Supporting Information for:

Facile Hydrogen Atom Abstraction and Sulfide Formation in a Methyl-Thiolate Capped Iron-Sulfur-Carbonyl Cluster

J. Patrick Shupp and Michael J. Rose

The University of Texas at Austin, Austin TX 78757

_____

Experimental
General Procedures and Reagents
All reactions were carried out in either an argon atmosphere glovebox or a N_2 atmosphere Schlenk line. GC measurements were performed with a Shimadzu GC2014 fuel cell analyzer, and NMR measurements utilized an Agilent MR400 with a OneNMR probe with Protune accessory. Mass Spectrometry and GCMS were carried out with a Waters Micromass AutoSpec Ultima interfaced with an Agilent 6890N GC system. All IR's were carried out on a Bruker FTIR spectrometer Alpha II. The starting materials $Fe(CO)_5$, KOH, K_2SO_3, CH_3I, 2-bromopropane, benzo-15-crown-5, and TEMPO were purchased from Strem, Fisher, Acros, Aldrich, Oakwood, or Chem-Impex and used without further purification. The isotopically labeled compounds CD_3I and $^{13}CH_3I$ were purchased from Aldrich and Acros, respectively, and stored over copper metal. KC_8 and $K_2[SFe_3(CO)_9]$ were prepared according to previous syntheses.[13,21] Deuterated MeCN was purchased from Cambridge Isotopes and used without further purification. HPLC grade solvents were purchased from EMD, Fischer, Macron, or J. T. Baker, which were then dried with an alumina column system from Pure Process Technology.
Caution: Iron carbonyl complexes are often pyrophoric and should be handled under an inert atmosphere.

Synthesis of K[(SR)Fe$_3$(CO)$_9$], where R = CH$_3$, ^{i}Pr, CD$_3$
These reactions were carried out according to a modification of a previously reported synthesis.[22] In a typical reaction, a Schlenk flask was charged with 250-500 mg of the bare potassium salt $K_2[SFe_3(CO)_9]$ and dissolved in 25 mL of THF (red solution). The reaction was chilled to 0 °C and 4-8 equivalents of RX (specifically, CH_3I, ^{i}PrBr or CD_3I) were added dropwise through a septum. The reactions were allowed to proceed over the course of 2 h, whereupon a copious precipitate formed. Color changes were subtle, ranging from red to red-brown or magenta. The suspension was filtered and the solvent was removed *in vacuo*. The desired mono-anionic products were extracted into Et_2O, and the solvent was again removed by vacuum, and the residual powder was washed with pentane. Crystals of these compounds were grown by vapor diffusion of pentane or Et_2O into a THF solution of the crude material in the presence of excess (4 equiv.) benzo-15-crown-5. IR for **1** (v_{CO} in cm^{-1}): 2037, 1959, 1910, 1763. ^{1}H NMR in d^3-MeCN (δ from TMS) for **1**: 2.65. ^{13}C NMR in d^3-MeCN (δ from TMS) for **1**: 51.26, 220.82. Yield for **1** (–CH$_3$): 22.54%. Yield for **1** (–CD$_3$): 32.95%. IR for **3** (v_{CO} in cm^{-1}): 2065, 1991, 1906, 1866, 1735. ^{1}H NMR in d^3-MeCN (δ from TMS) for **3**: 2.52. ^{13}C NMR in d^3-MeCN (δ from TMS) for **3**: 230.22. Yield for **3**: 34.80%.

Reaction of 1 with TEMPO:
Synthesis of [K(benzo-15-crown-5)$_2$]$_2$[(SFe$_2$(CO)$_{12}$)$_2$Fe(CO)$_2$]
The starting materials K[(CH$_3$S)Fe$_3$(CO)$_9$] (200 mg, 0.4 mmol) and TEMPO (63 mg, 0.4 mmol) were dissolved in THF in two separate vials. The vial containing K[(SCH$_3$)Fe$_3$(CO)$_9$] was frozen in a liquid argon cold-well chilled with N_2, and the TEMPO solution was added to the frozen slurry. The reaction was allowed to warm to room temperature and react over the course of 3 h. After this time the solvent was removed *in vacuo*, and the residual material was washed with Et_2O. The remaining powder was dissolved in MeCN and benzo-15-crown-5 (4 equiv.) was added. After slow diffusion of Et_2O, brown crystals of [K(benzo-15-crown-5)$_2$]$_2$[S$_2$Fe$_5$(CO)$_{14}$] were obtained. IR for **2** (v_{CO} in cm^{-1}): 2032, 1993, 1961, 1920, 1895, 1866. ^{13}C NMR in d^3-MeCN (δ from TMS) for **2**: 222.52. Yield for **2**: 36.48%.

Reaction of K[Fe$_3$(S^{i}Pr)(CO)$_9$] with TEMPO
A magenta THF solution containing 119 mg (0.223 mmol) K[Fe$_3$(S^{i}Pr)(CO)$_9$] was frozen at 87 K in a liquid argon cold-well. In a separate vial, 30 mg (0.192 mmol) TEMPO was dissolved in THF, and added to the frozen mixture. The reaction was allowed to warm to room temperature and proceed over the course 1.5 h. Afterwards, the solvent was removed *in vacuo,* to yield a magenta oil. The residual oil was dissolved in THF with 4 equiv. benzo-15-crown-5 and stirred overnight. This solvent was removed by vacuum and washed with Et_2O to yield a brown powder. Vapor diffusions of

pentane or Et$_2$O into THF afforded large numbers of magenta crystals, which were determined to be starting material by single crystal XRD.

NMR Scale Reaction to Determine Paramagnetism
A JY tube was used to dissolve 15 mg K[Fe$_3$(SCD$_3$)(CO)$_9$] in d^3-MeCN. A spectrum was obtained of this starting material, then the tube was returned to an argon atmosphere glovebox. The solution was mixed with 5 mg of TEMPO, then added back to the JY tube, which was then quickly sealed to capture any evolved gases. The solution was then rotated slowly over the course of 2 hours, at which time the product spectrum was obtained.

GC data
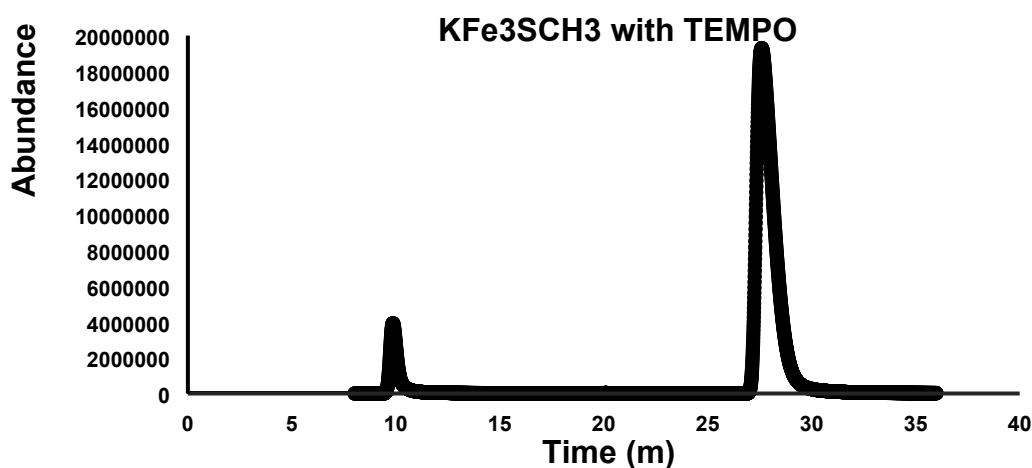
Figure S1. GC trace of the headspace after reaction between [K(benzo-15-crown-5)$_2$][(SCH$_3$)Fe$_3$(CO)$_9$] and TEMPO in <u>acetonitrile</u> using a FID detector. The first peak elutes at 9.5 minutes and corresponds to CO$_2$, while the second peak elutes at 27 minutes and is assigned as C$_3$H$_4$ or C$_4$H$_7$.
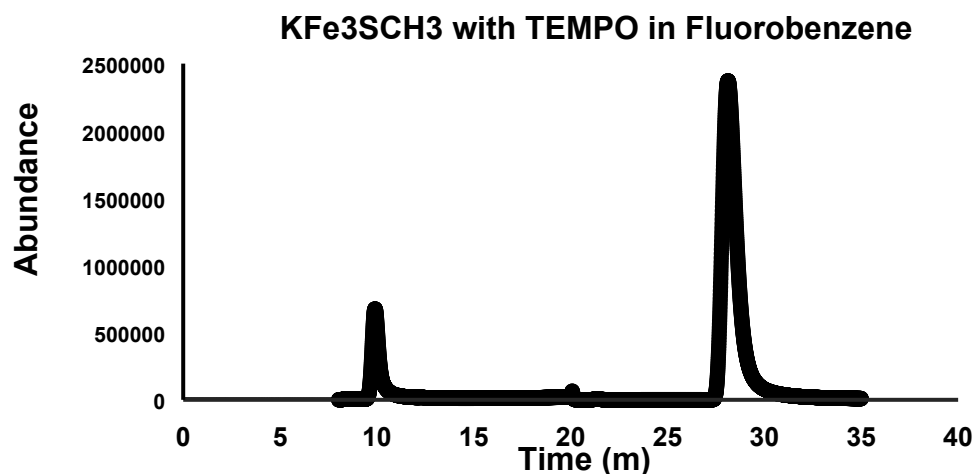

Figure S2. GC trace of the headspace after reaction between [K(benzo-15-crown-5)$_2$][(SCH$_3$)Fe$_3$(CO)$_9$] and TEMPO in <u>fluorobenzene</u> using a FID detector.
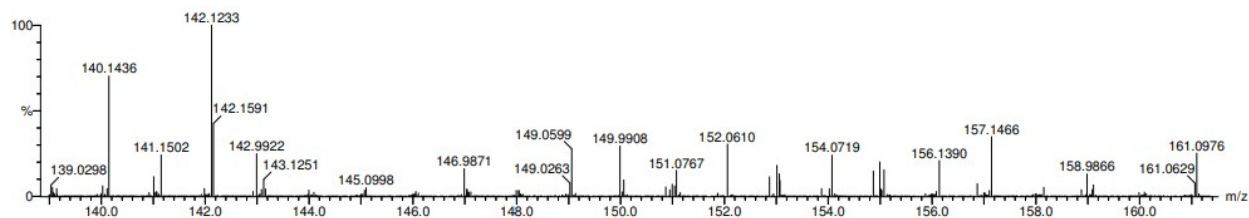
Mass Spectrometry Data

Figure S3. Mass spectrum of the reaction mixture in THF. Peaks at m/z = 140 and 142 correspond to the [M-H]$^+$ and MH$^+$ signals of 2,2,5,5-tetramethylpiperidine. The m/z = 156 and 157 peaks correspond to the [M-H]$^+$ and MH$^+$ fragments of TEMPOH.
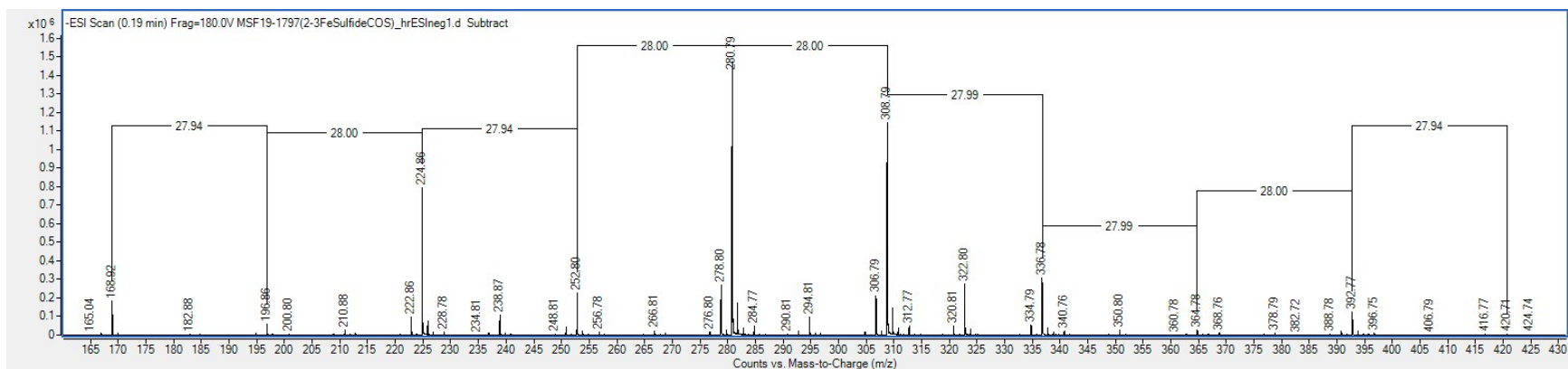

Figure S4. Mass spectrum of the Et$_2$O soluble products after reaction of [K(benzo-15-crown-5)$_2$][(SCH$_3$)Fe$_3$(CO)$_9$] and TEMPO in THF. The most intense species with a m/z = 420 was assigned as [HFe$_3$(CO)$_9$] as [M]$^-$ or [H$_2$Fe$_3$(CO)$_9$] as [M-H]$^-$. Subsequent loss of 9 COs can be traced, indicating the analyte in question is an iron carbonyl.
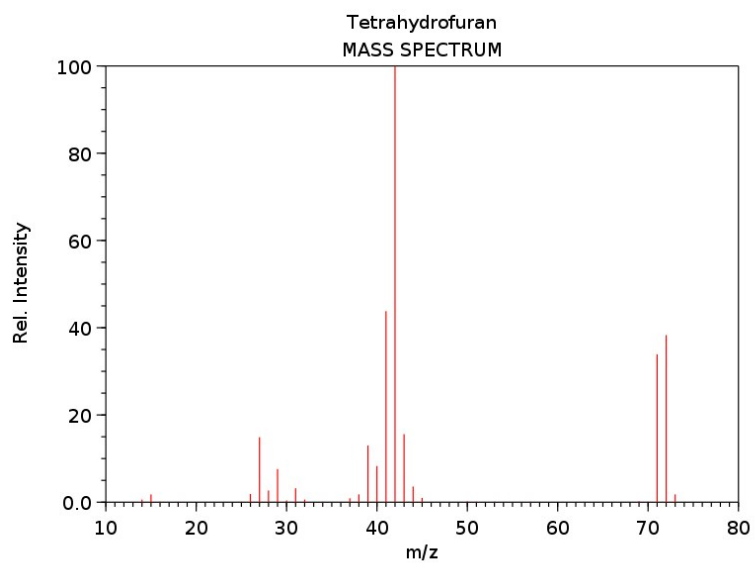
Figure S5. Mass spectrum of THF in EI mode. This spectrum is from the National Institute of Standards and Technology,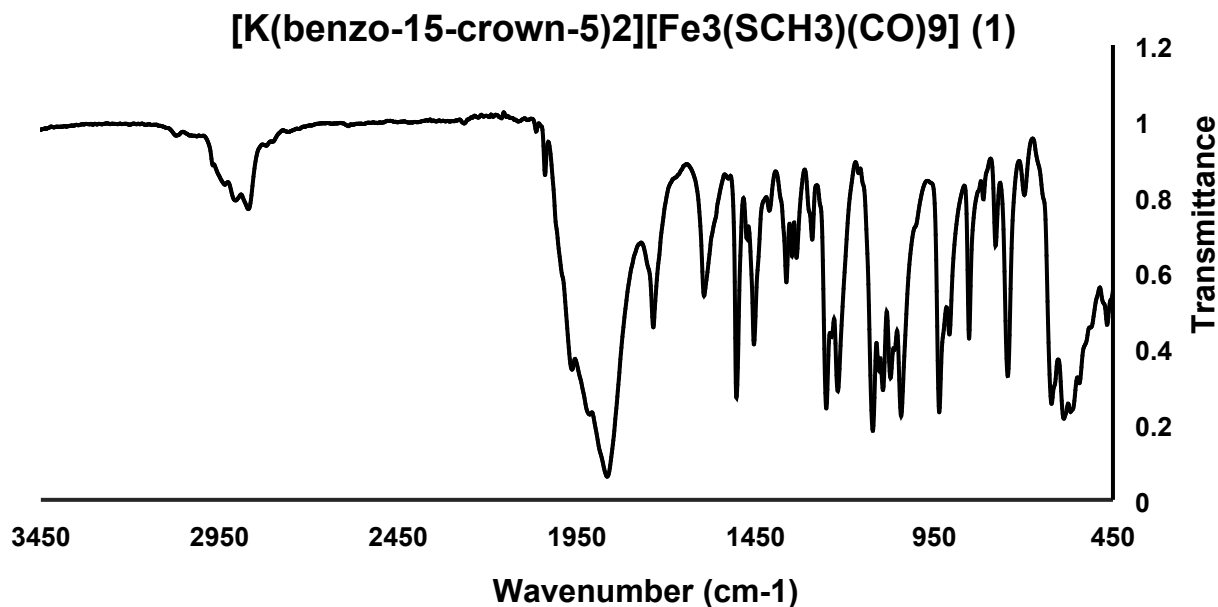 United States Department of Commerce's Internet WebBook (https://webbook.nist.gov/cgi/cbook.cgi?ID=C109999&Mask=200#Mass-Spec)

IR Data

[K(benzo-15-crown-5)2][Fe3(SCH3)(CO)9] (1)

Figure S6. FTIR spectrum of [K(benzo-15-crown-5)$_2$][(SCH$_3$)Fe$_3$(CO)$_9$] (**1**). Relevant CO stretches are 2037, 1959, 1910, and 1763 (v_{CO} in cm^{-1}).
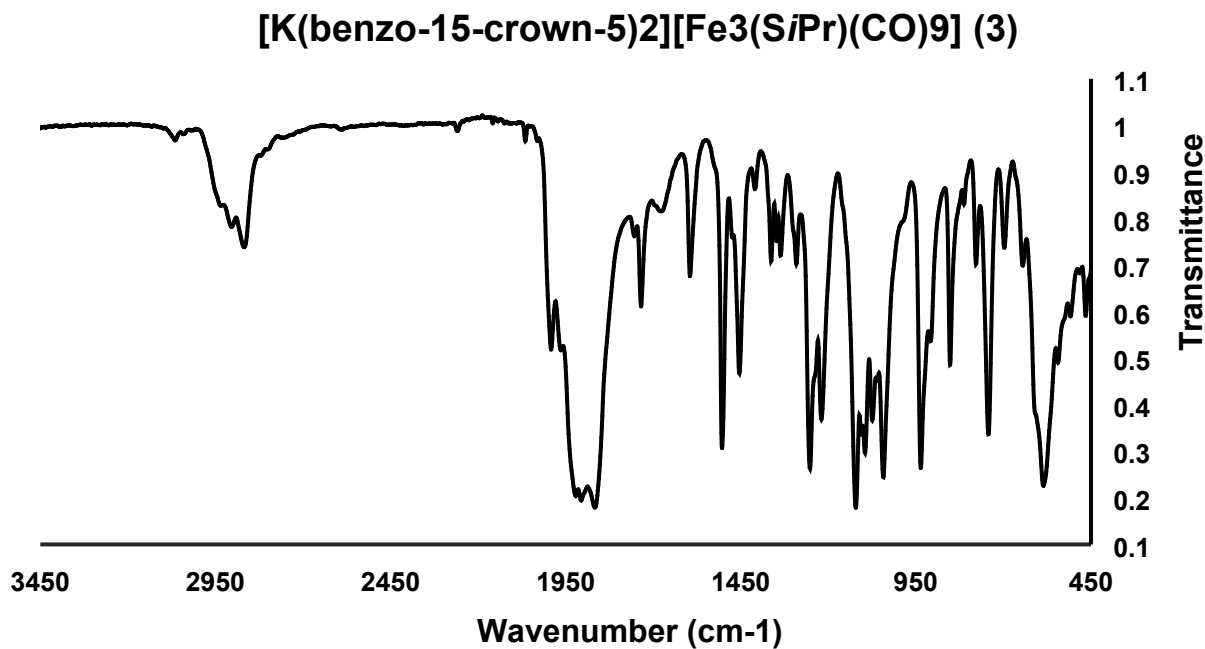
[K(benzo-15-crown-5)2][Fe3(S*i*Pr)(CO)9] (3)

Figure S7. FTIR spectrum of [K(benzo-15-crown-5)$_2$][(S^{i}Pr)Fe$_3$(CO)$_9$] (**3**). Relevant CO stretches are 2065, 1991, 1906, 1866, and 1735 IR (v_{CO} in cm^{-1}).
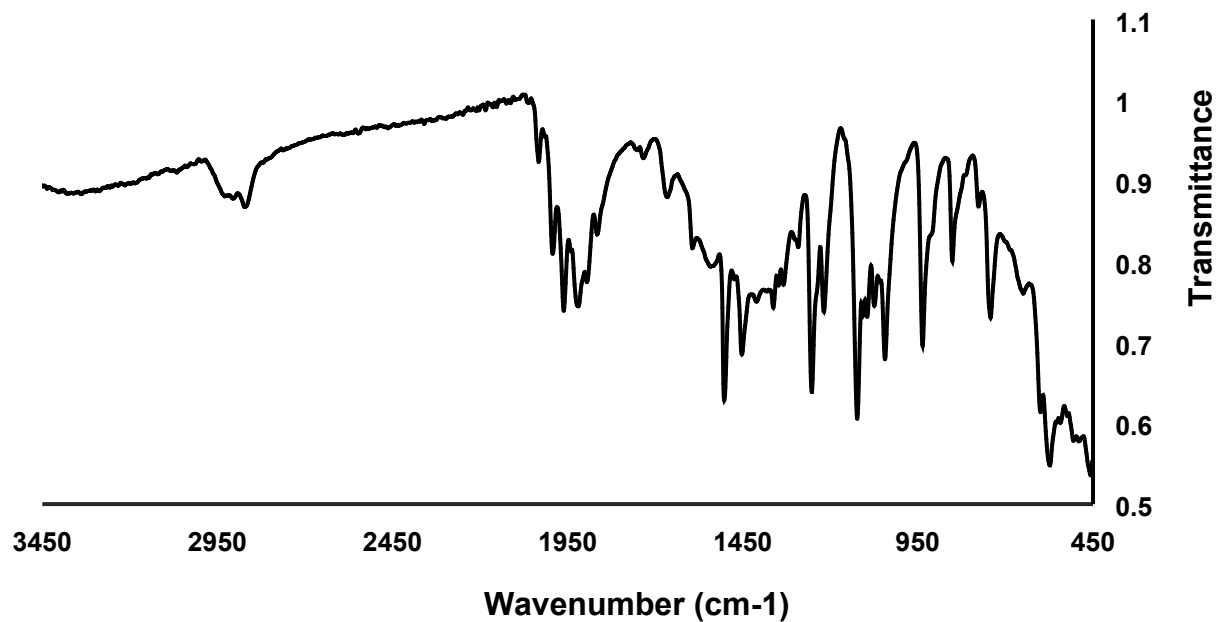
[K(benzo-15-crown-5)2]2[(SFe2(CO)6)2Fe(CO)2] (2)

Figure S8. FTIR spectrum of [K(benzo-15-crown-5)$_2$]$_2$[(SFe$_2$(CO)$_6$)$_2$Fe(CO)$_2$] (**2**). Relevant CO stretches are 2032, 1993, 1961, 1920, 1895, and 1866 IR (v_{CO} in cm^{-1}).

NMR Data
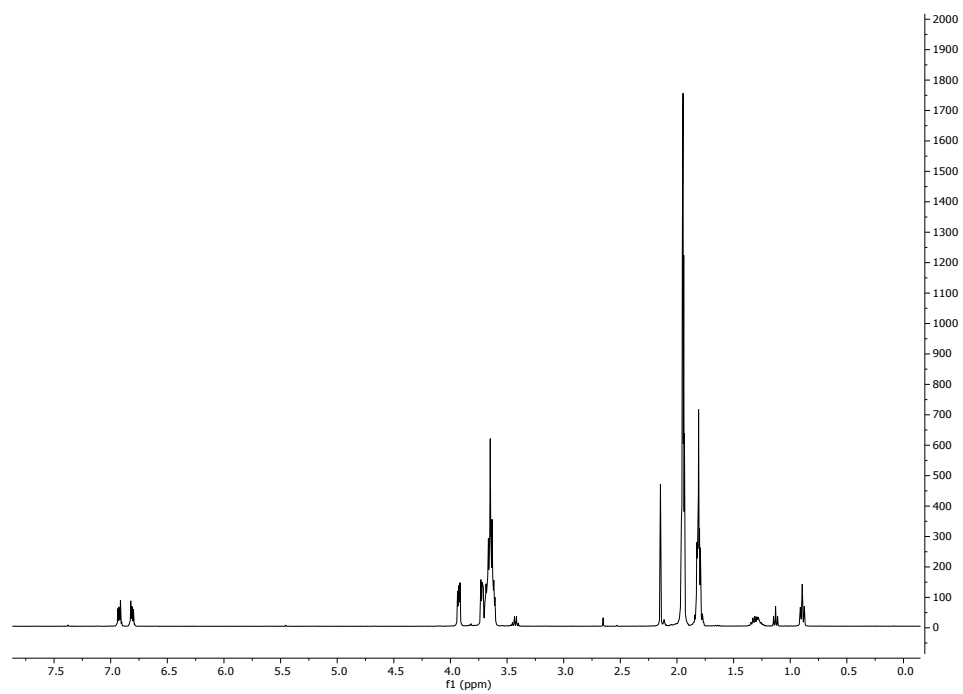
Figure S9. ^{1}H NMR spectrum of [K(benzo-15-crown-5)$_2$][(SCH$_3$)Fe$_3$(CO)$_9$] (**1**) in d^3-MeCN.
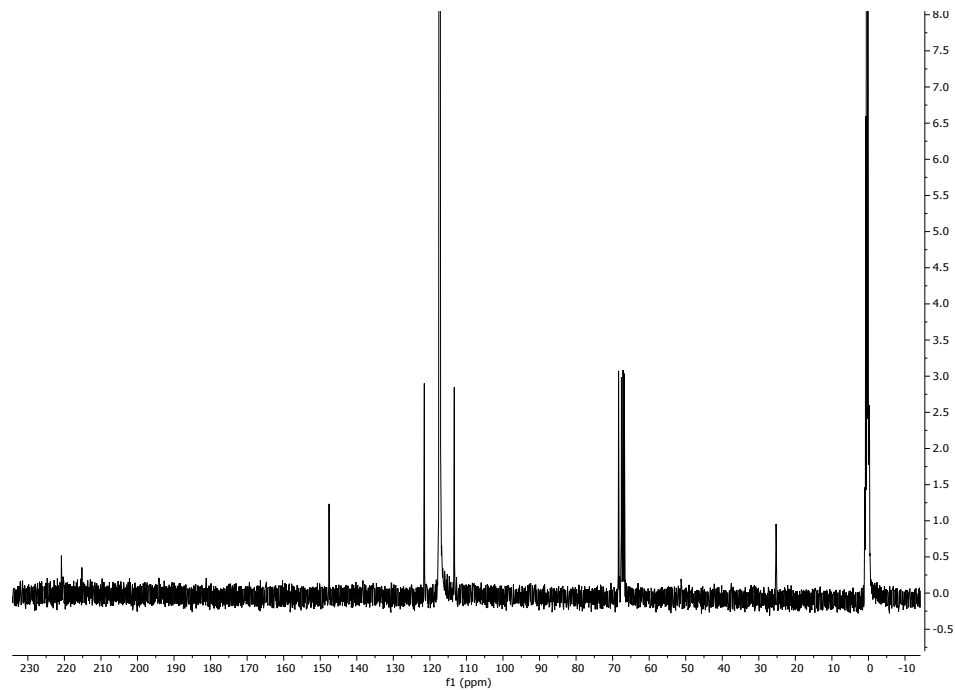
Figure S10. ^{13}C NMR spectrum of [K(benzo-15-crown-5)$_2$][(SCH$_3$)Fe$_3$(CO)$_9$] (**1**) in d^3-MeCN.
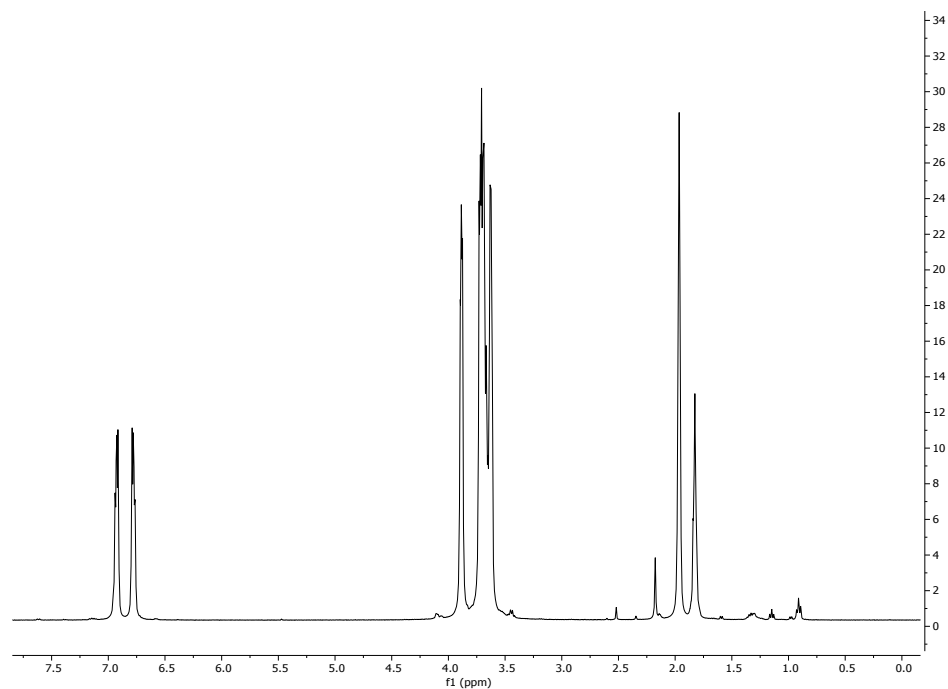
Figure S11. ^{1}H NMR spectrum of [K(benzo-15-crown-5)$_2$][(S^{i}Pr)Fe$_3$(CO)$_9$] (**3**) in d^3-MeCN.
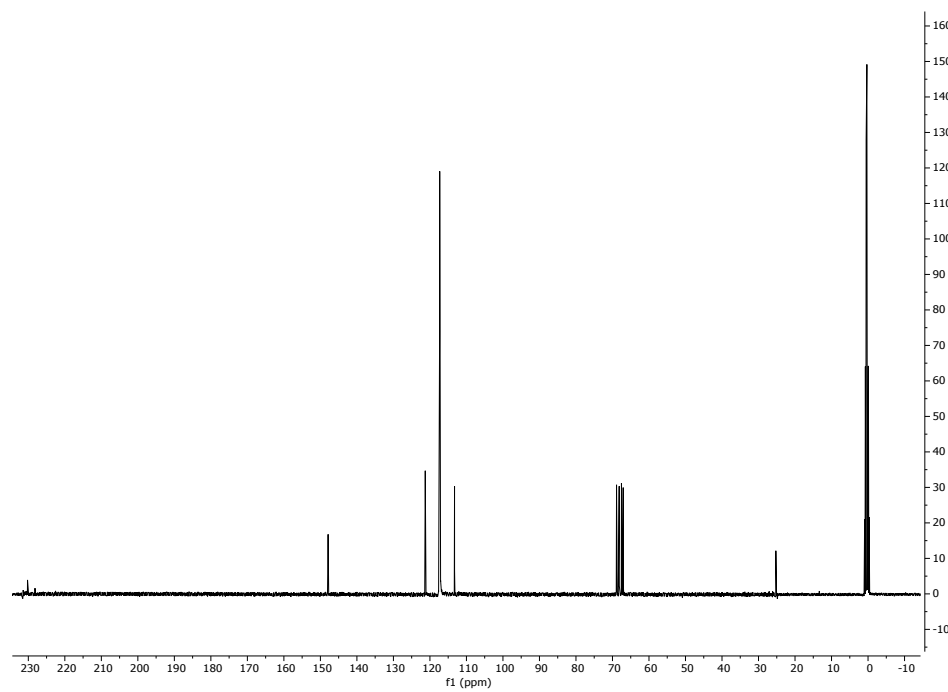
Figure S12. ^{13}C NMR spectrum of [K(benzo-15-crown-5)$_2$][(S^{i}Pr)Fe$_3$(CO)$_9$] (**3**) in d^3-MeCN.
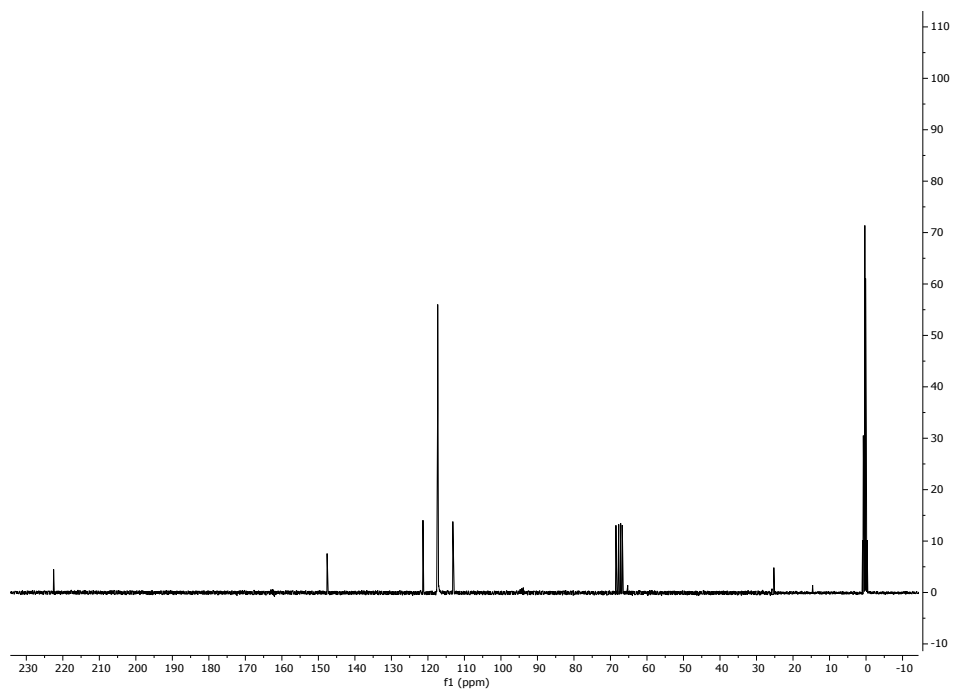
Figure S13. ^{13}C NMR spectrum of $[K(benzo-15-crown-5)_2]_2[(SFe_2(CO)_{12})_2Fe(CO)_2]$ (**2**) in d^3-MeCN.
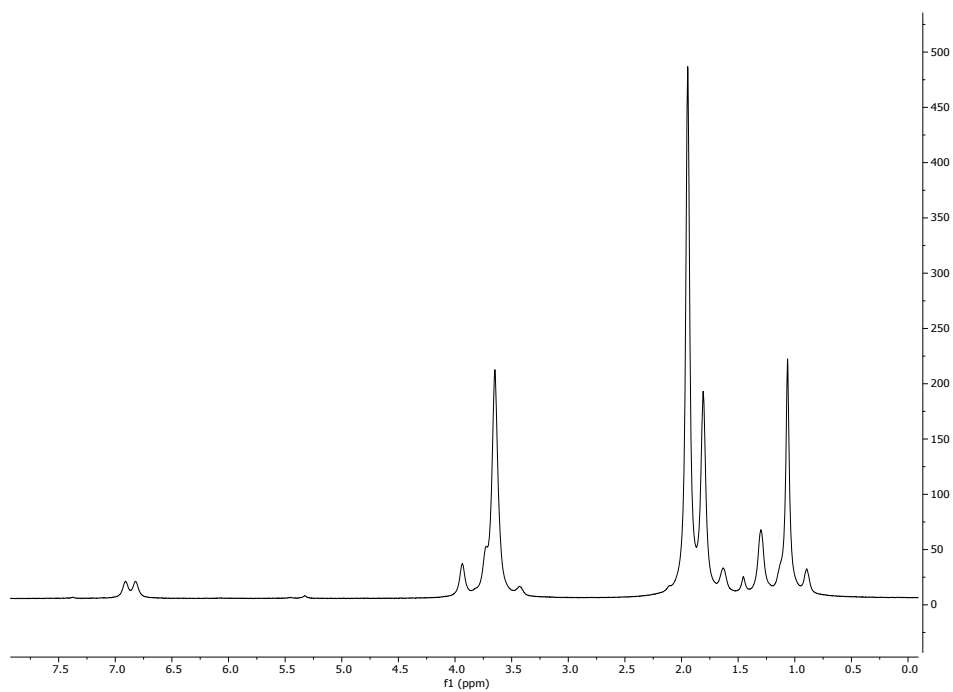
Figure S14. H^1 NMR spectrum taken in d^3-MeCN of $[K(benzo-15-crown-5)_2][(SCH_3)Fe_3(CO)_9]$ (**1**) after the reaction of TEMPO, with the broad peaks indicative of the sample's paramagnetism.

X-ray Data Collection

For complex **1**, The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a μ-focus Cu Kα radiation source (λ = 1.5418 Å) with collimating mirror monochromators. All frames of data were collected using ω-scans with a scan range of 1° and a counting time of 20 seconds per frame for low angle data, and up to 35 seconds for high angle data. The data were collected at 100 K using an Oxford Cryostream low temperature device. Data collection, unit cell refinement and data reduction for compound **1** were performed using Rigaku Oxford Diffraction's CrysAlisPro V 1.171.40.53, as well as unit cell refinement and data reduction for compound **3**. For complexes **2** and **3** the data were collected on a Rigaku ACF-12 with a Saturn 724+ CCD using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). All frames of data were collected using ω-scans with a scan range of 0.5° and a counting time of 45 seconds per frame. The data were collected at 100 K using a Rigaku XStream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table **S1**. Data reduction and unit cell refinement for compound **2** was performed using the Rigaku Americas Corporation's Crystal Clear version 1.40.1 The structure was solved by direct methods using SHELXT and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6. Structure analysis was aided by use of the programs OLEX2 and WinGX. The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2 × U_{eq} of the attached atom (1.5 × U_{eq} for methyl hydrogen atoms).

Table S1. Selected crystal data and refinement parameters for new complexes reported herein.

	K[Fe$_3$(SCH$_3$)] (1)	K$_2$[Fe$_5$S$_2$] (2)	K[Fe$_3$(S^{i}Pr)] (3)
Formula	C$_{38}$H$_{43}$Fe$_3$KO$_{19}$S	C$_{74}$H$_{90}$Fe$_5$K$_2$O$_{35}$S$_2$	C$_{40}$H$_{47}$Fe$_3$KO$_{19}$S
FW	1042.4	1961.03	1070.5
Color	Red	Brown	Red
Habit	Needle	Plate	Needle
T (K)	100	100	100
Lattice	Triclinic	Triclinic	Triclinic
Space Group	P-1	P-1	P-1
a (Å)	13.2480(24)	11.7472(7)	11.6950(3)
b (Å)	14.1411(17)	15.4129(6)	15.2437(4)
c (Å)	14.3224(28)	25.0874(8)	15.3863(4)
α (deg)	114.370(16)	80.089(3)	63.000(3)
β (deg)	110.071(18)	83.912(4)	70.310(2)
γ (deg)	94.339(15)	72.768(4)	87.375(2)
V (Å^3)	2220.42(333)	4266.3(3)	2282.27(49)
Z	2	2	2
d$_{calc}$ (g/cm$_3$)	1.56	1.527	1.56
μ (mm^{-1})	9.691	1.062	1.153
GOF on F^2	0.981	1.013	1.026
R indices [I > 2σ(I)]	R_1 = 0.088, wR_2 = 0.219	R_1 = 0.082, wR_2 = 0.2029	R_1 = 0.030, wR_2 = 0.074
R indices all data	R_1 = 0.127, wR_2 = 0.262	R_1 = 0.1202, wR_2 = 0.2281	R_1 = 0.036, wR_2 = 0.077

References

(1)   Jr., H. F. H. *Inorg. Synth.* 1966, VIII, 181–183.

(2)   Nametkin, N. S.; Tyurin, V. D.; Kukina, M. A. *J. Organomet. Chem.* 1978, 149 (3), 355–370.

(3)   CrysAlisPro. Rigaku Oxford Diffraction (2019). CrysAlicPro Software System, V 1.171.40.37a.

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

(5)   Sheldrick, G. M. (2015). SHELXL-2016/6. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 9-18.

(6)   CrystalClear 1.40 (2008). Rigaku Americas Corportion, The Woodlands, TX.

(7)   Sheldrick, G. M. (2015). SHELXL-2016/6. *Acta Cryst.*, C71, 9-18.

(8)   OLEX2. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. and Puschmann, H. A Complete Structure Solution, Refinement and Analysis Program. J. Appl. Cryst. 42, 339-341.

(9)   WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. *J. Appl. Cryst.* 32. 837-838.

(10) $Rw(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.

   $R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$.

   $S = [\Sigma w(|F_o|^2 - |Fc|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

(11)   International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.