Supplementary Information

Spin states, bonding and magnetism in mixed valence iron(0)–iron(II) complexes

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**General considerations**

All manipulations were performed in an argon-filled MBraun glovebox maintained below 1 ppm of O$_2$ and H$_2$O or under an N$_2$ atmosphere using standard Schlenk techniques unless mentioned otherwise. Glassware was oven-dried at 150 °C for at least 12 h prior to use. Celite and molecular sieves were dried above 200 °C under vacuum for at least 12 h. Pentane, THF, hexanes, benzene, toluene, and diethyl ether were purified by passage through activated alumina and Q5 columns from Glass Contour Co, under argon. Benzene-$d_6$ and THF-$d_8$ were vacuum transferred from a solution of potassium benzophenone ketyl and was stored over 4 Å molecular sieves. KC$_8$ was prepared in an N$_2$ glovebox by manually grinding stoichiometric amounts of potassium metal and graphene at 90 °C until observation of a homogenous bronze-colored powder. L$_3$H,$^{[1]}$ [L$_3$FeCl]$_2$,$^{[2]}$ FeCl$_2$(THF)$_{1.43}$,$^{[3]}$ and K[CpFe(CO)$_2$]$_2$$^{[4]}$ were synthesized according to literature procedures. NMR data were collected on Agilent 400 or 500 MHz spectrometers. Chemical shifts in $^1$H NMR spectra are referenced to the residual protiated solvent peaks of C$_6$D$_5$H (δ 7.16 ppm) and THF-$d_8$ (δ 3.58 ppm). Solution magnetic susceptibilities were determined by the Evans method. Elemental analyses were performed at the CENTC Elemental Analysis Facility at the University of Rochester. IR spectra were collected on an Alpha Platinum ATR IR Spectrometer. UV-vis spectra were recorded on a Cary 50 spectrometer using Schlenk-adapted quartz cuvettes with a 1, 2, or 10 mm path length.
**Synthetic procedures**

**Synthesis of \([L^bFeCl]_2\):**

1,3-bis(2,4,6-trimethylphenylimido)propane (\(L^bH\), 432 mg, 1.41 mmol) was dissolved in THF (5.5 mL). A solution of benzylpotassium (183 mg, 1.41 mmol) in THF (6.5 mL) was added dropwise to the \(L^bH\) solution and this mixture was stirred for 10 minutes. FeCl\(_2\)(THF)\(_{1.43}\) (324 mg, 1.41 mmol) was suspended in THF (5 mL) in a 100 mL bomb flask and stirred for 10 minutes. The solution of \(KL^b\) was added dropwise to the suspension of FeCl\(_2\)(THF)\(_{1.43}\) (N.B. the inverse addition produces significant amounts of \(L^b_2Fe\)). The reaction mixture was stirred at room temperature for 30 minutes and then was heated to 85 °C for 1 hour. The mixture was then concentrated under reduced pressure and the resulting red oil was heated at 85 °C under vacuum to give dark orange solids. The solids were extracted with toluene (12 mL), filtered, and concentrated to 8 mL. Pentane (11 mL) was layered on top and the solution was cooled to −40 °C overnight to yield orange crystalline solids (183 mg, 33%). The mother liquor was evaporated under reduced pressure and the solid was extracted with toluene (3 mL), filtered, and pentane (17 mL) was layered on top before cooling it to −40 °C overnight to yield a second crop of orange crystals (169 mg, total yield 63%).

\(^1H\) NMR (400 MHz, C\(_6\)D\(_6\)) δ ppm: 25.5 (6H, para-CH\(_3\)), 13.2 (4H, meta-ArCH), 2.97 (12H, ortho-CH\(_3\)), 36.0 (1H, α-CH). The resonance associated with the imine-CH was not found, likely due to its proximity to the paramagnetic Fe, as has previously reported for the analogous Co complex.\(^1\) \(\mu_{\text{eff}}\) (Evans, C\(_6\)D\(_6\), 298 K) = 4.3(2) \(\mu_B\). IR (ATR, neat): 1563, 1497, 1469, 1436, 1375, 1346, 1387, 1280, 1224, 1126, 1010, 849, 742, 517, 499 cm\(^{-1}\). UV-vis (hexane, \(\varepsilon\) in mM\(^{-1}\)cm\(^{-1}\)): 336 nm. **Elemental analysis** calculated for C\(_{21}\)H\(_{25}\)ClFeN\(_2\): C, 63.58%; H, 6.35%; N, 7.06. Found: C, 63.75%; H, 6.35%; N, 6.95%. Mössbauer (80 K, solid): \(\delta = 0.88\) mm s\(^{-1}\), |\(\Delta E_Q\)| = 2.39 mm s\(^{-1}\), \(\Gamma = 0.19\) mm s\(^{-1}\).
Synthesis of \( \text{L}^4\text{FeFeCp(CO)}_2 \) (1a)

\([\text{L}^\text{Me,Me,MeFeCl}]_2\) (238.2 mg, 0.290 mmol) was suspended in diethyl ether (6 mL, all solvents used must be free of THF). \( \text{K[CpFe(CO)}_2\) (133.3 mg, 0.617 mmol) was added and the residual solids washed with 5 mL of diethyl ether for quantitative transfer. To this suspension hexane (5 mL) was added. After stirring for 30 min, solution was filtered through a medium porosity frit and resulting red solution cooled to \(-40 \degree\) overnight. \( \text{Me,Me,MeLFeFeCp(CO)}_2\) was collected as dark red crystals in two crops (combined yield 204.4 mg, 62.2%).

\(^1\text{H NMR}\) (400 MHz, \( \text{C}_6\text{D}_6\)) \(\delta = 190.8\) (2H, para-ArH), 71.1 (4-5H, meta-ArH or CpH), 40.9 (6H, imine-CH\(_3\)), 1.27 (4H, residual Fp impurity), \(-5.96\) (5H, CpH or meta-ArH), \(-61.9\) (12H, ortho-CH\(_3\)), \(-77.4\) (2-3H, assigned as 3H, \(\alpha\)-CH\(_3\)). \(\mu_{\text{eff}}\) (Evans, \( \text{C}_6\text{D}_6\), 298 K) = 5.2(2) \(\mu_B\). \(\text{IR}\) (ATR, neat): 1941 (s, symmetric CO), 1877 (s, asymmetric CO), 1515, 1463, 1434, 1411, 1366, 1319, 1297, 1252, 1191, 1163, 991, 865, 828, 820, 790, 762, 648, 587, 537, 498 cm\(^{-1}\). \(\text{UV-vis}\) (hexane, \(\varepsilon\) in mM\(^{-1}\)cm\(^{-1}\))): 345, 272 nm. \(\text{Elemental analysis}\) calculated for \( \text{C}_{29}\text{H}_{32}\text{Fe}_2\text{N}_2\text{O}_2\): C, 63.07; H, 5.84; N, 5.07. Found: C, 62.92%; H, 5.83%; N, 4.96%.

\(\text{Mössbauer}\) (80 K, solid): Nested fit: Component 1 (53\%): \(\delta = 0.08\) mm s\(^{-1}\), |\(\Delta E_0\)| = 1.84 mm s\(^{-1}\) (FeCp(CO))\(_2\)). Component 2 (47\%): \(\delta = 0.60\) mm s\(^{-1}\), |\(\Delta E_0\)| = 0.90 mm s\(^{-1}\) (\(\text{L}^4\text{Fe}\)). Staggered fit: Component 1 (50\%): \(\delta = 0.03\) mm s\(^{-1}\), |\(\Delta E_0\)| = 1.80 mm s\(^{-1}\) (FeCp(CO))\(_2\)). Component 2 (50\%): \(\delta = 0.57\) mm s\(^{-1}\), |\(\Delta E_0\)| = 0.90 mm s\(^{-1}\) (\(\text{L}^4\text{Fe}\)).
Synthesis of L₆FeFeCp(CO)₂ (1b)

[L₆MesFeCl]₂ (126 mg, 0.159 mmol) was suspended in diethyl ether (6 mL, all solvents used must be THF free). K[CpFe(CO)₂] (73.1 mg, 0.338 mmol) was added and the residual solids washed with 5 mL of diethyl ether for quantitative transfer. After stirring for 30 minutes, the solution was filtered through a medium porosity frit and the filtrate was concentrated to 2 mL under reduced pressure. Cooling the red solution to −40 °C overnight yielded dark red crystals of L₆MesFeFeCp(CO)₂ in two crops (combined yield 151.2 mg, 88%).

¹H NMR (400 MHz, C₆D₆) δ (ppm) 94.5 (1H, β-CH), 77.1 (4-5H, CpH or meta-CH), 24.21 (6H, para-CH₃), 1.37 (residual Cp containing impurity), −8.81 (4-5H, CpH or meta-CH), −69.6 (12H, ortho-CH₃). The resonance associated with the imine-CH was not found. µₑₑₑ⁰ (Evans, C₆D₆, 298 K) = 5.3(2) µₑₑ. IR (ATR, neat): 1944 (s, symmetric CO), 1878 (s, asymmetric CO), 1766, 1568, 1506, 1471, 1437, 1345, 1308, 1228, 1126, 1010, 848, 824, 744, 733, 694, 648, 582, 542, 514, 495 cm⁻¹. UV-vis (hexane, ε in mM⁻¹cm⁻¹): 334 nm. Elemental analysis calculated for C₂₈H₃₀Fe₂N₂O₂ (%): C, 62.48; H, 5.62; N, 5.20. Found: C, 62.46; H, 5.57, N, 5.09. Mössbauer (80 K, solid). Nested fit: Component 1 (42%): δ = 0.12 mm s⁻¹, |ΔE₀| = 1.86 mm s⁻¹ (FeCp(CO)₂). Component 2 (46%): δ = 0.58 mm s⁻¹, |ΔE₀| = 0.65 mm s⁻¹ (L₆Fe). Component 3 (12%): δ = −0.35 mm s⁻¹, |ΔE₀| = 1.04 mm s⁻¹ (unknown impurity). Staggered fit: Component 1 (42%): δ = 0.05 mm s⁻¹, |ΔE₀| = 1.70 mm s⁻¹ (FeCp(CO)₂). Component 2 (46%): δ = 0.65 mm s⁻¹, |ΔE₀| = 0.79 mm s⁻¹ (L₆MesLFe). Component 3 (12%): δ = −0.35 mm s⁻¹, |ΔE₀| = 1.04 mm s⁻¹ (unknown impurity).
**1H NMR spectra of metal complexes**

**Figure S 1.** 1H NMR (400 MHz) spectrum of [L\textsuperscript{b}FeCl\textsubscript{2}] in benzene-\textit{d}_6.

**Figure S 2.** 1H NMR (400 MHz) spectrum of L\textsuperscript{a}FeFeCp(CO)\textsubscript{2} (1a) in benzene-\textit{d}_6.

**Figure S 3.** 1H NMR (400 MHz) spectrum of L\textsuperscript{b}FeFeCp(CO)\textsubscript{2} (1b) in benzene-\textit{d}_6.
FTIR spectra of metal complexes

Figure S 4. FTIR spectrum of solid \([\text{L}^b\text{FeCl}]_2\)

Figure S 5. FTIR spectrum of solid \(\text{L}^b\text{FeFeCp(CO)}_2\) (1a).

Figure S 6. FTIR spectrum of solid \(\text{L}^b\text{FeFeCp(CO)}_2\) (1b).
Table S1. Summary of FTIR data (solid samples).

| Compound      | 1a            | 1b            | K[FeCp(CO)₂] | Fe₂Cp₂(CO)₄ |
|---------------|---------------|---------------|--------------|-------------|
| ν₃CO (cm⁻¹)   | 1941, 1877    | 1944, 1878, 1766 | 1860, 1731   | 1972, 1751  |
UV/vis spectra of metal complexes

Figure S7. Top: UV-vis spectra of $[\text{H,Mes}^\text{LFeCl}]_2$ in 0.52-4.09 mM solutions in THF. Bottom: Beer-Lambert Law plot of selected UV-vis spectral features for $[\text{L}^\text{H,Mes}^\text{FeCl}]_2$ in THF solutions. Trendline equations are in the boxes to the right.
**Figure S 8.** Top: UV-vis spectra of L^4FeFeCp(CO)_2 (1a) in 0.07-1.31 mM solutions in THF. Bottom: Beer-Lambert Law plot of selected UV-vis spectral features for 1a in THF solutions. Trendline equations are in the insets.
**Figure S 9.** Top: UV-vis spectra of L^6FeFeCp(CO)₂ (1b) in 0.24-1.93 mM solutions in THF. Bottom: Beer-Lambert Law plot of selected UV-vis spectral features for 1b in THF solutions. Trendline equations are in the boxes to the right.
Mössbauer spectra and assignments

Figure S 10. Zero-field Mössbauer spectrum of \([L^\text{b} \text{FeCl}^2]_2\) recorded at 80 K. The red circles are the data, the black line is a one component simulation of the data (\(\delta = 0.88\) mm/s, \(|\Delta E_Q| = 2.39\) mm/s, \(\Gamma = 0.19\) mm/s), and the gray line is the residual.

Figure S 11. Zero-field Mössbauer spectra of \(L^\text{o} \text{FeCp(CO)}_2\) (1a) recorded at 220 K. Left spectrum has been modelled with a nested fit, while the right has been modelled using a staggered fit (See table). The circles represent the data, the solid colored lines are the fits, and the grey line represents the residual.
Table S 2. Zero-field Mössbauer fitting parameters for 1a at 220 K.

| Component        | Isomer shift ($\delta$) | Quadrupole Splitting ($\Delta E_Q$) | $I_{1R}$ FWHM | $a_{12}$ | Relative Area |
|------------------|--------------------------|-------------------------------------|----------------|---------|---------------|
| Nested Component 1 | 0.075 mm/s               | 1.84 mm/s                           | 0.19           | 0.5     | 53.2          |
| Component 1      | 0.60 mm/s                | 0.9 mm/s                            | 0.40           | 0.60    | 46.8          |
| Staggered Component 1 | 0.03 mm/s               | 1.80 mm/s                           | 0.19           | 0.5     | 49.8          |
| Component 2      | 0.57 mm/s                | 0.9 mm/s                            | 0.28           | 0.5     | 50.2          |

Figure S 12. Variable temperature Mössbauer spectra for 1a showing broadening upon decreasing temperature. Top: 220 K. Middle: 150 K. Bottom: 80 K.
Figure S 13. Zero-field Mössbauer spectra of L$^b$FeFeCp(CO)$_2$ (1b) recorded at 80 K. Left spectrum has been modelled with a nested fit, while the right has been modelled using a staggered fit (See table S 3). The circles represent the data, the solid, colored lines are the fits, and the grey line represents the residual.

Table S3. Zero-field Mössbauer fitting parameters for 1b at 80 K.

|                | Isomer shift (δ) | Quadrupole Splitting (ΔE$_Q$) | Ω$_{LR}$ (FWHM) | Relative Area |
|----------------|------------------|-------------------------------|-----------------|---------------|
| **Nested**     |                  |                               |                 |               |
| Component 1    | 0.12 mm/s        | 1.86 mm/s                     | 0.14            | 42.4          |
| Component 2    | 0.58 mm/s        | 0.65 mm/s                     | 0.15            | 45.7          |
| Component 3    | ~0.35 mm/s       | 1.04 mm/s                     | 0.12            | 11.9          |
| (impurity)     |                  |                               |                 |               |
| **Staggered**  |                  |                               |                 |               |
| Component 1    | 0.05 mm/s        | 1.70 mm/s                     | 0.14            | 42.4          |
| Component 2    | 0.65 mm/s        | 0.79 mm/s                     | 0.15            | 45.7          |
| Component 3    | ~0.35 mm/s       | 1.04 mm/s                     | 0.12            | 11.9          |
| (impurity)     |                  |                               |                 |               |
Figure S 14. Zero-field Mössbauer spectra of K[CpFe(CO)₂] recorded at 80 K. \( \delta = 0.15 \text{ mm s}^{-1}; \Delta E_O = 2.05 \text{ mm s}^{-1}; I_{LR} = 0.17 \). The circles represent the data, the solid, colored lines are the fits, and the grey line represents the residual.

Figure S 15. Zero-field Mössbauer spectra of L′FeBr recorded at 80 K.

\[
\delta = 0.69 \text{ mm s}^{-1}; \Delta E_O = 0.93 \text{ mm s}^{-1}; I_{LR} = 0.60/0.40
\]
Figure S 16. Zero-field Mössbauer spectra of $\text{L}^{\prime}\text{Fe}$ recorded at 80 K.

$\delta = 0.70 \text{ mm s}^{-1}$; $\Delta E_Q = 1.27 \text{ mm s}^{-1}$; $I_{L/R} = 0.56/0.54$.

Table S4. Experimental details of Mössbauer data presented in Figure 6

| R         | L     | $\delta$ (mm s$^{-1}$) | $\Delta E_Q$ (mm s$^{-1}$) | Temp (K) | Ref |
|-----------|-------|------------------------|-----------------------------|----------|-----|
| CH$_3$    | L$^c$ | 0.48                   | 1.42                        | 4.2      | [5] |
| PCy$_2$   | L$^d$ | 0.54                   | 1.21                        | 4.2      | [6] |
| PrPr$_2$  | L$^d$ | 0.55                   | 1.03                        | 4.2      | [6] |
| Fp        | L$^a$ | 0.57/0.60              | 0.90                        | 80       | This work |
| Fp        | L$^b$ | 0.58/0.65              | 0.65/0.79                   | 220      | This work |
| PPh$_2$   | L$^d$ | 0.58                   | 1.50                        | 4.2      | [6] |
| CPh$_3$   | L$^d$ | 0.58                   | 0.76                        | 80       | [7] |
| NHrBu     | L$^c$ | 0.63                   | 1.11                        | 4.2      | [5] |
| Br        | L$^c$ | 0.69                   | 0.93                        | 80       | This work |
| I         | L$^c$ | 0.70                   | 1.27                        | 80       | This work |
| NHTol     | L$^c$ | 0.71                   | 1.42                        | 4.2      | [5] |
| O(C$_6$H$_{12}$Bu$_3$) | L$^a$ | 0.77                   | 1.38                        | 173      | [8] |
| Cl        | L$^c$ | 0.78                   | 1.61                        | 4.2      | [5] |
Magnetic measurements.

Magnetic data were collected using a Quantum Design MPMS 3 superconducting quantum interference device (SQUID) magnetometer. Magnetic measurements for compounds 1a and 1b were performed on ground microcrystalline solids. The samples were prepared under an atmosphere of N₂ and restrained with eicosane in polyethylene capsules. Dc magnetic measurements were collected in the temperature range of 2–300 K. Variable field magnetization curves were collected at 100 K to check for curvature indicative of the presence of ferromagnetic impurities. Dc magnetic susceptibility measurements were performed under applied magnetic fields of 0.05 T and 0.10 T, and 0.5 T and corrected for the diamagnetism of each sample and eicosane, estimated using Pascal’s constants. Variable field, variable temperature magnetization measurements (reduced magnetization) were performed under applied magnetic fields of 1–7 T in 1 T increments, in the temperature range of 2–10 K. Dc magnetic susceptibility data and reduced magnetization data were simulated using the program MagProp in DAVE 2.0. The spin Hamiltonians employed accounted for g-anisotropy and axial and transverse zero-field splitting, D and E, respectively. Magnetic data for 1a and 1b were modelled according to the Van Vleck model using the following spin Hamiltonian: \( \hat{H} = D \hat{S}_z^2 + E (\hat{S}_x^2 - \hat{S}_y^2) + g_i \mu_B S \hat{H}, (i = x, y, z) \). In this Hamiltonian, D and E are the axial and transverse zero-field splitting parameters, respectively, and g is the electron g-value. No satisfactory simulation of the reduced magnetization data for 1b was achieved due to the presence of iron impurities, as evident by the 11.9% impurity determined from Mössbauer spectroscopy. However, simulation of the dc magnetic susceptibility data for 2 afforded a preliminary value for D, while E was fixed to be zero.
**Figure S 17.** Variable field magnetization collected on a polycrystalline sample of 1a at 100 K. The absence of curvature supports the absence of ferromagnetic impurities.

**Figure S 18.** Variable temperature dc magnetic susceptibility data of 1a collected under an applied magnetic field of 1000 Oe. The black line represents the simulated data using the spin Hamiltonian parameters in Table 1 in the manuscript.
Figure S 19. Variable field, variable temperature magnetization data of 1a in the temperature range of 2–10 K, under an applied magnetic field range of 1–7 T, in 1 T increments. The black lines represent the best simulation to the data using the spin Hamiltonian parameters in Table 1 in the main manuscript.

Figure S 20. Variable field magnetization collected on a polycrystalline sample of 1b at 100 K. The absence of curvature supports the absence of ferromagnetic impurities.
Figure S 21. Variable temperature dc magnetic susceptibility data of 1b collected under an applied magnetic field of 1000 Oe. The black line represents the simulated data using the spin Hamiltonian parameters in Table 1 in the manuscript.
Crystallographic data

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of [L₆FeCl]₂. Similar low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Dectris Pilatus3R detector with Mo Kα (λ = 0.71073 Å) for the structure of 1a and 1b. All diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The data for [L₆FeCl]₂ was refined as a 2-component twin. The fractional volume contribution of the minor twin component was freely refined to a converged value of 0.3502(13). The structure was solved with SHELXT and was refined against F² on all data by full-matrix least squares with SHELXL.¹¹ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme of compound 007b-18003 can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 2117732 ([L₆FeCl]₂), 2117733 (1a), 2117734 (1b) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S5. Selected bond lengths (Å) and angles (°) from the solid state structures of 1a and 1b. *centroids were calculated using the Mecury program and do not have associated standard deviations.

| Bond length (Å)/angle (°) | 1a           | 1b           |
|--------------------------|--------------|--------------|
| Fe1–Fe2                  | 2.4199(3)    | 2.4127(2)    |
| Fe1–N11                  | 1.9968(10)   | 2.0076(10)   |
| Fe1–N21                  | 1.9800(11)   | 2.0032(11)   |
| Fe2–C1                   | 1.7390(15)   | 1.7507(14)   |
| Fe2–C2                   | 1.7440(14)   | 1.7466(14)   |
| Fe-Cp(centroid)*         | 1.720        | 1.724        |
| N21-Fe1-N11              | 91.16(4)     | 95.13(4)     |
| N21-Fe1-Fe2              | 135.15(3)    | 136.74(3)    |
| N11-Fe1-Fe2              | 133.24(3)    | 128.13(3)    |
| C1-Fe2-C2                | 91.77(6)     | 93.45(6)     |
| Fe1-Fe2-Cp(centroid)*    | 113.4        | 119.2        |
Table S6. Crystal data and structure refinement for $[\text{L}^3\text{FeCl}]_2$, 1a, and 1b

| Complex          | $[\text{L}^3\text{FeCl}]_2$ | 1a               | 1b               |
|------------------|-------------------------------|------------------|------------------|
| Identification Code       | 007b-18003                   | 007c-20055       | 007c-20027       |
| CCDC number             | 2117732                      | 2117733          | 2117734          |
| Empirical formula       | $\text{C}_{42}\text{H}_{50}\text{Cl}_2\text{Fe}_2\text{N}_4$ | $\text{C}_{29}\text{H}_{32}\text{Fe}_2\text{N}_2\text{O}_2$ | $\text{C}_{25}\text{H}_{30}\text{Fe}_2\text{N}_2\text{O}_2$ |
| Formula weight         | 793.46                       | 552.26           | 538.24           |
| Temperature            | 93(2) K                      | 93(2) K          | 93(2) K          |
| Wavelength             | 1.54184 Å                    | 0.71073 Å        | 0.71073 Å        |
| Crystal system         | Monoclinic                   | Monoclinic       | Triclinic        |
| Space group            | $\text{C}2/c$                | $\text{P}2_1/c$  | $\text{P}1$      |
| a (Å)                  | 15.0560(4)                   | 10.0268(6)       | 9.29645(19)      |
| b (Å)                  | 18.5712(5)                   | 17.9172(3)       | 11.7447(3)       |
| c (Å)                  | 14.5565(6)                   | 20.2769(12)      | 12.4107(3)       |
| α (°)                  | 90                           | 90               | 90.0369(18)      |
| β (°)                  | 91.558(3)                    | 134.848(10)      | 103.7400(18)     |
| γ (°)                  | 90                           | 90               | 107.2310(19)     |
| Volume (Å³)            | 4068.6(2)                    | 2582.7(4)        | 1253.52(5)       |
| Z                       | 4                            | 4                | 2                |
| Density (calc, g/cm³)  | 1.295                        | 1.420            | 1.426            |
| Absorption coefficient | 7.175 mm⁻¹                   | 1.152 mm⁻¹       | 1.185            |
| F(000)                 | 1664                         | 1152             | 560              |
| θ range                | 3.780 to 67.179°             | 3.054 to 27.484° | 3.238 to 27.482° |
| Refractions collected  | 7860                         | 57312            | 48243            |
| Independent reflections| 7860 [R(int) = 0.0928]       | 5914 [R(int) = 0.0372] | 5729 [R(int) = 0.0338] |
| Observed reflections (I > 2σ(I)) | 6569 | 5517 | 5289 |
| Max./min. transmission | 1.00000 / 0.68613            | 1.00000 / 0.46715 | 1.00000 / 0.76436 |
| Data / restraints / parameters | 7860 / 0 / 236 | 5914 / 0 / 323 | 5729 / 0 / 313 |
| Goof                     | 1.097                        | 1.054            | 1.039            |
| R1 [I>2σ(I)]           | 0.0466                       | 0.0236           | 0.0228           |
| wR2 [I>σ(I)]           | 0.1379                       | 0.0592           | 0.0583           |
| R1 (all data)          | 0.0537                       | 0.0261           | 0.0253           |
| wR2 (all data)         | 0.1423                       | 0.0603           | 0.0594           |
| Largest diff. peak and hole (e/Å³) | 0.353 and -0.583 | 0.359 and -0.288 | 0.374 and -0.247 |
Figure S 22. Complete numbering scheme for $[L^bFeCl]_2$. The thermal ellipsoids are drawn at 50% probability level. The hydrogen atoms are shown as circles for clarity.
Figure S 23. The complete numbering scheme of 1a with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Figure S 24. The complete numbering scheme of 1b with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.
**Computational details**

Geometry optimizations, frequency calculations, and calculations of Mössbauer parameters were performed using the ORCA program package (Version 3.0.3).\(^{[12]}\) Optimized geometries were calculated using the B3LYP functional and the scalar relativistically recontracted version of the Aldrichs triple-z basis set (def2-TZVP). The scalar relativistic zero-order approximation (ZORA) was used to correct for relativistic effects. The atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ) was used on all atoms. The calculated structures were confirmed to be minima based on the absence of imaginary frequencies from frequency calculations on the optimized geometries. Mössbauer parameters were calculated using the correlations that were described previously.\(^{[13]}\) Unrestricted corresponding orbitals (UCOs) were calculated using the ORCA program package (Version 4.1.2) with the UCO keyword. Orbitals are plotted with an isosurface value of 0.05. The UCOs from the B3LYP/def2-TZVP calculation are shown in Figure 5 in the main text. Intrinsic atomic orbitals and intrinsic bond orbitals (IAOIBO) were calculated with B3LYP functional and def2-TZVP/D3BJ/ZORA basis set, as described above.\(^{[14]}\) The Fe–Fe bonding orbitals were identified by the contributions from Fe1 and Fe2, with 61α and 54β being the only orbitals with contributions from both metal centers.

**Table S6.** Comparison of bonding parameters between solid state and optimized structures.

| Bond length/angle | 1a XRD | 1a opt | 1b XRD | 1b opt |
|-------------------|--------|--------|--------|--------|
| Fe1–Fe2           | 2.42(1)| 2.40   | 2.41(1)| 2.41   |
| Fe1–N21           | 1.98(1)| 2.00   | 2.01(1)| 1.99   |
| Fe1–N11           | 2.00(1)| 2.00   | 2.00(1)| 1.99   |
| N21-Fe1-N11       | 91.2(1)| 89     | 95.1(1)| 95     |
| N21-Fe1-Fe2       | 135.2(1)| 135   | 136.7(1)| 132   |
| N11-Fe1-Fe2       | 133.2(1)| 135   | 128.1(1)| 132   |
| C1-Fe2-C2         | 91.8(1)| 92     | 93.5(1)| 92     |
**Table S7.** Comparison of spectroscopic and computed Mössbauer parameters for 1a and 1b.

|       | 1a         | 1b         |
|-------|------------|------------|
|       | Exp   | B3LYP | BP86 | Exp   | B3LYP | BP86 |
| Fe1   | δ (mm/s) | 0.08   | 0.60  | 0.09  | 0.48  | 0.59  | 0.64  | 0.12  | 0.58  | 0.08  | 0.46  | 0.59  | 0.64  |
| Fe2   | 1.84  | 0.90   | 2.05  | -2.03 | 1.60  | -1.85 | 1.86  | 0.65  | -2.05 | -2.04 | 1.58  | -2.06 |
| ΔE_Q (mm/s) |  |  | | | | | | | |

**Figure S 25.** Optimized structures of 1a and 1b.
Figure S 26. Larger version of UCO molecular orbitals (top) and IAOIBO (bottom) in Figure 5.
### Coordinates

**1a**

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| Fe   | -2.283360141 | 12.582490871 | 9.503470931 |
| Fe   | -4.223770562 | 13.930041265 | 9.902720878 |
| C    | -3.991260133 | 13.632851088 | 11.606104040 |
| O    | -3.889870301 | 13.464880849 | 12.744460914 |
| C    | -3.158090134 | 13.512104124 | 9.935830969 |
| O    | -2.503990012 | 16.262781052 | 9.970440748 |
| N    | -1.739239885 | 10.721820583 | 10.002180800 |
| N    | -0.759730251 | 12.644960774 | 8.210870832 |
| C    | -0.411510215 | 8.689780476  | 10.245640878 |
| H    | 0.365920247  | 8.702100780  | 11.02521075 |
| H    | -0.094930165 | 9.798830704  | 9.488210517 |
| C    | -1.322890203 | 8.313920693  | 10.79761025 |
| C    | -0.620240187 | 10.077006042 | 9.690008052 |
| C    | 0.383230164  | 10.650590874 | 8.849609036 |
| C    | 0.255050205  | 11.794051167 | 8.091550358 |
| C    | 1.332440267  | 12.106930628 | 6.410750592 |
| H    | 1.577020170  | 11.229891068 | 6.478840597 |
| C    | 2.251440169  | 12.422010991 | 7.557830616 |
| C    | 1.657520201  | 9.797570923  | 8.676960628 |
| H    | 1.895480097  | 9.231620836  | 10.15000924 |
| H    | 2.516430440  | 10.440830639 | 8.488360798 |
| H    | 1.607139881  | 9.082130480  | 7.848640538 |
| C    | -2.786270090 | 10.727506671 | 10.752970601 |
| C    | -3.780560273  | 9.382208983  | 10.089000794 |
| C    | -4.876740361  | 8.932890814  | 10.819420976 |
| H    | -5.652830565  | 8.371520578  | 10.312530556 |
| C    | -4.985620168  | 9.916330635  | 12.178170877 |
| H    | -5.849190341  | 8.489008747  | 12.73961073 |
| C    | -3.980660183  | 9.905306163  | 12.827280858 |
| H    | -4.059670051  | 10.10217033  | 13.888181228 |
| C    | -2.88240175  | 10.366670681 | 12.132860864 |
| C    | -3.644900394  | 9.055860534  | 8.628060416 |
| H    | -3.219570476  | 8.885031011  | 8.806120840 |
| H    | -4.609480850  | 8.796660710  | 8.195680799 |
| C    | -2.969230478  | 8.207820654  | 8.480210410 |
| C    | -1.764490207  | 11.097080808 | 12.842921221 |

**1b**

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| Fe   | 1.28692670138272 | 7.43688860483305 | 8.91792801644806 |
| C    | 3.37444121976293 | 7.44225044535140 | 10.10406790994542 |
| C    | 2.92652300170416 | 5.8593651561136 | 10.70101554797479 |
| O    | 2.69160638275271 | 4.82705422429875 | 11.15443162610160 |
| C    | 3.85455489768517 | 6.8301783937535 | 8.5459463267617 |
| O    | 4.21532661415769 | 6.4295738949959 | 7.5197340985701 |
| N    | 0.38299271577016 | 8.8825697338734 | 7.8418167310146 |
N -0.12635696219619 6.08903199566791 8.47746639648884
C -0.74037537034748 7.15559928825528 6.089034439309 6.62758763747955
H -1.1248317990318 9.57706464439306 6.5337639375819
C -1.50345685740647 7.54699183724551 7.1177686051774
H -2.41134613304946 7.5903520362075 6.5337639375819
C -1.18846011534149 8.71555992882558 7.18032431206736
H -1.8864120130511 9.57706464439306 6.62758763747955
C 0.2024460782553 10.1540348364420 7.8863006911498
H 2.05923952980913 10.36506997826186 6.89958063820489
C 2.73251799989512 11.58218355245876 6.89464963801260
H 3.53955238771615 11.74596150029613 6.1868279905833
C 2.40790878544346 12.58672811546635 7.8053153082737
H 1.36835479317163 12.35057261813860 8.69827086902736
C 1.10370624937327 11.2676250510793 7.91684028623180
C 0.66094664494957 11.14970158037991 8.7040538007805
H 2.44490013695942 9.29256268254070 5.8935636748550
H 2.79516154284581 8.3911302639344 6.3952041181296
C 3.24241053742481 9.63688286026208 5.2334907404356
H 1.5946870354948 9.89433270573232 5.26937653274145
C 3.15394100608714 13.89364608498603 7.8061894351978
H 4.23275607634283 13.73471472645749 7.75003579149578
C 2.94314958844727 14.4688503960896 8.7081628833800
H 2.87183907636577 14.50819974951510 6.9465705348266
C -0.46661843096635 10.92997437301894 9.67509325826490
H -1.43672246200688 10.95815049046225 9.17232919675402
H -0.467562789762743 11.69872813830104 10.44733644431998
C -0.4005282016803 9.95082440702326 10.1532055508688
C 0.02458375823548 4.78196502751742 9.02980473330660
C 0.70928977941433 3.79885548566348 8.30462997334714
C 0.87385362994775 2.54604572830962 8.88621116024247
H 1.40846495146057 1.7807767337025 8.32976472691323
C 0.39604958832798 2.25291944955805 10.15898525918628
C -0.27513305310546 3.52332848822993 10.8541644221176
C -0.64906860960353 3.04868263633277 11.85116304673478
C -0.46315104537700 4.52186747464917 10.3149197631803
C 1.26061959108884 4.09505034652071 6.93722823946692
H 0.47732383181505 4.4057957354239 6.24274046452728
H 1.75242916709993 3.21491029143430 6.52413623844687
H 1.99365781071426 4.90410526643924 6.9694376207739
C 0.63638915534699 0.90493313774836 10.78263063443460
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