Supporting information

Construction of diiron diamond-core complexes influenced by a fluoroalkoxide ligand

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Table of contents

A. GENERAL EXPERIMENTAL DETAILS 3
B. COMMERCIAL STARTING MATERIALS 3
C. SYNTHESIS OF STARTING MATERIALS 4
C.1. BIS(HEXAMETHYLDISILAZANE AMIDE)IRON(II) – [Fe(HMDS)$_2$] (2) 4
C.2. SYNTHESIS OF HMTOH 4
C.3. SYNthesis of [Fe(HMTO)$_2$] (3). 5
C.4. SYNTHESIS OF [Fe(HMTO)$_2$]·THF 5
D. Synthesis of the diamond-core complexes 4 and 5 6
D.1 Synthesis of (Ph(CF$_3$)$_2$CO)$_2$Fe$_2$[µ$_2$-(µ$_2$-N(SiMe$_3$)$_2$)$_2$] (4) 6
D.2 Synthesis of (Ph(CF$_3$)$_2$CO)$_2$Fe$_2$[µ$_2$-HMTO]$_2$. (5) 6
E. NMR spectra 7
F. Variable temperature $^1$H NMR analysis 12
G. SC-XRD analysis. 18
H. COMPUTATIONAL STUDIES 21
H.1 DFT CALCULATIONS 21
H.2 AIM CALCULATIONS 24
I. $^{57}$FE MÖSSBAUER SPECTROSCOPY 24
A. General experimental details

All air- and moisture-sensitive materials were manipulated in an argon-filled M Braun glovebox or on a dual-manifold Schlenk line. All glassware was dried in an oven prior to use (160 °C). Tetrahydrofuran and diethyl ether were refluxed and distilled from Na/benzophenone under argon and stored in a Schlenk flask with a potassium mirror layer. Pentane and n-hexane were refluxed and distilled from LiAlH₄ under argon and stored in a Schlenk with a potassium mirror layer. Toluene and benzene were obtained dry and degassed from a SPS M Braun system and storage under 3 Å molecular sieves in the glovebox. C₆D₆ was refluxed and distilled from LiAlH₄ under argon. CDCl₃ was dried over 3 Å molecular sieves. A freshly opened bottle of the fluorinated alcohol 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol (1) was degassed by three cycles of freeze-pump-thaw and stored over molecular sieves (4 Å) for several days prior to use. ¹H, ¹³C, and ¹⁹F NMR spectra were obtained on Agilent Mercury spectrometers (400 MHz). Chemical shifts for ¹H and ¹³C spectra are reported as parts per million relative to tetramethylsilane and referenced to the residual ¹H or ¹³C resonances of the deuterated solvent (¹H δ [ppm]: benzene 7.16, chloroform 7.26; ¹³C δ [ppm]: benzene 128.06, chloroform 77.16). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), integration. Elemental analyses were performed at the Warsaw University of Technology (Department of Catalysis and Organometallic Chemistry). Mössbauer spectra were recorded at the Institute of Microelectronics and Photonics (Łukasiewicz-IMIF). Diffraction data were collected at 100(2) K on an Agilent Technologies SuperNova Dual Source diffractometer with MoKα (λ = 0.71073) radiation using CrysAlis RED software.¹ The analytical numerical absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid,² implemented in SCALE3 ABSPACK scaling algorithm, were applied.³ The structural determination procedure was carried out using the SHELX package.⁴ The structures were solved with direct methods and then successive least-square refinement was carried out based on the full-matrix least-squares method on F2 using the SHELXL program.⁴ All H-atoms were positioned geometrically with C–H equal to 0.93, 0.96, and 0.97 Å for the aromatic, methyl and methylene H-atoms, respectively. The H-atoms were constrained to ride on their parent atoms with Uiso(H) = xUeq(C), where x = 1.2 for the aromatic and methylene H-atoms, and 1.5 for the methyl H-atoms. The figures for this publication were prepared using the ORTEP-3 program.⁵ The crystallographic data can be obtained free of charge via www.ccdc.cam.ac.uk/ data_request/cif, under the deposition numbers CCDC 2204464 (3-THF), 2155775 (4) and 2204465 (5).

B. Commercial starting materials

Reagents were purchased at the highest commercial quality. Solid compounds were used without further purification unless otherwise stated and liquids were distilled/degassed prior to be used and storage into the glovebox. Mg (turnings, 99.9+%), NaH (95%), palladium(II) acetylacetonate (35% Pd) were purchased from Acros Organics. FeCl₂ (10 mesh, 99.99% trace metal basis), 2-bromomesitylene (99%) and 1 (99+) were purchased from Alfa Aesar. 2,6-dibromophenol (98%) was purchased from Sigma Aldrich.

C. Synthesis of starting materials

C.1. Bis(hexamethyldisilazane amide)iron(II) – [Fe(HMDS)$_2$] (2)

\[
\begin{align*}
\text{FeCl}_2 + & \quad \text{Me}_3\text{SiN}^+\text{SiMe}_3^- \quad \text{Et}_2\text{O} \\
& \quad \text{Li}^+ \quad \text{2 equiv.} \\
& \quad \text{Et}_2\text{O} \quad \text{-20 °C to RT} \\
& \quad \text{24 h} \\
& \quad \text{-2 LiCl} \\
\rightarrow & \quad \text{Me}_3\text{SiN}^+\text{SiMe}_3^- \quad \text{Me}_3\text{Si}^+ \\
& \quad \text{N-Fe-N} \\
& \quad \text{SiMe}_3 \\
\end{align*}
\]

This compound was obtained following the procedure reported by Holland et al.\textsuperscript{6} and distilled inside the glovebox as suggested by Bukhryakov et al.\textsuperscript{7}

A Schlenk flask was charged with crushed anhydrous FeCl$_2$ beads (500 mg, 3.92 mmol) and Et$_2$O (50 mL). The suspension was cooled to 0 °C after which a solution of LiN(SiMe$_3$)$_2$ (830 mg, 7.85 mmol, 2.0 equiv.) in Et$_2$O (50 mL) was added dropwise under stirring. The suspension was allowed to reach ambient temperature slowly and it was stirred for 24 h. Volatile materials were removed under vacuum, and the dark green residue was extracted with pentane (3 x 25 mL). The dark green extracts were filtered, transferred into a round bottom Schlenk flask and concentrated under vacuum, returning a dark green oil. The Schlenk flask was connected to a distillation apparatus and the oil was distilled under reduced pressure (10 mTorr) to afford pyrophoric green oil at 80-90 °C (sole fraction, oil bath temperature 105-110 °C). The product was directly transferred into a freezer inside the glovebox where the oil solidified upon cooling to afford a light green solid (980 mg, 80% yield; reported yield: 88%). \textit{Note: [Fe(N(SiMe$_3$)$_2$)$_2$] is a highly reactive compound that reacts vigorously with water or oxygen. Care should be taken when handling this material in large quantities as it can spontaneously combust upon exposure to air.} \textsuperscript{1}H NMR (400 MHz, C$_6$D$_6$): $\delta$ [ppm] = 64.9 (36H, br).

C.2. Synthesis of HMTOH

\[
\begin{align*}
\text{Br} & \quad \text{ONa} \quad \text{Br} \\
& \quad \text{2} \\
& \quad \text{MgBr} \\
& \quad \text{Pd(acac)$_2$} \\
& \quad \text{THF} \\
& \quad \text{-2 MgBr$_2$} \\
& \quad \text{acidic work-up} \\
\rightarrow & \quad \text{HMTOH} \\
& \quad \text{1.9 g, 79% yield} \\
\end{align*}
\]

This compound was obtained following the procedure reported by Bukhryakov et al.\textsuperscript{7}

Sodium hydride (0.22 g, 8.65 mmol, 1.1 equiv.) was carefully added to a solution of 2,6-dibromophenol (2.00 g, 7.86 mmol, 1.0 equiv.) in THF (20 mL) under nitrogen stream. Pd(acac)$_2$ (0.12 g, 0.39 mmol, 0.05 equiv.) was added, followed by freshly prepared mesityl magnesium bromide in THF (~20 mL, ~1.0 M, \textit{vide infra}), and the resulting mixture was heated under reflux under a positive pressure of nitrogen for 12 h. Upon cooling to room temperature, 5% aqueous HCl (~100 mL) was carefully added to quench the excess of both the Grignard reagent and NaH. The mixture was extracted with CH$_2$Cl$_2$ (3x25 mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The resulting residue (yellow solid) was purified by recrystallization from hot methanol (100


\textsuperscript{7} Belov, D. S.; Mathivathanan, I.; Martin, W. B.; Bukhryakov, K. V. \textit{Angew. Chem. Int. Ed.} \textbf{2021}, 60, 2934 –2938.
mL) to obtain an off-white solid (1.33 g). The filtrate was evaporated, and the residue was purified by silica gel chromatography (20:1 hexanes/EtOAc) followed by recrystallization from hot methanol (~5 mL) to yield 0.56 g of product additionally. Combined yield 1.9 g, 79%. 

\[
\delta_{(\text{ppm})} = 2.09 (s, 12\text{H}), 2.36 (s, 6\text{H}), 4.57 (s, 1\text{H}), 7.01 (s, 4\text{H}), 7.06 (s, 3\text{H}).
\]

Preparation of the Grignard reagent. 2-Bromo-1,3,5-trimethylbenzene (3.68 mL, 4.79 g, 23.6 mmol, 3.0 equiv.) was dissolved in THF (25 mL), and ca. 1/3 of the solution was added to Mg turnings (0.63 g, 25.9 mmol, 3.3 equiv) under the flow of argon. Once the reaction started, the rest of the bromoarene solution was added dropwise. The freshly prepared organo-magnesium reagent was used as such upon removal of the unreacted Mg turnings by cannula filtration.

C.3. Synthesis of [Fe(HMTO)\(_2\)] (3).

This compound was obtained following the procedure reported by Bukhryakov et al.\(^7\)

In a Schlenk flask, [Fe(HMDS)\(_2\)] (500 mg, 1.33 mmol) was dissolved in toluene (10 mL) and solid HMTOH (890 mg, 2.66 mmol, 2.0 equiv.) was added. The reaction mixture was refluxed for 1 hour, cooled to room temperature, and then stirred overnight. Toluene was evaporated, and the residue was recrystallized from n-hexane (100 mL). The product was obtained as pale yellow-greenish crystals in two crops: 721 mg (first crop), 254 mg (second crop), 75% combined yield. 

\[
\delta_{(\text{ppm})} = -26.1 (\text{br}, s, 8\text{H}), -18.6 (\text{br}, 2\text{H}), 2.67 (\text{br}, 24\text{H}), 39.3 (\text{br}, 12\text{H}), 64.9 (\text{br}, 4\text{H}).
\]

\(^{13}\text{C}\{(\text{H})\} \text{NMR (C}_6\text{D}_6, 101 \text{MHz}): \text{Silent spectrum. Anal. Calcd for C}_{48}\text{H}_{50}\text{FeO}_2: C, 80.66\%; H, 7.05\%. Found: C, 80.75\%; H, 7.08\%.

C.4. Synthesis of [Fe(HMTO)\(_2\)]·THF

Inside the glovebox, [Fe(HMDS)\(_2\)] (500 mg, 1.33 mmol) was dissolved in pentane (10 mL) into a vial. THF (108 \(\mu\text{L}, 1.33 \text{ mmol}, 1.0 \text{ equiv.}) was added and the mixture was stored in the freezer at \(-40 \text{ °C}\) for 1 h. Then, solid HMTOH (877 mg, 2.66 mmol, 2.0 equiv.) was added portion-wise. The reaction mixture was stirred until it reached room temperature (about 30 min) and then it was allowed to stir for an additional 1.5 h. A white microcrystalline material was formed. The solid was removed by filtration and...
it was washed with one portion (1 ml) of cold pentane (−40 °C). Such pentane washing and the reaction mother liquors were combined and stored in the freezer (−40 °C). The first crop of the colourless microcrystalline solid returned 620 mg product, while the second crop, obtained from the mother liquors, returned 314 mg of 3·THF (89% combined yield). 1H NMR (CDCl₃, 400 MHz): δ [ppm] = −20.6 (br, 2H), −13.8 (br, 6H), −5.9 (br, 6H), 2.9 (br, 4OH), 56.9 (br, 4H). 13C{1H} NMR (CDCl₃, 101 MHz): Silent spectrum. Anal. Calcd for C₆₂H₆₁Fe₆O₁₂·C₆H₁₂O: C, 78.40%; H, 7.64%. Found: C, 78.84%; H, 7.53%. ⁵⁷Fe-Mössbauer (solid state, 298 K): δ = 1.15 mm s⁻¹, |ΔE₀| = 2.94 mm s⁻¹.

D. Synthesis of the diamond-core complexes 4 and 5

D.1 Synthesis of [(Ph(CF₃)₂CO)₂Fe₂][(μ²-N(SiMe₃))₂] (4)

In a vial, inside the glovebox, [Fe(HMDS)₂] (124 mg, 0.33 mmol) was dissolved in pentane (2 ml). Then, a solution of 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol (80.6 mg, 0.33 mmol, 1.0 equiv.) in pentane (1 ml) was added dropwise. The reaction mixture was stirred for 2 h at room temperature. A crystalline greenish solid was formed and it was removed by filtration. The solid was washed with cold pentane (2 x 0.5ml) and dried under vacuum. The reaction mother liquids were stored in the fridge (−40 °C) and pale greenish crystals were obtained overnight, suitable for X-ray measurements. The two crops of the Fe₂(μ-OR)₂ complex returned 120 mg product, 79% yield. 1H NMR (CDCl₃, 400 MHz): δ [ppm] = 23.61 (s, 4H), 11.34 (d, J_HH = 7.06 Hz, 4H), 10.18 (t, J_HH = 6.99 Hz, 2H), −1.50 (s, 36H). ¹³C{¹H} NMR (CDCl₃, 101 MHz): δ [ppm] = 147.9, 138.6, 134.3, 132.8, 52.9, 2.3. ¹⁹F{¹H} NMR (CDCl₃, 376 MHz): δ [ppm] = −41.02. Anal. Calcd for C₂₆H₁₆F₁₂Fe₂N₂O₂Si₆: C, 39.22%; H, 5.05%; N, 3.05%. Found: C, 38.92%; H, 5.09%; N, 4.33%. μ_eff = 3.02 μ₀, Evans’s method (298 K). ⁵⁷Fe-Mössbauer (solid state, 298 K) δ = 0.69 mm s⁻¹, |ΔE₀| = 1.25 mm s⁻¹.

D.2 Synthesis of [(Ph(CF₃)₂CO)₂Fe₂][(μ²-HMTO)] (5)

In a vial, inside the glovebox, [Fe(HMTO)₂] (71.5 mg, 0.1 mmol) was dissolved in hexane (2 ml). Then, a solution of 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol (24.4 mg, 0.1 mmol, 1.0 equiv.) in hexane (1 ml) was added dropwise. The reaction mixture was stirred for 3 h at room temperature. A colourless solid was formed and it was removed by filtration. The solid was washed with cold pentane (2 x 0.5ml) and dried under vacuum, giving 49 mg product, 78% yield. Suitable crystals for X-ray diffraction analysis were obtained by recrystallization from the solvent mixture diethyl ether/pentane (1:20) at −40 °C. ¹H NMR (CDCl₃, 400 MHz): δ [ppm] = 93.12 (s), 65.44 (s, complex 3), 47.47 (s), 39.77 (s, complex 3), 32.13 (s), 24.88 (s), 2.57 (s, complex 3), −13.44 (s), −18.78 (s, complex 3), −20.79 (s), −26.25 (s, complex 3), −55.68 (s). ¹³C{¹H} NMR (CDCl₃, 101 MHz) and ¹⁹F{¹H} NMR (CDCl₃, 376 MHz): Silent spectra. Anal. Calcd
for C_{66}H_{60}F_{12}Fe_{2}O_{4}·C_{4}H_{10}O: C, 63.17%; H, 5.30% Found: C, 62.67%; H, 5.54%. \textsuperscript{57}Fe Mössbauer (solid state, 298 K): \(\delta = 1.15 \text{ mm s}^{-1}\), \(|\Delta E_Q| = 2.92 \text{ mm s}^{-1}\).

**E. NMR spectra**

![NMR spectrum](image1)

**Figure S1.** \(^1\text{H} \text{NMR (CDCl}_3, 400 MHz)\) spectrum of the isolated compound HMTOH.

![NMR spectrum](image2)

**Figure S2.** \(^{13}\text{C} \{^1\text{H}\} \text{NMR (CDCl}_3, 101 MHz)\) spectrum of the isolated compound HMTOH.
**Figure S3.** $^1$H NMR (C$_6$D$_6$, 400 MHz) spectrum of the isolated compound [Fe(HMDS)$_2$], 2.

**Figure S4.** $^1$H NMR (C$_6$D$_6$, 400 MHz) spectrum of the isolated compound [Fe(HMTO)$_2$], 3.

**Figure S5.** $^{13}$C($^1$H) NMR (C$_6$D$_6$, 101 MHz) spectrum of the isolated compound [Fe(HMTO)$_2$]. Only the residual signal of the deuterated solvent is observed, i.e. the $^{13}$C($^1$H) NMR spectrum of 3 is silent.
Figure S6. $^1$H NMR (C$_6$D$_6$, 400 MHz) spectrum of the isolated adduct [Fe(HMTO)$_2$]·THF, 3·THF.

Figure S7. $^{13}$C($^1$H) NMR (C$_6$D$_6$, 101 MHz) spectrum of the isolated compound [Fe(HMTO)$_2$]·THF. Only the residual signal of the deuterated solvent is observed, i.e. the $^{13}$C($^1$H) NMR spectrum of 3·THF is silent.
Figure S8. $^1$H NMR (C$_6$D$_6$, 400 MHz) spectrum of the isolated compound [([Ph(CF$_3$)$_2$CO])$_2$Fe$_2$($\mu^2$-N(SiMe$_3$)$_2$)$_2$], 4. The inset displays the region from 11.5 to 10.1 ppm.

Figure S9. $^{13}$C($^1$H) NMR (C$_6$D$_6$, 101 MHz) spectrum of the isolated compound [([Ph(CF$_3$)$_2$CO])$_2$Fe$_2$($\mu^2$-N(SiMe$_3$)$_2$)$_2$], 4.
**Figure S10.** $^{19}$F$^1$H NMR (C$_6$D$_6$, 376 MHz) spectrum of the isolated compound $[(\text{Ph(CF}_3\text{CO)})_2\text{Fe}]^{II}[^{\mu^2-}\text{N(SiMe}_3\text{)}_2)]$, 5.

**Figure S11.** $^1$H NMR (C$_6$D$_6$, 400 MHz) spectrum of the isolated compound $[(\text{Ph(CF}_3\text{CO)})_2\text{Fe}]^{II}[^{\mu^2-}\text{HMTO})_2]$, 5. In solution, complex equilibria between monomeric, dimeric and homoleptic species were observed.
Figure S12. $^{13}$C$^1$H NMR (C$_6$D$_6$, 101 MHz) spectrum of the isolated compound [{$\text{Ph(CF}_3\text{CO)}_2\text{Fe}_2\text{[}\mu^2\text{-HMTO})_2$], 5. Only the residual signal of the deuterated solvent is observed, i.e. the $^{13}$C$^1$H NMR spectrum of 5 is silent.

Figure S13. $^{19}$F$^1$H NMR (C$_6$D$_6$, 376 MHz) spectrum of the isolated compound [{$\text{Ph(CF}_3\text{CO)}_2\text{Fe}_2\text{[}\mu^2\text{-HMTO})_2$], 5. Only noise is observed, i.e. the $^{19}$F$^1$H NMR spectrum of 5 is silent.

**F. Variable temperature $^1$H NMR analysis**

Magnetic susceptibility was determined using the Evans method for a sample of 10.8 mg of [{$\text{Ph(CF}_3\text{CO)}_2\text{Fe}_2\text{[}\mu^2\text{-N(SiMe}_3\text{)}_2$)] in 0.70 mL of Tol-d$_8$. The solvent resonances of pure solvent are $\delta$ [ppm] = 7.15; 7.07; 7.00 and 2.09. Diamagnetic corrections were not made.
**Figure S14.** Variable-temperature $^1$H NMR (toluene-$d_8$, 500 MHz) spectra of $[[\text{Ph(CF}_3\text{CO})_2\text{Fe}]_2\{\mu^2-\text{N(SiMe}_3\text{)}_2\}_2]$ (0.017 M) from 218.15 K (bottom) to 298.15 K (top). Full range measured.

**Figure S15.** Variable-temperature $^1$H NMR (toluene-$d_8$, 500 MHz) spectra of $[[\text{Ph(CF}_3\text{CO})_2\text{Fe}]_2\{\mu^2-\text{N(SiMe}_3\text{)}_2\}_2]$ (0.017 M) from 218.15 K (bottom) to 298.15 K (top). Insert $\delta$ [ppm] 2.6 – 1.8.
Table S1. Magnetic moment for complex 4 at different temperatures, calculated through Evan’s method.

<table>
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<tr>
<th>T (K)</th>
<th>Δδ (ppm)</th>
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<th>X_{mass} (x10^{-3})</th>
<th>μ_{eff}</th>
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Figure S16. Variable-temperature Evan’s plot for compound \([\text{Ph(CF}_3\text{CO)}_2\text{Fe}_{2}\{\text{μ}^2-\text{N(SiMe}_3\text{)}_2\}])_2\), 4.

Attempts to perform solution magnetometry with \([\text{Ph(CF}_3\text{CO)}_2\text{Fe}_{2}\{\text{μ}^2-\text{HMTO)}_2\}]\), 5

Magnetic susceptibility measurements using the Evans method were attempted for complex 5. A sample of 10.5 mg of \([\text{Ph(CF}_3\text{CO)}_2\text{Fe}_{2}\{\text{μ}^2-\text{HMTO)}_2\}]\) in 0.95 mL of Tol-d₈ was prepared. The solvent resonances of pure solvent are δ [ppm] = 7.15; 7.07; 7.00 and 2.09. Diamagnetic corrections were not made. Measurements at 278.15, 273.15, 268.15, 263.15 and 258.15 K had problems for shimming and locking. That issue and the existence of complex solution equilibria between monomeric, dimeric and
homoleptic species precluded a proper interpretation of the data obtained. For instance, see Table S2, abnormally high effective magnetic moments were calculated under the assumption that such equilibria can be neglected, thus suggesting that this premise is false.

**Figure S17.** Variable-temperature $^1$H NMR (toluene-$d_8$, 500 MHz) spectra of [[Ph(CF$_3$)$_2$CO]$_2$Fe$_2$($\mu^2$-HMTO)$_2$] (0.017 M) from 218.15 K (bottom) to 298.15 K (top). Full range measured. Signals marked with * correspond to complex [Fe(HMTO)$_2$], 3.
Figure S18. Variable-temperature $^1$H NMR (toluene-d$_8$, 500 MHz) spectra of $[[\text{Ph(CF}_3\text{)}_2\text{CO}]_2\text{Fe}_2(\mu^2\text{-HMTO})_2]$ (0.017 M) from 218.15 K (bottom) to 298.15 K (top). Insert $\delta$ (ppm) 3.9 – 1.4.

Table S2. Magnetic moment for complex 5 at different temperatures, calculated through Evan’s method, assuming that the solution equilibria between monomeric, dimeric and homoleptic species can be neglected.

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Poor shimming and difficult to make locking
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<td><strong>Empirical formula</strong></td>
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<td><strong>Crystal system</strong></td>
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<td><strong>Space group</strong></td>
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<td><strong>a/Å</strong></td>
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<td><strong>c/Å</strong></td>
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<td><strong>Volume/Å$^3$</strong></td>
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<td><strong>Z</strong></td>
</tr>
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<td><strong>ρ$\text{calc}$/g/cm$^3$</strong></td>
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<td><strong>μ/mm$^{-1}$</strong></td>
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<td><strong>Final R indexes [all data]</strong></td>
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<tr>
<td><strong>Largest diff. peak/hole / e Å$^{-3}$</strong></td>
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</table>
G. SC-XRD analysis.

*Figure S19.* Molecular structure of 3·THF shown with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. Side view (top) and top view (bottom) of 3·THF.
Figure S20. Solid-state molecular structure of 4 with thermal ellipsoids at 50% probability. Selected bond lengths [Å] and angles [°]: Fe1-N1 2.018(12), Fe1-N2 2.070(13), Fe1-O1 1.850(5), Fe···Fe 2.674(3), Fe1-N1-Fe1 81.7(2), N1-Fe1-O1 98.0(5), O1-Fe1-N1 146.2(2), O1-Fe1-N2 115.7(7), Fe1-O1-C7 143.7(5). Hydrogen atoms are omitted for clarity. Top view (top) and planar view (bottom) of the diamond-core scaffold.
Figure S21. (a) ORTEP drawing of the molecular structure of complex 5. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms and mesityl groups were omitted for clarity. Two independent molecules per unit cell were found. (b) Top view and (c) planar view of diamond-core moiety.
**Figure S22.** Packing of compound 5 within the unit cell: two sets of two molecules are paralleled with each other, while other two molecules are perpendicular. Hydrogen atoms and mesityl groups were omitted for clarity. Crystallographic axes: a, red; b, green; c, blue.

**H. Computational studies**

**H.1 DFT Calculations**

DFT calculations were carried out at the Mississippi Center for Supercomputing Research. Gaussian 16, revision B.01, and the B3LYP functional with the def2tzvpp basis set on iron and def2svp on all other atoms, were implemented. Grimme’s D3 dispersion correction with Becke-Johnson damping was included for all calculations. This methodology was selected because, upon canvassing geometry optimizations using several combinations of functionals and basis sets, it gave the closest agreement to geometry of the compound determined experimentally (SC-XRD). The B3LYP functional has also been reported to give satisfactory performance in predicting both spin states and magnetic exchange coupling constants in similar iron complexes.9 Frequency calculations were carried out on optimized

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structures to check for imaginary frequencies, to confirm that the structures correspond to local minima, and to corroborate the stability of the wavefunctions. The initial guess for the broken symmetry BS(2,2) wavefunction was generated using the Brokensym function in Orca, version 5.0.3, and subsequent geometry optimizations and single point calculations were carried out in Gaussian as described above. Biorthogonalization of spin-orbitals was carried out and overlap integrals were calculated using MultiWFN. Topology analysis (AIM) was also carried out using MultiWFN.

Table S4. Theoretical and experimental selected bond lengths (Å) and angles (°) of 4.

<table>
<thead>
<tr>
<th>Bond parameter (Distance, Å; angle, °)</th>
<th>Calculated (Broken Symmetry)</th>
<th>Calculated (High-Spin)</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-O</td>
<td>1.846</td>
<td>1.849</td>
<td>1.850(5)</td>
</tr>
<tr>
<td>Fe-N</td>
<td>2.024, 2.088</td>
<td>2.045, 2.128</td>
<td>2.018(12), 2.070(13)</td>
</tr>
<tr>
<td>Fe···Fe</td>
<td>2.716</td>
<td>2.886</td>
<td>2.674(3)</td>
</tr>
<tr>
<td>N-Fe-N</td>
<td>97.3</td>
<td>92.5</td>
<td>98.0(5)</td>
</tr>
<tr>
<td>Fe-N-Fe</td>
<td>82.6</td>
<td>87.5</td>
<td>81.7(2)</td>
</tr>
<tr>
<td>O-Fe-N</td>
<td>116.0, 146.6</td>
<td>116.7, 150.6</td>
<td>115.7(7), 146.2(2)</td>
</tr>
</tbody>
</table>

The electronic structure of the compound was probed by DFT to provide insight into the nature of the interaction between the two iron centers. Using the crystallographically determined structure as a starting point, the geometry of the compound was optimized on either a high-spin (ferromagnetically coupled, $S = 4$) surface or a broken symmetry (BS(2,2), antiferromagnetically coupled, $S = 0$) surface. The metrical parameters of the Fe$_2$N$_2$ core for the broken symmetry geometry are in generally good agreement with the crystallographically determined structure, including a calculated Fe-Fe distance of 2.716 Å, compared to the experimental value of 2.674 Å. The calculated high-spin geometry gave a much longer Fe-Fe distance of 2.886 Å. The broken symmetry solution lies lower in energy by 3.8 kcal/mol compared to the high-spin solution, corresponding to a magnetic coupling $J$-value of -84 cm$^{-1}$ according to the Yamaguchi formalism for the Heisenberg-Dirac-van Vlack magnetic exchange Hamiltonian $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$. This calculated value is in good agreement with the experimental value, which was estimated as 83 cm$^{-1}$ based on fitting of the variable-temperature Evans method data.

The Yamaguchi formula for the estimation of the $J$-value is:

$$J_{ab} = \frac{(E_{BS} - E_{HS})}{\langle S^2 \rangle_{HS} - \langle S^2 \rangle_{BS}}$$

where HS refers to the high-spin (ferromagnetically coupled) and BS refers to the broken-symmetry (antiferromagnetically coupled) state. $E$ and $\langle S^2 \rangle$ are the energy and spin expectation values of the corresponding states, respectively, which are both determined by the DFT calculations for each state.$^{1,2}$

Table 5. Theoretical and experimental selected bond lengths (Å) and angles (deg) of 5

<table>
<thead>
<tr>
<th>Parameter (Distance, Å; angle, °)</th>
<th>Calculated</th>
<th>Measured[a]</th>
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</thead>
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<td>1.858(13)</td>
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<tr>
<td>Fe1-O1</td>
<td>2.056</td>
<td>2.055(12)</td>
</tr>
<tr>
<td>Fe···Fe</td>
<td>3.086</td>
<td>3.089(3)</td>
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<tr>
<td>Fe···C7ipso</td>
<td>2.636</td>
<td>2.465(7)</td>
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<tr>
<td>O1-Fe-O1</td>
<td>83.2</td>
<td>82.5(5)</td>
</tr>
<tr>
<td>Fe-O1-Fe</td>
<td>96.8</td>
<td>96.7(2)</td>
</tr>
<tr>
<td>O1-Fe1-O2</td>
<td>131.9</td>
<td>127.5(2)</td>
</tr>
</tbody>
</table>

[a] Average of two independent molecules in the asymmetric unit.

Figure S23. Spin density isosurfaces for compound 5. (A) High-spin state, isovalue 0.01 e/Å³; (B) High-spin state, isovalue 0.001 e/Å³; (C) Broken-symmetry state, isovalue 0.01 e/Å³; (D) Broken-symmetry state, isovalue 0.001 e/Å³.

The structure of 5 was optimized in the high-spin state (ferromagnetically coupled, S = 4; each iron center locally high-spin S = 2). Likewise, a broken-symmetry DFT (BS-DFT) approach was used to explore the nature of magnetic coupling between the iron centers and the sign and magnitude of the exchange parameter $J_{ab}$, which can be approximated using equation 1. In this case, the energies of the high-spin (ferromagnetic) and broken-symmetry (antiferromagnetic) solutions were very close, with the high-spin state lying approximately 0.04 kcal/mol below the broken-symmetry state. This suggests that there may be weak ferromagnetic coupling between the two iron centers, with an approximate $J$-value of 7 cm⁻¹.
H.2 AIM calculations

Atoms-in-molecules analysis of the electron density of compound 4 did not identify a bond critical point between the two iron centers. A ring critical point was identified near the midpoint of the iron-iron axis.

I. $^{57}$Fe Mössbauer Spectroscopy

The $^{57}$Fe Mössbauer spectroscopy measurements were performed in transmission geometry at room temperature. A $^{57}$Co source in a rhodium matrix was used. The Mössbauer spectra were fitted with Lorentzian functions by a non-linear least square method. The spectra were fitted with quadrupole doublets related to Fe$^{2+}$ species. The values of the hyperfine parameters of the quadrupole doublets, such as isomer shift ($\delta$) and quadrupole splitting ($\Delta E_Q$) were determined. The values of isomer shifts are given relatively to the $\alpha$-Fe standard at room temperature (293K).

Mossbauer calculations: A single-point calculation was carried out in Orca on the optimized geometries to predict the Mössbauer parameters for the compound in the broken-symmetry state. The b3lyp function was used, and the CP(PPP) basis set was used on iron and the def2tzvp basis set on all other atoms. The resolution of identity approximation and chain-of-spheres integration (RIJCOSX) were used, and relativistic effects were neglected since their inclusion has been shown to have a negligible effect on the accuracy of DFT-calculated iron Mössbauer parameters.$^{3,4}$ The published linear correlation from Papai and Vanko between the calculated electron density at iron and the isomer shift was used.$^{4}$ Since this correlation is based on data taken at 4.2 K, a correction for the temperature-dependence of the second-order Doppler shift can be applied to estimate the predicted Mössbauer isomer shift at 298 K (data acquisition temperature for compound 3). These calculations predict an isomer shift of 0.69 mm/s at 4.2 K, or 0.57 mm/s at 298 K.$^{4,5}$ The predicted quadrupole splitting is 1.6 mm/s. Since the mean absolute errors and maximum deviations for Mössbauer parameters determined using this DFT correlation were 0.06 mm/s and 0.15 mm/s for the isomer shift, and 0.24 mm/s and 1.29 mm/s for the quadrupole splitting, respectively,$^{4}$ these calculated values agree within the error with the experimentally measured parameters.
Table S6. Hyperfine parameters of the spectral components (quadrupole doublets) determined from fitting of the Mössbauer spectra of different three-fold trigonal planar iron(II) complexes.

<table>
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<tr>
<th>Complex</th>
<th>SC&lt;sup&gt;a&lt;/sup&gt;</th>
<th>δ&lt;sub&gt;Fe&lt;/sub&gt; (mm.s&lt;sup&gt;-1&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>∆E&lt;sub&gt;Q&lt;/sub&gt; (mm.s&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>RSF(%)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>T (K)</th>
<th>Ref.</th>
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<td>0.60</td>
<td>100</td>
<td>100</td>
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<td>0.59</td>
<td>100</td>
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<td>1.97</td>
<td>100</td>
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<td>[12]</td>
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<td>1.25</td>
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<td>4.2</td>
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<sup>a</sup> SC = Spectral component. <sup>b</sup> Isomer shift relative to metallic iron at 298 K. <sup>c</sup> RSF = Relative spectral fraction. <sup>d</sup> Pseudo trigonal-pyramidal geometry around each Fe(II) core.

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