# Supporting Information

# A monometallic iron(I) organoferrate

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# Contents

# 1. General considerations

All the operations were carried out under a pure dinitrogen atmosphere using either a glove box or standard Schlenk techniques. The solvents were purified using solvent purification system (Innovative Technology, NJ, USA). UV-Visible spectra were recorded on Varian Cary 50 Bio spectrophotometer. IR spectra were measured using Varian 800 FT-IR spectrometer. Elemental analyses were performed using a Flash 2000 CHNS Analyzer by Thermo Scientific. Nuclear Magnetic Resonance spectra were recorded on a Bruker Avance 400 MHz instruments at ambient temperature.

The diffraction data were measured at low temperature [100(2) K] using Mo K$_\alpha$ radiation on a Bruker APEX II CCD diffractometer equipped with a kappa geometry goniometer. The dataset was reduced by EvalCCD[1] and then corrected for absorption.[2] The solution and refinement were performed by SHELX.[3] The crystal structure was refined using full-matrix least-squares based on $F^2$ with all non-hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the "riding" model.

Solvents were purified using a two-column solid-state purification system (Innovative Technology, USA) and transferred to glove box without exposure to air by the aid of a Straus flask.

All chemicals used in preparation of ligands and complexes were commercially available and used without further purification, unless stated otherwise. The phenyllithium solution (1.8M in dibutyl ether) was purchased from Aldrich. Cluster **7** (TBA)$_2$[Fe$_4$S$_4$Cl$_4$] was prepared according to the literature procedure.[4]

Iron standard solution for ICP-AES (c(Fe) = 1.000 g/L, in nitric acid) was purchased from Fluka.

# 2. Synthesis of tetra-*n*-butylammonium (η<sup>6</sup>-biphenyl)diphenylferrate (complex 11)

Cluster **7** (196 mg, 0.2 mmol, 1.0 equiv.) was suspended in 7-9 mL of diethyl ether and PhLi solution (0.9 mL, 1.8M in dibutyl ether, 1.6 mmol, 8.0 equiv.) was added at once at ambient temperature. The mixture was allowed to stir for 30 min at ambient temperature and then filtered. The solid was washed with ca. 20 mL of diethyl ether and extracted with ca. 20 mL of THF. The extract was concentrated *in vacuo* to ca. 5 mL volume, filtered through a glassy cotton filter and allowed to crystallize by vapor diffusion (THF/pentane). The large black needle-shaped crystals formed were collected by filtration, washed with pentane and dried *in vacuo* to yield complex **11** (152 mg, 63%). $\mu_{eff} = 1.75 \; \mu_B$ (Evans method, in THF-$d_8$).

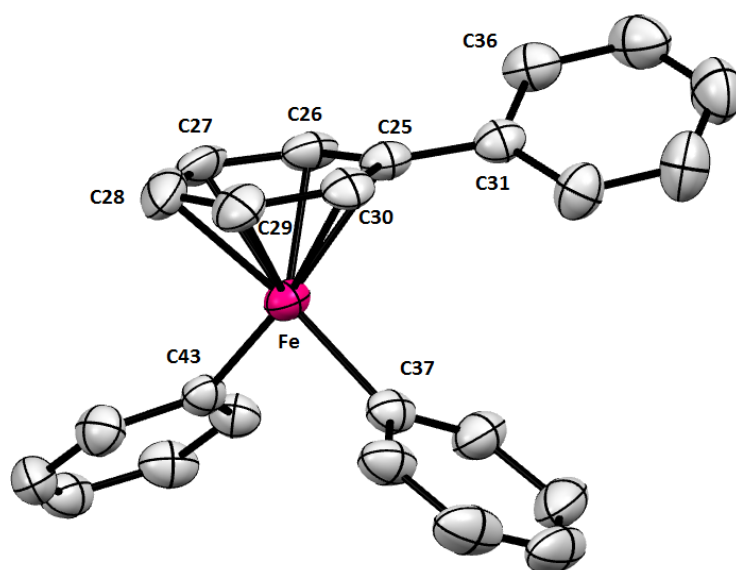**Elemental analysis.** Calcd for $C_{40}H_{56}FeN$: C, 79.18; H, 9.30; N, 2.31. Found: C, 73.62; H, 8.86; N, 2.08.

**Fe content by ICP-AES.** Calcd. for $C_{40}H_{56}FeN$: Fe, 9.20. Found: Fe, 9.60.

**IR**, cm$^{-1}$: 3028, 2961, 2941, 2874, 1553, 1506, 1472, 1452, 1379, 1047, 1014, 991, 974, 878, 770, 754, 731, 721, 696, 667, 642, 606.

**UV-Vis**, nm ($\varepsilon$ in M$^{-1}$·cm$^{-1}$): 346 ($8.17 \cdot 10^3$), 506 ($1.83 \cdot 10^3$), 718 ($5.46 \cdot 10^2$).

# 3. Selected structural parameters of complex 11



**Figure S1.** X-Ray crystal structure of the anion in complex **11**. Only one of the two molecules is shown. The ellipsoids are drawn at a 50% probability level.

**Table S1**. Selected bond length and angle of **11**.

| Parameter | Value | Parameter | Value |
|---|---|---|---|
| Fe-C43 | 1.977(2) Å | C29-C30 | 1.411(4) Å |
| Fe-C37 | 1.971(3) Å | C30-C25 | 1.420(4) Å |
| Fe-($\eta^6$-Ph plane)$^{a)}$ | 1.578 Å | C37-C43 | 2.874 Å |
| C25-C26 | 1.421(4) Å | C25-C31 | 1.470(4) Å |
| C26-C27 | 1.411(5) Å | <(C37-Fe-C43) | 93.43(10)° |
| C27-C28 | 1.398(5) Å | <(C30-C25-C31-C36) | -147.4(3)° |
| C28-C29 | 1.423(5) Å | | |

a) estimated as the distance between the Fe atom and the $\eta^6$-phenyl ring centroid.

# 4. Determination of the iron content in complex 11 by ICP-AES

*Sample solution preparation:*

A sample of complex **11** (of around 30 mg) was dissolved in a freshly-prepared "piranha" solution (obtained by mixing cold solution of $H_2O_2$ (30wt%, 1 mL) and $H_2SO_4$ (conc., 3 mL); **warning:** *extreme caution must be taken during this manipulation!*. The resulting homogeneous solution was quantitatively transferred to a 100.0 mL volumetric flask and diluted with bidistilled water until the mark.

*Standard solutions preparation:*

Using commercially available iron standard solution (c(Fe) = 1.000 g/L), five standard solution with concentrations 1.000 mg/L, 2.000 mg/L, 3.000 mg/L, 4.000 mg/L and 5.000 mg/L were prepared.

*Measurements and calculations:*

The intensities at 238.15 nm[49] were measured thrice for each of prepared solutions (the sample solution and the standard solutions). The mean values were used to establish the calibration curve I = K·c + W. The mass content of iron in the sample was calculated, using the following formula (for the calibration curve established in mg/L concentration units):

$$wt\%(Fe) = \frac{1}{10} \times \frac{I(sample) - W}{K} \times \frac{1}{m(sample), mg}$$

# 5. Determination of the effective magnetic moment of complex 11 by Evans method

A sample of complex **11** (around 25 mg) was placed in a weighed J. Young NMR tube. The tube with the complex was weighed again. 0.60 mL of THF-$d_8$ was placed in the tube. The solution was homogenized and a sealed capillary insert, containing THF-$d_8$ was placed inside the tube. NMR spectrum of the resulting sample was registered and the shift of the solvent residual peaks was calculated ($\Delta f$, Hz).

Molar magnetic susceptibility calculation:

$$\chi_M = \frac{477 \cdot \Delta f}{2 \cdot f_w \cdot c}$$

where $f_w = 4 \cdot 10^8$ Hz (NMR working frequency), $c$ – concentration of the complex (M).

Measured magnetic moment:

$$\mu_{meas} = \sqrt{8 \cdot \chi_M \cdot T} = 1.62\ \mu_B$$

where $\chi_M$ – molar magnetic susceptibility, $T$ – absolute temperature (K).

The diamagnetic susceptibility was estimated using the following formula:[5]

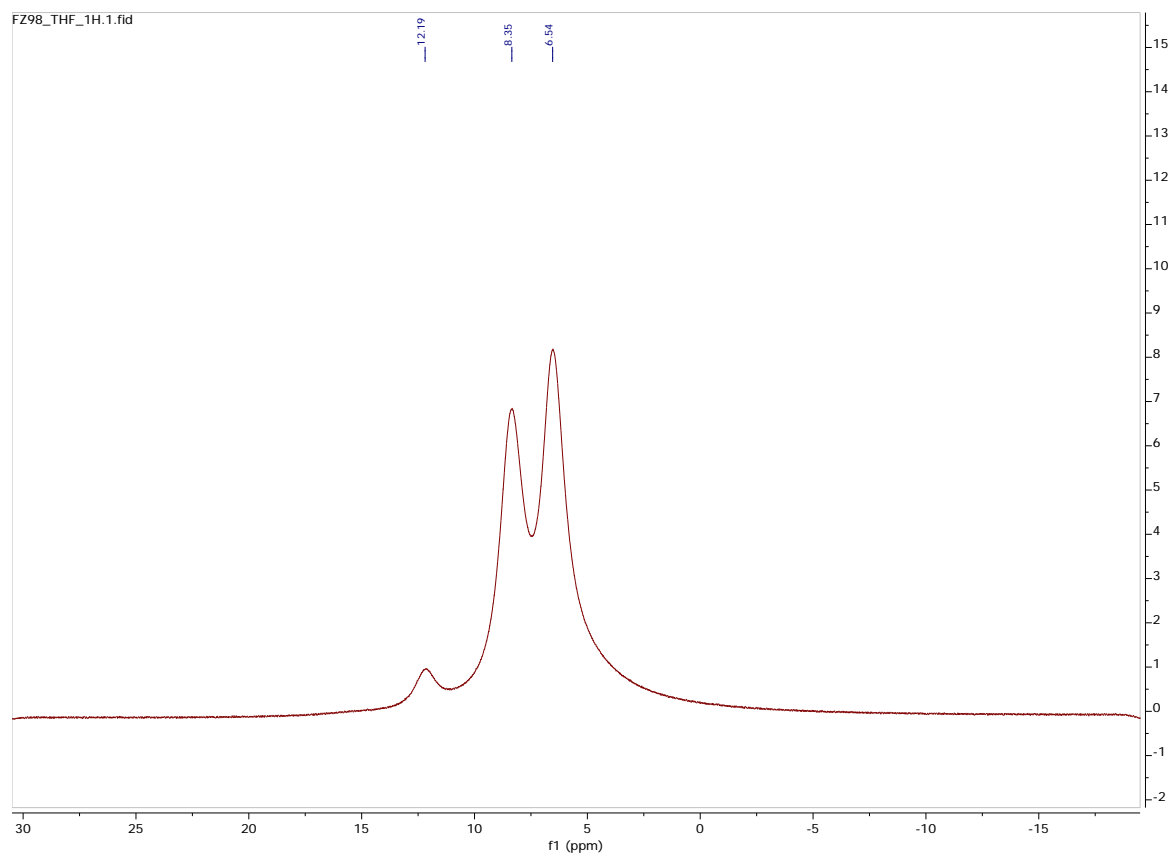$$\chi_D \approx -\frac{MW}{2} \times 10^{-6}\ emu \cdot mol^{-1} = -182.14 \cdot 10^{-6}\ emu \cdot mol^{-1}$$

The corrected effective magnetic moment was calculated as follows:

$$\mu_{eff} = \sqrt{\mu_{meas} - 8 \cdot \chi_D \cdot T} = \sqrt{(1.62\ \mu_B)^2 - 8 \cdot (-0.05339\ emu \cdot K \cdot mol^{-1})} = 1.75\ \mu_B$$

Theoretical spin-only values for the effective magnetic moment are calculated as follows:

$$\mu_{eff} = \sqrt{n(n+2)}, \text{ where } n \text{ – number of unpaired electrons.}$$
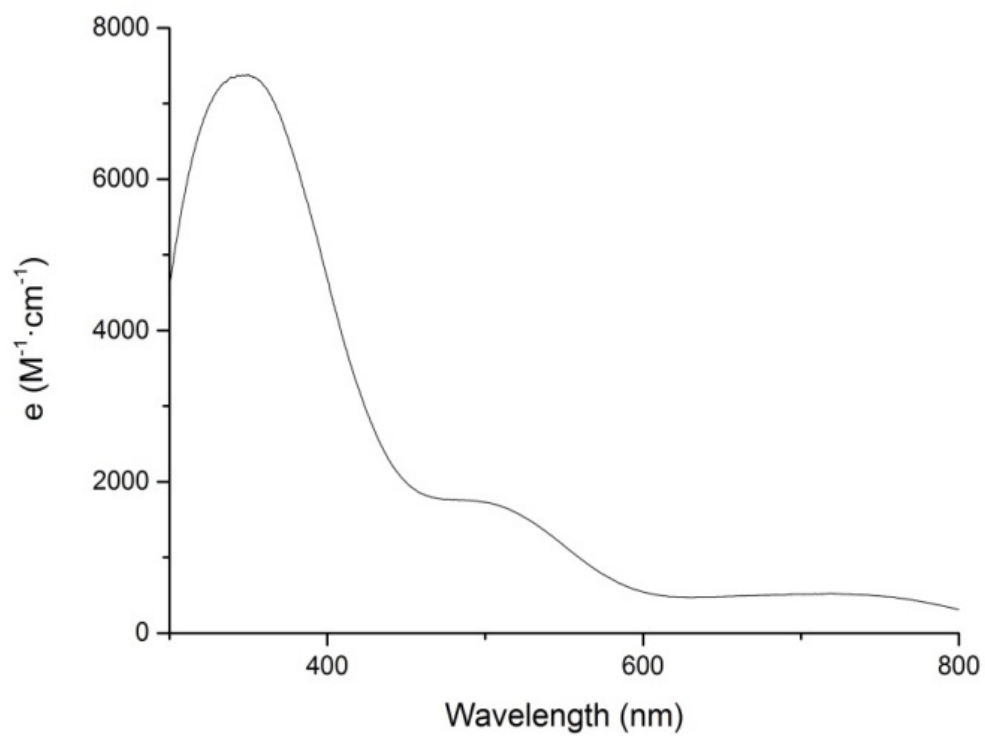
# 6. $^{1}$H NMR spectrum



**Figure S2**. $^{1}$H NMR spectrum of complex **11** in THF-d$_8$

# 7. UV-Vis spectrum

**Figure S3**. UV-Vis spectrum of complex **11** in THF.

# 8. Reactivity of complex 11 towards organic electrophiles

A solution of complex **11** in THF or acetonitrile (0.03-0.08 M) was treated with an excess (>10 equiv.) of the corresponding organic halide (PhCl, 2-PyBr, $n$-BuBr or $p$-(MeO)C$_6$H$_4$Br) at r.t. The reaction mixture was stirred at room temperature, quenched with TFA (diluted acetone solution) or (in case of 2-bromopyridine) exposed to the air, evaporated to dryness and extracted with benzene. The obtained solution was analyzed by GC-MS.

Estimated yields of the cross-coupling products (GC):

1) 2-phenylpyridine: 6% yield, 1 h reaction time;

2) 4-methoxy-1,1'-biphenyl: 8% yield, 20 h reaction time;

3) $n$-butylbenzene: 23% yield, 18 h reaction time.

# 9. Computational details

The geometries of both the low-spin doublet and high-spin quartet states of **11** were optimized at the OPBE[6]/def2-TZVPP level in Gaussian09.[7] The choice of this density functional was motivated by its use of OPTZ exchange, which helps in accurately reproducing the energies of inorganic complexes with different spin states.[8] The computations were corrected for the influence of solvent (diethylether) using the SMD implicit solvent model.[9]

**Table S2**. Computed electronic energies of the doublet and quartet spin states of **11** at the OPBE/def2-TZVPP theoretical level.

| | |
|---|---|
| Doublet | -2190.621975 |
| Quartet | -2190.590455 |

**Table S3**. Comparison of experimental and computed geometries of **11**. Computations at the OPBE/def2-TZVPP theoretical level.

| Parameter | Experimental Value | Computed Value (Doublet) |
|---|---|---|
| Fe-C43 | 1.977(2) Å | 1.961Å |
| Fe-C37 | 1.971(3) Å | 1.967Å |
| Fe-($\eta^6$-Ph plane)[a)] | 1.578 Å | 1.533Å |
| C25-C26 | 1.421(4) Å | 1.429Å |
| C26-C27 | 1.411(5) Å | 1.415Å |
| C27-C28 | 1.398(5) Å | 1.417Å |
| C28-C29 | 1.423(5) Å | 1.416Å |
| C29-C30 | 1.411(4) Å | 1.415Å |
| C30-C25 | 1.420(4) Å | 1.429Å |
| C37-C43 | 2.874 Å | 2.707Å |
| C25-C31 | 1.470(4) Å | 1.478Å |
| <(C37-Fe-C43) | 93.43(10)° | 87.12° |
| <(C30-C25-C31-C36) | -147.4(3)° | -149.2° |

# 9. References

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