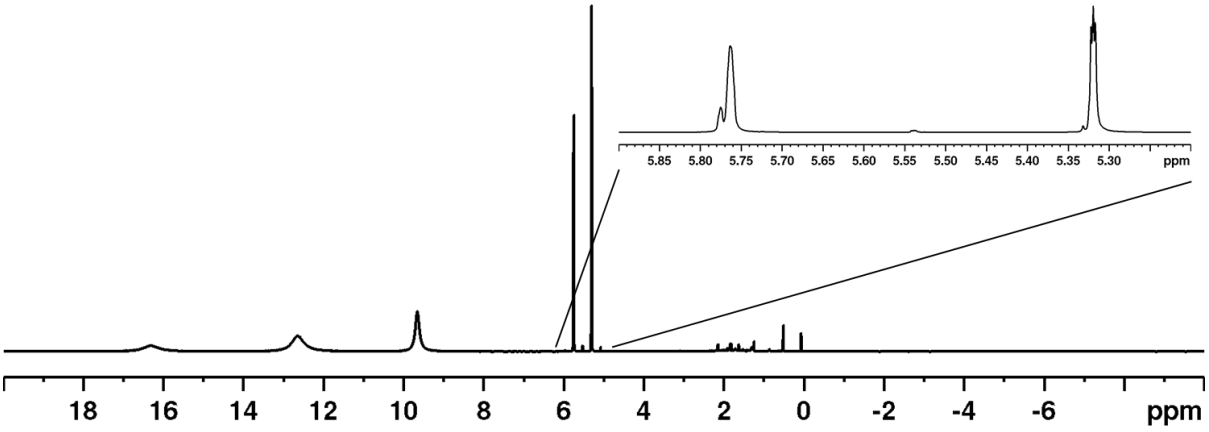


*Figure S 25: ^{1}H NMR spectrum of **1-Ni** in CD_2Cl_2 recorded at room temperature; 18 mg of substance were dissolved in 0.6 mL of CD_2Cl_2 inside the NMR tube and a coaxial capillary filled with CD_2Cl_2 was added to determine the number of unpaired electrons in **1-Ni** via the Evans method.*

3.6. 2-Fe

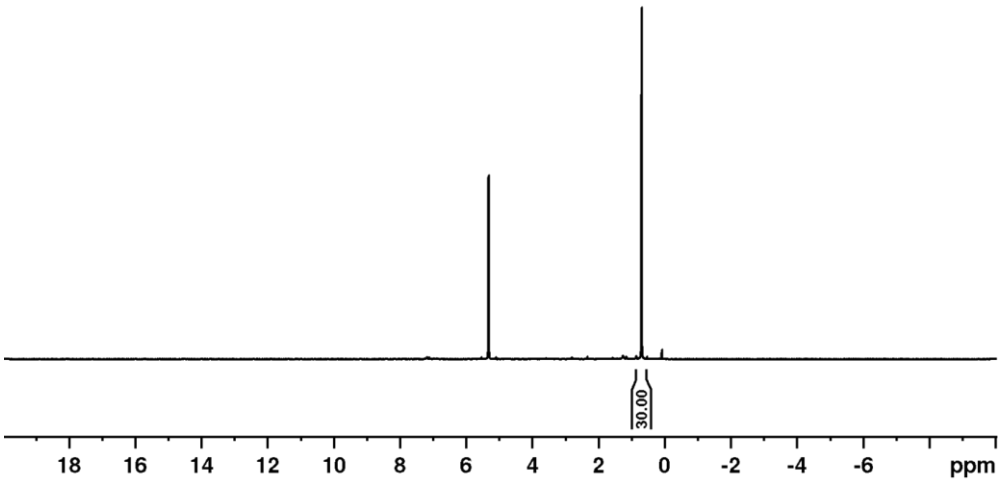


*Figure S 26: ^{1}H NMR spectrum of **2-Fe** in CD_2Cl_2 recorded at room temperature.*

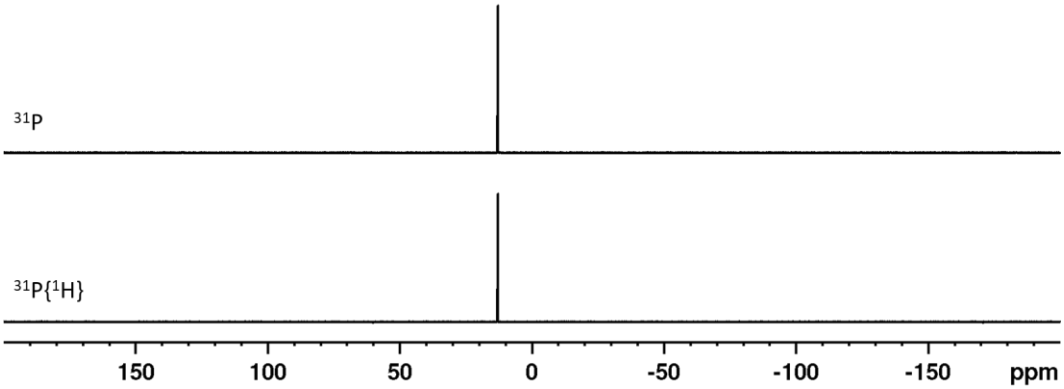


*Figure S 27: ^{31}P (top) and $^{31}P\{^{1}H\}$ (bottom) NMR spectrum of **2-Fe** in CD_2Cl_2 recorded at room temperature.*

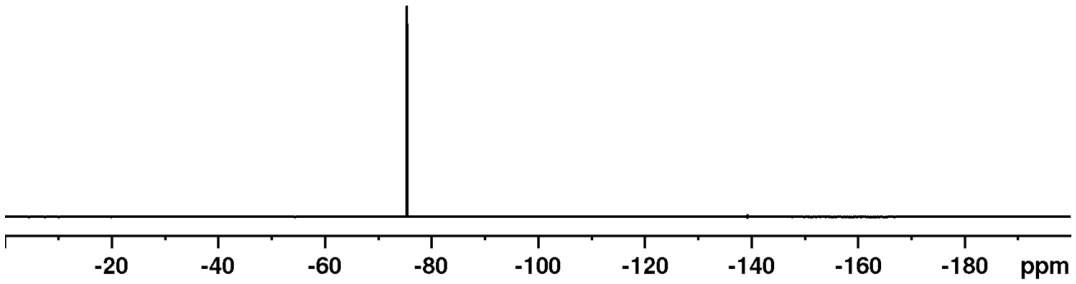


*Figure S 28: $^{19}F\{^{1}H\}$ NMR spectrum of **2-Fe** in CD_2Cl_2 recorded at room temperature.*

3.7. 2-Co

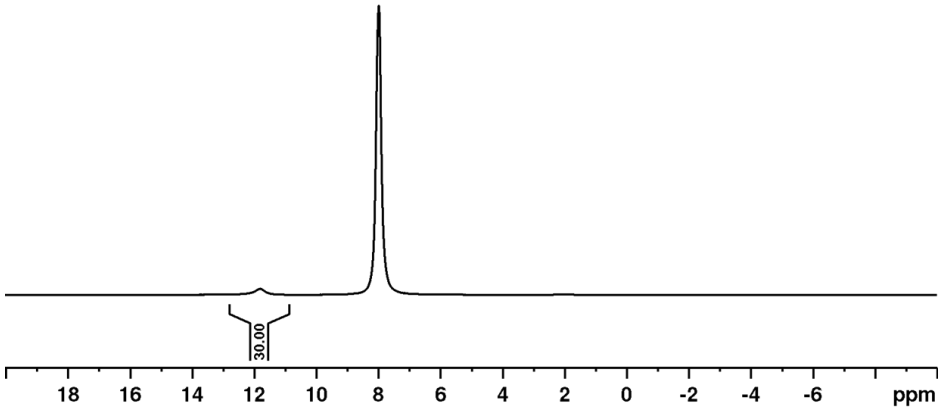


*Figure S 29: ^{1}H NMR spectrum of **2-Co** in o-DFB with added C_6D_6* capillary *recorded at room temperature.*

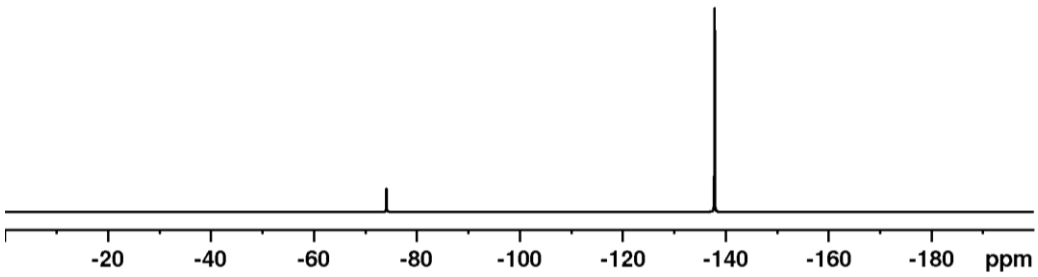


*Figure S 30: $^{19}F\{^{1}H\}$ NMR spectrum of **2-Co** in o-DFB with added C_6D_6* capillary *recorded at room temperature.*

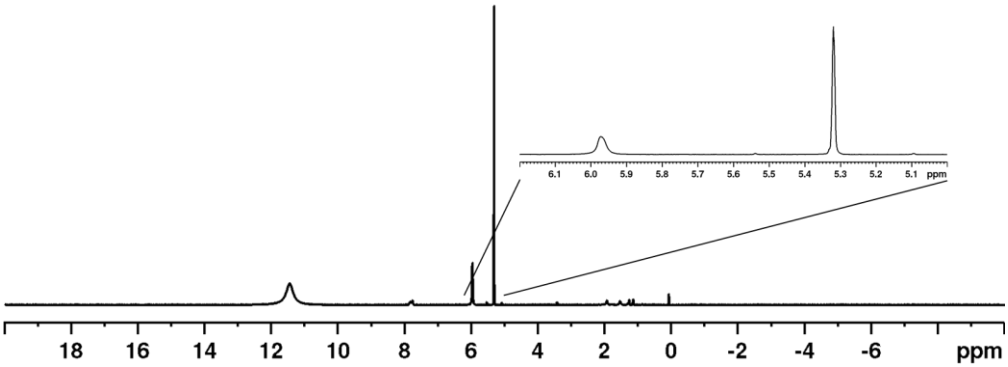


*Figure S 31: ^{1}H NMR spectrum of **2-Co** in CD_2Cl_2 recorded at room temperature; 20 mg of substance were dissolved in 0.2 mL of CD_2Cl_2 inside the NMR tube and a coaxial capillary filled with CD_2Cl_2 was added to determine the number of unpaired electrons in **2-Co** via the Evans method.*

3.8.3

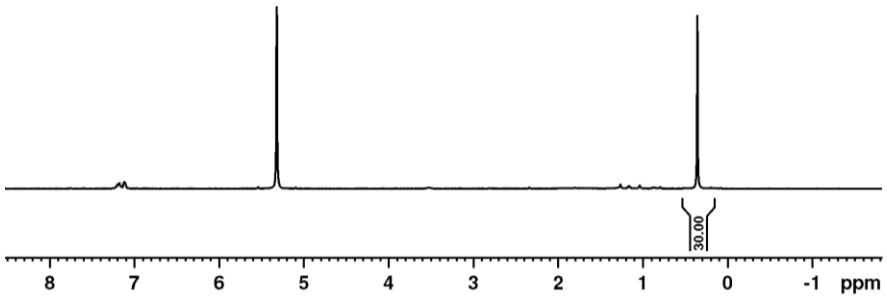


*Figure S 32: ^{1}H NMR spectrum of **3** in CD_2Cl_2 recorded at room temperature with traces of o-DFB at δ = 7.1 ppm.*

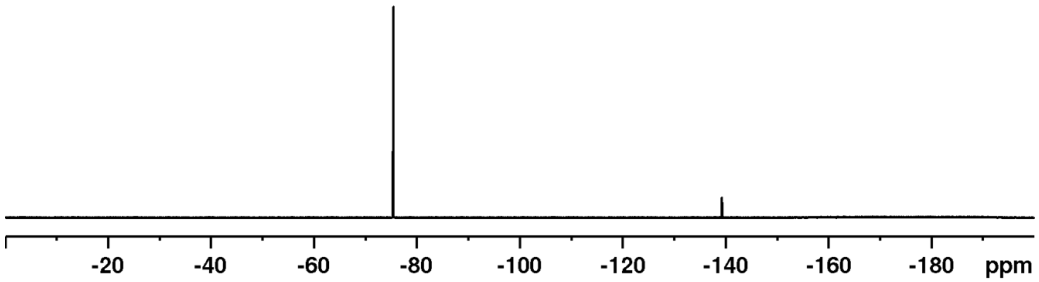


*Figure S 33: $^{19}F\{^{1}H\}$ NMR spectrum of **3** in CD_2Cl_2 recorded at room temperature with traces of o-DFB at δ = 140 ppm.*

3.9. [Fe(tol)$_2$][*pf*]$_2$

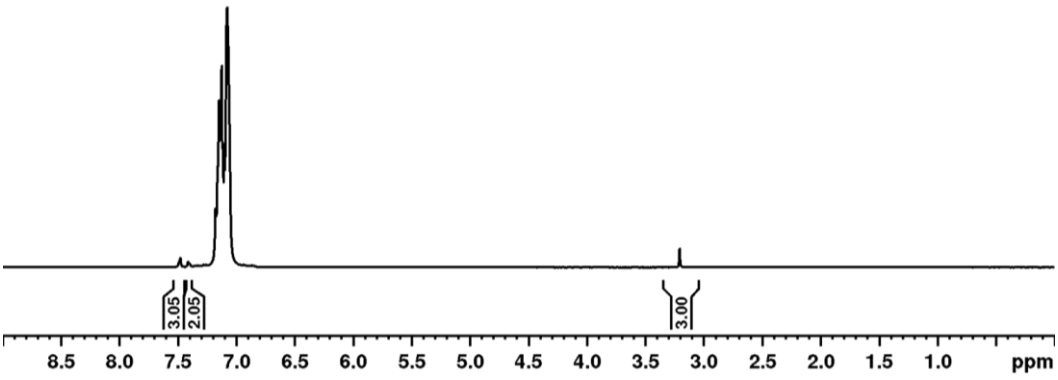


*Figure S 34: ^{1}H NMR spectrum of **[Fe(tol)$_2$][pf]$_2$** in o-DFB with added C_6D_6* capillary *recorded at room temperature.*

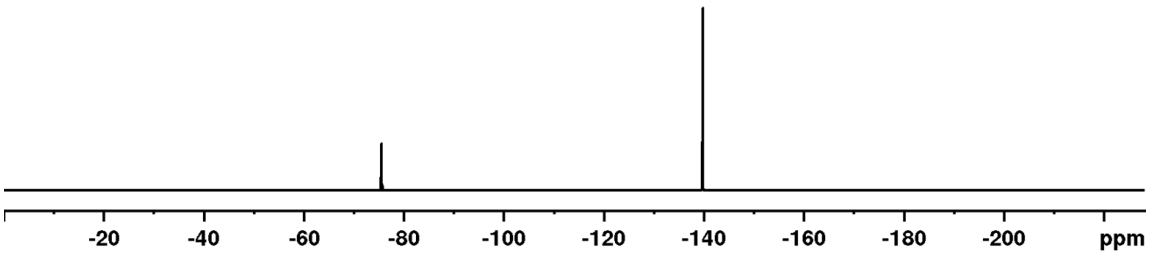


*Figure S 35: $^{19}F\{^{1}H\}$ NMR spectrum of **[Fe(tol)$_2$][pf]$_2$** in o-DFB with added C_6D_6* capillary *recorded at room temperature.*

4. Computational Data

4.1. General Remarks

DFT calculations were performed using the Orca 5.0 software package.[16] The sterically demanding Cp* ligands in **2-Fe** and **2-Co** were replaced with unsubstituted Cp ligands to save computational resources. Geometry optimizations were performed at the ωB97X-D3[17]/def2-TZVP[18] level of theory with PCM solvent correction for CH_2Cl_2.[19] Stationary points were verified by analytical frequency calculations. Single point calculations were performed at the ωB97X-D3/def2-TZVP level of theory with solvent correction as described above.

4.2. Spin Density Distribution and Energetic Comparison

To gain insight into the electronic structure of especially the paramagnetic species **1-Mn**, **1-Ni** and **2-Co**, their spin densities were analysed (Figure S36). While the spin density in **1-Mn** is clearly localized at the Mn atom, the two unpaired electrons in **1-Ni** and **2-Co** are centred at the Ni and Co atoms, respectively. Only in **1-Ni**, minor contributions from the Cp‴ ligand are apparent. As for both latter species a hypothetical singlet electron configuration would be possible and is transiently even observed for **1-Ni** in the solid state, the energetic separation between this singlet configuration and the experimentally observed triplet ground state was of interest. Thus, both the compounds **1-Ni** and **2-Co** were optimized as singlet as well as triplet configuration, the geometries compared, and the energetic separation determined (Figure S37). In both cases, the triplet configuration is 55.31 kJ/mol (**1-Ni**) and 127.17 kJ/mol (**2-Co**) more stable, respectively.

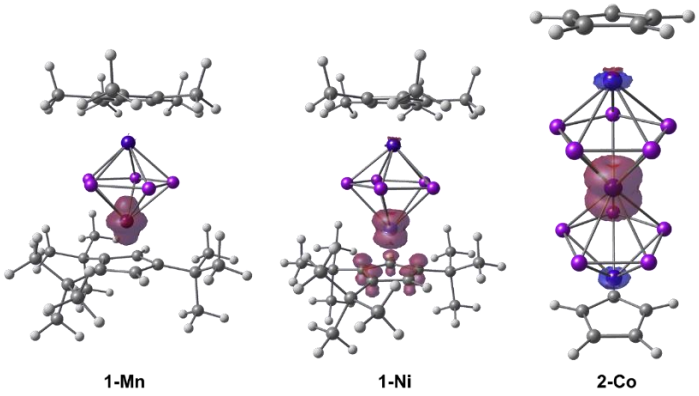


*Figure S 36: Calculated spin density distribution for **1-Mn**, **1-Ni** and **2-Co**; surfaces are drawn at isovalues of 0.02, 0.01 and 0.01, respectively.*

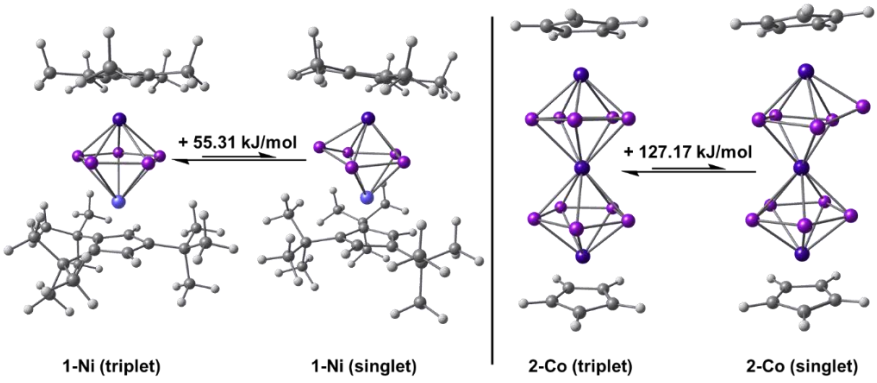
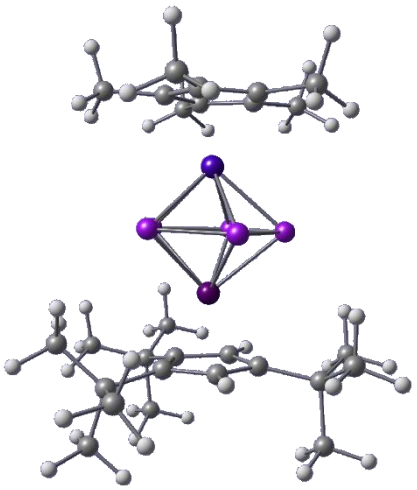


*Figure S 37: Comparison of optimized molecular structures for **1-Ni** (left) and **2-Co** (right) in case of a singlet or triplet electronic configuration, each.*

4.3. Optimized Geometries

1-Mn

ωB97XD/def2TZVP (CPCM (CH_2Cl_2)): Energies/H = -5176.41492301, Enthalpies/H = -5176.41397880, Free Energies/H = -5176.51963493, ZPVE/ kcal/mol = 441.30



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P	11.907417000	7.105424000	23.481035000
P	10.299426000	8.466773000	23.081553000
P	11.776838000	5.500057000	22.072764000
P	9.180285000	7.685969000	21.436635000
P	10.067029000	5.830692000	20.840639000
C	7.707775000	5.666106000	23.631510000
C	8.481336000	4.499285000	23.434186000
H	8.294496000	3.766067000	22.668105000
C	6.349321000	5.958460000	23.023769000
C	9.520927000	4.405682000	24.410581000
C	8.319411000	6.347626000	24.705442000
H	7.980915000	7.291468000	25.098481000
C	11.753465000	9.480438000	20.164545000
C	12.877701000	9.264115000	21.013326000
C	10.315698000	3.096722000	24.561365000
C	11.679533000	8.393674000	19.246168000
C	9.415428000	5.597417000	25.230491000
C	8.983985000	5.515516000	27.640096000
H	8.873435000	4.432065000	27.601079000
H	7.999267000	5.960832000	27.484914000
H	9.326815000	5.788155000	28.640442000
C	11.845267000	3.233284000	24.580950000
H	12.238938000	3.291853000	23.566848000
H	12.278019000	2.343569000	25.043475000
H	12.201043000	4.101243000	25.123190000
C	5.967831000	7.433335000	23.158982000
H	5.949269000	7.749406000	24.203420000

H	4.967972000	7.588491000	22.749361000
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C	12.760610000	7.507749000	19.524673000
C	9.989981000	6.029348000	26.590508000
C	9.826442000	2.415849000	25.852270000
H	10.160820000	2.933762000	26.748914000
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H	8.735694000	2.362603000	25.875222000
C	11.384119000	5.512854000	26.939925000
H	12.129597000	5.850583000	26.218129000
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H	10.764397000	7.996559000	26.019554000
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H	8.940845000	1.834105000	23.404428000
H	10.595973000	1.241337000	23.513156000
H	10.223105000	2.583901000	22.433244000
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H	12.531814000	10.734421000	22.540154000
H	14.055816000	10.912161000	21.669261000
H	13.874111000	9.641536000	22.877936000
C	10.854121000	10.671616000	20.187289000
H	9.838075000	10.414405000	19.887723000
H	11.226169000	11.426169000	19.490172000
H	10.813034000	11.123557000	21.177985000
C	14.751667000	7.470743000	21.192736000
H	14.846302000	7.697020000	22.254706000
H	15.620157000	7.894430000	20.682877000
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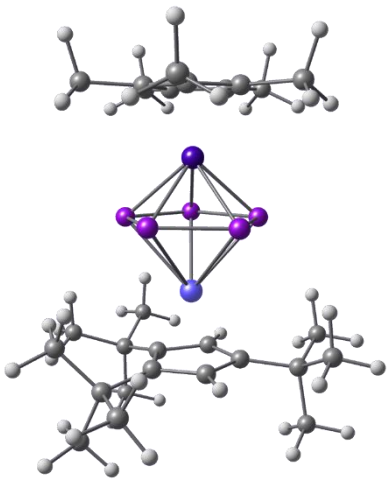
1-Ni (triplet)

ωB97XD/def2TZVP (CPCM (CH_2Cl_2)): Energies/H = -5533.77609673, Enthalpies/H = -5533.77515253, Free Energies/H = -5533.88116412, ZPVE/ kcal/mol = 439.97



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P	5.678036000	5.291258000	20.574025000
P	5.937916000	5.113278000	18.479408000
P	8.811134000	6.435977000	19.793535000
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C	6.999883000	9.088230000	18.754917000
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H	10.584211000	0.564925000	18.017468000

C	11.365329000	3.910753000	18.404663000
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C	7.158599000	3.177534000	23.448501000
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H	9.096899000	9.541603000	18.858619000
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H	8.539090000	9.040281000	17.259958000

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H	5.406724000	9.271757000	16.106727000
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H	3.109755000	7.101782000	19.448897000
H	3.528911000	7.104436000	17.733158000
H	2.821911000	8.541589000	18.472248000
C	4.531625000	8.548623000	21.529197000
H	3.797649000	7.743895000	21.500069000
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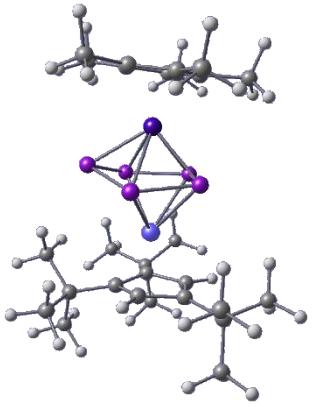
1-Ni (singlet)

ωB97XD/def2TZVP (CPCM (CH_2Cl_2)): Energies/H = -5533.75348611, Enthalpies/H = -5533.75254190, Free Energies/H = -5533.86009630, ZPVE/ kcal/mol = 440.62



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C	9.327822000	2.633908000	19.166084000
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H	4.836895000	2.471897000	21.466877000
C	8.267035000	9.599290000	18.155115000
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H	8.539090000	9.040281000	17.259958000

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H	5.406724000	9.271757000	16.106727000
H	5.174806000	7.531842000	16.280469000
C	3.511007000	7.710305000	18.638618000
H	3.109755000	7.101782000	19.448897000
H	3.528911000	7.104436000	17.733158000
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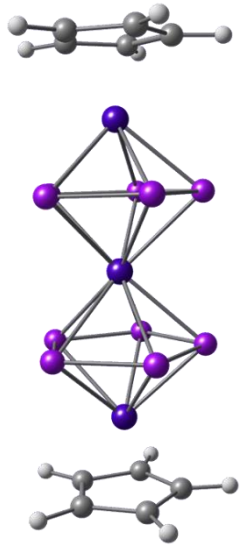
H	3.797649000	7.743895000	21.500069000
H	3.994011000	9.488967000	21.671654000
H	5.173315000	8.395043000	22.396549000

2-Fe'

ωB97XD/def2TZVP (CPCM (CH_2Cl_2)): Energies/H = -7591.66093026, Enthalpies/H = -7591.65998606, Free Energies/H = -7591.73656363, ZPVE/ kcal/mol = 124.09



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Fe	3.790546000	8.385606000	14.662908000
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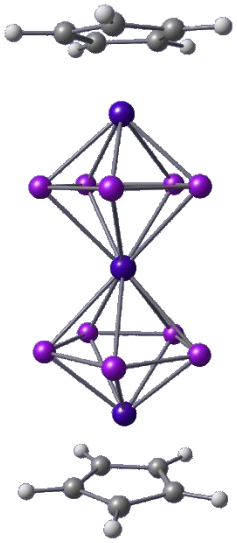
P	2.532311000	3.603941000	13.166905000
P	2.509027000	6.903730000	13.329164000
P	2.202119000	6.799588000	15.429352000
P	4.603273000	6.933537000	12.971410000
P	4.126091000	3.465271000	16.209118000
P	4.627220000	3.632686000	12.812439000
P	5.590300000	6.852922000	14.851766000
P	5.612336000	3.549021000	14.692867000
P	4.106910000	6.767194000	16.370100000
C	2.995844000	0.370799000	13.418235000
C	4.021607000	0.280729000	15.469761000
C	4.398681000	0.388197000	13.208236000
C	2.762899000	0.303750000	14.816011000
C	5.032479000	0.332946000	14.476081000
H	4.896448000	0.453919000	12.252641000
H	6.097009000	0.349619000	14.654507000
C	4.970652000	10.066872000	14.910977000
H	2.238500000	0.421224000	12.650655000
C	2.909602000	10.097164000	13.901483000
C	4.306971000	10.119792000	13.658353000
H	4.181687000	0.251168000	16.536923000
C	2.709780000	10.030880000	15.304277000
H	1.797225000	0.294329000	15.298293000
C	3.983600000	10.011946000	15.928175000
H	6.039332000	10.048992000	15.062015000
H	4.781597000	10.148373000	12.689268000

H	1.756099000	9.980607000	15.807564000
H	4.168903000	9.945178000	16.989501000
H	2.134565000	10.105497000	13.150093000

2-Co' (triplet)

ωB97XD/def2TZVP (CPCM (CH_2Cl_2)): Energies/H = -7710.95679967, Enthalpies/H = -7710.95585546, Free Energies/H = -7711.03591349, ZPVE/ kcal/mol = 123.19



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Fe	11.974036000	16.328787000	15.913898000
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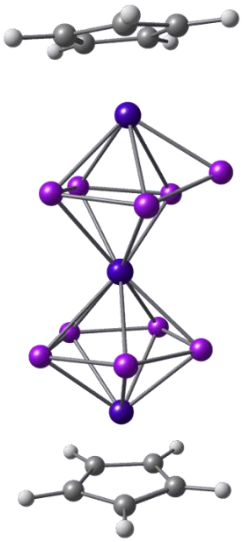
P	10.911286000	14.284925000	16.524974000
P	12.225338000	14.203733000	14.865862000
P	8.524832000	12.208109000	14.724003000
P	9.831632000	12.136245000	13.058601000
P	11.771595000	15.833612000	13.590770000
P	9.647310000	15.966567000	16.277686000
P	10.177761000	16.921645000	14.463326000
P	7.255268000	13.887160000	14.488150000
P	9.368022000	13.769000000	11.791424000
P	7.776578000	14.851581000	12.675701000
C	6.959468000	11.799005000	10.711671000
C	7.272053000	10.704155000	11.557324000
C	5.893657000	12.521672000	11.306074000
C	13.050173000	16.513178000	17.669842000
C	6.399380000	10.750102000	12.674434000
C	5.547800000	11.873657000	12.519350000
H	7.461076000	12.052135000	9.790523000
H	8.052992000	9.978227000	11.391954000
C	13.933523000	16.448977000	16.562042000
C	12.208608000	17.641176000	17.494659000
H	5.443043000	13.420839000	10.915281000
H	4.787046000	12.193986000	13.214224000
H	6.400238000	10.065498000	13.508416000
C	13.637854000	17.537589000	15.702246000
C	12.571691000	18.274274000	16.278426000
H	13.009032000	15.812440000	18.489295000
H	14.682248000	15.691048000	16.391219000
H	11.414847000	17.948222000	18.157875000
H	12.102553000	19.148237000	15.853800000
H	14.122589000	17.752394000	14.762531000

2-Co' (singlet)

ωB97XD/def2TZVP (CPCM (CH_2Cl_2)): Energies/H = -7710.90921936, Enthalpies/H = -7710.90827516, Free Energies/H = -7710.98747581, ZPVE/ kcal/mol = 123.07



Fe	7.619011000	12.475142000	12.650199000
Fe	11.864829000	16.385590000	15.837958000
Co	9.736019000	14.309834000	14.246688000
P	10.822598000	14.337733000	16.381160000
P	12.084765000	14.329193000	14.695537000
P	8.632946000	12.114136000	14.781731000
P	9.913733000	12.055851000	13.119032000
P	11.335827000	15.938651000	13.464929000
P	9.436045000	15.948722000	15.998734000
P	10.179517000	17.329122000	14.572449000
P	7.399194000	13.851844000	14.585855000
P	9.486059000	13.774950000	11.920305000
P	7.856161000	14.839078000	12.766486000
C	7.091087000	11.780117000	10.774894000
C	7.306979000	10.688882000	11.653649000
C	6.045552000	12.574159000	11.311462000
C	12.981564000	16.368799000	17.579902000
C	6.395003000	10.808255000	12.734193000
C	5.616445000	11.973846000	12.523170000
H	7.643621000	11.983655000	9.870517000
H	8.051455000	9.917081000	11.533334000
C	13.840617000	16.342441000	16.448713000
C	12.202101000	17.549931000	17.510693000
H	5.659136000	13.486928000	10.884889000
H	4.850460000	12.352351000	13.182473000
H	6.324454000	10.144951000	13.582455000
C	13.591422000	17.508108000	15.682126000
C	12.582396000	18.257366000	16.340461000
H	12.921057000	15.613502000	18.348226000
H	14.549166000	15.564680000	16.208785000
H	11.434367000	17.843859000	18.209641000
H	12.168242000	19.193545000	16.001336000
H	14.064572000	17.765196000	14.746815000

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