

Supporting Information

CO Substitution by PPh₃ in Fe₂S₂(CO)₆ Proceeds via a Novel Fe₂S Intermediate

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I. General Information

Manipulations were conducted using standard Schlenk-line techniques or an MBraun glovebox under N₂ atmosphere. Solvents were deoxygenated by N₂ sparging and purified by passage through an activated alumina column using solvent purification system. ¹H (500 MHz) and ³¹P{¹H} (202 MHz) NMR spectra were recorded on Varian VXR500 or U500 spectrometer. Chemical shifts (δ/ppm) were referenced to residual solvent peaks (for ¹H) or external 85% H₃PO₄ (for ³¹P). Solution IR spectra were recorded on a PerkinElmer Spectrum 100 FTIR spectrometer. Elemental analysis was performed utilizing an Exeter CE-440 elemental Analyzer. A Waters Micromass Quattro II spectrometer was used to acquire ESI-MS data for analytes. Crystallographic data were collected using a Siemens SMART diffractometer equipped with a Mo Kα source (λ = 0.71073 Å) and an Apex II detector. All chemicals were purchased from commercial sources and used without further purification. CD₂Cl₂ was degassed by three times freeze-pump-thaw and dried using 4Å molecular sieves. Fe₂(μ-S)₂(CO)₆ were prepared according to the literature methods.¹

References

1. a) Bogan, L. E.; Lesch, D. A.; Rauchfuss, T. B. Synthesis of Heterometallic Cluster Compounds from Fe₃(μ₃-Te)₂(CO)₉ and Comparisons with Analogous Sulfide Clusters. *J. Organomet. Chem.* 1983, 250, 429–438; b) Seyferth, D.; Henderson, R. S.; Song, L.-C. Chemistry of μ-Dithio-bis(tricarbonyliron), a Mimic of Inorganic Disulfides. 1. Formation of Di-μ-thiolato-bis(tricarbonyliron) Dianion. *Organometallics* 1982, 1, 125–133.

II. Preparation, Characterization and Reactivities

Reaction of $\text{Fe}_2(\mu\text{-S})_2(\text{CO})_6$ with 2 equivalents of PPh_3 . $\text{Fe}_2(\mu\text{-S})_2(\text{CO})_6$ (35 mg, 0.1 mmol) and PPh_3 (53 mg, 0.2 mmol) were dissolved in 5 mL THF in a vial under N_2 . It was stirred at rt and detected by ^{31}P NMR, which show full conversion of $\text{Fe}_4\text{S}_3(\text{CO})_8(\text{PPh}_3)_3$ after 4 h, gave $\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_4(\text{PPh}_3)_2$ as the product. The yield was determined to be 54% using $\text{O}=\text{PPh}_3$ as internal standard.

$\text{Fe}_2(\mu\text{-S})(\text{CO})_6(\text{PPh}_3)_2$ (4). $\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_6$ (150 mg, 0.44 mmol) and PPh_3 (229 mg, 0.87 mmol) were dissolved in 5 mL THF ($-30\text{ }^\circ\text{C}$) in a vial under N_2 . Then 20 mL hexanes was layered on top of the solution, and the vial was kept at $-30\text{ }^\circ\text{C}$ for 2 days to gave red precipitates. It was filtered, washed with hexanes for 3 times and dried under vacuum. $\text{Fe}_2\text{S}(\text{CO})_6(\text{PPh}_3)_2$ was obtained as red microcrystals in the yield of 59% (215 mg). ^1H NMR (600 MHz, CD_2Cl_2): δ 7.62, m, 7.46, m. ^{31}P NMR (202 MHz): δ 64.9. IR (THF): ν_{CO} = 2033 w, 1971 vs, 1950 sh, 1915 w. Anal. Calcd for $[\text{C}_{42}\text{H}_{30}\text{Fe}_2\text{O}_6\text{P}_2\text{S} + \text{THF}]$: C, 60.82; H, 4.22; Found: C, 60.87; H, 3.91; ESI-MS m/z calcd for $[\text{Fe}_2\text{S}(\text{CO})_6(\text{PPh}_3)_2 + \text{H}^+]$, 837.0015. Found, 837.0038. Single crystals suitable for X-ray diffraction study were grown by slow diffusion of pentane into a THF solution at $-30\text{ }^\circ\text{C}$.

Reaction of $\text{Fe}_2(\mu\text{-S})(\text{CO})_6(\text{PPh}_3)_2$ with 1 equivalent of $\text{S}=\text{PPh}_3$. $\text{Fe}_2(\mu\text{-S})(\text{CO})_6(\text{PPh}_3)_2$ (26 mg, 0.03 mmol) and $\text{S}=\text{PPh}_3$ (9.0 mg, 0.03 mmol) were dissolved in 2 mL THF in a vial under N_2 . It was stirred at rt and detected by ^{31}P NMR, which show full conversion of $\text{Fe}_2(\mu\text{-S})(\text{CO})_6(\text{PPh}_3)_2$ and $\text{S}=\text{PPh}_3$ after 2 h, gave $\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_4(\text{PPh}_3)_2$ as the product. The yield was determined to be 66% using $\text{O}=\text{PPh}_3$ as internal standard.

Protonation of $\text{Fe}_2(\mu\text{-S})(\text{CO})_6(\text{PPh}_3)_2$ with HOTf. $\text{Fe}_2(\mu\text{-S})(\text{CO})_6(\text{PPh}_3)_2$ (51 mg, 0.06 mmol) in 2 mL CH_2Cl_2 was treated with HOTf (9.2 mg, 0.06 mmol) at rt. After stirring for 20 min, 20 mL pentane was added to give red precipitates. It was filtered, washed with pentane and dried under vacuum. Recrystallization from CH_2Cl_2 /pentane gave $[\text{Fe}_2(\mu\text{-SH})(\text{CO})_6(\text{PPh}_3)_2]\text{OTf}$ (**[H4]OTf**) as red solid in the yield of 78% (47 mg). ^1H NMR (500 MHz, CD_2Cl_2): δ 7.63-7.59 (m, 30 H), 1.96 (s, 1H). ^{31}P NMR (202 MHz): δ 51.8. ESI-MS m/z calcd for $[\text{Fe}_2\text{SH}(\text{CO})_6(\text{PPh}_3)_2]^+$, 837.0; Found, 836.9. IR (CH_2Cl_2): ν_{CO} = 2089 w, 2046w, 2023 vs. Anal. Calcd for $[\text{C}_{43}\text{H}_{31}\text{F}_3\text{Fe}_2\text{O}_9\text{P}_2\text{S}_2 + \text{CH}_2\text{Cl}_2]$: C, 49.33; H, 3.10; Found: C, 49.6; H, 3.41. Single crystals suitable for X-ray diffraction study were grown by slow diffusion of pentane into a CH_2Cl_2 solution at -30°C .

Methylation of $\text{Fe}_2(\mu\text{-S})(\text{CO})_6(\text{PPh}_3)_2$ with MeOTf. $\text{Fe}_2(\mu\text{-S})(\text{CO})_6(\text{PPh}_3)_2$ (34 mg, 0.04 mmol) in 2 mL CH_2Cl_2 was treated with MeOTf (6.6 mg, 0.04 mmol) at rt. The mixture was stirred at rt for 20 min and filtered through a short pad of celite. 10 mL pentane was added to precipitate the product as red solid. Recrystallization from CH_2Cl_2 /diethyl ether gave $[\text{Fe}_2(\mu\text{-SMe})(\text{CO})_6(\text{PPh}_3)_2]\text{OTf}$ (**[Me4]OTf**) as microcrystals in the yield of 86% (36 mg). ^1H NMR (500 MHz, CD_2Cl_2): δ 7.65-7.60 (m, 30 H), 1.10 (s, 3H). ^{31}P NMR (202 MHz): δ 50.9. ESI-MS m/z calcd for $[\text{Fe}_2\text{SMe}(\text{CO})_6(\text{PPh}_3)_2]^+$, 851.0; Found, 850.9. IR (CH_2Cl_2): ν_{CO} = 2085 w, 2042 w, 2019 vs. Anal. Calcd for $\text{C}_{44}\text{H}_{33}\text{F}_3\text{Fe}_2\text{O}_9\text{P}_2\text{S}_2$: C, 52.82; H, 3.32; Found: C, 52.48; H, 3.25. Single crystals suitable for X-ray diffraction study were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution at -30°C .

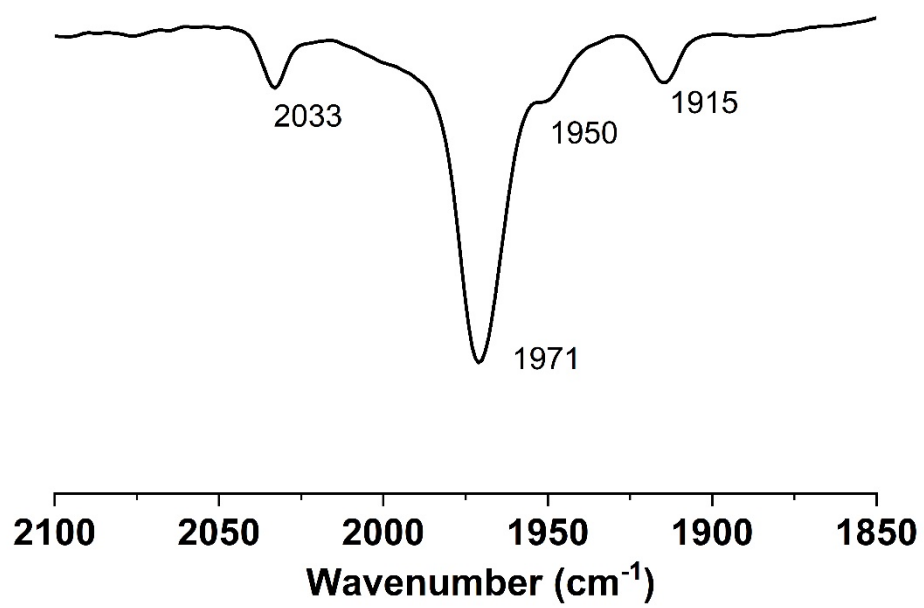


Figure S1. IR spectrum of $\text{Fe}_2(\mu\text{-S})(\text{CO})_6(\text{PPh}_3)_2$ (**4**) in THF solution.

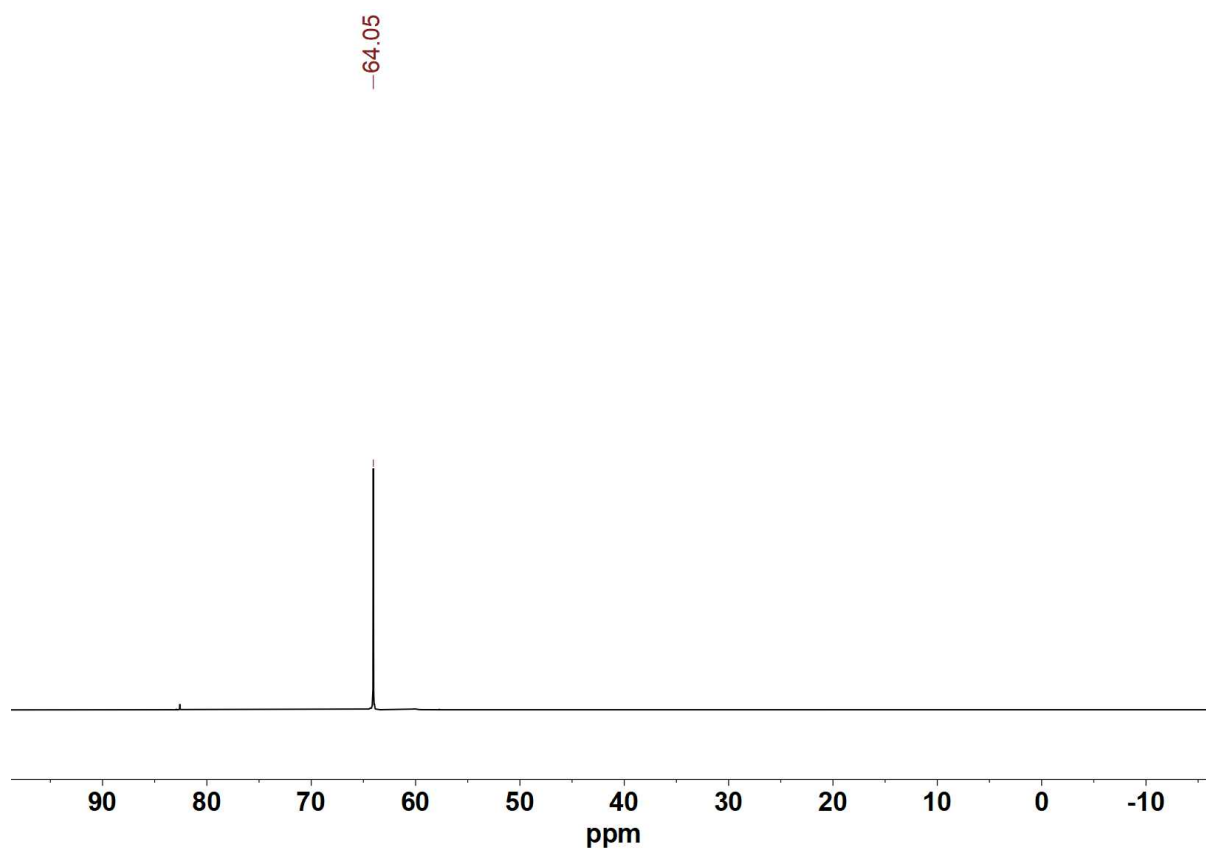


Figure S2. ^{31}P NMR spectrum of $\text{Fe}_2(\mu\text{-S})(\text{CO})_6(\text{PPh}_3)_2$ (**4**) in CD_2Cl_2 solution.

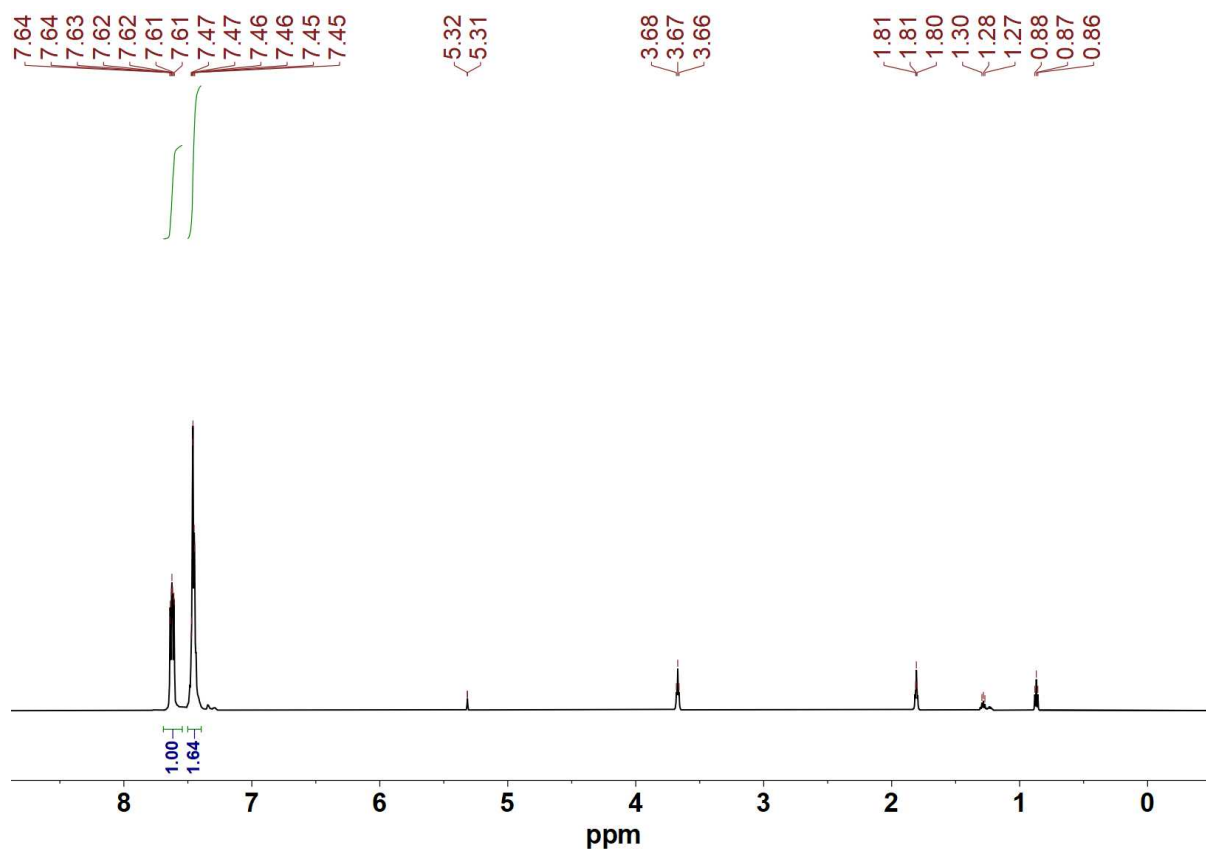


Figure S3. ^1H NMR spectrum of $\text{Fe}_2(\mu\text{-S})(\text{CO})_6(\text{PPh}_3)_2$ (**4**) in CD_2Cl_2 solution.

Assignment: THF (δ 3.67, 1.81), pentane (δ 1.28, 0.87).

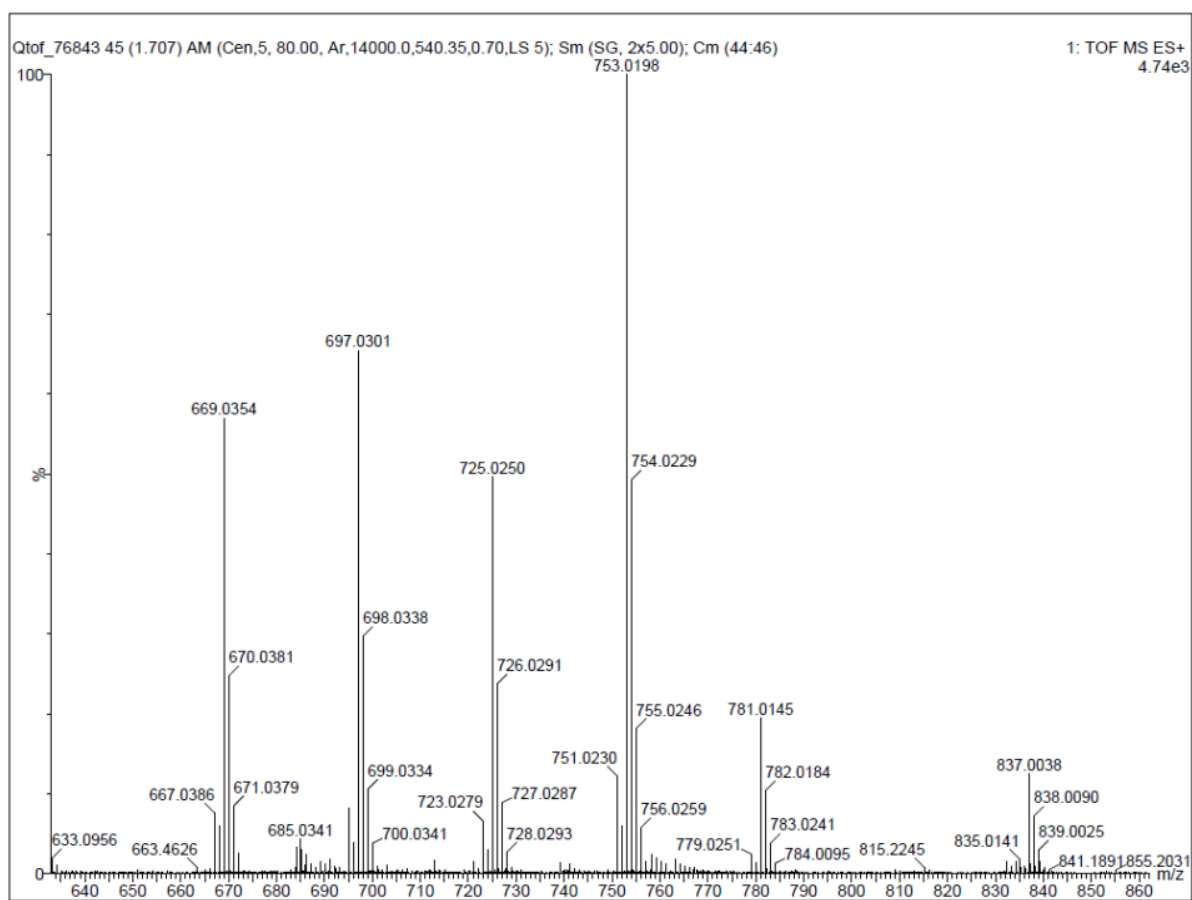


Figure S4. HR-ESI spectrum of $\text{Fe}_2(\mu\text{-S})(\text{CO})_6(\text{PPh}_3)_2$ (**4**) in THF solution.

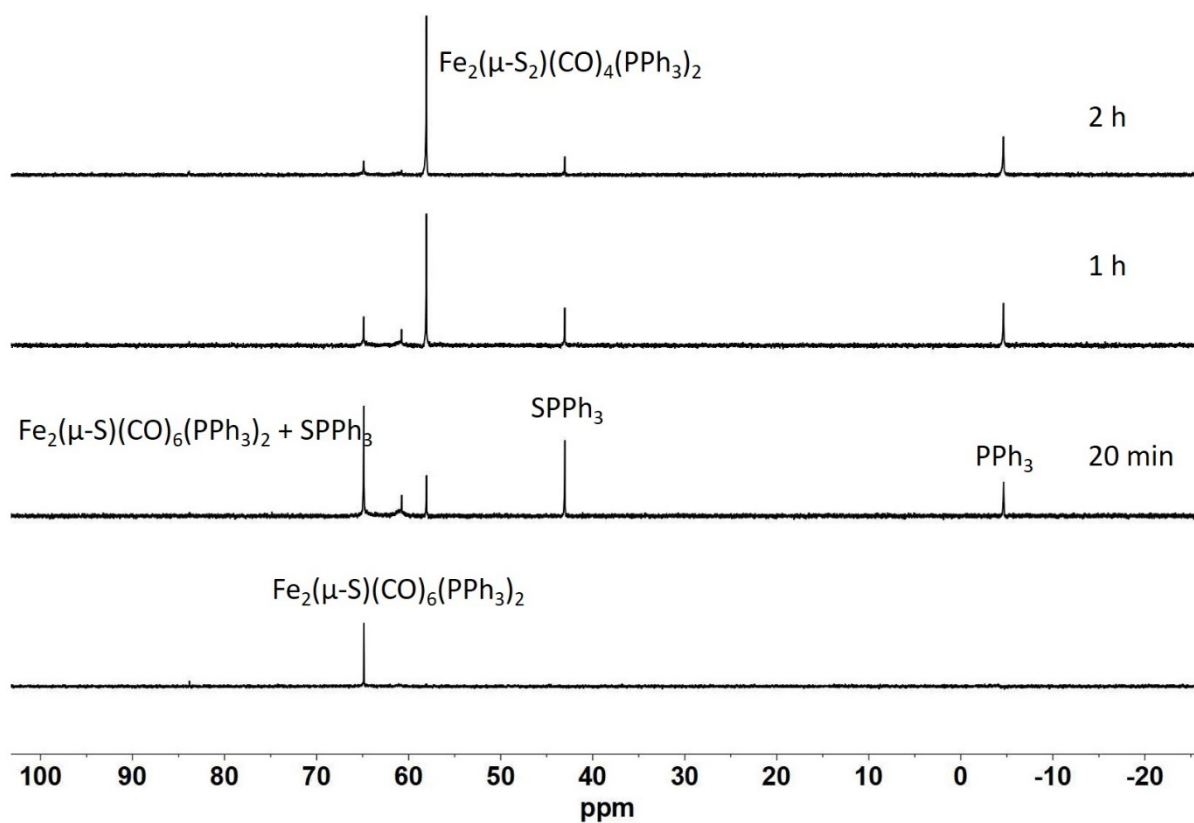


Figure S5. ^{31}P NMR spectrum of $\text{Fe}_2(\mu\text{-S})(\text{CO})_6(\text{PPh}_3)_2 + \text{S}=\text{PPh}_3$ (1 : 1) in THF solution vs time at rt.

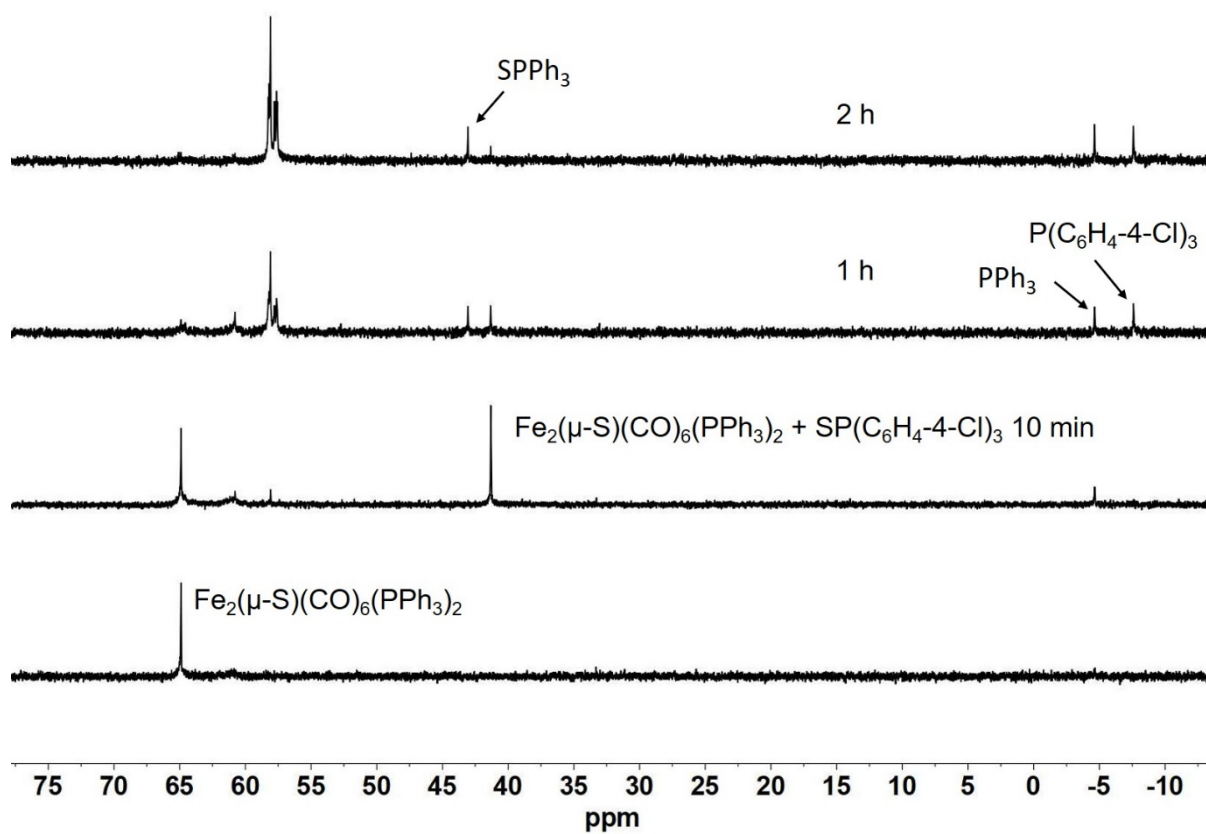


Figure S6. ^{31}P NMR spectrum of $\text{Fe}_2(\mu\text{-S})(\text{CO})_6(\text{PPh}_3)_2 + \text{S}=\text{P}(\text{C}_6\text{H}_4\text{-4-Cl})_3$ (1 : 1) in THF solution vs time at rt.

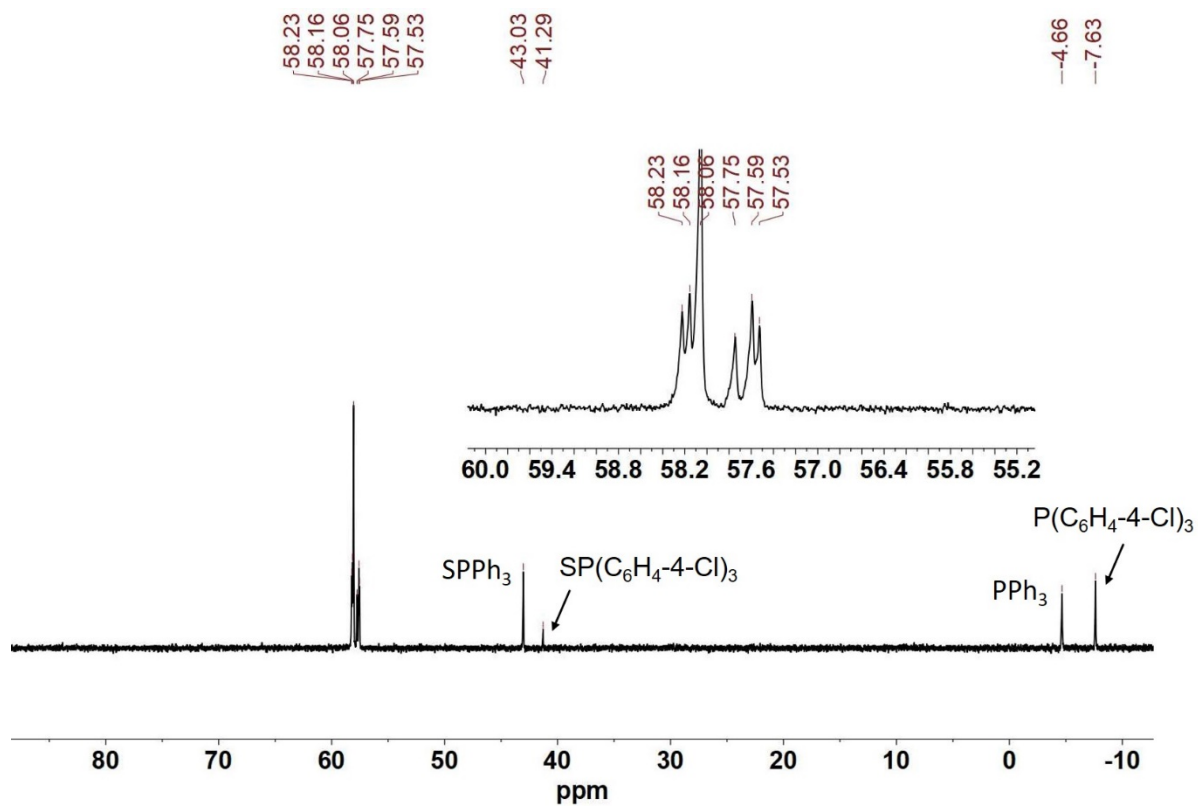


Figure S7. ^{31}P NMR spectrum of $\text{Fe}_2(\mu\text{-S})(\text{CO})_6(\text{PPh}_3)_2 + \text{S}=\text{P}(\text{C}_6\text{H}_4\text{-4-Cl})_3$ (1 : 1) in THF solution for 2 h at rt.

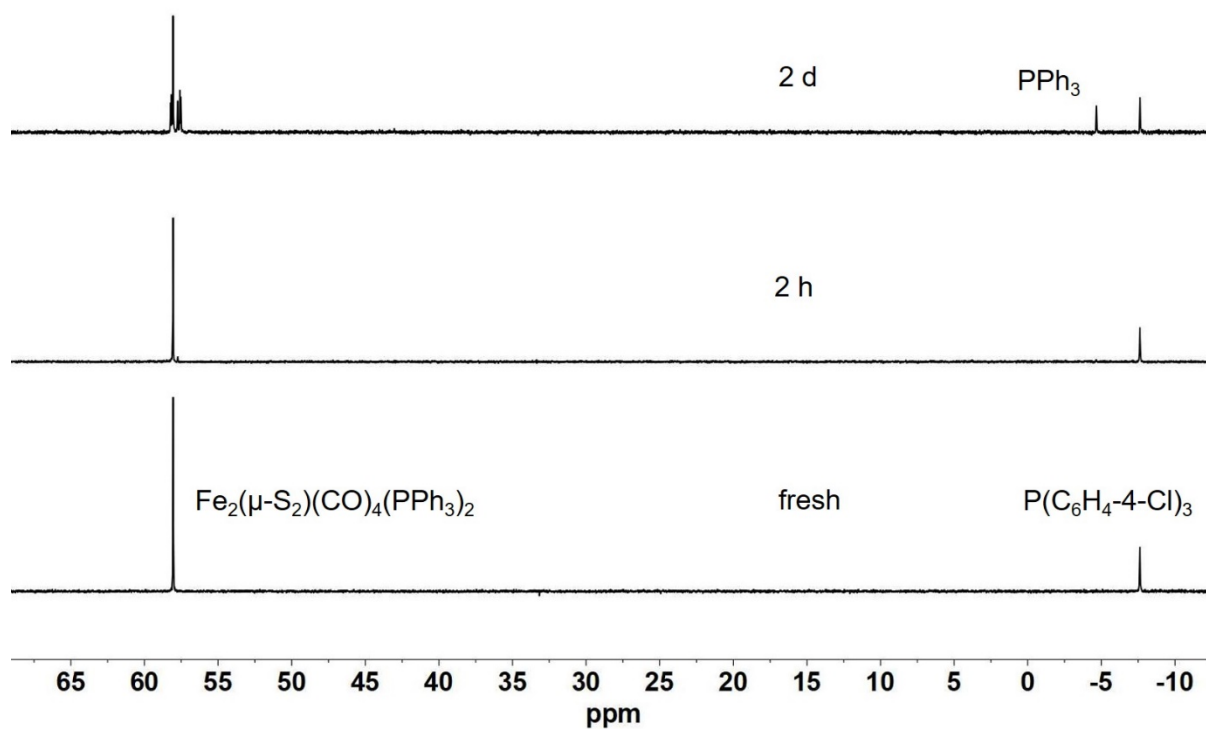


Figure S8. ^{31}P NMR spectrum of $\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_4(\text{PPh}_3)_2 + \text{P}(\text{C}_6\text{H}_4\text{-4-Cl})_3$ (1 : 1) in THF solution vs t at rt.

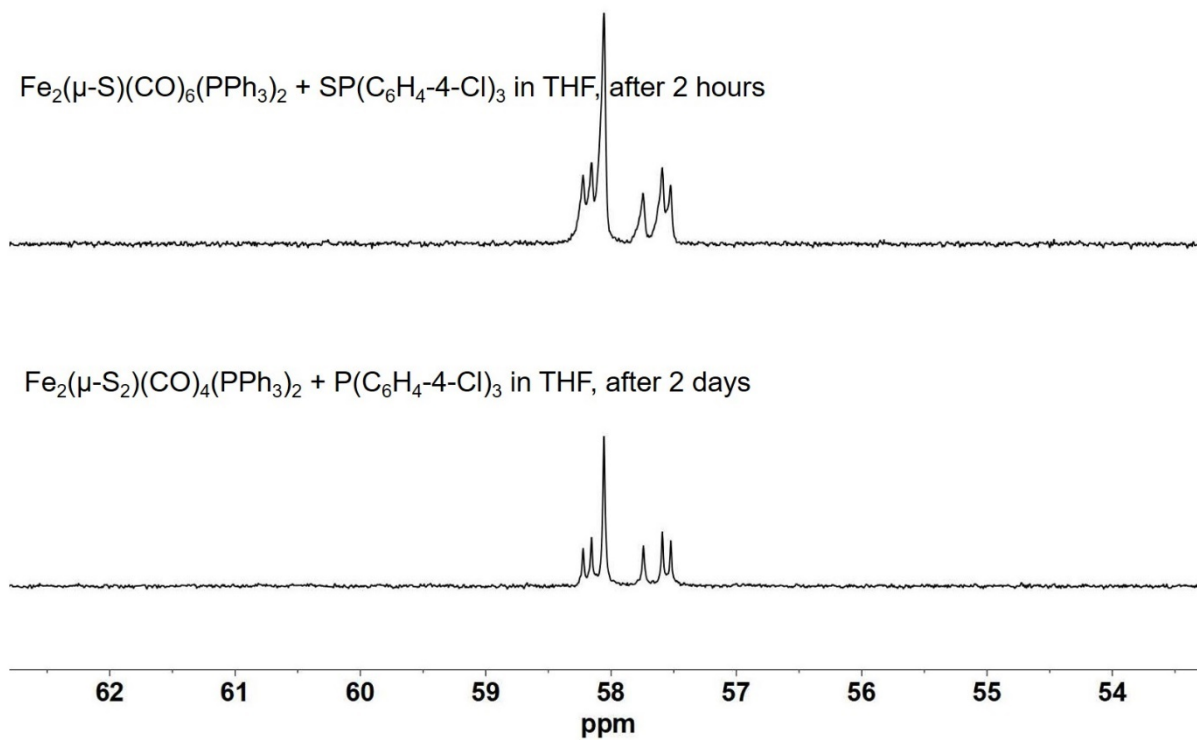


Figure S9. Exemplified ^{31}P NMR spectrum of $\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_4(\text{PPh}_3)_2 + \text{P}(\text{C}_6\text{H}_4\text{-4-Cl})_3$ in THF after 2 days and $\text{Fe}_2(\mu\text{-S})(\text{CO})_6(\text{PPh}_3)_2 + \text{SP}(\text{C}_6\text{H}_4\text{-4-Cl})_3$ in THF for 2 hours.

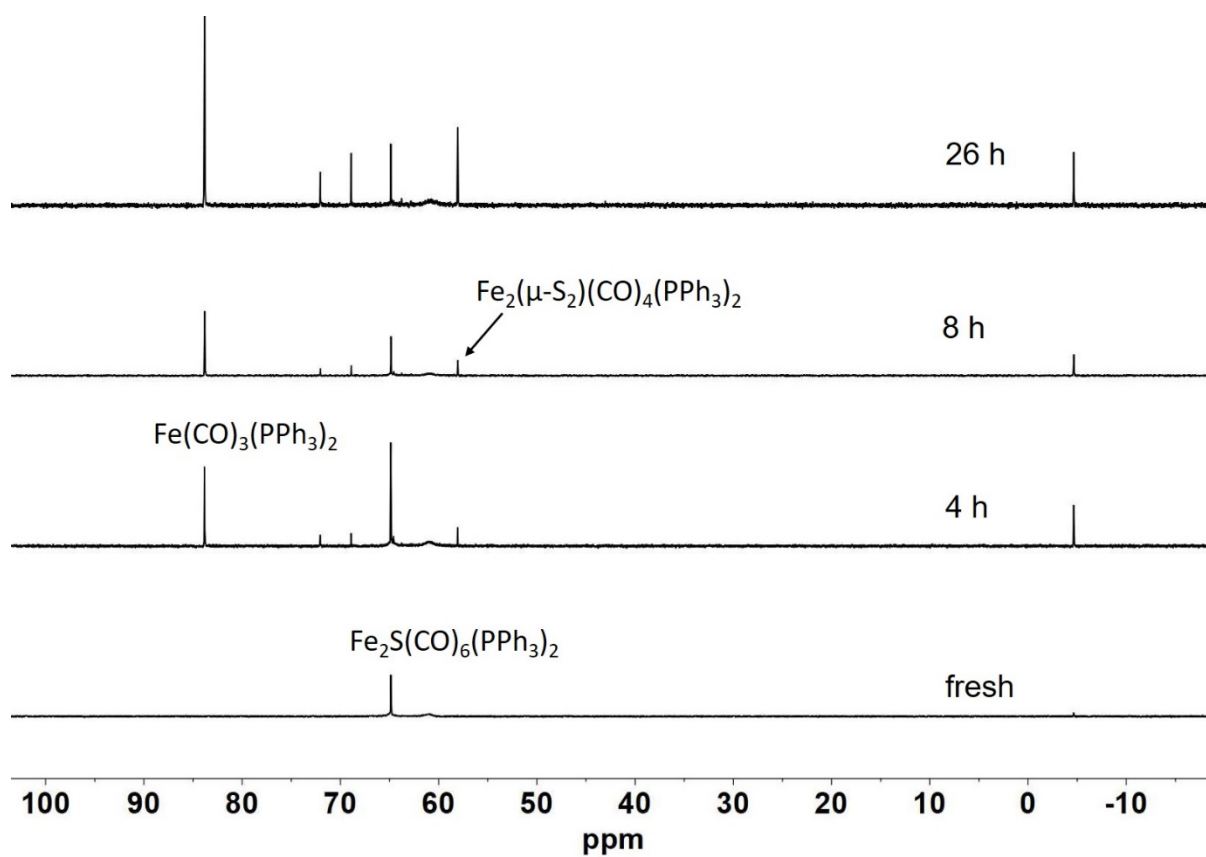


Figure S10. ^{31}P NMR spectrum of $\text{Fe}_2(\mu\text{-S})(\text{CO})_6(\text{PPh}_3)_2$ (**4**) in THF solution vs time.

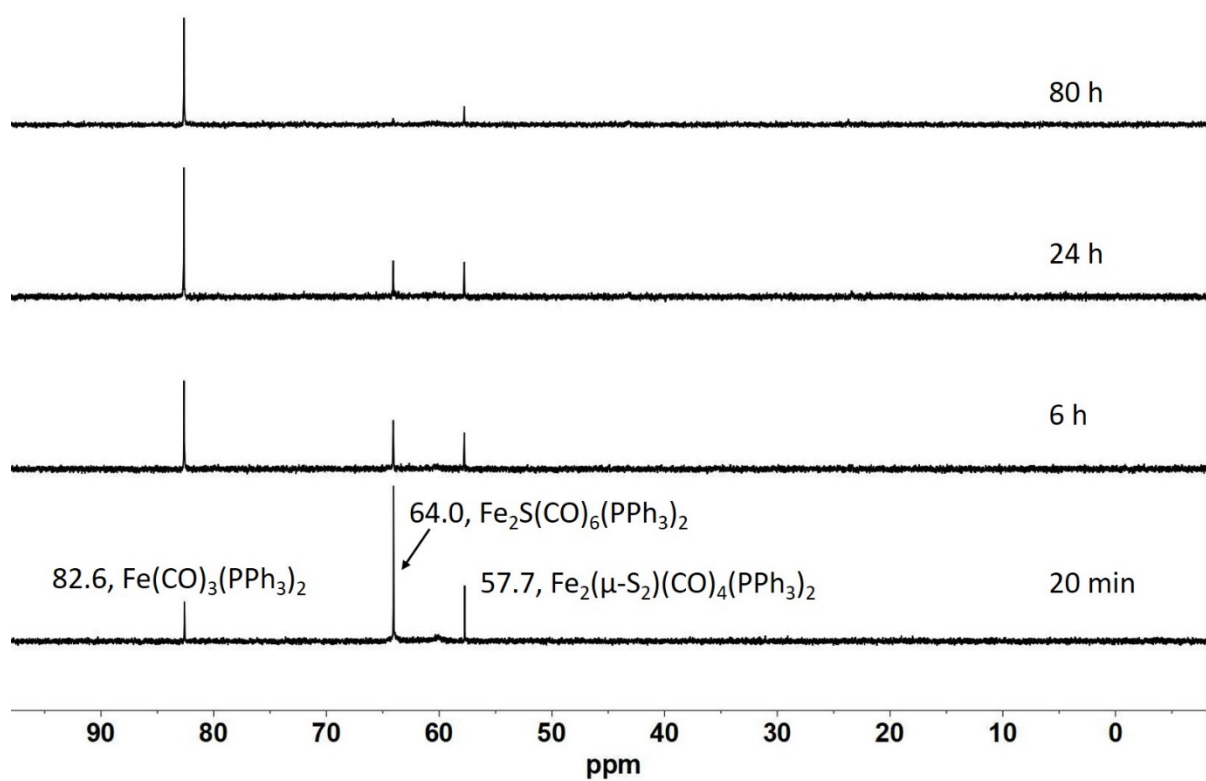


Figure S11. ^{31}P NMR spectrum of $\text{Fe}_2(\mu\text{-S})(\text{CO})_6(\text{PPh}_3)_2$ (**4**) in CH_2Cl_2 solution vs time.

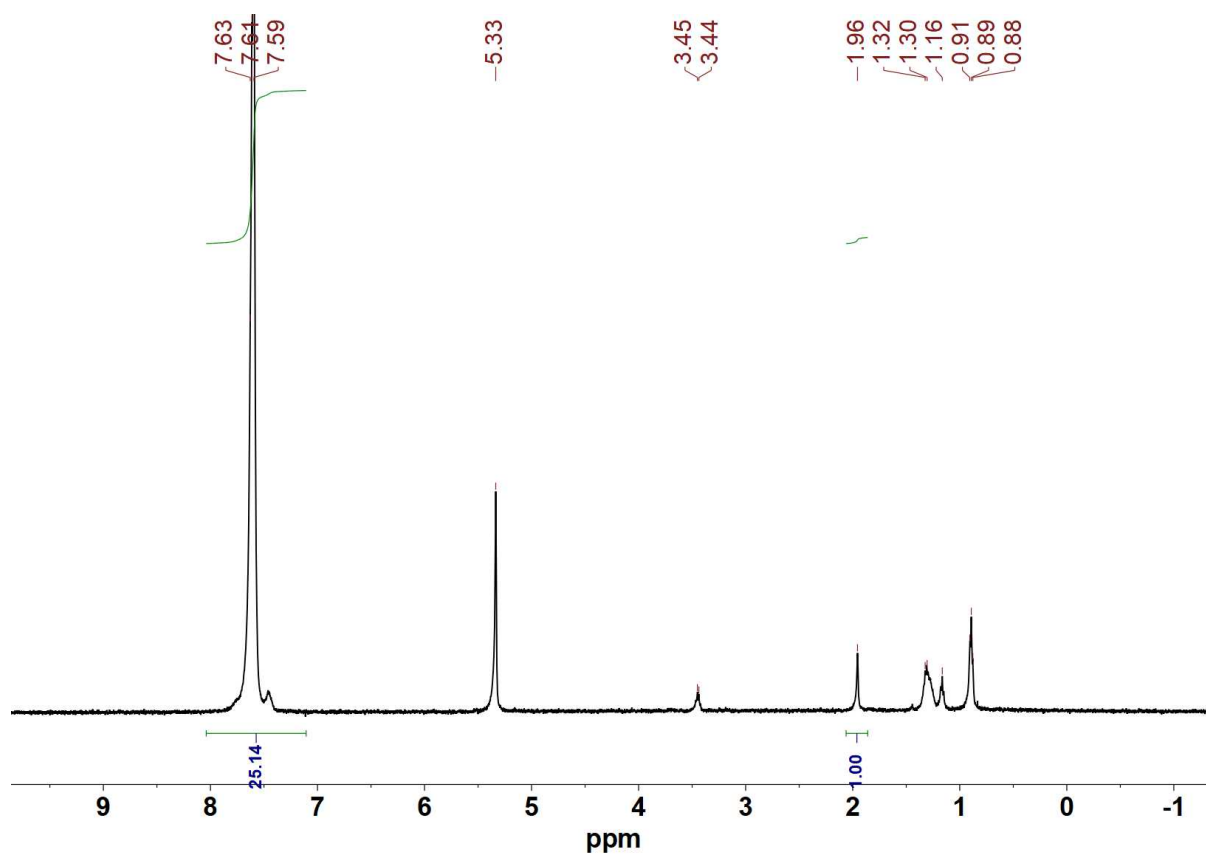


Figure S12. ^1H NMR spectrum of $[\text{Fe}_2(\mu\text{-SH})(\text{CO})_6(\text{PPh}_3)_2]\text{OTf}$ ($[\text{H4}]\text{OTf}$) in CD_2Cl_2 solution.
Assignment: diethyl ether (δ 3.44, 1.16), pentane (δ 1.32, 0.89).

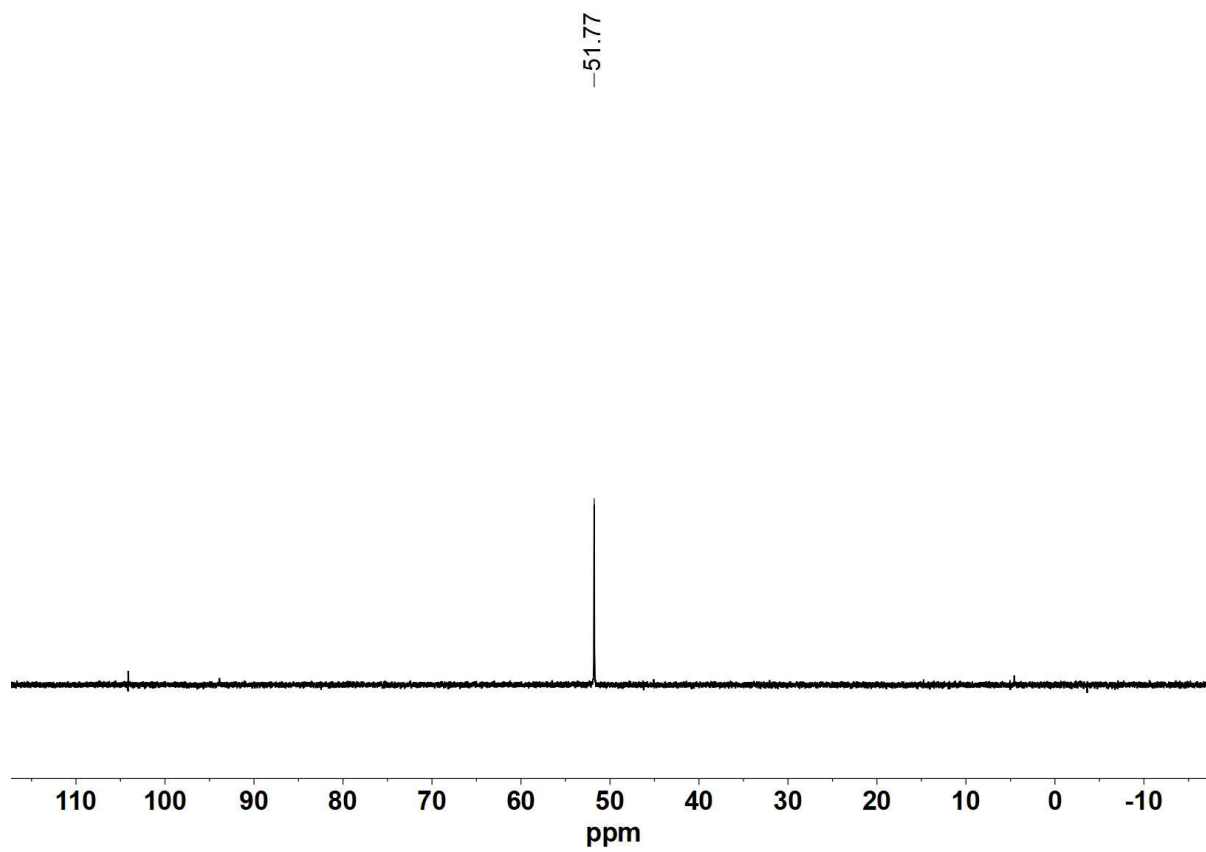


Figure S13. ^{31}P NMR spectrum of $[\text{Fe}_2(\mu\text{-SH})(\text{CO})_6(\text{PPh}_3)_2]\text{OTf}$ ($[\text{H}_4]\text{OTf}$) in CD_2Cl_2 solution.

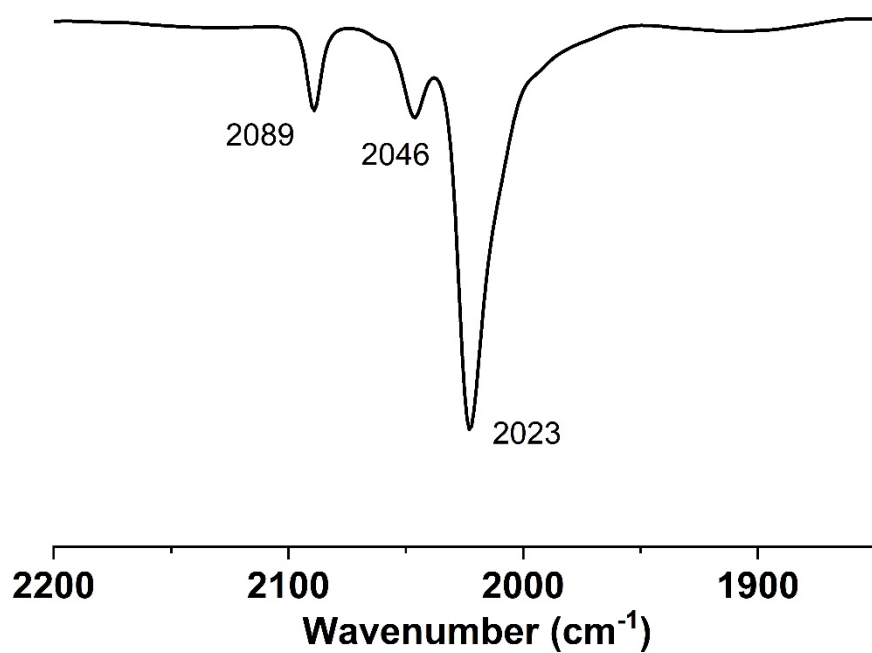


Figure S14. IR spectrum of $[\text{Fe}_2(\mu\text{-SH})(\text{CO})_6(\text{PPh}_3)_2]\text{OTf}$ ($[\text{H}_4]\text{OTf}$) in CH_2Cl_2 solution.

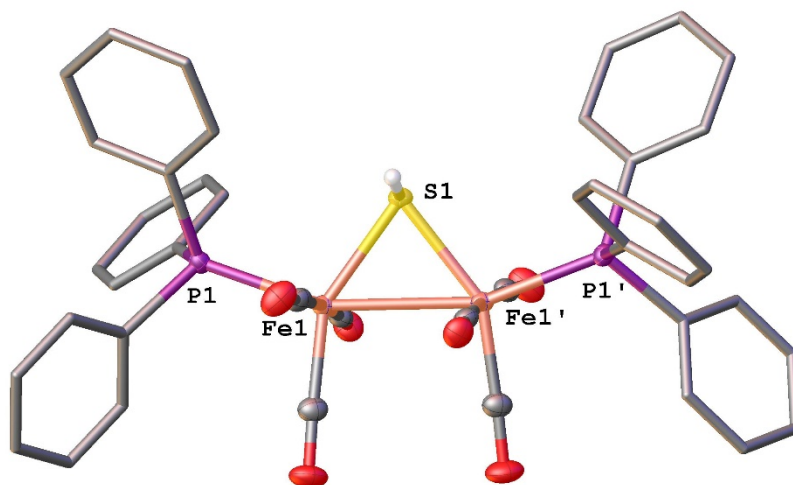


Figure S15. ORTEP of the $[\text{Fe}_2(\mu\text{-SH})(\text{CO})_6(\text{PPh}_3)_2]\text{OTf}$ ($[\text{H4}]\text{OTf}$). Thermal ellipsoids are drawn at 50% probability. The anion CF_3SO_3^- and hydrogen atoms except for SH are omitted for clarity. Selected bond lengths (\AA): Fe1-Fe1', 2.7089(10); Fe1-S1, 2.2612(11); Fe1-P1, 2.2701(10). Selected angles ($^\circ$): Fe1-S1-Fe1', 73.59(4); S1-Fe1-Fe1', 53.20(2).

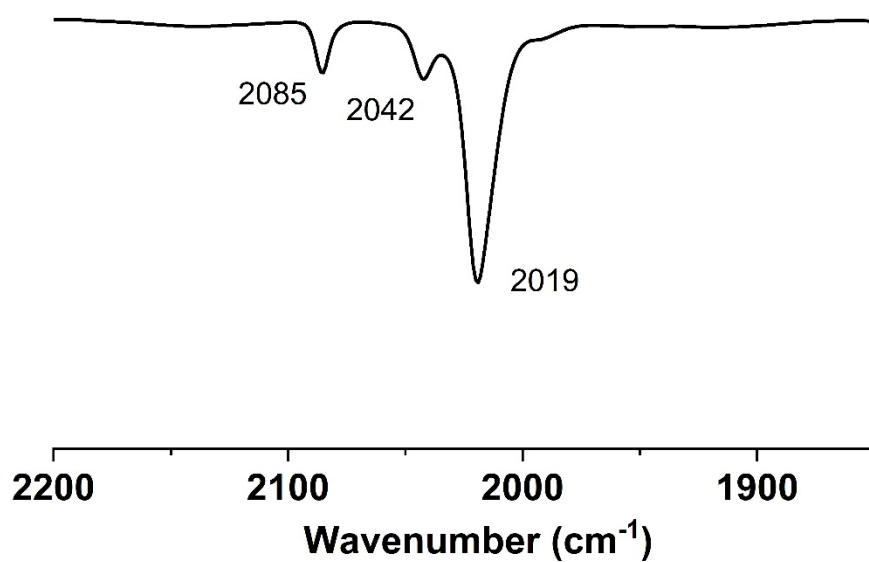


Figure S16. IR spectrum of $[\text{Fe}_2(\mu\text{-SMe})(\text{CO})_6(\text{PPh}_3)_2]\text{OTf}$ (**[Me4]OTf**) in CH_2Cl_2 solution.

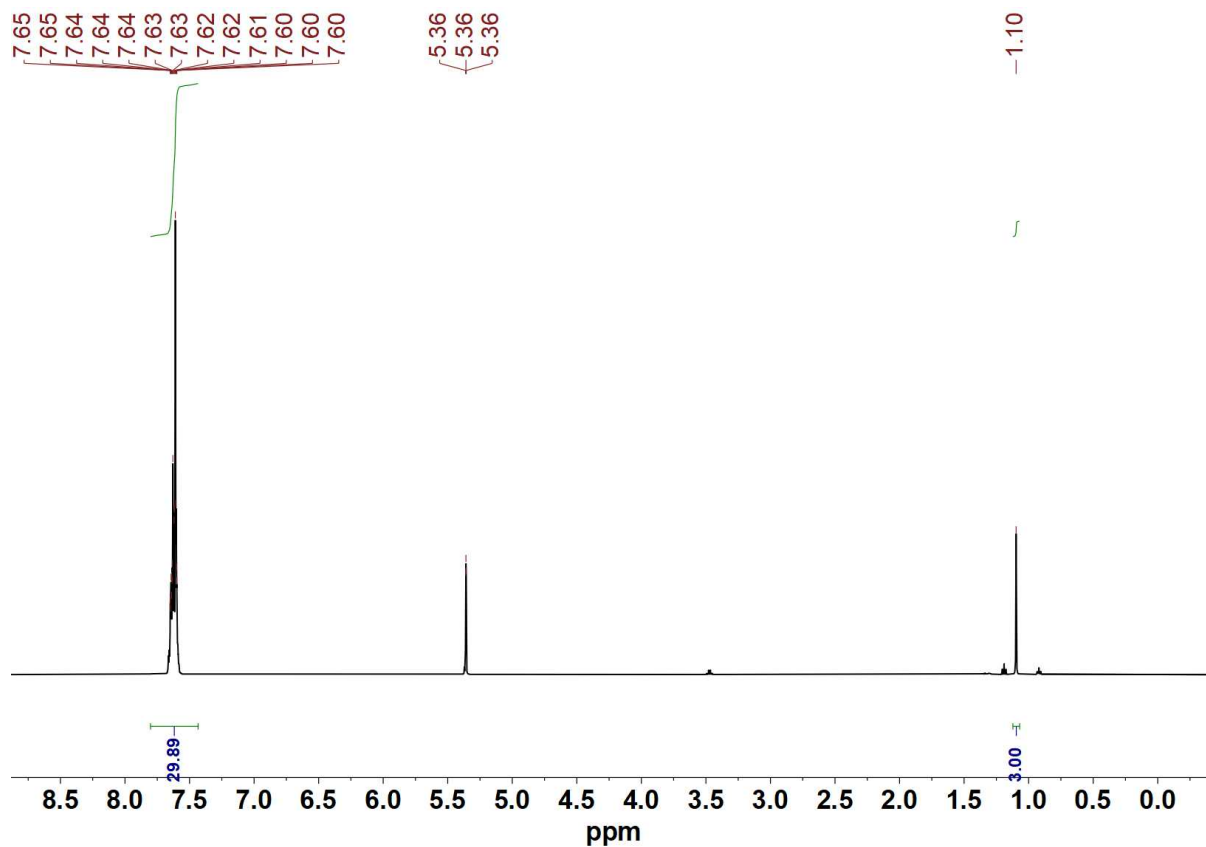


Figure S17. ^1H NMR spectrum of $[\text{Fe}_2(\mu\text{-SMe})(\text{CO})_6(\text{PPh}_3)_2]\text{OTf}$ ($[\text{Me}_4]\text{OTf}$) in CD_2Cl_2 solution.

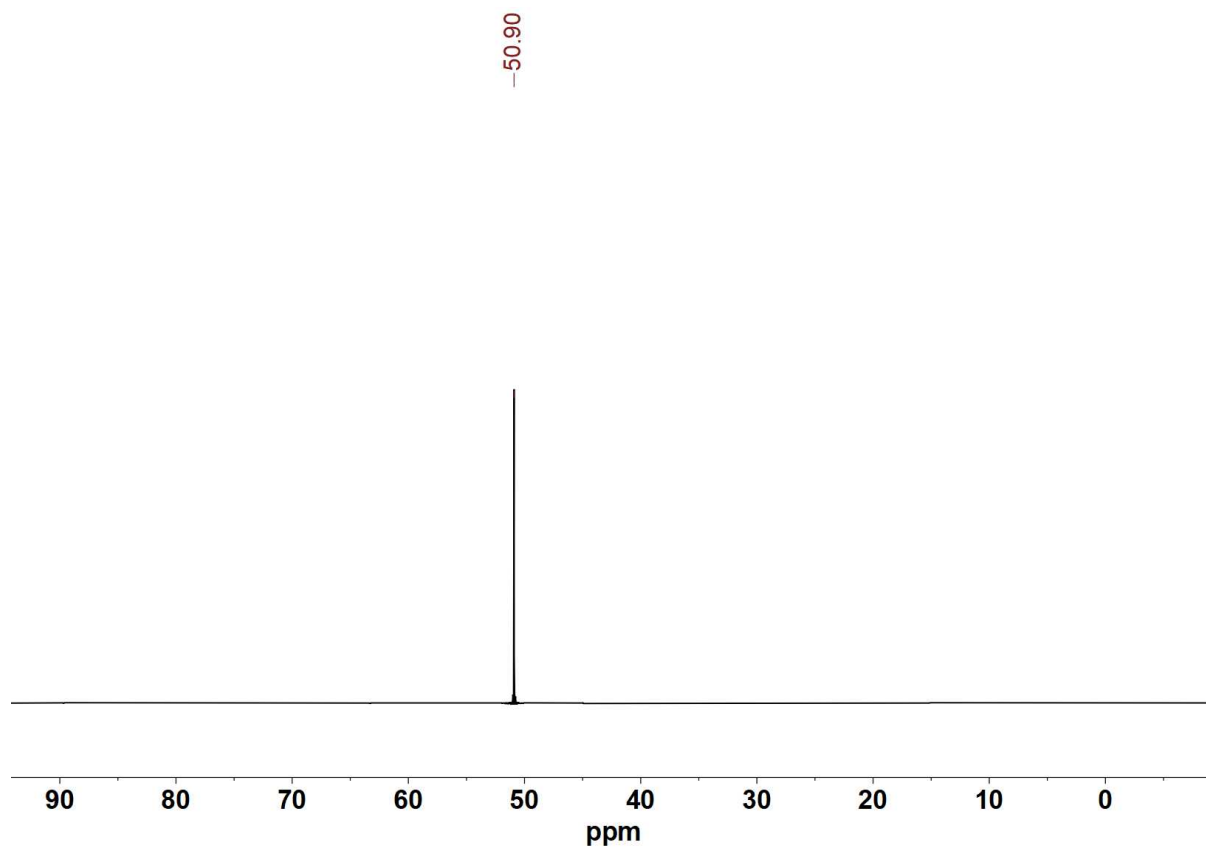


Figure S18. ^{31}P NMR spectrum of $[\text{Fe}_2(\mu\text{-SMe})(\text{CO})_6(\text{PPh}_3)_2]\text{OTf}$ (**[Me4]OTf**) in CD_2Cl_2 solution.

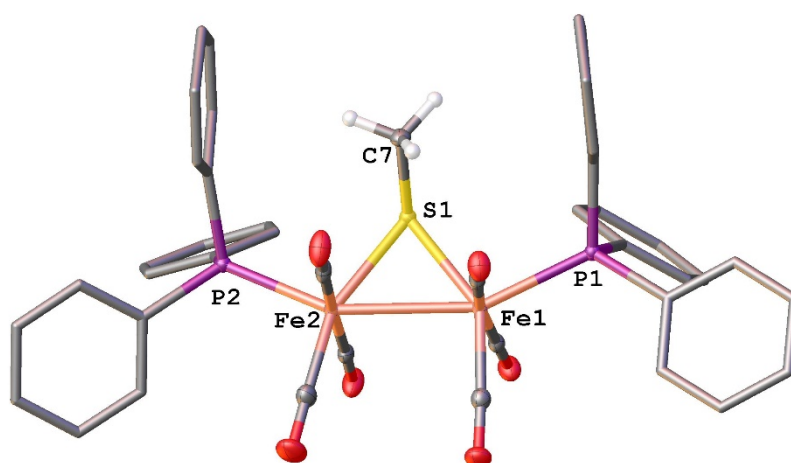


Figure S19. ORTEP of the [Fe₂(μ-SMe)(CO)₆(PPh₃)₂]OTf ([Me₄]OTf). Thermal ellipsoids are drawn at 50% probability. The anion CF₃SO₃⁻ and hydrogen atoms except for CH₃ are omitted for clarity. Selected bond lengths (Å): Fe1-Fe2, 2.7074(2); Fe1-S1, 2.2558(3); Fe2-S1, 2.2614(3); S1-C7, 1.8221(12); Fe1-P1, 2.2909(3); Fe2-P2 2.2719(3). Selected angles (°): Fe1-S1-Fe2, 73.646(10); S1-Fe1-Fe2, 53.272(8); S1-Fe2-Fe1, 53.082(8).

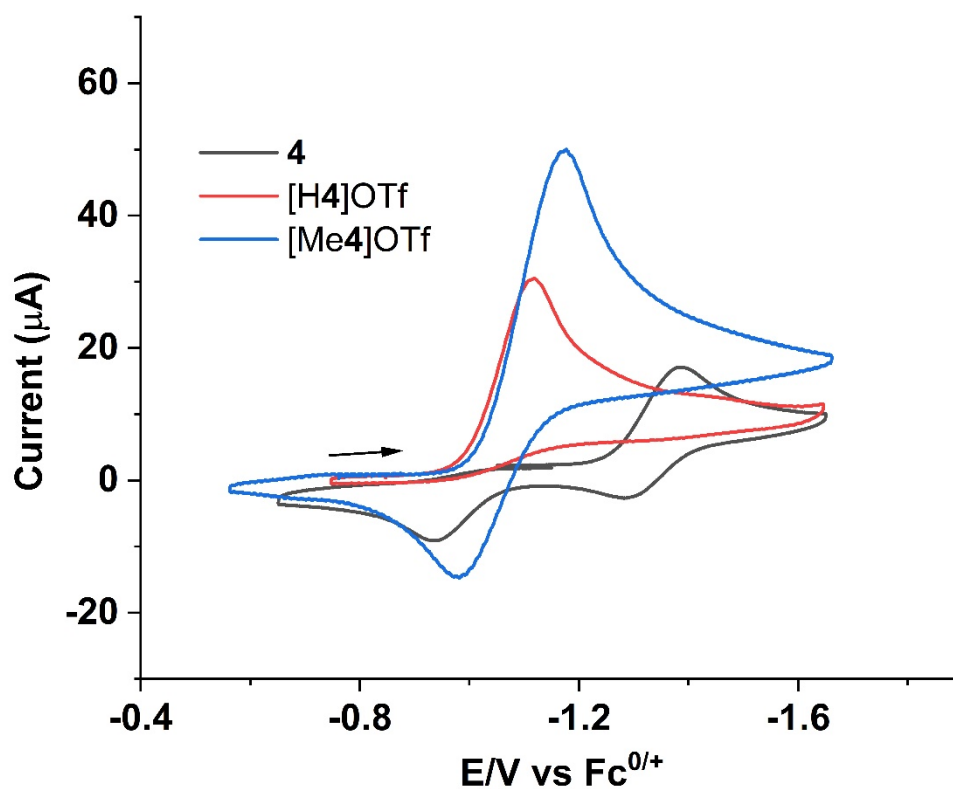


Figure S20. Cyclic voltammogram of **4**, [H4]OTf and [Me4]OTf. Conditions: 1.0 mM in CH₂Cl₂, 0.1 M Bu₄NPF₆, scan rate 200 mV/s, glassy carbon working electrode (*d* = 3.0 mm), Ag wire pseudoreference electrode with internal Fc standard, and Pt wire counter electrode.

III. Crystallography

CCDC number for $\text{Fe}_2(\mu\text{-S})(\text{CO})_6(\text{PPh}_3)_2$: 2063553;

$[\text{Fe}_2(\mu\text{-SH})(\text{CO})_6(\text{PPh}_3)_2]\text{OTf}$: 2063552;

$[\text{Fe}_2(\mu\text{-SMe})(\text{CO})_6(\text{PPh}_3)_2]\text{OTf}$: 2063554.

Intensity data were collected on a Bruker D8 Venture kappa diffractometer equipped with a Photon-II CPAD detector. An $1\ \mu\text{s}$ microfocus Mo source ($\lambda = 0.71073\ \text{\AA}$) coupled with a multi-layer mirror monochromator provided the incident beam. The sample was mounted on a 0.3 mm nylon loop with the minimal amount of Paratone-N oil. Data was collected as a series of φ and/or ω scans. Data was collected at 100 K using a cold stream of $\text{N}_{2(g)}$. The collection, cell refinement, and integration of intensity data was carried out with the APEX3 software.¹ A multi-scan absorption correction was performed with SADABS.² The structure was phased with intrinsic phasing methods using SHELXT³ and refined with the full-matrix least-squares program SHELXL.⁴

(1) Bruker (2018). APEX3. Bruker AXS, Inc., Madison, Wisconsin, USA.

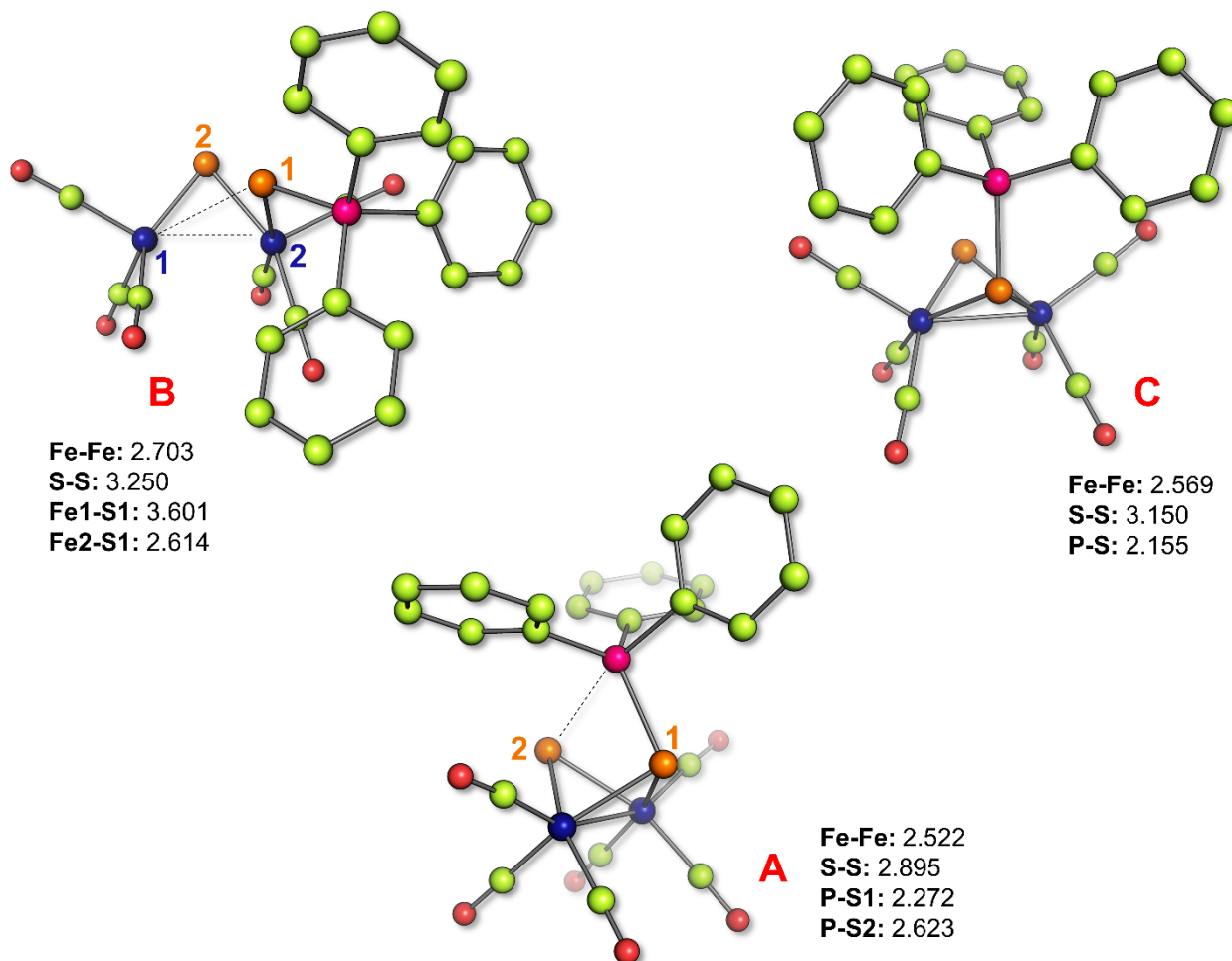
(2) Krause, L., Herbst-Irmer, R., Sheldrick, G. M. and Stalke, D. *J. Appl. Cryst.*, 2015, 48, 3-10.

(3) Sheldrick, G. M. *Acta Cryst.* 2015, A71, 3-8.

(4) Sheldrick, G. M. *Acta Cryst.* 2015, C71, 3-8.

IV. DFT Calculation

Relative free energies (**bold values**) in kcal/mol, ν_{CO} in cm^{-1} .



Optimized structures of structures A, B and C (see above). Selected distances in Å.

Computational details

DFT calculations were carried out with the TURBOMOLE 7.2.1 suite of programs.¹ The scheme BP86^{2,3}/def-TZVP⁴ was chosen, since it proved suited for the modelling of the electronic structure of multi-iron complexes bearing carbonyl and/or phosphine ligands.⁵⁻⁷ The D3 correction⁸ was added to calculations, to accurately account for dispersion forces. The implicit solvent model COSMO (COnductor-like Screening Model)^{9,10} was used, setting the value of ϵ at 7.58 (for THF). Calculations were accelerated thanks to the Resolution-of-Identity approximation (RI).¹¹ Each optimized structure was characterized as pure minimum with a full vibrational analysis. The latter also allowed us to evaluate the partition function Q , calculated as the product $Q_{\text{translational}}$, $Q_{\text{rotational}}$, $Q_{\text{vibrational}}$, and thus to correct SCF energies with thermal and entropic contributions, in order to calculate free energies (G) at $p=1$ bar and $T=298.15\text{K}$.

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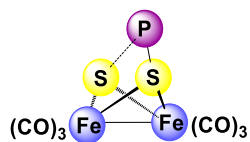
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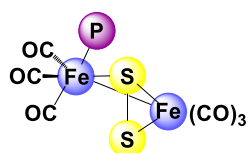
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XYZ coordinates of relevant minima.



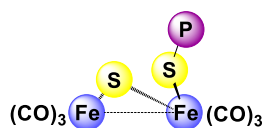
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O	-0.264426	1.742773	-1.178730
C	-1.499105	0.490014	-4.335556
O	-1.003379	0.635019	-5.372006
S	-3.820892	-0.502287	-1.265207
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C	-3.506609	-1.966637	-4.970133
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C	-3.397037	-3.446711	0.025580
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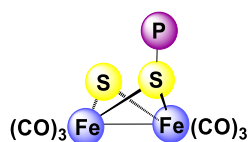
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C	-0.626417	7.697832	0.114249
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C	1.051804	9.020782	1.260028
C	0.963261	8.176247	2.371906
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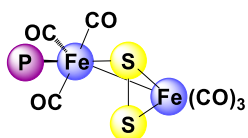
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