

SUPPORTING INFORMATION

(Electrochemical) Properties and Computational Investigations of Ferrocenyl-Substituted $\text{Fe}_3(\mu_3\text{-PFc})_2(\text{CO})_9$ and $\text{Co}_4(\mu_4\text{-PFc})_2(\text{CO})_9$ Clusters and their Reduced Species

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NIR Spectroelectrochemistry

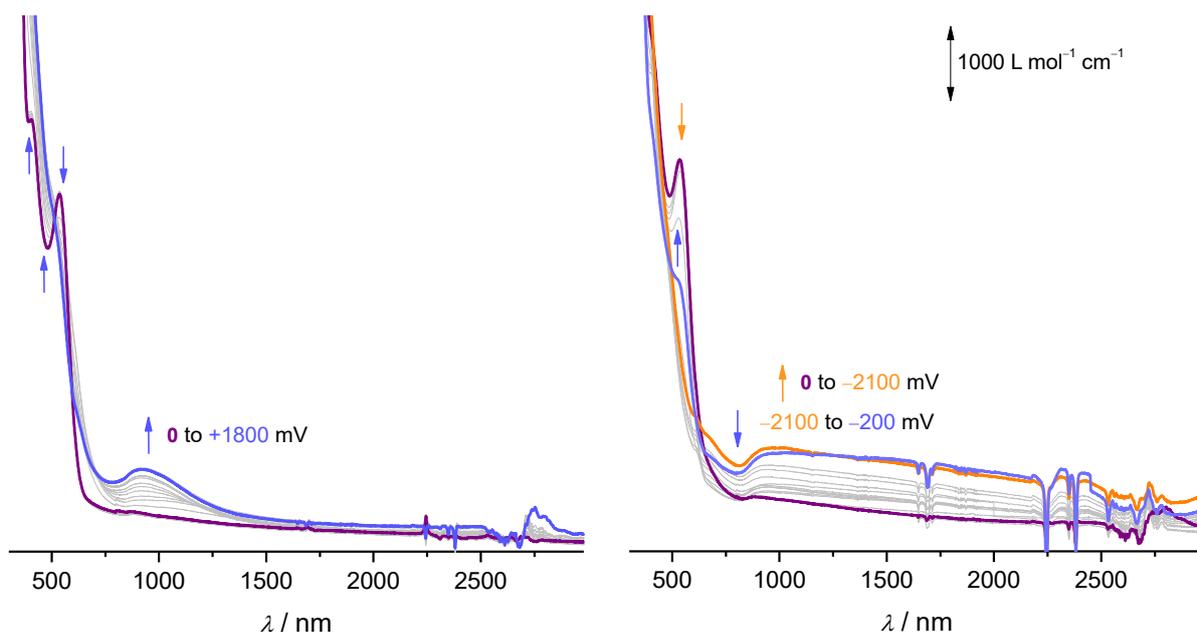


Figure S1. NIR spectra of **4** at 25 °C in dichloromethane (2 mmol L^{-1}) at rising (left) and decreasing potentials (right). All potentials vs. Ag/AgCl; supporting electrolyte 0.1 mol L^{-1} of $[\text{N}^n\text{Bu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$; Pt working electrode.

CV Measurements

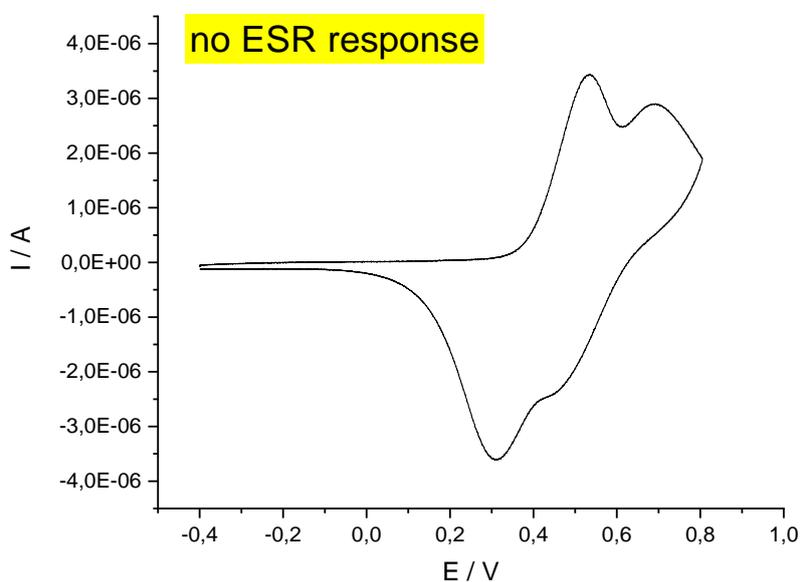


Figure S2. Cyclic voltammogram of **4** measured in a spectroelectrochemical cell (sweep rate 3 mV s^{-1}) in a dichloromethane solution (0.5 mmol L^{-1}) at 25 °C with a Pt working electrode. Supporting electrolyte 0.5 mol L^{-1} of $[\text{N}^n\text{Bu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$. All potentials vs. the AgCl-coated Ag wire. An EPR signal could neither be obtained during the first, nor the second oxidation process.

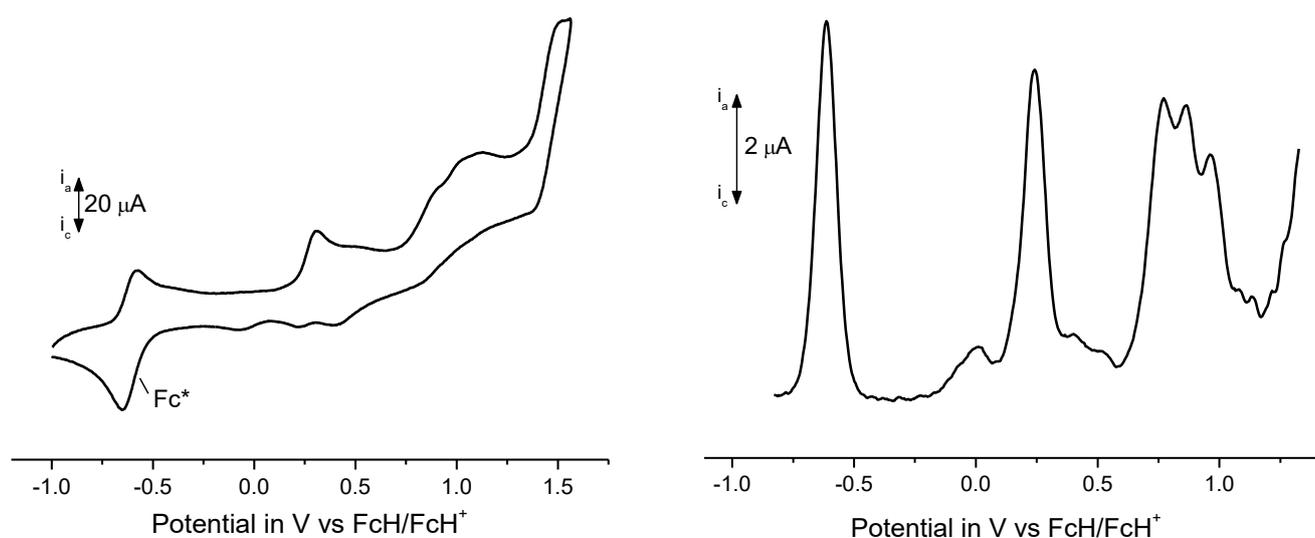


Figure S3. Cyclic voltammogram (left: scan rate 100 mV s^{-1}) and square-wave voltammogram (right: step-height 25 mV , pulse-width 2 s , amplitude 5 mV) of **5** in a dichloromethane solution (1.0 mmol L^{-1}) at $25 \text{ }^\circ\text{C}$ measured with a glassy carbon working electrode. Supporting electrolyte 0.1 mol L^{-1} of $[\text{N}^n\text{Bu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$. ($\text{Fc}^* = \text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2$)

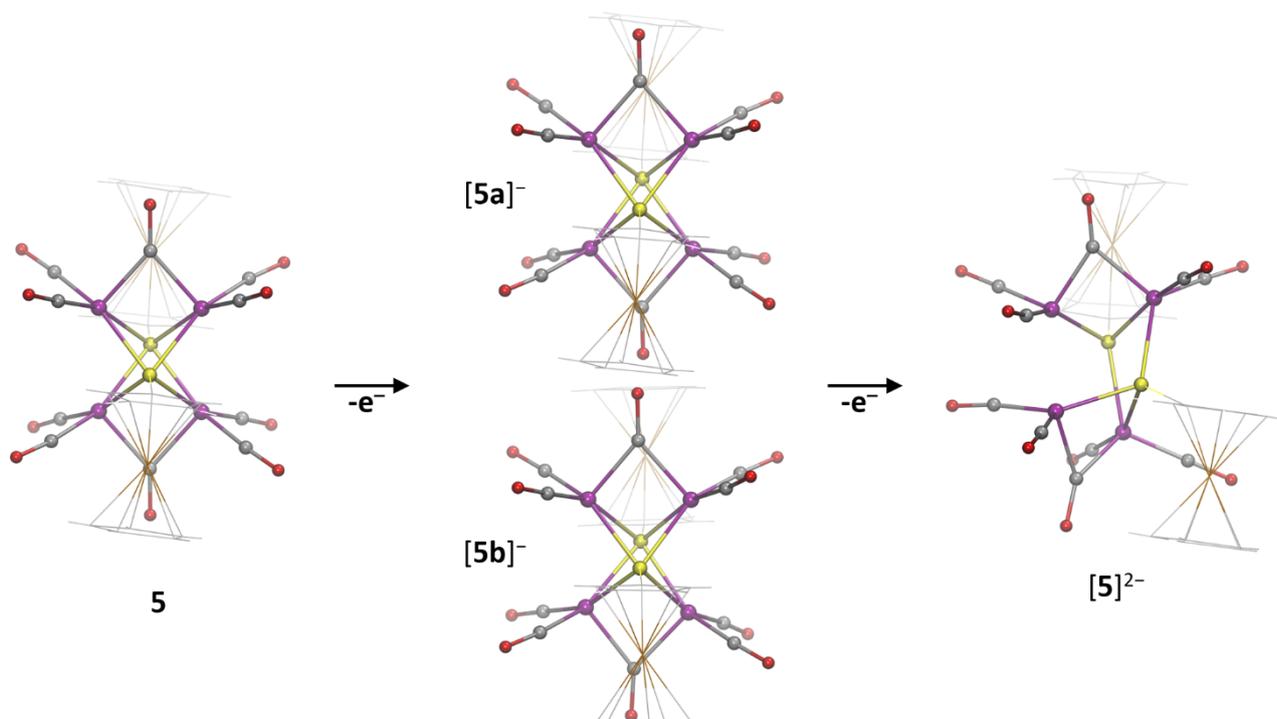


Figure S4. DFT optimized structures of **5**, $[\mathbf{5}]^-$ and $[\mathbf{5}]^{2-}$.

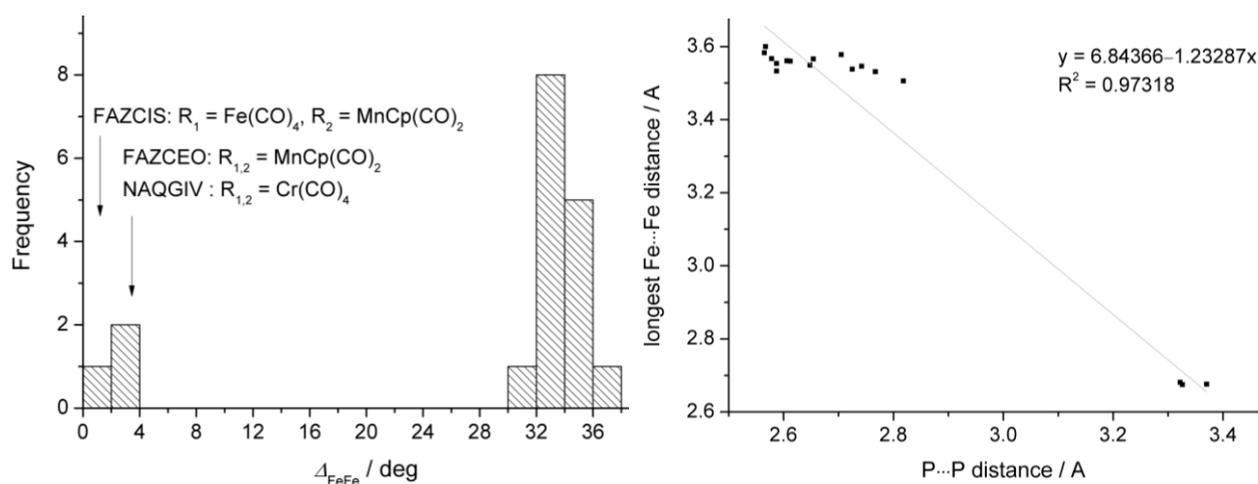
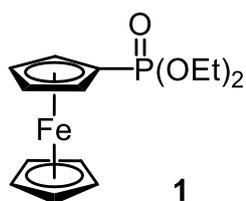


Figure S5. The histogram (left) shows the difference (Δ_{FeFe}) between the longest and the shortest Fe–Fe bond distance ($\Delta_{\text{FeFe}} = 0$, perfectly trigonal bipyramidal with a trigonal Fe_3 plane; $\Delta_{\text{FeFe}} > 0$, square pyramidal with a square planar Fe_2P_2 plane, capped by a phosphine) and selected substituents R bonded to the P atoms within the cluster core. The right diagram shows the relationship between longest Fe...Fe and the P...P distance. Further CSD ref codes, which are not shown in the Diagram are: BINMUG, BINMUG, FAZCEO, FAZCIS, FOBWEY, JOGZIO, JOGZOU, JOGZOU, MEFWUP, MEFXAW, NAQGIV, NAQHAO, PIFGOA, TOPXEB, VUPLIB, WEZLAO, YUVHOM, YUVHOM, featuring C-, S-, P-, Au- based groups R, or $\{\text{FeCp}(\text{CO})_2\}$, $\{\text{MnCp}(\text{CO})_2\}$ and H substituents.

Synthesis of the Starting Materials

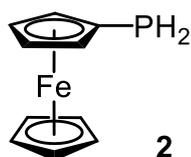
Synthesis of diethyl ferrocenylphosphonate (**1**)



In a Schlenk tube, ferrocene (4.00 g, 22 mmol) and KO^tBu (0.54 g, 5 mmol) were dissolved in 100 mL THF and cooled to $-80\text{ }^\circ\text{C}$ followed by the dropwise addition of $^t\text{BuLi}$ (10 mL, 19 mmol). After stirring of the reaction mixture at this temperature for 30 minutes, $\text{ClP}(\text{O})(\text{OEt})_2$ (3 mL, 20 mmol) was added. The solution was allowed to warm to ambient temperature where stirring was continued for 12 h. The dark mixture was poured into 200 mL of an aqueous 1 M NaOH solution, extracted with dichloromethane (3 x 30 mL) and dried over MgSO_4 . After filtration and removal of all volatiles the dark precipitate was purified by column chromatography (Silica, 4 x 12 cm column size). The excess of ferrocene was removed using dichloromethane, followed by a 7/3 dichloromethane/THF mixture to remove the product. After removal of all volatiles the title compound was obtained as a brown oil.

Yield: 4.9 g (15 mmol, 79 % based on $^t\text{BuLi}$). Spectroscopic data are in agreement with those reported in literature.¹ ^1H NMR (CDCl_3 , δ in ppm): 1.37 (t, $^3J(\text{H}, \text{H}) = 7.1$ Hz, 6H, CH_3), 4.16 (m, 4H, CH_2), 4.34 (s, 5H, C_5H_5), 4.42 (m, 2H, C_5H_4), 4.54 (m, 2H, C_5H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ in ppm): 16.9 (d, $^3J(\text{C}, \text{P}) = 6.5$ Hz), 62.0 (d, $^2J(\text{C}, \text{P}) = 6$ Hz), 67.3 (d, $^1J(\text{C}, \text{P}) = 215.3$ Hz), 70.2 (s), 71.6 (d, $^2J(\text{C}, \text{P}) = 14.1$ Hz), 71.9 (d, $^3J(\text{C}, \text{P}) = 15.6$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ in ppm): 27.0.

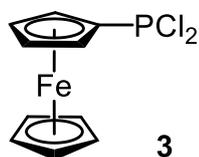
Synthesis of ferrocenylphosphane (**2**)



In a Schlenk tube, **1** (3.00 g, 9.32 mmol) was dissolved in 25 mL of degassed diethyl ether and the solution was cooled to 0 °C using an ice bath. A tablet of LiAlH₄ (~ 600 mg, 15.8 mmol) and ClSiMe₃ (1.2 mL, 9.3 mmol) was added in a single portion and the mixture was allowed to warm to ambient temperature where stirring was continued for 18 h. A water bath was placed under the reaction vessel and ~ 5 mL of degassed water was carefully added. Caution: the initial drops may cause an intense gas formation. Afterwards, degassed H₂SO₄ (*w* = 30%) was added until the pH value turned below 4. The now clear aqueous phase was extracted with degassed diethyl ether under an argon atmosphere until the organic phases stayed colourless. They were dried by filtering them through a plug of MgSO₄ into a Schlenk tube. After washing of the MgSO₄ plug with degassed diethyl ether and removal of all volatiles in vacuo, the title compound was obtained as a red oil, which solidified slowly.

Yield: 2.0 g (9.2 mmol, 97 % based on **1**). Spectroscopic data are in agreement with those reported in literature.² ¹H NMR (CDCl₃, δ in ppm): 4.31–4.29 (m, 4H, C₅H₄), 4.20 (s, 5H, C₅H₅), 3.86 (d, ¹*J*(H, P) = 203 Hz, 2H, PH₂). ¹³C{¹H} NMR (CDCl₃, δ in ppm): 75.7 (d, *J*(C, P) = 14.0 Hz, C₅H₄), 70.7 (d, *J*(C, P) = 3.6 Hz, C₅H₄), 69.3 (s, C₅H₅), 64.1 (d, ¹*J*(C, P) = 4.7 Hz, C–P). ³¹P NMR (CDCl₃, δ in ppm): –143.6 (t, ¹*J*(P, H) = 203 Hz).

Synthesis of dichloro ferrocenylphosphine (**3**)



A solution of compound **2** (2.00 g, 9.17 mmol) and 30 mL of degassed dichloromethane was cooled to –10 °C and a phosgene solution (10 mL, 18.34 mmol in toluene) was dropwise added. After completion of the addition the solution was allowed to warm to ambient temperature where stirring was continued overnight. All volatiles were removed in vacuo **3** was obtained as a red oil, which solidified slowly.

Yield: 2.6 g (9.17 mmol, 99 % based on **2**). Spectroscopic data are in agreement with those reported in literature.² ¹H NMR (CDCl₃, δ in ppm): 4.61–4.59 (m, 4H, CH an C₅H₄), 4.30 (s, 5H, CH an C₅H₅). ¹³C{¹H} NMR (CDCl₃, δ in ppm): 79.5 (d, ¹*J*(C, P) = 52.3 Hz, C–P), 73.3 (d, ³*J*(C, P) = 4.5 Hz, CH an C₅H₄), 71.1 (d, ²*J*(C, P) = 22.5 Hz, CH an C₅H₄), 70.0 (s, CH an C₅H₅). ³¹P NMR (CDCl₃, δ in ppm): 164.6 (s).

Table S1. Crystallographic data for clusters **4** and **5**.

| Compound | 4 | 4 | 5 |
|--|---|---|--|
| CCDC | 1935472 | 1935473 | 1935474 |
| empirical formula | C ₂₉ H ₁₈ Fe ₅ O ₉ P ₂ | C ₂₉ H ₁₈ Fe ₅ O ₉ P ₂ | C ₃₀ H ₁₈ Co ₄ Fe ₂ O ₁₀ P ₂ |
| formula weight | 851.62 g/mol | 851.62 g/mol | 947.8 g/mol |
| temperature | 125(2) K | 300 K | 299 K |
| wavelength | 0.71073 Å | 1.54178 Å | 1.54184 Å |
| crystal system | orthorhombic | orthorhombic | monoclinic |
| space group | <i>Cmc2</i> ₁ | <i>Cmc2</i> ₁ | <i>P2</i> ₁ / <i>c</i> |
| unit cell dimensions | | | |
| <i>a</i> / Å | 20.5877(7) | 20.7092(17) | 10.267(5) |
| <i>b</i> / Å | 15.1700(6) | 15.4436(13) | 10.871(5) |
| <i>c</i> / Å | 9.6197(3) | 9.6876(8) | 14.812(5) |
| α / ° | 90 | 90 | 90 |
| β / ° | 90 | 90 | 107.563(5) |
| γ / ° | 90 | 90 | 90 |
| volume / Å ³ | 3004.38(18) | 3098.3(4) | 1576.1(12) |
| <i>Z</i> | 4 | 4 | 2 |
| Density / Mg/m ³ | 1.883 | 1.826 | 1.997 |
| absorption coefficient / mm ⁻¹ | 2.517 | 19.767 | 24.758 |
| <i>F</i> (000) | 1696 | 1696 | 936 |
| crystal size /mm | 0.2 x 0.2 x 0.2 | 0.20 x 0.20 x 0.10 | 0.10 x 0.10 x 0.10 |
| θ range for data collection | 3.258–25.996° | 3.570–65.489° | 5.135–65.499° |
| | –25 ≤ <i>h</i> ≤ 25 | –24 ≤ <i>h</i> ≤ 23 | –11 ≤ <i>h</i> ≤ 12 |
| limiting indices | –18 ≤ <i>k</i> ≤ 18 | –18 ≤ <i>k</i> ≤ 18 | –12 ≤ <i>k</i> ≤ 12 |
| | –11 ≤ <i>l</i> ≤ 11 | –11 ≤ <i>l</i> ≤ 11 | –17 ≤ <i>l</i> ≤ 17 |
| collected reflections | 12938 | 10204 | 24910 |
| independent reflections | 3012 | 2508 | 2689 |
| <i>R</i> (int) | 0.0303 | 0.0579 | 0.0426 |
| completeness to θ | 99.50% | 99.30% | 99.30% |
| data/restraints/parameters | 3012 / 1 / 217 | 2508 / 1 / 218 | 2689 / 0 / 217 |
| goodness-of-fit on <i>F</i> ² | 1.021 | 1.128 | 1.112 |
| $\Delta\rho_{\max}$; $\Delta\rho_{\min}$ / eÅ ⁻³ | 0.278; –0.178 | 0.426; –0.433 | 0.283; –0.270 |
| <i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)] | 0.0174 | 0.0421 | 0.0245 |
| ωR_2 (all data) | 0.0420 | 0.0992 | 0.0561 |
| abs. struct. parameter ³ | –0.007(8) | 0.075(13) | – |

References

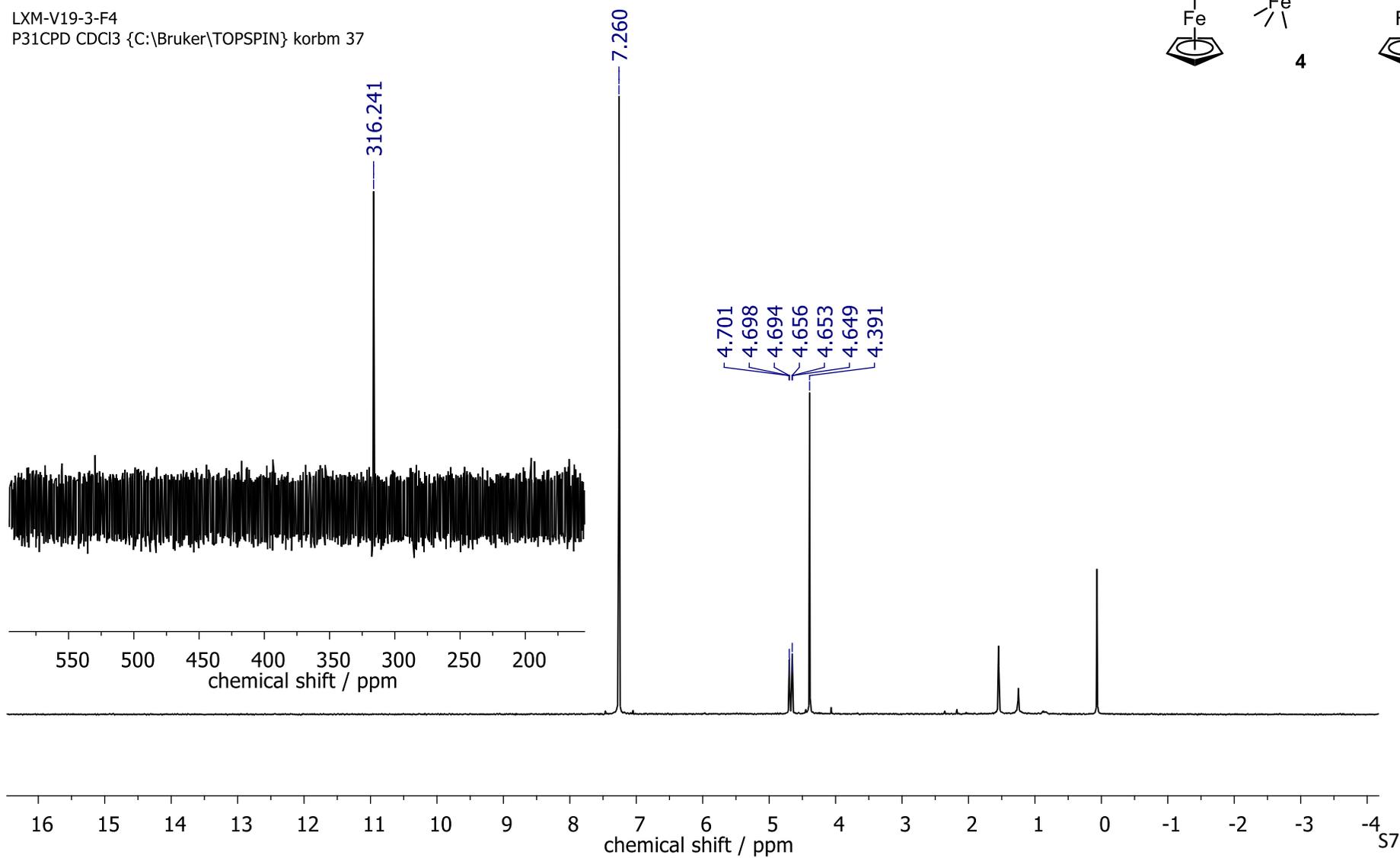
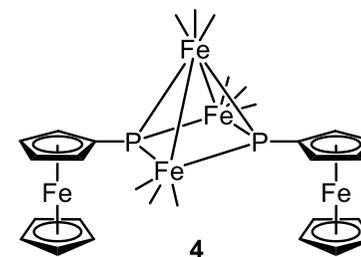
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^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of new compounds 4 and 5

^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of 4

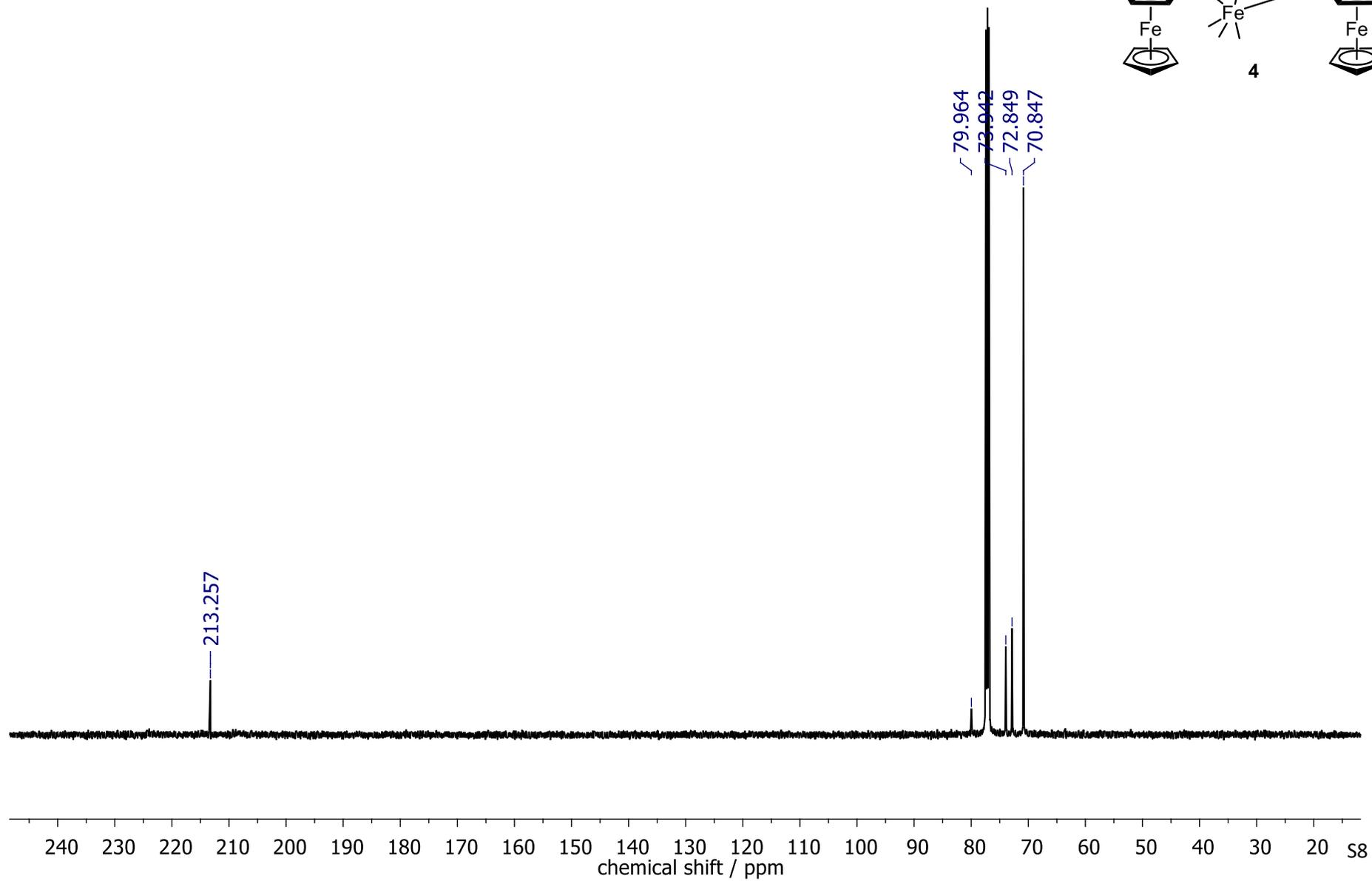
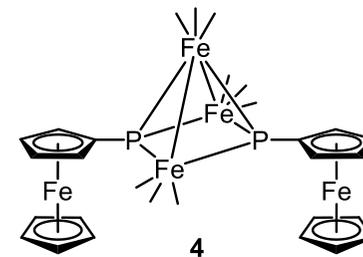
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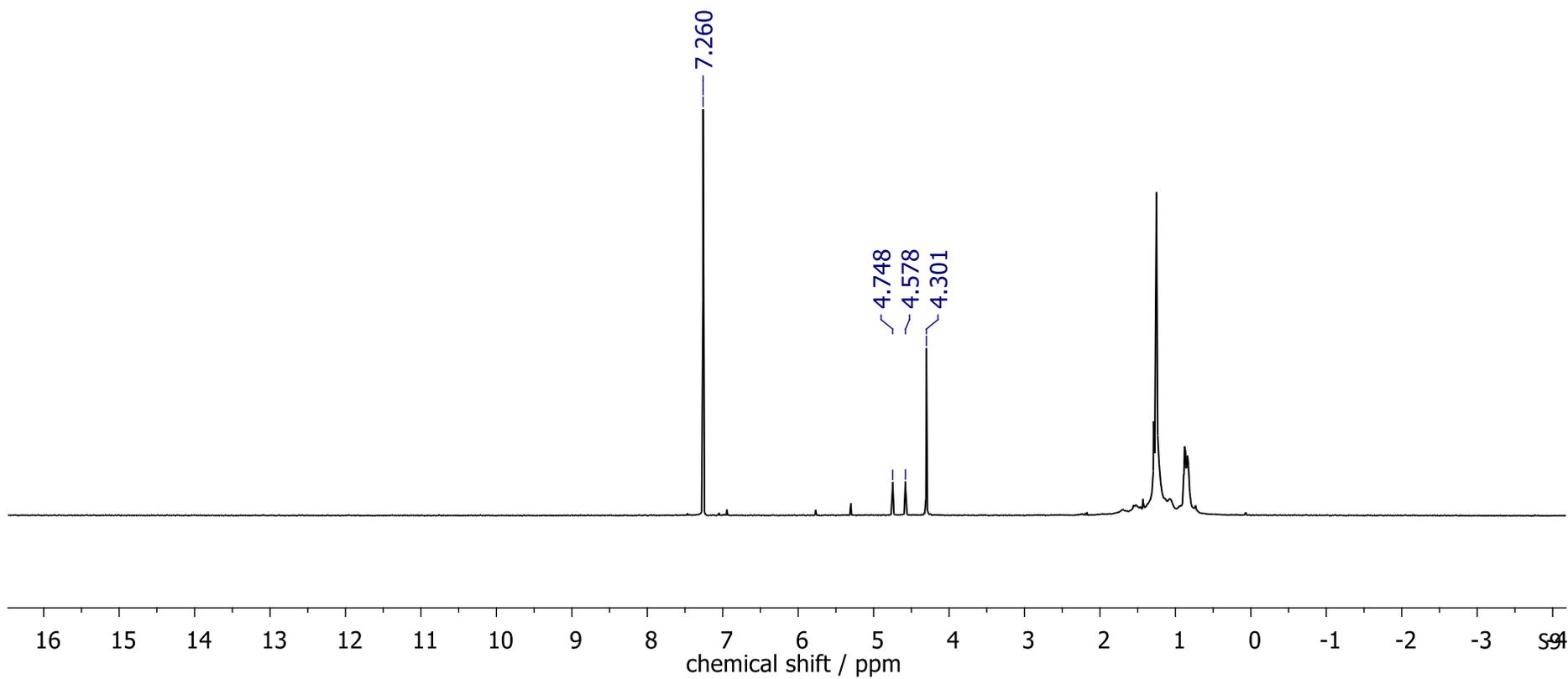
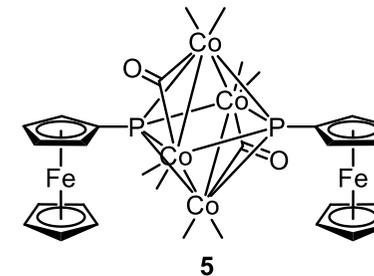
$^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 4

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^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of 5

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PROTON CDCl₃ {C:\Bruker\TOPSPIN} korbm 25



$^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 5

LXM-V21-F2
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