Experimental Protocols

General Considerations

Unless otherwise noted, all compounds were prepared by literature procedures or purchased from commercial sources. All manipulations were carried out under a dinitrogen atmosphere by utilizing standard glovebox or schlenk techniques. Solvents were dried and de-oxygenated by an argon sparge followed by passage through an activated alumina column purchased from S.G. Waters Company. All non-halogenated solvents were tested with a standard sodium-benzophenone ketyl solution to ensure the absence of oxygen and water.

NMR

NMR measurements were obtained on Varian 300 or 500 MHz or Bruker 400 MHz spectrometers. Deuterated solvents for these measurements were obtained from Cambridge Isotope Laboratories and were dried and degassed prior to use. All ^{1}H spectra were referenced to residual solvent peaks.

Electrochemistry

All experiments were conducted with a CH Instruments 630-C Electrochemical Analyzer and the CHI Version 8.09 software package. All experiments were conducted under an atmosphere of dinitrogen with 0.1 M [TBA][PF$_6$] in THF as the electrolyte. Cyclic Voltammetry experiments were conducted in a single cell setup with a platinum wire as the auxiliary electrode, a Ag/[TBA][PF$_6$]/THF pseudo-reference electrode separated from the solution by a Vycor frit (Bioanalytical Systems, Inc.), and a 0.078 cm^2 glassy carbon electrode (Bioanalytical Systems, Inc.). Ferrocene was included in scans as an internal standard of potential.

EPR

EPR X-band spectrometry was obtained on a Bruker EMX spectrometer with the aid of Bruker Win-EPR software suite version 3.0. The spectrometer was equipped with a rectangular cavity which operated in the TE$_{102}$ mode. Temperature control was achieved with the use of an Oxford continuous-flow helium cryostat (temperature range 3.6 – 300 K). The microwave bridge came equipped with a frequency counter which enabled accurate measurement of the frequency values. The sample was prepared in a 9:1 THF:2-MeTHF solution in an EPR tube sealed with a Teflon stopcock.

Magnetic Measurements

Data was obtained using a Quantum Designs SQUID magnetometer running MPMSR2 software (Magnetic Property Measurement System Revision 2) at a field strength of 5000 G. Samples were inserted into the magnetometer in plastic straws sealed under nitrogen with polycarbonate capsules. Loaded samples were centered within the magnetometer using the DC centering scan at 35 K and 5000 gauss. Data were acquired at 2-20 K (one data point every 2 K), and 20-310 K (one data point every 5 K). The magnetic susceptibility was adjusted for diamagnetic contributions using the constitutive corrections of Pascal's constants as well as a diamagnetic subtraction due to the holder diamagnetism. Data workup, including simulations,

was performed in the JulX software package.[1] Magnetic data were fit with the following spin exchange Hamiltonian: $H = -2J \cdot S_{Fe1} \cdot S_{Fe2}$. Intermolecular interactions were simulated using a Weiss temperature, ΘW, for the simulations as a perturbation of the temperature scale, $kT' = k(T-\Theta W)$.

Mössbauer Spectroscopy.

Spectra were recorded on a spectrometer from SEE Co (Edina, MN) operating in the constant acceleration mode in a transmission-geometry. Spectra were recorded with the temperature of the sample maintained at 80 K. The sample was kept in an SVT-400 dewar from Janis (Wilmington, MA), at zero field. Application of a magnetic field of 54 mT parallel to the γ-beam did not cause detectable changes in the spectra recorded at 80 K. The quoted isomer shifts are relative to the centroid of the spectrum of a metallic foil of α-Fe at room temperature. Samples were prepared by grinding polycrystalline material into a fine powder and then mounted in a cup fitted with a screw-cap as a boron nitride pellet. Data analysis was performed using the program WMOSS (www.wmoss.org) and quadrupole doublets were fit to Lorentzian lineshapes.

X-Ray Crystallography

Data was obtained at low temperatures on a Siemens or Bruker Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo or Cu Kα radiation ($\lambda = 0.71073$ or 1.54178 Å, respectively), performing φ- and ω-scans. All structures were solved by standard direct or Patterson methods and refined against F^2 using the SHELX program package.[2,3,4] All atoms, with the exception of hydrogens, have been anisotropically refined. All hydrogen atoms were calculated using a standard riding model.

Several disordered ligand and solvent molecules were refined with the use of standard restraints. It is noteworthy that in the structure of **1** additional electron density was found in the central core of the molecule. This was modeled as a small percentage of a disordered bis-thiolate. While the bond lengths in **1** seem longer than what would be expected for similar molecules, these models fit the data quite well and were left in. Additionally, there is a small component of disorder present in the phosphine ligands of **2**. This disorder may be a manifestation of localization of the inter-valence species.

Synthesis of ([PhBP₃]Fe)₂(μ-S) , 1

[PhBP₃]FeCl (0.301 g, 0.39 mmol) and NEt₃ (0.1 mL, 0.72 mmol) were dissolved in 10 mL of benzene to form a bright yellow solution. To this, a 5 mL suspension of [TBA][SH] (0.081 g, 0.29 mmol) in THF was added dropwise over 5 minutes. The solution rapidly turned dark brown and was allowed to stir at RT for 2 hours. After this time, solvent was removed in vacuo and the remaining residue was extracted into 10 mL of benzene and filtered through a silica plug. The benzene solution was frozen and lyophilized to yield **1** as a dark brown powder (0.150 g, 0.01 mmol, 51%). X-ray quality crystals were grown from pentane diffusion into a

[1] http://ewww.mpi-muelheim.mpg.de/bac/logins/bill/julX_en.php
[2] Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467.
[3] Sheldrick, G. M. *Acta Cryst.* **2004**, *A64*, 112.
[4] Müller, P. *Crystallography Reviews* **2009**, *15*, 57.

concentrated benzene solution of **1**. ^{1}H NMR (C_6D_6, δ): 28.29 (s), 14.67 (s), 10.50 (t, J = 7 Hz), 9.75 (t, J = 7 Hz), 5.56 (s), 4.20 (t, J = 7 Hz), 2.76 (br s). UV-vis (THF) λ_{max}, nm (ε, M^{-1} cm^{-1}): 944 (sh), 905 (5550), 637 (2140), 350 (13310), 301 (16580), 263 (sh). Anal. Calc. for $C_{90}H_{82}B_2Fe_2P_6S$: C 71.36; H 5.46. Found: C 71.04; H 5.45.

Synthesis of {([PhBP₃]Fe)₂(μ-S)}{Na(12-crown-4)₂}, 2

A 5 mL THF solution of **1** (0.050 g, 0.03 mmol) was placed over an amalgam of sodium and mercury (0.010:3 g, 0.4 mmol). The amalgam was stirred for 15 min over which time the solution turned dark green. The THF solution was then decanted from the amalgam and filtered through a celite plug before volatiles were removed. The resulting dark green solid was triturated and washed 3x with ether and benzene (3 ml) before being taken up in a minimum of THF. 12-crown-4 (0.1 mL, 0.6 mmol) was then added before the solution was layered with pentane and cooled to -35 °C to crystallize overnight. After 12 hours the mother liquor was removed and the dark crystals were washed 3x with benzene (3 mL) to provide **2** as a black solid (0.047 g, 0.025 mmol, 76%). [1]H (THF-d^8, δ): 53.68 (br s), 10.54 (s), 9.64 (s), 1.93 (s), 0.053 (br s). UV-vis (THF) λ_{max}, nm (ε, M^{-1} cm^{-1}): 944 (sh), 905 (5550), 740 (sh), 638 (8463), 511 (sh), 346 (24420), 296 (28560). Elemental analysis was obtained on the bis-THF adduct obtained prior to 12-crown-4 addition, Anal. Calc. for $C_{114}H_{124}B_2Fe_2NaO_6P_6S$: C 69.70, H 6.36. Found: C 69.08, H 6.41.

Synthesis of {([PhBP₃]Fe)₂(μ-S)} {Na(12-crown-4)₂}₂, 3

A 5 mL THF solution of **1** (0.050 g, 0.03 mmol) in THF was cooled to -35 °C for 30 minutes. After this time a freshly prepared 0.35 M solution of $NaC_{10}H_8$ in THF (2 mL, 0.07mmol) was filtered into the solution of **1**. The solution was allowed to stir for 10 minutes during which time the color of the solution darkened to black. The solution was then concentrated to half volume before 12-crown-4 (0.012 g, 0.06 mmol) was added. The solution was then layered with 3 mL of pentane before being cooled to -35 °C overnight to yield a black crystalline material which was then washed 3x with benzene (3 mL) to yield **3** (0.037 g, .015 mmol, 49%). The resulting solid is very poorly soluble in THF. Solution NMR data was taken by using the preparation described above, but removing volatiles prior to the addition of 12-crown-4. The resulting black solid was washed with pentane (3x3 mL) to remove $C_{10}H_8$ and taken up in THF-d^8. The 12-crown-4 was then added and the solution was rapidly analyzed by NMR spectroscopy before precipitation. ^{1}H NMR (THF-d^8, δ): 10.36 (br s), 8.63 (br s), 7.83 (s), 7.23 (br s), 7.04 (br s), 0.04 (br s), -1.75 (br s). Anal. Calc. for $C_{122}H_{146}B_2Fe_2Na_2O_{16}P_6S$: C 64.67, H 6.50. Found: C 63.98, H 6.85. The poor solubility of the product precluded acquisition of high quality UV-Visible data.
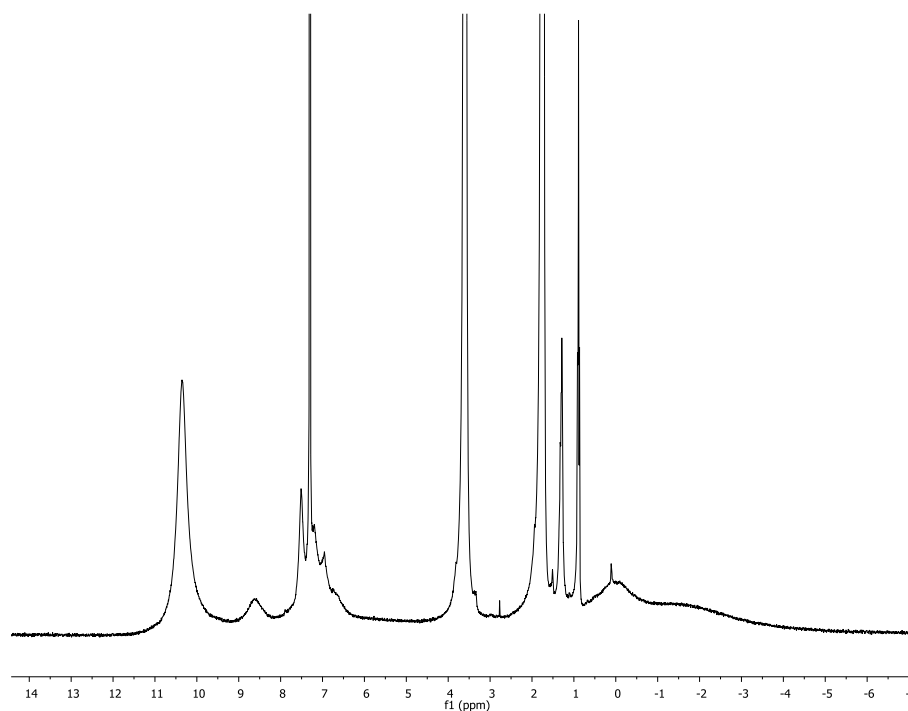
Figure 1. ^{1}H NMR Spectrum of ([PhBP$_3$]Fe)$_2$(μ-S) (**1**)
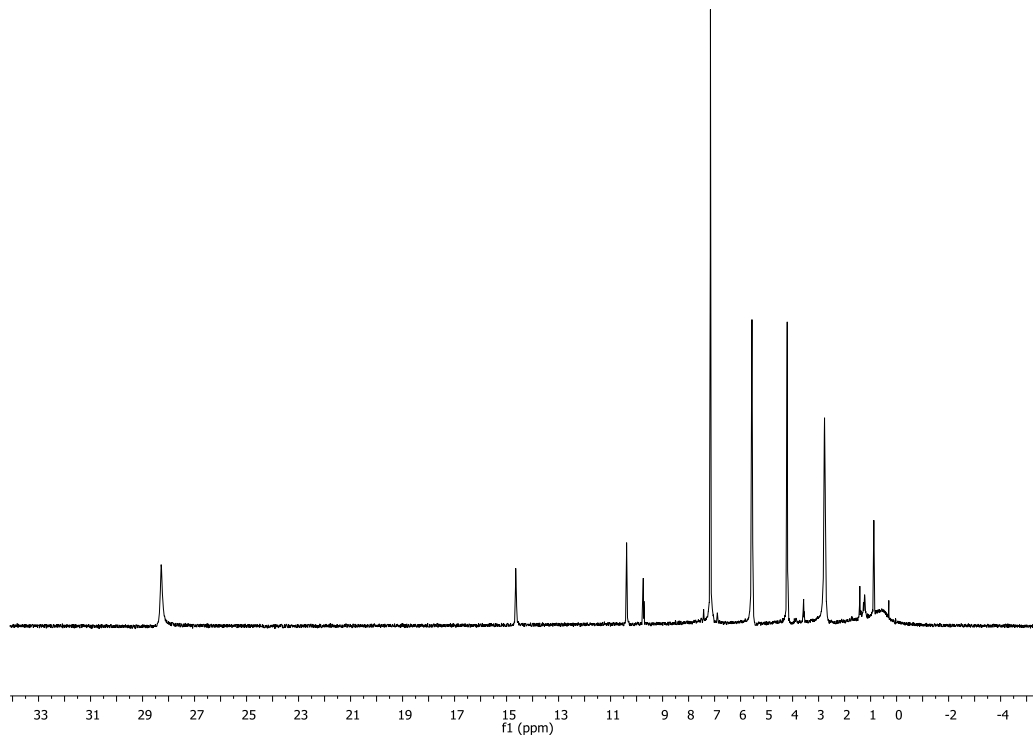
Figure 2. ^{1}H NMR Spectrum of {([PhBP$_3$]Fe)$_2$(μ-S)}{Na(12-crown-4)$_2$} (**2**)
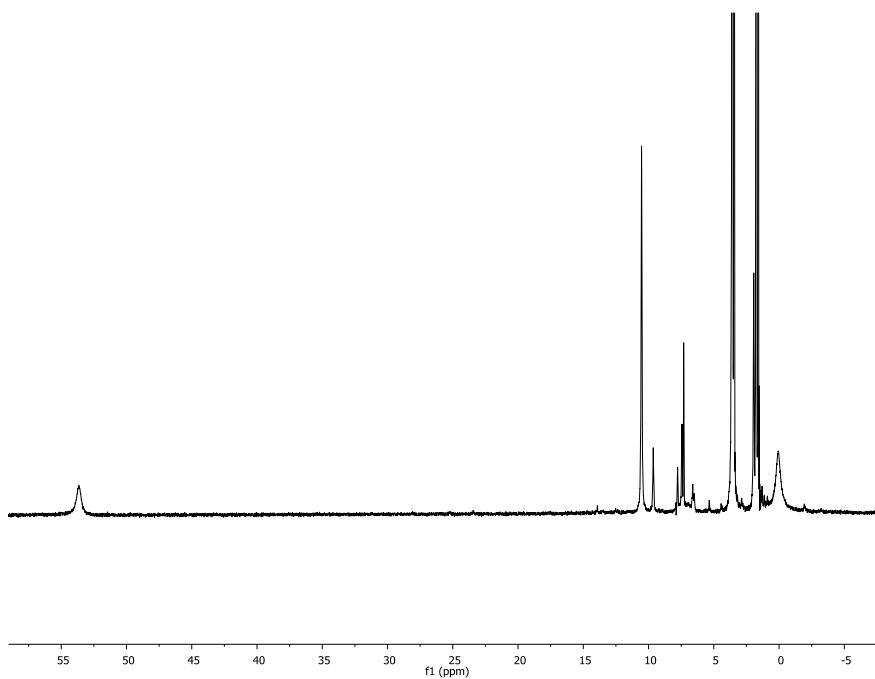
Figure 3. ^{1}H NMR Spectrum of {([PhBP$_3$]Fe)$_2$(μ-S)}{Na(12-crown-4)$_2$}$_2$ (**3**)

Figure 4. UV-Visible Spectrum of ([PhBP$_3$]Fe)$_2$(μ-S) (**1**)
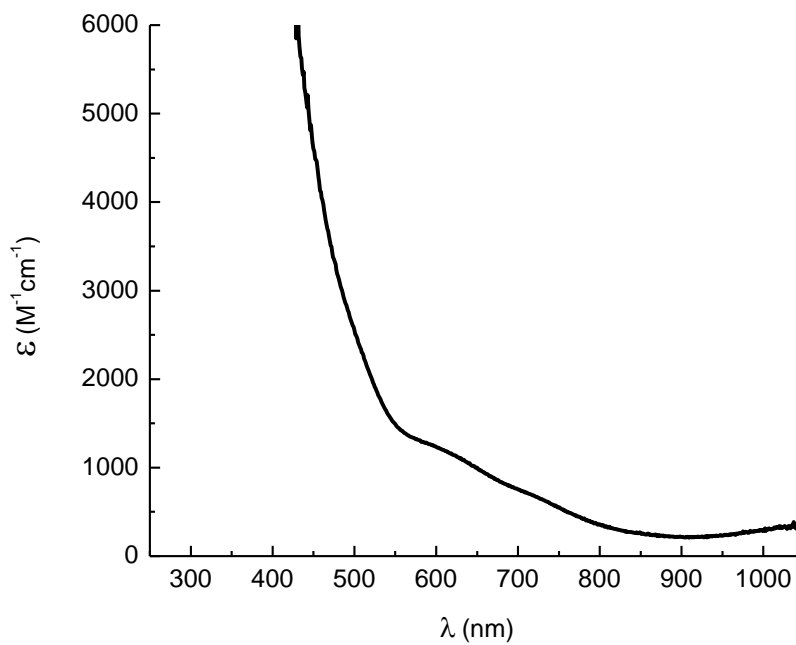
Conditions: THF, 0.46 mM

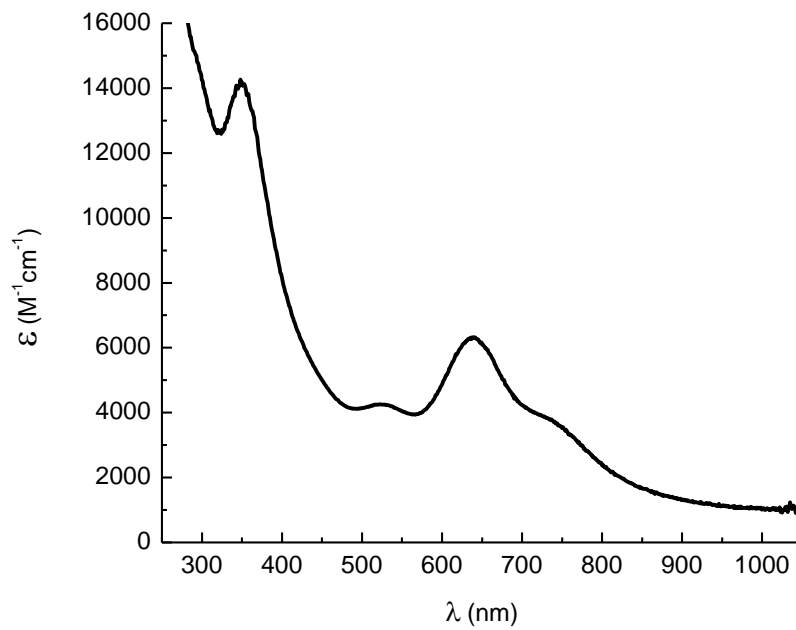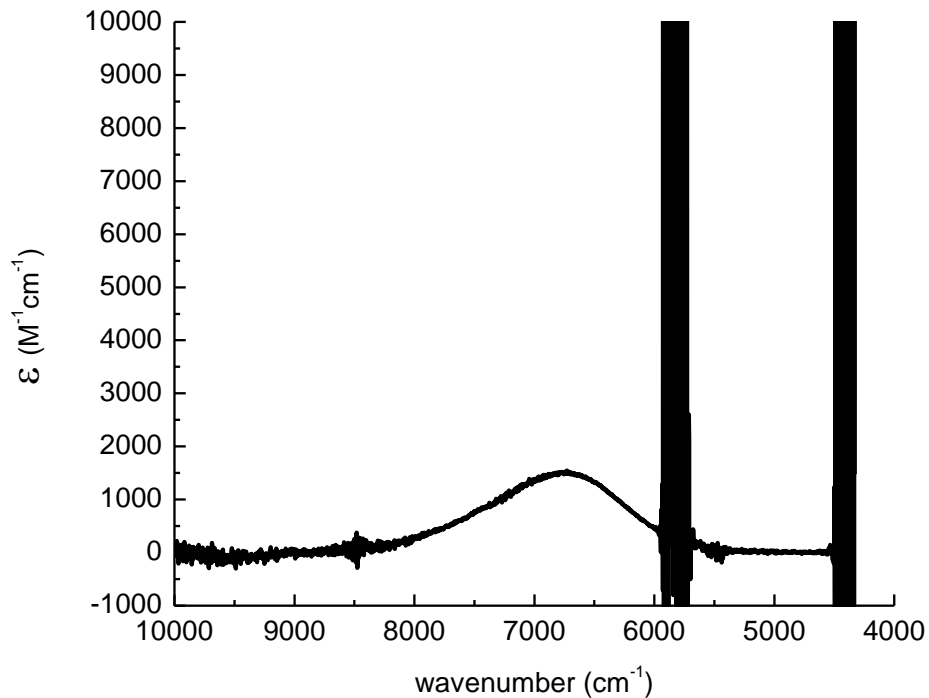**Figure 5.** UV-Visible Spectrum of $\{([PhBP_3]Fe)_2(\mu\text{-}S)\}\{Na(12\text{-crown-}4)_2\}$ (**2**)

Conditions: THF, 0.13 mM

Figure 6. Near-IR Spectrum of $\{([PhBP_3]Fe)_2(\mu\text{-}S)\}\{Na(12\text{-crown-}4)_2\}$ (**2**)

Conditions: THF, 0.13 mM

H_{ab} can be calculated using an equation[5] defined as follows:

$$H_{ab} = (0.0206(\nu_{max}\varepsilon_{max}\Delta\nu_{1/2})^{1/2})/r_{ab}$$

The parameters for this equation can be obtained from the above spectrum and the crystal structure of complex **2**:

The distance between the iron centers: $r_{ab} = 4.2$ Å

The wavelength of the maximum absorbance: $\nu_{max} = 6740$ cm^{-1}

The maximum absorbance: $\varepsilon_{max} = 1500$ M^{-1}cm^{-1}

The full width at half maximum of the band: $\Delta\nu_{1/2} = 1300$ cm^{-1}

Using these parameters, $H_{ab} = 562$ cm^{-1}

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[5] B. S. Brunschwig, C. Creutz, N. Sutin, *Chem. Soc. Rev.* **2002**, *31*, 168-184.

Figure 7. 4 K EPR Spectra of {([PhBP$_3$]Fe)$_2$(μ-S)}{Na(12-crown-4)$_2$} (**2**)
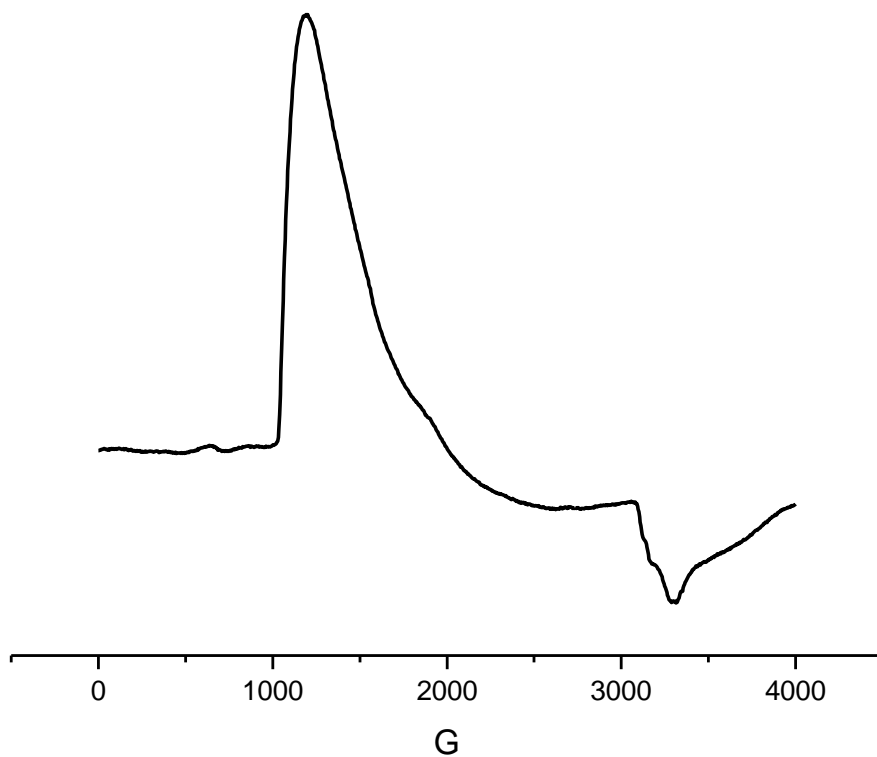
Experimental Parameters: microwave power, 20.313 mW; microwave frequency, 9.380 GHz; modulation amplitude, 4.00 G; gain, 5020.

Figure 8. Cyclic Voltammogram of ([PhBP$_3$]Fe)$_2$(μ-S) (**1**)
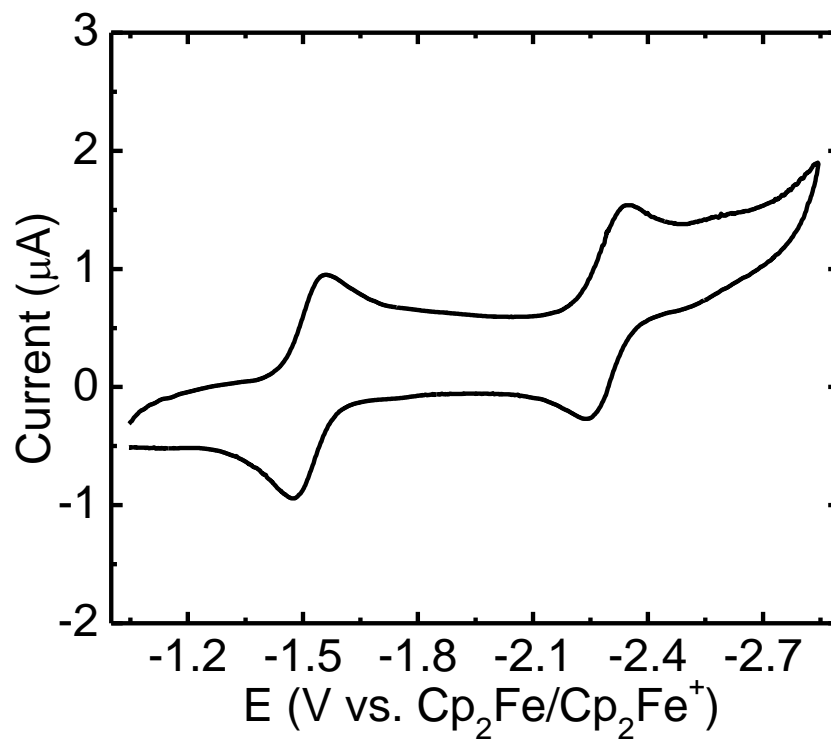
Conditions: 100 mV/s THF, 0.01 M [NBu$_4$][PF$_6$], THF, glassy carbon working, Pt auxiliary, Ag/[Ag][NO$_3$] reference.

Figure 9. Comparison of Variable Temperature Magnetic Fits of {([PhBP$_3$]Fe)$_2$(μ-S)}{Na(12-crown-4)$_2$} (**2**)
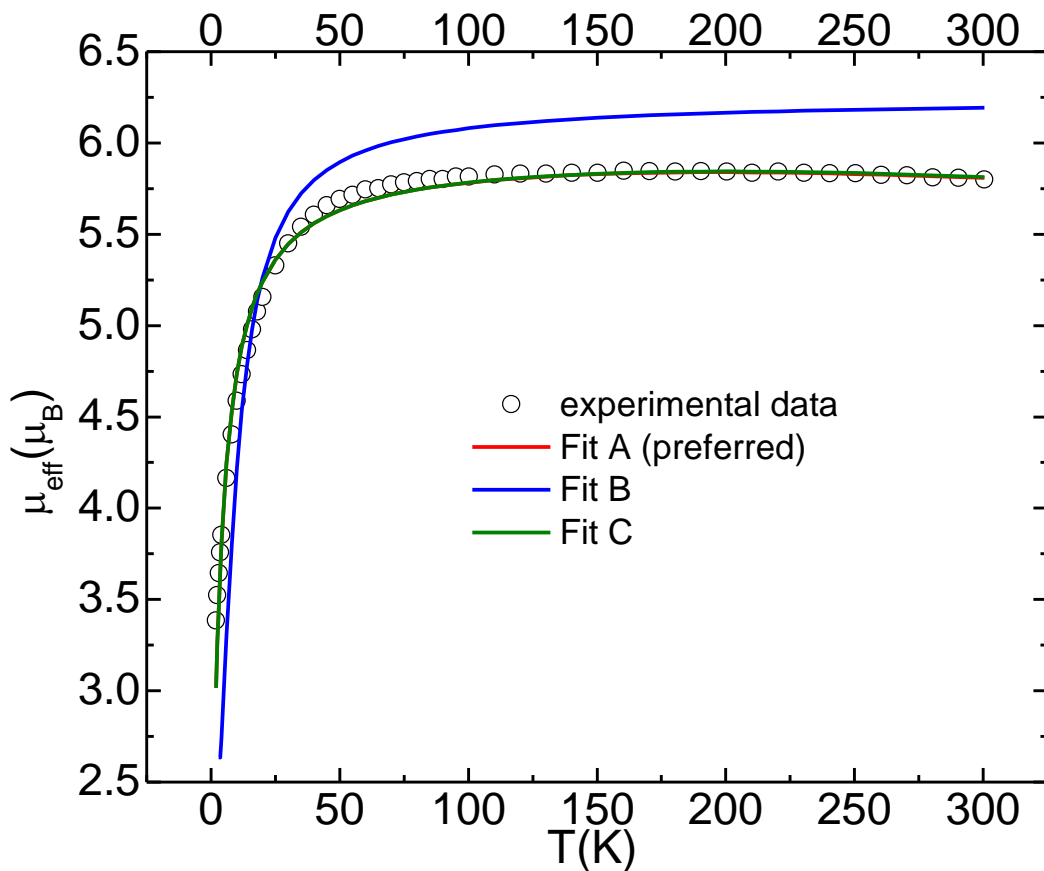
Fit Parameters	A	B	C
g	2.02	2.00	2.01
S_1	2	2	1
S_2	0.5	1.5	1.5
J_{12} (cm$^{-1)}$	100	-1.5	118
Θ (K)	-5.5	1.6	-5.7

Table 1. Magnetic and Mössbauer Fit Parameters for **1**-**3**.

	1	**2**	**3**
g	2.00	2.01	2.06
S_1	2	2	0.5
S_2	2	0.5	0.5
J_{12} (cm$^{-1)}$	-154	110	197
Θ (K)	0	-5.7	-1
δ (mm/s)	0.49	0.53/0.16	0.22
ΔE_q (mm/s)	1.91	1.02/0.01	0

Note that the magnetic fit for **1** had a small (1.3 %) S = 2 with Θ = -2 impurity included to fit the data below 50K.

Table 2. Crystal data and structure refinement for ([PhBP$_3$]Fe)$_2$(μ-S) (**1**)

Identification code	temp
Empirical formula	C90 H82 B2 Fe2 P6 S1.11
Formula weight	1518.28
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 12.9215(13) Å $\qquad$ α= 90°.
	b = 13.3515(14) Å $\qquad$ β= 92.191(2)°.
	c = 22.126(2) Å $\qquad$ γ = 90°.
Volume	3814.4(7) Å^3
Z	2
Density (calculated)	1.322 Mg/m^3
Absorption coefficient	0.584 mm^{-1}
F(000)	1584
Crystal size	0.30 x 0.20 x 0.05 mm^3
Theta range for data collection	1.78 to 31.44°.
Index ranges	-18<=h<=18, -19<=k<=18, -31<=l<=31
Reflections collected	66507
Independent reflections	11930 [R(int) = 0.1232]
Completeness to theta = 31.44°	94.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9714 and 0.8444
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11930 / 15 / 467
Goodness-of-fit on F^2	1.010
Final R indices [I>2sigma(I)]	R1 = 0.0702, wR2 = 0.1559
R indices (all data)	R1 = 0.1644, wR2 = 0.1971
Largest diff. peak and hole	1.222 and -0.566 e.Å^{-3}

Table 3. Crystal data and structure refinement for {([PhBP$_3$]Fe)$_2$(μ-S)}{Na(12-crown-4)$_2$} (**2**)

Identification code	jsa01_0m
Empirical formula	C6.62 H7.12 B0.12 Fe0.12 Na0.06 O0.50 P0.38 S0.06
Formula weight	118.14
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/C
Unit cell dimensions	a = 25.1189(12) Å α= 90°.
	b = 13.2882(6) Å β= 94.365(2)°.
	c = 28.3900(13) Å γ = 90°.
Volume	9448.7(8) Å^3
Z	64
Density (calculated)	1.329 Mg/m^3
Absorption coefficient	0.493 mm^{-1}
F(000)	3972
Crystal size	0.57 x 0.34 x 0.26 mm^3
Theta range for data collection	1.73 to 26.43°.
Index ranges	-31<=h<=31, -16<=k<=16, -35<=l<=35
Reflections collected	74372
Independent reflections	9722 [R(int) = 0.0624]
Completeness to theta = 26.43°	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9722 / 4000 / 1059
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0472, wR2 = 0.1148
R indices (all data)	R1 = 0.0751, wR2 = 0.1329
Largest diff. peak and hole	1.020 and -0.341 e.Å^{-3}

Table 4. Crystal data and structure refinement for $\{([PhBP_3]Fe)_2(\mu\text{-}S)\}\{Na(12\text{-crown-}4)_2\}_2$ (**3**)

Table 1. Crystal data and structure refinement for jsa42_0m.

Identification code	jsa42_0m
Empirical formula	C138 H178 B2 Fe2 Na2 O20 P6 S
Formula weight	2553.98
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 12.5634(6) Å α= 82.174(3)°.
	b = 18.2367(10) Å β= 79.885(3)°.
	c = 29.0547(17) Å γ = 88.640(2)°.
Volume	6492.4(6) Å^3
Z	2
Density (calculated)	1.306 Mg/m^3
Absorption coefficient	0.387 mm^{-1}
F(000)	2712
Crystal size	0.5 x 0.2 x 0.1 mm^3
Theta range for data collection	1.42 to 24.71°.
Index ranges	-14<=h<=14, -21<=k<=21, -34<=l<=34
Reflections collected	113949
Independent reflections	21981 [R(int) = 0.1035]
Completeness to theta = 24.71°	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6813
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	21981 / 1697 / 1544
Goodness-of-fit on F^2	1.011
Final R indices [I>2sigma(I)]	R1 = 0.0623, wR2 = 0.1286
R indices (all data)	R1 = 0.1182, wR2 = 0.1507
Largest diff. peak and hole	0.919 and -0.767 e.Å^{-3}