Supporting Information:

Diiron Oxo Reactivity in a Weak-Field Environment

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**General Considerations.** All manipulations of metal complexes were carried out in the absence of water and dioxygen using standard Schlenk techniques, or in an MBraun inert atmosphere drybox under a dinitrogen atmosphere. Ligand and ligand precursor syntheses were carried out in air, except where noted. All glassware was oven dried for a minimum of 6 h and cooled in an evacuated antechamber prior to use in the drybox. Benzene, hexanes, tetrahydrofuran, dichloromethane and toluene were dried and deoxygenated on a Glass Contour System (SG Water USA, Nashua, NH) and stored over 4 Å molecular sieves (Strem) prior to use. Tetrahydrofuran-\(d_8\), and \(\text{D}_2\text{O}\) were purchased from Cambridge Isotope Labs and used as received. Benzene-\(d_6\) and dichloromethane-\(d_2\) were purchased from Cambridge Isotope Labs, degassed and stored over 4 Å molecular sieves prior to use. Pentane and 2-methyltetrahydrofuran was purchased from Sigma-Aldrich and stored over 4 Å molecular sieves prior to use. Celite® 545 (J. T. Baker) and \(\text{MgSO}_4\) were dried in a Schlenk flask for 24 h under dynamic vacuum while heating to at least 190 °C prior to drybox use. 9\(H\)-xanthen-9-one was purchased from TCI America. Iodobenzene and sodium hypochlorite (available chloride 10-15%) were purchased from Sigma Aldrich and cobaltocene and decamethylcobaltocene were purchased from Strem. Tetrabutylammonium chloride was purchased from Sigma-Aldrich and heated to 50 °C under high vacuum overnight prior to use. Tetraethylammonium chloride was purchased from Sigma-Aldrich and heated to 80 °C under high vacuum overnight prior to bringing into the glovebox. The solid was then recrystallized from acetonitrile layered with diethyl ether. Distilled \(\text{H}_2\text{O}\), \(\text{D}_2\text{O}\) and \(\text{H}_2\text{O}^{18}\) were degassed by sparging with argon prior to use. Tetraphenylphosphonium chloride was purchased from Sigma Aldrich and recrystallized from an anhydrous dichloromethane/hexanes mixture before use. KBr was purchased from International Crystal Laboratories and used without further purification. Silica gel 40–63 μm (Silicycle Inc.) and neutral aluminum oxide, Brockmann Grade I, 58–60 mesh powder (Alfa Aesar) were used as received.
2-(Tert-butyl)-1H-pyrrole\textsuperscript{1}, 9,9-dimethyl-9H-xanthene\textsuperscript{2} and 9,9-dimethyl-9H-xanthene-4,5-dicarbaldehyde\textsuperscript{3} were synthesized as previously reported. 2,6-Lutidinium tetraphenylborate\textsuperscript{4} and Fe\textsubscript{2}(Mes)\textsubscript{4}\textsuperscript{5} were synthesized following previously reported procedures.

**Characterization and Physical Measurements.** \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded on Agilent DD2 600 MHz or Varian Unity/Inova 500 MHz spectrometers. \textsuperscript{1}H and \textsuperscript{13}C NMR chemical shifts are reported relative to SiMe\textsubscript{4} using the chemical shift of residual solvent peaks as reference. Elemental analyses (%CHN) were obtained on a PerkinElmer 2400 Series II CHNS/O Analyzer.

Zero-field \textsuperscript{57}Fe Mössbauer spectra were measured with a constant acceleration spectrometer (SEE Co, Minneapolis, MN) at 90 K. Isomer shifts are quoted relative to Fe foil at room temperature. Data were analyzed and simulated with Igor Pro 6 software (WaveMetrics, Portland, OR) using Lorentzian fitting functions. Samples were prepared by suspending 20–50 mg of compound in sufficient Paratone oil or by dissolving 20–40 mg in benzene and immobilizing by rapid freezing in liquid nitrogen.

Electrochemical experiments were carried out using a CH Instruments CHI660C Electrochemical Workstation. The electrolyte used was 0.1 M (\textsuperscript{n}Bu\textsubscript{4}N)(PF\textsubscript{6}) in THF. The working electrode was glassy carbon and a platinum wire was used as the counter electrode. Cyclic voltammograms were referenced against a ferrocene standard. Cyclic voltammetry was performed with scan rates of 10 mV/s to 500 mV/s.

Infrared spectra were acquired on a Varian 1000 FT-IR spectrometer by pressing the samples into KBr pellets (~3–4 mg of dried sample and ~80 mg of KBr).

UV/Visible spectra were recorded on a Varian Cary 50 UV/Vis spectrometer using quartz cuvettes and a scan rate of 600 nm/min.

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(3) C. J. Chang, Y. Deng, A. F. Heyduk, C. K. Chang and D. G. Nocera, *Inorg. Chem.* 2000, **39**, 959.
(4) K. L. C. Gronberg, R. A. Henderson and K. E. Oglieve, *J. Chem. Soc.*, *Dalton Trans.* 1998, 3093.
(5) R. Hernández Sánchez, S.-L. Zheng and T. A. Betley, *J. Am. Chem. Soc.* 2015, **137**, 11126.
EPR spectra were obtained on a Bruker EleXsys E-500 CW-EPR spectrometer. Spectra were measured as frozen glass in 2-methyltetrahydrofuran at a microwave power of 0.6325–2 mW. Simulation and fitting were performed with the EasySpin 3.0.0 ToolBox for MATLAB® R2008a. The spectrum was simulated by optimizing g values, the FWHM value for the isotropic magnetic-field domain broadening, and the FWHM of the Gaussian distribution of g values.

**Theoretical Measurements.** All calculations were performed using the density functional theory and the quantum chemical program package Gaussian16 using the unrestricted B3LYP hybrid functional (which includes the Becke three-parameter exchange and the Lee, Yang, and Parr correlation functional) and GD3BJ dispersion of Grimme et al. with Becke-Johnson damping. The SDD basis set was used in the investigation, which combines the Dunning/Huzinaga valence double-zeta basis for elements up to Ar, with the Stuttgart/Dresden effective core potentials for the remainder of the periodic table. This particular method and level of theory was reported by Smith et al. in 2008 and was found to provide appropriate accuracy in similar thermodynamic estimations of pKₐ values for iron complexes. Solvation of the molecular species was modelled using continuum parameters designed to describe tetrahydrofuran solvent (ε = 7.43). Geometry optimizations were performed in order to obtain electronic energies, followed by frequency calculations to compute zero-point energies and derive values for thermal and entropic corrections at 298.15 K.

Considering a general acid-base reaction between a bridging hydroxide species (denoted

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(6) S. Stoll and A. Schweiger, *J. Magn. Reson.* 2006, **178**, 42.
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(8) Gaussian, Inc., Revision B.01 (2016), Wallingford CT.
(9) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comp. Chem.* 2011, **32**, 1456.
(10) T. H. Dunning Jr. and P. J. Hay, in *Modern Theoretical Chemistry*, Ed. H. F. Schaefer III, Vol. 3 (Plenum, New York, 1977) pp. 1-28.
(11) U. Wedig, M. Dolg, H. Stoll, and H. Preuss in *Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry*, Ed. A. Veillard, Reidel and Dordrecht: 1986, pp. 79.
(12) A. Bergner, M. Dolg, W. Kuchle, H. Stoll, and H. Preuss, *Mol. Phys.*, 1993, **80**, 1431.
(13) I. Naito, F. Ding, R. P. Bontchev, H. Wang and J. M. Smith, *J. Am. Chem. Soc.*, 2008, **130**, 2716.
below as \([\text{hydroxide}]^+\) and a bridging oxo species (denoted as \(\text{oxo}\)):

\[
[\text{hydroxide}]^+ + [A]^- \rightarrow \text{oxo} + \text{HA} \quad (S1)
\]

where HA is a weak acid whose \(pK_a\) value in THF has previously been reported.\(^{14}\) The overall free energy of the reaction is thus satisfied by the relationship:

\[
\Delta G = 2.303RT \left[ pK_a([\text{hydroxide}]^+) - pK_a(\text{HA}) \right] \quad (S2)
\]

where \(pK_a([\text{hydroxide}]^+)\) and \(pK_a(\text{HA})\) denote the \(pK_a\) values for the \([\text{hydroxide}]^+\) and HA, respectively. As described by Smith et al., using this method one evaluates the relative free energy with respect to a known weak acid, HA, and thus bypasses the explicit treatment of the solvated proton.\(^{14}\)

Although many experimental \(pK_a\) values for weak acids have been determined in solvents such as H\(_2\)O, dimethyl sulfoxide, and acetonitrile, unfortunately the stability of the species of interest (3 and 4) hindered experimental acid/base reactions under these solvation conditions. The stability of 3/4 in dry solvents such as benzene and diethyl ether is greatly improved, but unfortunately the poor solubility of the complexes limited effective spectroscopic evaluation of acid/base reactivity in these cases. THF is suitably solvating for both reactants and products, but experimental \(pK_a\) values are limited in number. Smith et al. recently reported accurate theoretical determination of numerous \(pK_a\) values for acids in THF\(^{14}\), so we were able to use these values in order to estimate the \([\text{hydroxide}]^+\) \(pK_a\) theoretically.

In order to estimate the \(pK_a\) of the diiron hydroxide-bridged species 4, it is important to define the respective conjugate base as differing simply by one proton. Experimentally, protonation of species 3 (in which binding of solvent molecules to iron is not demonstrated in the solid state structure) to yield 4 is concomitant with the binding of one THF molecule to each iron center (as featured in the solid state structure of 4). Therefore, two options are presented in order to effectively model the acid/base reactivity of 3 and 4:

1) Protonation of the bridging oxo 3 to yield 4a (a model of the bridging hydroxide 4 with no THF bound). It is worth noting that experimentally, this species (4a) was

\(^{14}\) F. Ding, J. M. Smith and H. Wang, \textit{J. Org. Chem.}, 2009, \textbf{74}, 2679.
not isolable, and it seems that THF binding upon protonation is highly favorable. In fact, addition of two THF molecules to 4a, yielding 4, is shown to be energetically favorable by 96 kJ mol\(^{-1}\):

\[
4a + 2 \text{THF} \rightarrow 4 \quad \Delta G = -96 \text{kJ mol}^{-1}
\]

The following acid-base reaction between 4a and 3 is thus considered:

\[
[(^\text{Bu}dmx)\text{Fe}_2(\mu-\text{OH})]^+ + \text{A}^- \rightarrow (^\text{Bu}dmx)\text{Fe}_2(\mu-\text{O}) + \text{HA} \quad (S3)
\]

and the overall free energy of the reaction is satisfied by the relationship:

\[
\Delta G = 2.303RT \left[ pK_a(\text{Fe}_2(\mu-\text{OH})^+) - pK_a(\text{HA}) \right] \quad (S4)
\]

where \( pK_a(\text{Fe}_2(\mu-\text{OH})^+) \) and \( pK_a(\text{HA}) \) denote the \( pK_a \) values for 4a and HA, respectively.\(^\text{14} \)

This method was tested with a series of acids spanning a range of \( pK_a \) values (Table S-1) and yielded a \( pK_a \) value for 4a which was consistent across this series. The derived value of \( pK_a \) by this method was shown to be 15.3(6) for (\(^\text{Bu}dmx)\text{Fe}_2(\mu-\text{OH})^+\) (4a) in THF.

2) Protonation of a bridging oxo 3a (in which THF molecules are bound to each iron center) to yield the bridging hydroxide 4. Again, the free energy change upon addition of two molecules of THF to 3 (yielding 3a) was found to be energetically favorable by 30 kJ/mol, which supports experimental evidence that 3 binds THF in solution.

\[
3 + 2 \text{THF} \rightarrow 3a \quad \Delta G = -30 \text{kJ mol}^{-1}
\]

The acid-base reaction between 4 and 3a now takes the form:

\[
[(^\text{Bu}dmx)\text{Fe}_2(\mu-\text{OH})(\text{thf})_2]^+ + \text{A}^- \rightarrow (^\text{Bu}dmx)\text{Fe}_2(\mu-\text{O})(\text{thf})_2 + \text{HA} \quad (S5)
\]

and the free energy is satisfied by the relationship:

\[
\Delta G = 2.303RT \left[ pK_a(\text{Fe}_2(\mu-\text{OH})(\text{thf})_2^+) - pK_a(\text{HA}) \right] \quad (S6)
\]
where $pK_a(\text{Fe}_2(\mu-\text{OH})(\text{thf})_2^+)$. Using the same series of acids, (see Table S-2), a $pK_a$ value of 26.7(6) for 4 in THF was derived.\textsuperscript{14}

3) Protonation of a bridging oxo 6 to yield 6a (a model of the conjugate acid of 6, a diferric bridging hydroxide). It is worth noting that experimentally, this species (6a) was not isolable, and it seems that deprotonation is highly favorable due to its negative $pK_a$.

The acid-base reaction between 6a and 6 is considered:

$$[(t\text{Budmx})\text{Fe}_2(\mu-\text{OH})\text{Cl}_2]^+ + A^- \rightarrow (t\text{Budmx})\text{Fe}_2(\mu-\text{O})\text{Cl}_2 + HA \quad (S7)$$

and the free energy is satisfied by the relationship:

$$\Delta G = 2.303RT [pK_a(\text{Fe}_2(\mu-\text{OH})\text{Cl}_2^+) – pK_a(HA)] \quad (S8)$$

where $pK_a(\text{Fe}_2(\mu-\text{OH})\text{Cl}_2^+)$ denotes the $pK_a$ value for species 6a. Using the same series of acids, (see Table S-3), a $pK_a$ value of −1.8(6) for 6a in THF was derived.\textsuperscript{14}
Table S-1. Calculated $pK_a$ values of $[\text{(}^{t}{\text{Bu-dm}}\text{x)}\text{Fe}_2(\mu-$OH$)]^+$ (4a) with respect to different reference acids.

| Reference Acid       | Calculated $pK_a$ of $[\text{Fe}_2(\mu-$OH$)]^+$ |
|----------------------|-----------------------------------------------|
| Lutidinium           | 16.1                                          |
| Benzoic Acid         | 15.5                                          |
| Acetic Acid          | 15.2                                          |
| Phenol               | 14.4                                          |
| 2,2,2-trifluoroethanol | 15.4                                        |

Table S-2. Calculated $pK_a$ values of $[\text{(}^{t}{\text{Bu-dm}}\text{x)}\text{Fe}_2(\mu-$OH$)(\text{thf})_2]^+$ (4) with respect to different reference acids.

| Reference Acid       | Calculated $pK_a$ of $[\text{Fe}_2(\mu-$OH$)(\text{thf})_2]^+$ |
|----------------------|---------------------------------------------------------------|
| Lutidinium           | 27.6                                                          |
| Benzoic Acid         | 27.0                                                          |
| Acetic Acid          | 26.7                                                          |
| Phenol               | 25.9                                                          |
| 2,2,2-trifluoroethanol | 26.8                                        |

Table S-3. Calculated $pK_a$ values of $[\text{(}^{t}{\text{Bu-dm}}\text{x)}\text{Fe}_2(\mu-$OH$)\text{Cl}_2]^+$ (6a) with respect to different reference acids.

| Reference Acid       | Calculated $pK_a$ of $[\text{Fe}_2(\mu-$OH$)\text{Cl}_2]^+$ |
|----------------------|-------------------------------------------------------------|
| Lutidinium           | −1.0                                                        |
| Benzoic Acid         | −1.6                                                        |
| Acetic Acid          | −1.9                                                        |
| Phenol               | −2.7                                                        |
| 2,2,2-trifluoroethanol | −1.7                                        |
To validate these findings, calculation of $^{57}\text{Fe} \text{Mössbauer isomer shifts (δ)}$ for complexes 3, 3a, 4, 4a, 6, and 6a were carried out as described previously$^{15}$ via linear regression of DFT calculated electron density at the nucleus to experimental values of δ. Mössbauer calculations were carried out using the ORCA 4.0.1.2 program package$^{16}$ and were initiated from spin-unrestricted single-point calculations that employed the B3LYP functional$^{17}$ with the def2-TZVP (Fe, N, O) and def2-SV(P) (C, H) basis sets.$^{18}$ Further, the def2-TSVP/J (Fe, N, Cl) and def2-SV(P)/J (C, H) auxiliary basis sets were employed to utilize the RIJCOSX approximation for accelerating the calculation.$^{19}$ A broken symmetry solution (see below for more details) was used to model antiferromagnetic coupling between the iron centers, and the continuum solvation model CPCM was implemented to model the solvent as tetrahydrofuran.$^{20}$ All geometries were taken from the optimized structures used for the pK$_a$ determinations (Figure S-29 – 34, Table S-8).

Table S-4. Calculated Mössbauer parameters for 4a, 4, 3, 3a, 6, and 6a.

| Complex | δ (Exp), mm/s | δ (Calc), mm/s | |ΔE|Q| (Exp), mm/s | |ΔE|Q| (Calc), mm/s |
|---------|----------------|---------------|----------------|----------------|----------------|
| 4a      | --             | 0.80, 0.83    | --             | 0.804, 1.01    |
| 4       | 1.01           | 1.07, 1.07    | 3.02           | 2.700, 2.700   |
| 3       | 0.68           | 0.75, 0.75    | 0.88           | 0.646, 0.648   |
| 3a      | 0.94           | 1.05, 1.05    | 2.01           | 1.821, 1.830   |
| 6       | 0.30           | 0.33, 0.33    | 1.38           | 1.081, 1.081   |
| 6a      | --             | 0.33, 0.33    | --             | 0.528, 0.505   |

(15) F. Neese, *Inorg. Chim. Acta*, 2002, **337**, 181.
(16) F. Neese in *The ORCA program system*, Wiley Interdiscip. Rev.: Comput. Mol. Sci., 2012, vol. 2, pp. 73.
(17) (a) A. D. *Becke, J. Chem. Phys.*, 1993, **98**, 5648; (b) C. T. Lee, W. T. Yang, and R. G. Parr, *Phys Rev. B*, 1988, **33**, 785.
(18) F. Weigand, *Phys. Chem. Chem. Phys.* 2006, **8**, 1057.
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Broken symmetry solutions were used to model the antiferromagnetic coupling present in these complexes. The standard notation BS\((m,n)\) represents the \((m+n)\) unpaired electrons within a system and net spin of \((m-n)/2\) for an antiferromagnetically coupled system.\(^2\) As such, one fragment will bear \(m\) \(\alpha\) electrons while the other bears \(n\) \(\beta\) electrons. The appropriate description for each case was as high spin iron centers (i.e., high-spin Fe\(\text{II}\) for 4\(a\), 4, 3, 3\(a\) and high spin Fe\(\text{III}\) for 6, 6\(a\)). The exchange coupling constant \(J\) was determined from the energy difference between the high-spin and broken-symmetry states, using the spin Hamiltonian in equation S8 and formula in equation S9:\(^2\)

\[
H = -2JS_{Fe(1)} \cdot S_{Fe(2)} \quad (S7)
\]

\[
J = - \frac{E_{HS} - E_{BS}}{S_{\text{max}}} \quad (S7)
\]

**Table S-5.** Broken symmetry solution information for 4\(a\), 4, 3, 3\(a\), 6, and 6\(a\).

| Complex | Broken symmetry description | \(E_{HS} - E_{BS}\) (cm\(^{-1}\)) | \(J\) (cm\(^{-1}\)) |
|---------|-----------------------------|----------------------------------|------------------|
| 4\(a\)  | BS(4,4)                     | 162.284                         | –10.1            |
| 4       | BS(4,4)                     | 236.530                         | –14.8            |
| 3       | BS(4,4)                     | 1055.057                        | –65.9            |
| 3\(a\)  | BS(4,4)                     | 1107.937                        | –69.3            |
| 6       | BS(5,5)                     | 2408.881                        | –96.4            |
| 6\(a\)  | BS(5,5)                     | 442.437                         | –17.7            |

The bond orders and orbital overlaps of the diiron oxo complexes were also considered using the results of the spin-unrestricted single-point calculations. Bond distance and bond order indicate that the strength of the Fe–O bonds increase from 3\(a\) to 3 to 6 (as indicated by a shorter Fe–O distance and larger Mayer bond order), which is consistent with the trend of decreasing basicity across the series. Furthermore, the overlap between corresponding orbitals was seen to increase across the series of 3\(a\) to 3 to 6. This value represents the

\(^{(21)}\) B. Kirchner, F. Wenmohs, S. Ye and F. Neese, *Curr. Opin. Chem. Biol.* 2007, 11, 134.

\(^{(22)}\) A.P. Ginsberg, *J. Am. Chem. Soc.* 1980, 102, 111.

\(^{(23)}\) L. Noodleman, *J. Chem. Phys.* 1981, 74, 5737.

\(^{(24)}\) L. Noodleman and E.R. Davidson, *Chem. Phys.* 1986, 109, 131.
overlap between orbitals involved in coupling of the system; since in this case coupling between iron centers is through the oxo bridge, this metric also provides insight into the strength of the Fe–O interactions. Each of these data is consistent with the conjecture that Fe–O covalency is increasing with decreased basicity.

**Table S-6.** Assessment of Fe–O covalency in 3, 3a, and 6.

| Complex | Fe–O distances (Å) | Mayer bond orders (Fe–O) | Orbital overlaps of UCOs |
|---------|-------------------|--------------------------|-------------------------|
| 3a      | 1.858, 1.859*     | 0.798, 0.797             | 0.141 – 0.170           |
| 3       | 1.7941(17)        | 0.811, 0.811             | 0.149 – 0.165           |
| 6       | 1.7734(10)        | 0.947, 0.947             | 0.226 – 0.265           |

*Bond metrics based on geometry optimized structure.

**Table S-7.** Orbital overlap of UCOs in 3a.

| Orbital | Orbital overlap |
|---------|----------------|
| 259     | 0.169          |
| 260     | 0.155          |
| 261     | 0.141          |

**Table S-8.** Orbital overlap of UCOs in 3.

| Orbital | Orbital overlap |
|---------|----------------|
| 219     | 0.165          |
| 220     | 0.155          |
| 221     | 0.149          |

**Table S-9.** Orbital overlap of UCOs in 6.

| Orbital | Orbital overlap |
|---------|----------------|
| 235     | 0.265          |
| 236     | 0.236          |
| 237     | 0.226          |
Syntheses.

**Iodobenzene dichloride:** The synthesis for iodobenzene dichloride was adapted from a published procedure.⁵ Iodobenzene (2.04 g, 10.0 mmol, 1.00 equiv) was dissolved in a mixture of 30 mL of sodium hypochlorite (available chloride 10–15%) and 30 mL of water. 20 mL of concentrated HCl was added dropwise to the stirring solution. A yellow solid precipitated over the course of ten minutes. The resulting yellow solid was collected by filtration, washed with water and hexanes. The solid was dissolved in dichloromethane and dried over MgSO₄ and filtered. The product was crystallized overnight in the dark at −35 °C. The following morning, the mother liquor was removed and the solid was brought into a nitrogen filled glovebox. It was again dissolved in dichloromethane, dried over MgSO₄, filtered and crystallized. The product was stored at −35 °C in the dark.

((Bu)dmx)H₂: Under inert atmosphere, a 350 mL pressure tube was charged with 2-(tert-butyl)-1H-pyrrole (6.89 g, 55.9 mmol, 4.10 equiv), 9,9-dimethyl-9H-xanthene-4,5-dicarbaldehyde (3.63 g, 13.6 mmol, 1.00 equiv) and 100 mL of dry dichloromethane. Pyridinium p-toluenesulfonate (685 mg, 2.73 mmol, 20.0 mol%) was added and the reaction mixture was sealed, removed from the glovebox and placed in an oil bath kept at 35 °C for 16 h. The crude reaction mixture was filtered through a plug of silica gel in a medium porosity frit (360 mL), concentrated *in vacuo* and used for the next step without further purification (9.71 g, 98.5%). The dipyrromethane (9.71 g, 13.4 mmol, 1.00 equiv) was

(21) X.-F. Zhao, C. Zhang, *Synthesis* 2007, 551.
dissolved in 200 mL of dichloromethane and 2,3-dichloro-5,6-dicyanoquinone (DDQ) (6.19 g, 27.3 mmol, 2.03 equiv) was added as a solid resulting in an immediate color change to dark brown. After stirring at room temperature for two hours, the reaction mixture was filtered through a plug of neutral alumina in a medium porosity frit (600 mL) and eluted with dichloromethane containing 1% triethylamine. Fractions containing product (TLC analysis, basic alumina, Rf (DCM) = 0.1, orange spot) were combined and the solvent was removed in vacuo. The resulting solid was triturated with methanol three times to remove residual triethylamine. The orange solid was recrystallized from a mixture of hot methanol/dichloromethane. The orange crystals that formed upon cooling to –10 °C were collected by filtration and washed with a small amount of methanol to give pure (tBu-dm)H2 (4.20 g, 43.9%). 1H NMR (500 MHz, C6D6): δ/ppm 13.25 (s, 2H), 7.17 (dd, J = 7.9, 1.6 Hz, 2H), 7.09 (dd, J = 7.5, 1.6 Hz, 2H), 6.79 (m, 2H), 6.54 (dd, J = 4.1, 0.8 Hz, 4H), 6.07 (dd, J = 4.1, 1.2 Hz, 4H), 1.50 (s, 9H), 1.40 (s, 36H). 13C{1H} NMR (126 MHz, C6D6): δ/ppm 165.05, 148.84, 140.31, 135.09, 132.40, 130.43, 128.59, 128.35, 126.51, 126.21, 122.40, 113.61, 34.69, 33.48, 32.29, 30.21. HRMS (ESI⁺) m/z Calc. 719.4689 [C49H58N4O + H⁺], Found 719.4718 [M+H⁺].
(tBudmx)Fe2(Mes)2 (1): To a 50 mL pressure vessel was added (tBudmx)H2 (500 mg, 695 μmol, 1.00 equiv), Fe2(Mes)4 (409 mg, 695 μmol, 1.00 equiv) and 10 mL benzene. The vessel was equipped with a magnetic stir bar, capped, removed from the glovebox and placed in an oil bath kept at 65 °C for four hours. The reaction mixture was cooled to room temperature, returned to the glovebox and filtered through Celite and the filter cake was washed with excess benzene until the eluent was nearly colorless. The solvent was frozen and removed in vacuo to yield a dark red powder. The residue was washed with hexanes (4×3 mL), filtered through Celite with benzene and lyophilized to yield a dark red powder (601 mg, 81.0%). Crystals suitable for X-ray diffraction were grown from a concentrated solution of toluene layered with hexanes at −35 °C. 1H NMR (500 MHz, 295 K, C6D6): δ/ppm 134.64, 74.56, 27.63, 11.84, 8.25, 3.36, 1.23, 0.88, −2.18, −13.65. Zero-field 57Fe Mössbauer (90 K) (δ, |ΔE_Q| (mm/s)): 0.46, 0.95 (γ = 0.16 mm/s). %CHN Calculated for C67H78Fe2N4O: C 75.42 H 7.37 N 5.25; Found: C 74.88 H 7.45 N 5.40.

(tBudmx)Fe2(μ-OH)(Mes)(thf) (2): In a 20 mL vial, (tBudmx)Fe2(Mes)2 (1) (100 mg, 93.7 μmol, 1.00 equiv) was dissolved in 4 mL of THF. A saturated solution of water in
benzene$^{26}$ (2.64 mL, 93.7 μmol, 1.00 equiv) was added dropwise to a vigorously stirred solution. The reaction mixture was stirred at room temperature for 20 minutes and concentrated in vacuo. The residue was recrystallized at −35 °C from 1 mL of diethyl ether. After 48 hours, the mother liquor was decanted and the residue was dried in vacuo to afford ($^{t}$Bu-dmx)Fe$_2$(μ-OH)(Mes)(thf) (2) as red-brown crystals (76.0 mg, 78.3%).$^1$H NMR (500 MHz, 295 K, THF-$d_8$): δ/ppm 82.43, 74.75, 72.37, 63.87, 47.17, 42.47, 37.95, 16.85, 14.29, 8.56, 6.02, 5.05, 3.35, 1.07, −1.23, −1.91, −8.08, −11.76. Zero-field $^{57}$Fe Mössbauer (90 K) (δ, |ΔE$_Q$| (mm/s)): 0.79, 3.22; 1, 2.95 (γ = 0.129, 0.166 mm/s). FTIR (KBr): 3638 cm$^{-1}$ (νO−H); 2685 cm$^{-1}$ (νO−D). %CHN Calculated for C$_{62}$H$_{76}$Fe$_2$N$_4$O$_3$: C 71.81 H 7.39 N 5.40; Found: C 71.44 H 7.76 N 5.39.

($^{t}$Bu-dmx)Fe$_2$(μ-O) (3): To a J. Young tube was added ($^{t}$Bu-dmx)Fe$_2$(μ-OH)(Mes)(thf) (2) (50 mg, 48 μmol, 1.0 equiv) and 1.5 mL of benzene. The tube was sealed, removed from the glovebox and heated to 45 °C for 30 minutes. The reaction mixture was cooled to room temperature, returned to the glovebox, transferred to a vial, frozen and concentrated in vacuo. The residue was dissolved in benzene and lyophilized three times to remove residual mesitylene to give ($^{t}$Bu-dmx)Fe$_2$(μ-O) (3) as a red powder (37 mg, 91%). Crystals suitable for X-ray diffraction were grown from a concentrated diethyl ether solution at −35 °C. $^1$H NMR (500 MHz, 295 K, C$_6$D$_6$): δ/ppm 19.51, 13.96, 8.05, 4.96, −2.27, −3.00, −6.40. Zero-field $^{57}$Fe Mössbauer (90 K) (δ, |ΔE$_Q$| (mm/s)): 0.68, 0.88 (γ = 0.15 mm/s). %CHN Calculated for C$_{49}$H$_{56}$Fe$_2$N$_4$O$_2$: C 69.67 H 6.68 N 6.63; Found: C 70.75 H 6.76 N 6.65.

(26) R. Karlsson, J. Chem. Eng. Data 1973, 18, 290–292.
[\textsuperscript{tBu}dmx]Fe_2(\textmu-OH)(thf)_2[BPh_4] (4): In a 20 mL vial, 2,6-lutidinium tetraphenylborate (41.2 mg, 96.4 \mu mol, 1.00 equiv) was dissolved in 2 mL of THF. A solution of [\textsuperscript{tBu}dmx]Fe_2(\textmu-OH)(Mes)(thf) (2) (100 mg, 96.4 \mu mol, 1.00 equiv) in 2 mL of THF was added dropwise. The reaction mixture was allowed to stir at room temperature for 45 minutes and filtered through Celite before being concentrated \textit{in vacuo}. The residue was washed with hexanes, filtered through Celite in THF, and concentrated \textit{in vacuo}. The residue was taken up in minimal ether to afford a saturated solution to which drops of THF were added. This solution was filtered through Celite and recrystallized at \(-35^\circ C\). After 48 hours, the mother liquor was decanted and [\textsuperscript{tBu}dmx]Fe_2(\textmu-OH)(thf)_2[BPh_4] (4) was recovered as orange crystals (78.6 mg, 62.4%). \textsuperscript{1}H NMR (600 MHz, 295 K, THF-\textit{d}_8): \delta/ppm 43.84, 28.15, 6.56, 6.28, 3.29, 2.64, 2.26, \(-3.04, \text{-}16.96\). Zero-field \textsuperscript{57}Fe Mössbauer (90 K) (\(\delta, |\Delta E_Q|^{(\text{mm/s})}\)): 1.01, 3.02 (\(\gamma = 0.145 \text{ mm/s}\)). FTIR (KBr): 3548 cm\(^{-1}\) (\(\nu_{O-H}\)); 2587 cm\(^{-1}\) (\(\nu_{O-D}\)). %CHN Calculated for C\(_{81}\)H\(_{93}\)BFe\(_2\)N\(_4\)O\(_4\): C 74.31 H 7.16 N 4.28; Found: C 74.66 H 7.34 N 4.31.

[Et_4N][\textsuperscript{tBu}dmx]Fe_2(\textmu-OH)Cl_2] (5b): In a 20 mL vial, tetraethylammonium chloride (5.1 mg, 31 \mu mol, 2.0 equiv) was dissolved in 2 mL of DCM and frozen in the cold well (\(-78^\circ C\)). A solution of [\textsuperscript{tBu}dmx]Fe_2(\textmu-OH)(thf)_2][BPh_4] (4) (20 mg, 15 \mu mol, 1.0 equiv) in 2 mL
of DCM was added dropwise and frozen in a layer on top. The reaction mixture was thawed and allowed to stir for 10 minutes. At this point, the reaction mixture was filtered through Celite and concentrated in vacuo. The residue was recrystallized at −35 °C from 4 mL of DCM layered with 1 mL of THF. After 48 hours, the mother liquor was decanted and the crystals were dried in vacuo to afford [Et₄N][((Bu)dmx)Fe₂(μ-OH)Cl₂] (5b) as an orange-brown residue (11.2 mg, 73.2%). Crystals suitable for X-ray diffraction were grown from a concentrated solution in THF upon cooling from 60 °C to room temperature. ¹H NMR (500 MHz, 295 K, CD₂Cl₂): δ/ppm 40.50, 12.55, 6.31, 6.00, 4.26, 1.71, −2.44, −13.91. Zero-field ⁵⁷Fe Mössbauer (90 K) (δ, |ΔE₀| (mm/s)): 1.00, 3.53 (γ = 0.152 mm/s). FTIR (KBr): 3629 cm⁻¹ (νO−H); 2675 cm⁻¹ (νO−D). %CHN Calculated for C₅₇H₇₇Cl₂Fe₂N₅O₂: C 65.40 H 7.41 N 6.69; Found: C 65.54 H 7.32 N 6.85.

((Bu)dmx)Fe₂(μ-O)Cl₂ (6): In a 20 mL vial, iodoobenzene dichloride (19.2 mg, 69.8 μmol, 1.00 equiv) was frozen in 2 mL of benzene. A solution of ((Bu)dmx)Fe₂(μ-O) (3) (59.0 mg, 69.8 μmol, 1.00 equiv) was added while stirring. The mixture was thawed and stirred at room temperature for ten minutes. The reaction was filtered through Celite and the filter cake washed with excess benzene until the eluent was nearly colorless. The solvent was frozen and removed in vacuo to yield a purple-brown powder. The residue was washed with hexanes (3×2 mL) and THF (3×0.5 mL) to give ((Bu)dmx)Fe₂(μ-O)Cl₂ (6) as a dark purple powder (31.2 mg, 48.8%). Crystals suitable for X-ray diffraction were grown from a concentrated solution of THF layered with diethyl ether at −35 °C. ¹H NMR (500 MHz, 295 K, C₆D₆): δ/ppm 13.87. Zero-field ⁵⁷Fe Mössbauer (90 K) (δ, |ΔE₀| (mm/s)): 0.30, 1.38 (γ = 0.17 mm/s). %CHN Calculated for C₄₉H₅₆Fe₂N₄O₂Cl₂: C 64.28 H 6.17 N 6.12; Found: C 63.76 H 6.41 N 5.83.
[Cp₂Co][[^tBu-dmx]Fe₂(μ-O)Cl₂] (7): In a 20 mL vial, a solution of cobaltocene (2.7 mg, 14 mmol, 1.0 equiv) in 1 mL of THF was added dropwise to a just-thawed suspension of[^tBu-dmx]Fe₂(μ-O)Cl₂ (6) (13 mg, 14 µmol, 1.0 equiv) in 2 mL of THF. The reaction mixture was stirred at room temperature for ten minutes and concentrated to give an orange solid. Crystals suitable for X-ray diffraction were grown from a concentrated solution of THF at 70 °C. ^1H NMR (500 MHz, 295 K, THF): δ/ppm 15.47, 8.27, 7.71, 7.19, 6.90, 1.29, 0.85.

[Cp^*₂Co][[^tBu-dmx]Fe₂(μ-OH)Cl₂] (5c): In a 20 mL vial, a solution of decamethylcobaltocene (8.6 mg, 26 µmol, 2.0 equiv) in 1 mL of THF was added dropwise to a just-thawed suspension of[^tBu-dmx]Fe₂(μ-O)Cl₂ (6) (12 mg, 13 mmol, 1.0 equiv) in 2 mL of THF. The reaction mixture was stirred at room temperature for ten minutes and concentrated to give an orange solid. The solid was triturated with hexanes twice to give [Cp^*₂Co][[^tBu-dmx]Fe₂(μ-OH)Cl₂] (5c) as an orange powder (12 mg, 75%). ^1H NMR (500 MHz, 295 K, THF): δ/ppm 38.80, 23.06, 9.36, 1.26, 0.85, −1.06, −10.35. Zero-field ^57Fe Mössbauer (90 K) (δ, |ΔE_Q|/(γ)): 1.00, 3.55 (γ = 0.16 mm/s). FTIR (KBr): 3625 cm⁻¹ (νO−H); 3616 cm⁻¹ (νO18−H).
Oxidation of \([(t^{Bu}dmx)Fe_2(\mu-OH)(thf)_2][BPh_4]\) (4): In a 20 mL vial, iodobenzene dichloride (12.4 mg, 45.1 µmol, 1.00 equiv) was frozen in 2 mL of benzene. A solution of \([(t^{Bu}dmx)Fe_2(\mu-OH)(thf)_2][BPh_4]\) (4) (58.9 mg, 45.1 µmol, 1.00 equiv) was added while stirring. The mixture was thawed and stirred at room temperature for ten minutes. The reaction was filtered through Celite, after which the solvent was frozen and removed in vacuo to yield a purple-brown powder. The residue was washed with hexanes (2×2 mL) and THF (2×0.5 mL) to give \([(t^{Bu}dmx)Fe_2(\mu-O)Cl_2]\) (6) as a dark purple powder (21.2 mg, 51%). Crystals suitable for X-ray diffraction were grown from a concentrated solution of diethyl ether with drops of THF at −35 °C.

Addition of 2,4,6-tri-tert-butylphenoxyl radical to \([Et_4N][(t^{Bu}dmx)Fe_2(\mu-OH)Cl_2]\) (5b): In a J. Young tube, 2,4,6-tri-tert-butylphenoxyl radical (3.7 mg, 14.1 µmol, 0.98 equiv) was combined with a 1.5 mL THF solution of \([Et_4N][(t^{Bu}dmx)Fe_2(\mu-OH)Cl_2]\) (5b) (14.8 mg, 14.1 µmol, 1.00 equiv). \(^1\)H NMR and EPR spectra were collected immediately. The reaction vessel was heated to 60 °C for 12 hours, over the course of which multiple time points were taken to monitor the reaction (Figure S-18).
Figure S-1: Zero-field $^{57}$Fe Mössbauer spectrum of ($^{t}$Bu-dmx)Fe$_2$(Mes)$_2$ (1). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature.

Figure S-2: Zero-field $^{57}$Fe Mössbauer spectrum of ($^{t}$Bu-dmx)Fe$_2$(μ-OH)(Mes)(thf) (2). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature.
**Figure S-3:** Zero-field $^{57}$Fe Mössbauer spectrum of ($^{t}$Bu$^n$dmx)Fe$_2$(μ-O) (3). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature.

**Figure S-4:** Zero-field $^{57}$Fe Mössbauer spectrum of ($^{t}$Bu$^n$dmx)Fe$_2$(μ-O)(thf)$_2$ (3a) (blue trace) after exposing ($^{t}$Bu$^n$dmx)Fe$_2$(μ-O) (3) (green trace) to THF for 30 minutes. The small amount of a third species present (yellow trace) has been assigned as an impurity formed upon
reaction of 3 with trace water. Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature.

Figure S-5: Zero-field $^{57}$Fe Mössbauer spectrum of [(t^{B}dmx)Fe$_2$(μ-OH)(thf)$_2$][BPh$_4$] (4). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature.
Figure S-6: Zero-field $^{57}$Fe Mössbauer spectrum of $[\text{Et}_4\text{N}][(\text{tBudmx})\text{Fe}_2(\mu-\text{OH})\text{Cl}_2]$ (5b). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature.

Figure S-7: Zero-field $^{57}$Fe Mössbauer spectrum of $(\text{tBudmx})\text{Fe}_2(\mu-\text{O})\text{Cl}_2$ (6). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature.
**Figure S-8:** Zero-field $^{57}$Fe Mössbauer spectrum of [Cp$_2$Co][($^6$Bu-dmx)Fe$_2$(μ-O)Cl$_2$] (7) at 90 K. Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature.

**Figure S-9:** Zero-field $^{57}$Fe Mössbauer spectrum of [Cp$_2$Co][($^6$Bu-dmx)Fe$_2$(μ-O)Cl$_2$] (7) at 4 K. Isomer shift and quadrupole splitting are reported relative to Fe foil at room
temperature. This data is fit to reflect 66% of the mixed-valent complex 7, with equal amounts of a four-coordinate high spin Fe(II) ($\delta = 0.98^{\text{mm/s}}$, $|\Delta E_Q| = 2.62^{\text{mm/s}}$) and a four-coordinate high spin Fe(III) center ($\delta = 0.52^{\text{mm/s}}$, $|\Delta E_Q| = 2.46^{\text{mm/s}}$). The remaining 33% is attributed to the formation of hydroxide 5c by hydrolysis of 7 ($\delta = 0.90^{\text{mm/s}}$, $|\Delta E_Q| = 3.42^{\text{mm/s}}$, see Figure S-10 for authentic sample).

Figure S-10: Zero-field $^{57}$Fe Mössbauer spectrum of $[\text{Cp}^{*}_2\text{Co}]\left[(^{\text{tBu}}\text{dmx})\text{Fe}_2(\mu-\text{OH})\text{Cl}_2\right]$ (5c). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature.
Figure S-11: UV/Vis absorption spectrum of \((t^\text{Bu} \text{dmx})\text{Fe}_2(\mu-\text{O})\) (3) in THF.
Figure S-12: FTIR spectrum of ($^{t}$Bu$_{2}$dmx)Fe$_{2}$(μ-OH)(Mes)(thf) (2) (top, red) and ($^{t}$Bu$_{2}$dmx)Fe$_{2}$(μ-OD)(Mes)(thf) (bottom, black), with inset of overlaid spectra in region featuring OH and OD stretches.

Figure S-13: FTIR spectrum of ($^{t}$Bu$_{2}$dmx)Fe$_{2}$(μ-O) (3).
**Figure S-14:** FTIR spectrum of $\text{[(Bu}_3\text{dmx)}\text{Fe}_2(\mu-\text{OH})(\text{thf})_2][\text{BPh}_4]$ (4) (top, red) and $\text{[(Bu}_3\text{dmx)}\text{Fe}_2(\mu-\text{OD})(\text{thf})_2][\text{BPh}_4]$ (bottom, black) with inset of overlaid spectra in region featuring OH and OD stretches.

**Figure S-15:** FTIR spectrum of $\text{[Et}_4\text{N}][\text{[(Bu}_3\text{dmx)}\text{Fe}_2(\mu-\text{OH})\text{Cl}_2]}$ (5b) (top, red) and
[Et₄N][((₃Bu)dmx)Fe₂(μ-OD)Cl₂] (bottom, black) with inset of overlaid spectra in region featuring OH and OD stretches.
Figure S-16: FTIR spectrum of $(^\text{Bu} \text{dmx})\text{Fe}_2(\mu\text{-O})\text{Cl}_2$ (6). Inset: Fingerprint region for $(^\text{Bu} \text{dmx})\text{Fe}_2(\mu\text{-O})\text{Cl}_2$ (6) (red) and $(^\text{Bu} \text{dmx})\text{Fe}_2(\mu\text{-O}^{18})\text{Cl}_2$ (black).
Figure S-17: FTIR spectrum of \([\text{Cp}^*\text{Co}][({}^{\text{d}}\text{Bu}dx)\text{Fe}_2(\mu-\text{OH})\text{Cl}_2] (5c)\) (top, red) and \([\text{Cp}^*\text{Co}][({}^{\text{d}}\text{Bu}dx)\text{Fe}_2(\mu-\text{O}^{18}\text{H})\text{Cl}_2] \) (bottom, black), with inset of region featuring OH stretches.
Figure S-18: EPR spectrum of \([\text{Cp}_2\text{Co}][\text{tBu}_{\text{dmx}}\text{Fe}_2(\mu-O)\text{Cl}_2]\) (7). Spectrum collected in a frozen 2-methyltetrahydrofuran glass at 77 K. The black line represents a simulation with EasySpin.\(^6\) Simulation parameters: \(S = \frac{1}{2}, \; g_x = 1.77, \; g_y = 1.96, \; g_z = 1.97.\) Spectral broadening was accounted for by inclusion of FWHM value for the isotropic magnetic-field domain broadening, and the FWHM of the Gaussian distribution of g values.
**Figure S-19:** EPR reaction monitoring of $[\text{Et}_4\text{N}][{(}^{t\text{Bu}}\text{dmx})\text{Fe}_2(\mu-\text{OH})\text{Cl}_2)]$ (5b) with 2,4,6-tri-tert-butylphenoxyl radical. Spectra collected in a frozen tetrahydrofuran solution at 77 K at indicated time points. Inset: Final spectrum after 12 h. Over the course of 12 h, conversion of the organic radical to the identical spectrum of 7, with g-values of 1.95 and 1.76, was observed.
Figure S-20: Cyclic voltammogram of [(^tBu^dmx)Fe$_2$(μ-O)Cl$_2$] (6). The data were obtained in THF at 25 °C using a carbon working electrode and 0.1 M [^nBu$_4$N][PF$_6$] as supporting electrolyte.

Figure S-21: Differential pulse voltammetric response for [(^tBu^dmx)Fe$_2$(μ-O)Cl$_2$] (6). The data were obtained in THF at 25 °C with 0.1 M [^nBu$_4$N][PF$_6$] as supporting electrolyte. The parameters for DPV were as follows: pulse amplitude of 50 mV, step size of 4 mV, pulse width of 50 ms and pulse period of 0.5 s.
Figure S-22: Scan rate dependence of \([{(t^\text{Bu}d\text{mx})Fe_2(\mu-O)Cl_2]}\) (6). The data were obtained in THF at 25 °C using a carbon working electrode and 0.1 M \([^\text{tBu}_4\text{N}][\text{PF}_6]\) as supporting electrolyte.
Figure S-23. Magnetometry data for (\(^{1\text{Bu}}\text{dmx}\))Fe\(_2\)Mes\(_2\) (1). (top, left) M vs. H at 100 K is linear, showing absence of ferromagnetic impurity even at low fields (top, left, inset). (top, right) Variable temperature magnetic susceptibility data (\(\chi_T\) vs. T) was recorded at 0.5 T and 1.0 T across the temperature range of 5 K – 300 K. At 0.5 T (red circles), \(\chi_T = 6.41\) cm\(^3\)K/mol at 295 K and at 1.0 T, \(\chi_T = 6.32\) cm\(^3\)K/mol at 295 K. These values exceed the spin-only value magnetic susceptibility value for two uncoupled \(S = 2\) centers (\(\chi_T = 6.00\) cm\(^3\)K/mol, dotted line) and are consistent with our hypothesis that the iron centers in this compound are non-interacting, given the large Fe–Fe distance in the solid state structure and lack of direct bridging unit. (bottom) Reduced magnetization data (M vs. H/T) was collected at 3 fields (1, 4, and 7 T) over the temperature range of 1.8 K – 10 K. The data was best fit
(black trace) as $S = 2$ centers with $g = 2.10$ using PHI$^{27}$ with to give the following parameters: $D = 16.8$ cm$^{-1}$ and $|E/D| = 0.25$.

(27) Chilton, N. F.; Anderson, R. P.; Turner, L. D.; Soncini, A.; Murray, K. S. J. Comput. Chem. 2013, 34, 1164.
Figure S-24. Magnetometry data for ($^{15}$Bu$^{13}$dmx)Fe$_2$(μ-O) (3). (left) M vs. H at 100 K is linear, showing absence of ferromagnetic impurity even at low fields (left, inset). (right) $\chi_M$T vs. T at 0.5 T with $\chi_M$T = 1.53 cm$^3$K/mol and 1.0 T with $\chi_M$T = 1.57 cm$^3$K/mol at 295 K. $\chi_M$T vs. T was best fit as two weakly coupled $S = 2$ centers using PH1$^{23}$ (black trace), including 3% of an $S = 2$ impurity, with the following parameters: $g = 1.90$, $J = -53.2$ cm$^{-1}$, $D = 0.64$ cm$^{-1}$, and $|E/D| = 0.016$. 
Figure S-25. Magnetometry data for \([\text{([}^{11}{\text{Bu}}\text{dmx})\text{Fe}_2(\mu-\text{OH})(\text{thf})_2][\text{BPh}_4]\) (4). (left) M vs. H at 100 K is linear, showing absence of ferromagnetic impurity even at low fields (left, inset). (right) Variable temperature magnetic susceptibility data (\(\chi_M T\) vs. T) was recorded at 0.5 T and 1.0 T across the temperature range of 5 K – 300 K. At 0.5 T (red circles), \(\chi_M T = 3.56\) cm\(^3\)K/mol at 295 K and at 1.0 T, \(\chi_M T = 3.48\) cm\(^3\)K/mol at 295 K. \(\chi_M T\) vs. T was best fit as two weakly coupled \(S = 2\) centers using PHI\(^23\) (black trace) with the following parameters: \(g = 1.80, J = -13.3\) cm\(^{-1}\), \(D = 0.47\) cm\(^{-1}\), and \(|E/D| = 0.23\). Due to the low \(g\)-tensor value in this fit, additional fits with \(g = 1.85\) and \(g = 1.90\) were attempted to confirm the presence of weak antiferromagnetic coupling by exemplifying minimally affected \(J\) coupling values: green trace, \(\chi_M T\) vs. T fit parameters: \(g = 1.85, J = -13.9\) cm\(^{-1}\), \(D = 0.56\) cm\(^{-1}\), and \(|E/D| = 0.11\); red trace, \(\chi_M T\) vs. T fit parameters: \(g = 1.90, J = -14.5\) cm\(^{-1}\), \(D = 0.45\) cm\(^{-1}\), and \(|E/D| = 0.16\).
Figure S-26. Magnetometry data for (βu-dmx)Fe₂(μ-O)Cl₂ (6). (left) \(M \) vs. \(H\) at 100 K is linear, showing absence of ferromagnetic impurity even at low fields (left, inset). (right). Variable temperature magnetic susceptibility data (\(χ_M T\) vs. \(T\)) was recorded at 0.5 T and 1.0 T across the temperature range of 5 K – 300 K. At 0.5 T (red circles), \(χ_M T = 0.687\) cm³K/mol at 295 K and at 1.0 T (blue circles), \(χ_M T = 0.677\) cm³K/mol at 295 K. \(χ_M T\) vs. \(T\) was fit as two weakly coupled \(S = \frac{5}{2}\) centers using PHI²³ (black trace), including a 3% \(S = 5/2\) impurity, with the following parameters: \(g = 1.90\), \(J = -122\) cm⁻¹, \(D = 0.38\) cm⁻¹, and \(|E/D| = 0.29\).
X-ray Diffraction Techniques. Structures of 1–7 were collected on a Bruker three-circle platform goniometer equipped with an Apex II CCD and an Oxford cryostream cooling device. Radiation was from a graphite fine focus sealed tube Mo Kα (0.71073 Å) source. Crystals were mounted on a cryoloop or glass fiber pin using Paratone N oil. Structures were collected at 100 K. Data were collected as a series of φ and/or ω scans.

Data were integrated using SAINT\textsuperscript{28} and scaled with either a numerical or multi-scan absorption correction using SADABS.\textsuperscript{28} The structures were solved by intrinsic phasing, direct methods or Patterson maps using SHELXS-2014\textsuperscript{29} and refined against $F^2$ on all data by full matrix least squares with SHELXL-2014.\textsuperscript{29} All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were constrained to be 1.2 times the parameter of the atoms they were linked to (1.5 times for methyl groups). Further details on particular structures are noted below.

\((\text{tBudmx})\text{Fe}_2(\text{Mes})_2\) (1): The structure was solved in the triclinic space group $P\overline{1}$ with two molecules per unit cell and one molecule in the asymmetric unit. The asymmetric unit contained several strongly disordered hexanes molecules. Due to apparent low occupancy and high disorder, an acceptable model could not be refined. A solvent mask was applied in Platon to reduce unrefined electron density. (CCDC 1554783)

\((\text{tBudmx})\text{Fe}_2(\mu-\text{OH})(\text{Mes})(\text{thf})\) (2): The structure was solved in the monoclinic space group $P2_1/n$ with four molecules per unit cell and one molecule in the asymmetric unit. Several disordered diethyl ether solvent molecules were modeled with similarity constraints. (CCDC 1554784)

\((\text{tBudmx})\text{Fe}_2(\mu-\text{O})\) (3): The structure was solved in the monoclinic space group $C2/c$ with four molecules per unit cell and half a molecule in the asymmetric unit. (CCDC 1554786)

\([((\text{tBudmx})\text{Fe}_2(\mu-\text{OH})(\text{thf})_2][\text{BPh}_4]\) (4): The structure was solved in the monoclinic space group $P2_1/c$ with four molecules per unit cell and one molecule in the asymmetric unit. Several disordered tetrahydrofuran solvent molecules were modeled with similarity constraints. (CCDC 1554785)

(28) APEX2 Software Suite; Bruker AXS: Madison, WI, 2009.
(29) Sheldrick, G. M. *Acta Crystal.* 2015, 71, 3-8.
[Et₄N][([Bu_dmx]Fe₂(μ-OH)Cl₂)] (5b): The structure was solved in the monoclinic space group Cc with four molecules per unit cell and one molecule in the asymmetric unit. Several disordered tetrahydrofuran solvent molecules were modeled with similarity restraints. (CCDC 1554789)

([Bu_dmx]Fe₂(μ-O)Cl₂) (6): The structure was solved in the monoclinic space group C2/c with four molecules per unit cell and half a molecule in the asymmetric unit. (CCDC 1554787)

[Cp₂Co][([Bu_dmx]Fe₂(μ-O)Cl₂)] (7): The structure was solved in the monoclinic space group P2₁/n with four molecules per unit cell and one molecule in the asymmetric unit. (CCDC 1554788)
Table S-10. X-ray diffraction experimental details.$^a$

| Moiety                  | Formula                                      | FW         | $\lambda$ (nm) | T (K) | Crystal System | Space Group | a (Å)      | b (Å)      | c (Å)      | $\alpha$ (°) | $\beta$ (°) | γ (°)      | Volume (Å$^3$) | Calc. $\rho$ (mg/m$^3$) | $\mu$ (mm$^{-1}$) | Crystal Size (mm) | Reflections | Completeness (to 2θ) | GOF on F$^2$ | R1, wR2$^a$ [I > 2σ(I)] | R1, wR2 [all data] |
|-------------------------|----------------------------------------------|------------|----------------|-------|----------------|-------------|------------|------------|------------|--------------|-------------|------------|----------------|--------------------------|---------------------|-----------------------|-------------|------------------------|-------------|------------------------|---------------------|
| ($^{\text{thd}}$dmx)Fe$_2$(Mes)$_2$ | C$_{67}$H$_{78}$Fe$_2$N$_4$O                   | 1067.03    | 0.71073        | 100(2) | triclinic      | $P\bar{1}$ (2) | 12.6756(9) | 13.0518(8) | 21.4971(15) | 80.777(2)    | 87.931(2)   | 73.976(2)  | 3374.0(4)       | 1.050                     | 0.469                | 0.20×0.10×0.07          | 12034        | 99.0%                  | 25.19°       | 0.0409, 0.1001        | 0.0623, 0.0924         |
| ($^{\text{thd}}$dmx)Fe$_2$(μ-OH)(Mes)(thf) | C$_{62}$H$_{74}$Fe$_2$N$_4$O$_3$; 1.677(C$_4$H$_{10}$O) | 1161.27    | 0.71073        | 100(2) | monoclinic     | $P2_1/n$ (4)  | 17.416(3)  | 15.512(2)  | 24.559(4)   | 106.397(3)   | 115.027(3)  | 90         | 6364.9(17)      | 1.212                     | 0.506                | 0.11×0.06×0.02          | 11474         | 98.9%                  | 25.20°       | 0.0836, 0.1915        | 0.2133, 0.1477         |
| ($^{\text{thd}}$dmx)Fe$_2$(μ-O) | C$_{49}$H$_{56}$Fe$_2$N$_4$O$_2$; (C$_{24}$H$_{20}$B) | 844.68     | 0.71073        | 100(2) | monoclinic     | $C2/c$ (4)   | 19.775(2)  | 12.6596(14) | 18.9582(17) | 90           | 90          | 90         | 4300.5(8)       | 1.305                     | 0.718                | 0.09×0.03×0.02          | 3827          | 99.4%                  | 25.11        | 0.0836, 0.1915        | 0.2133, 0.1477         |
| ($^{\text{thd}}$dmx)Fe$_2$(μ-OH)(thf)$_2$][BPh$_4$] | C$_{57}$H$_{73}$Fe$_2$N$_4$O$_4$·(C$_{24}$H$_{20}$B); 3.5(C$_4$H$_{10}$O) | 1561.46    | 0.71073        | 100(2) | monoclinic     | $P2_1/c$ (4)  | 18.8507(10)| 21.1660(11) | 21.1905(11) | 18.507(2)    | 19.775(2)   | 90         | 8422.0(8)       | 1.231                     | 0.403                | 0.09×0.03×0.02          | 14924         | 99.9%                  | 25.06°       | 0.0836, 0.1915        | 0.2133, 0.1477         |

$^a$R1 = $\sum ||F_o|| - |F_c|/\sum |F_o|$, wR2 = $\sum [w(F_o^2 - F_c^2)]^2/\sum [w(F_o^2)]^1/2$
Table S-11. X-ray diffraction experimental details.$^a$

| Moiety            | [Et₄N][]**(thdmx)**Fe₂(μ-OH)Cl₂ (5b) | **(thdmx)**Fe₂(μ-O)Cl₂ (6) | [Cp₂Co][]**(thdmx)**Fe₂(μ-O)Cl₂ (7) |
|-------------------|-----------------------------------|--------------------------|----------------------------------|
| Formula           | C₄₉H₅₂Cl₂Fe₂N₄O₂·(C₈H₂₀N); 2(C₄H₈O) | C₄₀H₅₀Cl₂Fe₂N₄O₂         | C₄₀H₅₂Cl₂Fe₂NaO₂·(C₆H₈O)        |
| FW                | 1189.02                           | 915.58                   | 1176.79                          |
| λ (nm)            | 0.71073                           | 0.71073                  | 0.71073                          |
| T (K)             | 100(2)                            | 100(2)                   | 100(2)                           |
| Crystal System    | monoclinic                        | monoclinic               | monoclinic                       |
| Space Group (Z)   | Cc                                | C2/c (4)                 | P2₁/n (4)                        |
| a (Å)             | 19.2846(13)                       | 19.178(3)                | 12.7553(7)                       |
| b (Å)             | 12.6737(9)                        | 13.2068(14)              | 25.2117(13)                      |
| c (Å)             | 26.2797(18)                       | 20.033(3)                | 17.9429(10)                      |
| a (°)             | 90                                | 90                       | 90                               |
| β (°)             | 102.8790(10)                      | 118.6000                 | 92.873(1)                        |
| γ (°)             | 90                                | 90                       | 90                               |
| Volume (Å³)       | 6261.4(7)                         | 4454.9(11)               | 5762.9(5)                        |
| Calc. ρ (mg/m³)   | 1.261                             | 1.365                    | 1.356                            |
| μ (mm⁻¹)          | 0.598                             | 0.815                    | 0.923                            |
| Crystal Size (mm) | 0.11×0.08×0.04                    | 0.12×0.08×0.07           | 0.12×0.11×0.04                   |
| Reflections       | 10845                             | 3963                     | 10211                            |
| Completeness (to 2θ) | 25.04°                          | 25.11°                   | 25.05°                           |
| GOF on F²         | 1.018                             | 1.027                    | 1.011                            |
| R1, wR2$^a$       | 0.0450, 0.0956                    | 0.0717, 0.1862           | 0.0328, 0.0872                   |
| [all data]        | 0.0612, 0.0895                    | 0.1298, 0.1593           | 0.0475, 0.0829                   |

$^a R1 = \Sigma|F_0| - |F_c|/\Sigma|F_0|, wR2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$
**Table S-12.** Bond metrics for 2–7.

| Complex | Fe–Fe (Å)    | Fe–O (Å)   | < Fe–O(H)–Fe (°) |
|----------|--------------|------------|-------------------|
| \((t^{Bu}dmx)Fe_2(\mu-OH)(Mes)(thf) \) (2) | 3.7427(13)  | 2.045(3), 1.942(4) | 139.7(2)          |
| \((t^{Bu}dmx)Fe_2(\mu-O) \) (3) | 3.0425(10)  | 1.7939(14) | 116.00(14)        |
| \([\{t^{Bu}dmx\}Fe_2(\mu-OH)(thf)_2][BPh_4]\) (4) | 3.5934(6)  | 1.969(2), 1.957(2) | 132.49(11)        |
| \([Et_4N][\{t^{Bu}dmx\}Fe_2(\mu-OH)Cl_2]\) (5b) | 3.9767(12)  | 1.991(5), 1.999(5) | 144.20(17)        |
| \((t^{Bu}dmx)Fe_2(\mu-O)Cl_2 \) (6) | 3.5244(17)  | 1.7734(10) | 167.1(3)          |
| \([Cp_2Co][\{t^{Bu}dmx\}Fe_2(\mu-O)Cl_2]\) (7) | 3.5616(7)  | 1.8034(15), 1.8928(15) | 148.98(10)        |
Figure S-27: Solid-state molecular structure for \((\text{t}^\text{Bu-dmx})\text{Fe}_2(\text{Mes})_2\) (1) with thermal ellipsoids at 50% probability level. Hydrogen atoms omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, oxygen = red.
**Figure S-28:** Solid-state molecular structure for (\(^{8}\text{Bu}dmx)\text{Fe}_2(\mu-\text{OH})(\text{Mes})(\text{thf})\) (2) with thermal ellipsoids at 40% probability level. Hydrogen atoms omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, oxygen = red, hydrogen = white.
Figure S-29: Solid-state molecular structure for \((^{\text{tBu}}\text{dmx})\text{Fe}_2(\mu-\text{O})\) (3) with thermal ellipsoids at 50% probability level presented at two different orientations. Hydrogen atoms omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, oxygen = red.
Figure S-30: Side view of the solid-state molecular structure for \((\text{^Bu}d\text{mx})\text{Fe}_2(\mu\text{-O})\) (3) with thermal ellipsoids at 50% probability level presented at two different orientations. Iron = orange, nitrogen = blue, carbon = gray, oxygen = red, hydrogen = white.
Figure S-31: Solid-state molecular structure for [(\text{B}^\text{d}dmx)Fe_2(\mu-OH)\text{(thf)}_2][\text{BPh}_4] (4) with thermal ellipsoids at 40% probability level. All hydrogen atoms except the \(\mu\)-hydroxo proton have been omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, oxygen = red, boron = pink.
**Figure S-32:** Solid-state molecular structure for $[\text{Et}_4\text{N}][((\text{Bu})\text{dmx})\text{Fe}_2(\mu-\text{OH})\text{Cl}_2]$ (5b) with thermal ellipsoids at 50% probability level. All hydrogen atoms except the $\mu$-hydroxo proton have been omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, chlorine = green, oxygen = red.
**Figure S-33:** Solid-state molecular structure for \((^{15}\text{Bu}dmx)\text{Fe}_2(\mu-O)\text{Cl}_2\ (6)\) with thermal ellipsoids at 50\% probability level. Hydrogen atoms omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, chlorine = green, oxygen = red.
Figure S-34: Solid-state molecular structure for [Cp₂Co][(⁴Bu-dmz)Fe₂(μ-O)Cl₂] (7) with thermal ellipsoids at 50% probability level. Hydrogen atoms omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, oxygen = red, chlorine = green, cobalt = aquamarine.
Figure S-35: Geometry optimized molecular structure $[({}^{t}{d}_{u}dmx)Fe_{2}(\mu-OH)]^+ (4a)$
**Figure S-36:** Geometry optimized molecular structure $\left[\left({\text{Bu}}\text{dmx}\right)\text{Fe}_2(\mu\text{-OH})(\text{thf})_2\right]^+ (4)$
Figure S-37: Geometry optimized molecular structure (^{11}Bu-dm)Fe₂(μ-O) (3)
Figure S-38: Geometry optimized molecular structure \((^{\text{Bu}}\text{dmx})\text{Fe} \(_2\)(\mu-O)(\text{thf})\(_2\) \text{(3a)}\)
Figure S-39: Geometry optimized molecular structure ($^{tBu}_2$dmx)Fe$_2$(μ-O)Cl$_2$ (6)
Figure S-40: Geometry optimized molecular structure $[(\text{Bu}^d\text{dmx})\text{Fe}_2(\mu-\text{OH})\text{Cl}_2]^+$ (6a)
Table S-13: Coordinates of optimized molecular structures for complexes 4a, 4, 3, 3a, 6, and 6a.

\[ \left( ^{18}\text{Bdmx}\right) \text{Fe}_2(\mu-\text{OH})^+ \text{(4a)} \]

| Element | X   | Y    | Z    |
|---------|-----|------|------|
| Fe      | -1.99662500 | 0.86733700 | -1.39437900 |
| Fe      | -2.13753200 | -0.81817500 | 1.40508500 |
| O       | -3.13079000 | 0.06664400 | -0.02787900 |
| H       | -4.10366900 | 0.11625400 | -0.05095600 |
| O       | 2.69895500 | -0.03437400 | 0.02302500 |
| N       | -0.64514800 | 0.04921300 | 2.39881000 |
| N       | -1.08514700 | 2.61683000 | -1.09920900 |
| N       | -0.82324600 | -2.42527800 |
| H       | 2.63106600 | 0.25171300 | 3.06951700 |
| C       | 1.17749300 | 1.60913700 | -1.55275700 |
| C       | 2.51388200 | -1.90040700 | 1.46395200 |
| C       | 0.33590000 | 2.59975400 | -0.99855300 |
| C       | 3.43492800 | 0.91077700 | -0.69491000 |
| C       | 1.04121900 | -1.63036500 | 1.53939700 |
| C       | 0.17195900 | -2.59627300 | 0.98267100 |
| C       | 2.65704300 | 1.81938300 | -1.44338000 |
| C       | -1.70656700 | -1.92354700 | -3.69908900 |
| C       | 4.83743700 | 0.95414200 | -0.66280900 |
| C       | -0.57053100 | 1.15552800 | 3.20444000 |
| C       | 3.36045900 | -1.02336700 | 0.75351300 |
| C       | -0.49890400 | -1.13500000 | -3.22506200 |
| C       | -0.62651800 | -4.53099600 | 0.06865100 |
| H       | -0.70178500 | -5.50127900 | -0.39953800 |

\[ E = -2518.90158573 \text{ a.u.} \]
\[ G = -2518.028445 \text{ a.u.} \]

Charge = +1, Multiplicity = 9
| Element | X         | Y         | Z         | Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|---------|-----------|-----------|-----------|
| H       | -2.134962 | -0.523786 | -5.341284 | H       | 7.207474  | -1.58387  | 0.454348  |
| H       | -2.800169 | -2.15886  | -5.580052 | H       | 7.250772  | -0.120575 | -1.449479 |
| H       | -1.060824 | -1.861987 | -5.803521 | C       | -1.436724 | 3.484570  | 3.469731  |
| C       | 5.462753  | 2.000545  | -1.373754 | H       | -0.555943 | 3.786859  | 4.046646  |
| H       | 6.546099  | 2.073660  | -1.373113 | H       | -2.284728 | 4.095086  | 3.804367  |
| C       | -2.982280 | -1.575647 | -2.906715 | H       | -1.241908 | 3.700945  | 2.413792  |
| H       | -2.850411 | -1.756194 | -1.835925 | C       | -3.987534 | 3.157549  | -0.795772 |
| H       | -3.815080 | -2.197927 | -3.254666 | H       | -3.826238 | 2.545790  | -1.695278 |
| H       | -3.289648 | -0.530957 | -3.068124 | H       | -4.996705 | 3.576233  | -0.884573 |
| C       | 0.791659  | 1.384269  | 3.583223  | H       | -3.966128 | 2.516518  | 0.090705  |
| H       | 1.141546  | 2.183257  | 4.220550  | C       | -1.964060 | 1.701061  | 5.195391  |
| C       | -3.563408 | -4.957833 | -0.676119 | H       | -2.181023 | 0.639753  | 5.370765  |
| H       | -3.497544 | -4.307049 | -1.554340 | H       | -2.806994 | 2.295389  | 5.570623  |
| H       | -4.594217 | -5.323127 | -0.592982 | H       | -1.070534 | 1.968149  | 5.770560  |
| H       | -2.914020 | -5.823947 | -0.842856 | C       | 6.549178  | 0.592624  | 1.156038  |
| C       | -2.961394 | 4.305607  | -0.686193 | H       | 7.225387  | 1.319903  | 0.693247  |
| C       | 4.494267  | -3.133717 | 2.168136  | H       | 7.161071  | -0.141377 | 1.691675  |
| H       | 4.941546  | -3.958703 | 2.713551  | H       | 5.921543  | 1.118466  | 1.884811  |
| C       | -3.052925 | 1.632228  | 2.922565  | C       | -3.051661 | 5.181980  | -1.973294 |
| H       | -2.938782 | 1.774804  | 1.843937  | H       | -2.364314 | 6.033684  | -1.915148 |
| H       | -3.865321 | 2.284565  | 3.263204  | H       | -4.072617 | 5.566821  | -2.091577 |
| H       | -3.378501 | 0.600726  | 3.128890  | H       | -2.795202 | 4.592015  | -2.861958 |
| C       | -0.408265 | 4.567075  | -0.109648 | H       | -0.456480 | 5.544255  | 0.347411  |
| C       | 5.310641  | -2.214139 | 1.490752  | E       | -2983.86526288 | a.u. |
| H       | 6.388752  | -2.337884 | 1.527676  | G       | -2982.765575 | a.u. |
| C       | 4.714944  | 2.950423  | -2.087674 | Charge = +1, Multiplicity = 9 |
| H       | 5.219737  | 3.748405  | -2.623037 | Fe      | 1.674618 | 1.744587 | 0.3189410 |
| C       | -3.302077 | -5.159275 | 1.835811  | Fe      | 1.674685 | -1.744535 | -0.3190160 |
| H       | -2.646724 | -6.029352 | 1.715011  | O       | 2.552551 | 0.000540 | -0.0001160 |
| H       | -4.336853 | -5.513641 | 1.925314  | H       | 3.527737 | 0.000780 | -0.0001330 |
| H       | -3.026231 | -4.647175 | 2.766037  | O       | 2.376717 | 3.606866 | 0.9414200 |
| C       | 6.583907  | -0.833179 | -0.952012 | O       | 2.376763 | -3.606797 | -0.9415800 |
| H       | 5.980881  | -1.335527 | -1.717169 | O       | -3.151334 | 0.000620 | -0.0006200 |

\[[(\text{BuDmx})\text{Fe}_2(\mu-\text{OH})(\text{thf})_2]^+ \] (4)
\[(\text{tdm})\text{Fe}_2(\mu-\text{O})\] (3)

E = $-2518.43671246$ a.u.

G = $-2517.574964$ a.u.

Charge = 0, Multiplicity = 9

Fe  
2.04284200  0.84724000  1.27918600  
4.77067100  4.26947300  2.01725000

O  
-2.68615900  -0.00001200  0.00002200  
3.73309700  2.84620900  2.19700800

O  
3.07300100  0.00000800  -0.00004400  
0.58827500  4.61546600  0.00489700

N  
1.18625500  2.66309400  1.03923600  
0.67484900  5.58433000  -0.46387500

N  
0.58050300  0.13854300  2.48127800  
3.04149400  -1.13524500  3.37202300

C  
-1.63831400  -0.20704800  3.03634300  
2.95968500  5.94625800  -0.76776300

H  
-2.71083800  -0.08642500  3.08740000  
3.86410100  -1.74843100  3.76060500

C  
0.50772400  -0.90559000  3.35543900  
3.18978200  -0.11104000  3.74023700

C  
-0.86293600  -1.14150700  3.72033300  
3.32579800  5.70469800  0.23755500

H  
-1.21098800  -1.90309300  4.40372300  
2.95968500  5.94625800  -0.76776300

C  
3.15317300  4.19890200  0.55326000  
4.38954200  5.96922900  0.27951000

C  
-3.38527200  1.01571700  0.65861900  
2.78742300  6.32933600  0.96141100

C  
-3.20604200  3.05068900  1.95402200  
1.53284000  -3.17044200  3.34599900

H  
-2.59878600  3.77742900  2.48424100  
0.61653200  -3.62402100  3.74228200

C  
-4.78792800  1.09216300  0.64068200  
2.38636300  -3.77923300  3.67103500

C  
-0.59214300  3.89727800  0.23270500  
1.47625800  -3.19868100  2.25360800

H  
-1.59810200  4.19382900  -0.02619300  
3.95710800  3.37692700  -0.49397000

C  
-4.60680200  3.18105700  1.91664000  
5.02618700  3.60838900  -0.39478700

H  
-5.08671300  4.02655100  2.39970400  
3.64551400  3.63470600  -1.51114500

C  
1.67397600  3.83081600  0.51697800  
3.82342600  2.29846200  -0.35727400

C  
-5.38282700  2.20051500  1.27968500  
-0.74327100  0.60952300  2.26051800

H  
-6.46449400  2.29615400  1.28480800  
1.10435000  1.72798400  1.47745900

C  
1.68191700  -1.70862800  5.41097900  
-0.22860000  2.68308100  0.90707200

H  
1.79005700  -0.68838700  5.80035200  
-2.57876700  1.95652100  1.33648000

H  
2.51605500  -2.31395500  5.78898300  
1.18624100  -2.66309200  -1.03927200

H  
0.74993900  -2.12893000  5.80595500  
0.58043100  -0.13852900  -2.48130100

C  
-5.65785700  -0.00001500  0.00005700  
-1.63840700  0.20703400  -3.03630800

C  
-6.55614300  0.63557400  -1.10236400  
-2.71093200  0.08639800  -3.08733500

H  
-7.20331700  1.41060500  -0.67690400  
0.50761200  0.90561200  -3.35541000

H  
-7.19873700  -0.12224400  -1.56387600  
-0.86306200  1.14151200  -3.72030500
(Bu₄dmx)Fe₂(μ-O)(thf)₂ (3a)

E = −2983.37141801 a.u.
G = −2982.287126 a.u.
Charge = 0, Multiplicity = 9
| Atom | X         | Y         | Z         | Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|------|-----------|-----------|-----------|
| H    | 5.57066400| -4.40377400| -1.35285400| H    | -1.79095300| -3.61558000| 3.66774400|
| C    | -2.39998300| -0.94457500| 3.20553100 | H    | -2.33436700| -2.85296600| 5.18090600|
| H    | -2.16557500| -0.01068100| 2.69275700 | H    | -0.63907000| -3.36627400| 4.99807000|
| C    | -3.18258500| -0.75680900| 3.95213200 | C    | 7.03109200 | -0.26870000| 1.19603100|
| H    | -2.81581600| -1.63574900| 2.46529300 | H    | 7.66214800 | 0.58256400 | 1.47514000|
| C    | -3.42220100| 5.50199700 | -1.97878100| H    | 7.69073300 | -1.10270500| 0.93166300|
| H    | -4.27296200| 6.18166900 | -1.87400500| H    | 6.43706000 | -0.56042700| 2.06983100|
| C    | -3.15974600| 5.43720000 | -3.04081600| C    | -2.80597600| 4.60260600 | 2.80039600|
| C    | -0.14221700| 2.75693400 | 3.52567000 | C    | -2.10461100| 5.11505900 | 3.47034000|
| H    | -0.20853200| 2.96491000 | 4.58383400 | H    | -3.82530000| 4.92929900 | 3.04703800|
| C    | 5.85753200 | 2.34551600 | -0.75492900| H    | -2.58381400| 4.90450000| 1.77064400|
| H    | 6.93986400 | -2.41030800| -0.82055500| C    | -1.26886000| -4.70198000| 0.95944600|
| C    | 4.94737800 | 3.62141900 | 1.11556000 | H    | -0.59366700| -4.50328400| 1.79761900|
| H    | 5.39790600 | 4.55810600 | 1.42989200 | H    | -0.72449900| -4.60703700| 0.01862700|
| C    | -2.64141400| -4.69096100| -2.85119100| C    | -3.61206000| -4.19317100| 1.41576200|
| H    | -1.92881200| -5.17558200| -3.52991500| H    | -4.28164800| -4.24222900| 0.54986000|
| C    | -3.65341700| -5.03408800| -3.10562000| H    | -4.02434800| -3.50892200| 2.16163600|
| H    | -2.41432600| -5.00882100| -1.82710500| C    | -3.27758300| -5.58849000| 1.96664600|
| C    | -2.19520900| 5.95259100 | -1.14666400| H    | -4.11875400| -6.27972200| 1.86026100|
| H    | -1.61166000| 6.72871900 | -1.65073300| H    | -3.00913300| -5.53088200| 3.02755300|
| H    | -2.51814500| 6.33975400 | -0.17311900| C    | -2.04936500| -6.01233200| 1.12243300|
| C    | 6.96955500 | 0.51529100 | -1.22345300| H    | -1.45082700| -6.78432400| 1.61516300|
| H    | 6.33127400 | 0.77679700 | -2.07542400| H    | -2.37256600| -6.39463700| 0.14704600|
| H    | 7.63081500 | -0.30480600| -1.52554500| C    | 7.59499800 | 1.38171500 | -0.98042800 | $(\text{Budmx})\text{Fe}_2(\mu-\text{O})\text{Cl}_2$ (6) | E = -3438.91434721 a.u. |
| C    | -0.74307000| -0.59167800| 5.05935000 | C    | 7.59499800 | 1.38171500 | -0.98042800 | $(\text{Budmx})\text{Fe}_2(\mu-\text{O})\text{Cl}_2$ (6) | G = -3438.052343 a.u. |
| H    | 0.10338000 | -0.99733600| 5.62573200 | H    | -1.58542700| -0.47206400| 5.75378500 | Charge = 0, Multiplicity = 11 |
| H    | -0.46274700| 0.39477600 | 4.67682500 | Fe   | 1.83890300 | 0.81078700 | -1.54360000 |
| C    | -3.72929900| 2.40046300 | 2.00785700 | Cl   | 3.46524000| 1.10959100 | -3.15325400 |
| H    | -3.60135200| 2.74619100 | 0.97857800 | O    | -2.88578600| -0.00004100| -0.00001900 |
| H    | -4.73818400| 2.68969500 | 2.33138600 | O    | 2.39748500| -0.00008400| -0.00011100 |
| H    | -3.65984400| 1.31043300 | 2.00188300 | N    | 0.26472700 | -0.05392400| -2.40136700 |
| C    | -1.49885800| -2.93330000| 4.47216100 | N    | 1.03510800 | 2.56324200 | -1.03925600 |
| X   | Y   | Z   |        | X   | Y   | Z   |        |        |
|-----|-----|-----|--------|-----|-----|-----|--------|--------|
| C   | 4.04941700 | -3.09387600 | 0.20267300 | H  | 1.88059000 | 2.57039000 | 1.70685100 |
| H   | 4.00940200 | -2.85716100 | -0.86248000 | C  | 0.54840200 | 3.49888900 | 3.97291200 |
| H   | 5.04994800 | -3.48185700 | 0.43104700 | H  | 0.09061300 | 3.90297100 | 3.06255400 |
| H   | 3.93013100 | -2.16642600 | 0.76226500 | H  | 1.34005800 | 4.18599000 | 4.29582300 |
| C   | -1.96869900 | 0.18848900 | 2.97317900 | H  | -0.20852500 | 3.47112400 | 4.76444700 |
| H   | -3.02094400 | -0.04140600 | 3.04830800 | Fe | 1.83900600 | -0.81075000 | 1.54352000 |
| C   | -2.76194400 | -1.98543100 | 1.26659500 | Cl | 3.46541000 | -1.10952200 | 3.15311000 |
| C   | 3.00090100 | -4.17191100 | 0.58202500 |        |        |        |        |        |
| C   | 0.49422900 | -4.44210500 | -0.15010200 |        |        |        |        |        |
| H   | 0.60715600 | -5.37002800 | -0.68799300 |        |        |        | E = -3439.34367578 a.u. |
| C   | -1.30126200 | -1.69573200 | 1.43230300 |        |        |        | G = -3438.468656 a.u. |
| C   | -4.77110400 | -3.26335300 | 1.77456800 |        |        |        | Charge = +1, Multiplicity = 11 |
| H   | -5.24185600 | -4.13541100 | 2.21736400 | Fe  | 1.79895000 | -0.85433500 | 1.56838200 |
| C   | -3.37155500 | -3.11612200 | 1.83204300 | Cl  | 3.41358000 | -1.13165900 | 3.13522300 |
| H   | -2.75913400 | -3.85357000 | 2.34121000 | O   | -2.90464300 | 0.01526300 | 0.01652000 |
| C   | 1.74130500 | 0.54561200 | 5.04677300 | O   | 2.62391100 | 0.01585800 | 0.00600600 |
| H   | 0.95303700 | 1.47650000 | 5.80674800 | N   | 0.25615500 | 0.05112600 | 2.34369500 |
| H   | 2.52236200 | 2.22219500 | 5.41770700 | N   | 1.03140300 | -2.55962900 | 1.00018300 |
| H   | 2.18175800 | 0.55459400 | 4.90401300 | C   | -3.59846300 | -1.04053700 | 0.60084400 |
| C   | 3.21402600 | -4.61368200 | 2.06242700 | C   | -4.99678300 | -1.12957800 | 0.56547000 |
| H   | 3.09166000 | -3.76972400 | 2.74629900 | C   | -1.02361100 | -0.57099500 | 2.17696900 |
| H   | 4.22921400 | -5.01312900 | 2.18268200 | C   | 1.55849100 | -3.70796300 | 0.42025500 |
| H   | 2.49733800 | -5.39813200 | 2.33669700 | C   | -0.38794600 | -2.58492900 | 0.79527500 |
| C   | -6.74957500 | 0.58043400 | 1.13252300 | C   | 0.07898700 | 1.14524700 | 3.18444500 |
| H   | -7.39424800 | -0.19870600 | 1.55389600 | C   | -5.57106400 | -2.29042500 | 1.12638400 |
| H   | -7.39472500 | 1.37720000 | 0.74589400 | H   | -6.65027800 | -2.40846200 | 1.12312000 |
| H   | -6.13373500 | 0.99437800 | 1.93930400 | C   | -1.28817900 | 1.21873800 | 3.56603200 |
| C   | 3.23473200 | -5.39927300 | -0.33483600 | H   | -1.71512200 | 1.96227900 | 4.22007800 |
| H   | 2.60922300 | -6.25052600 | -0.04148500 | C   | -0.69418200 | -3.73933100 | 0.02022900 |
| H   | 4.28266800 | -5.71161600 | -0.25571400 | H   | -1.68207700 | -4.01806200 | -0.31454900 |
| H   | 3.02953400 | -5.15993500 | -1.38541000 | C   | -5.86933500 | 0.00592000 | 0.00062100 |
| C   | 2.29389600 | 2.27417800 | 2.67187000 | C   | 1.16105500 | 2.08779000 | 3.68157000 |
| H   | 2.88823400 | 1.36899700 | 2.53740700 | C   | 4.06933800 | -3.12962500 | 0.24193700 |
| H   | 2.98098200 | 3.05864400 | 3.01222900 | H   | 4.01779200 | -2.80582500 | -0.79950600 |

\[([\text{Bi dmx}]\text{Fe}_2(\mu-OH)\text{Cl}_2]^+ (6a)\]

\[E = -3439.34367578 \text{ a.u.}\]

\[G = -3438.468656 \text{ a.u.}\]

[SI-71]
| Atoms | x     | y     | z     | Atoms | x     | y     | z     |
|-------|-------|-------|-------|-------|-------|-------|-------|
| H     | 5.05973000 | -3.56724500 | 0.41367500 | H     | 0.09412800 | 3.89461000 | 3.02126500 |
| H     | 3.99844600 | -2.25784000 | 0.89251500 | H     | 1.33505200 | 4.17513400 | 4.26315600 |
| C     | -1.96789700 | 0.16505200 | 2.94766500 | H     | -0.21829000 | 3.46754200 | 4.72133100 |
| H     | -3.01778500 | -0.06992100 | 3.03636800 | N     | 0.26955200 | -0.06477200 | -2.32569600 |
| C     | -2.77435500 | -2.00125300 | 1.22401200 | N     | 1.02858200 | 2.56730600 | -1.01118000 |
| C     | 2.99430800 | -4.43354700 | -0.19972900 | C     | -3.59933000 | 1.04948800 | -0.60430600 |
| C     | 0.50273300 | -4.33547000 | -0.19972900 | C     | -4.99816900 | 1.13178700 | -0.58345400 |
| H     | 0.61508800 | -5.36022100 | -0.73893700 | C     | -1.01758300 | 0.54211900 | -2.15523000 |
| C     | -1.31665600 | -1.70380100 | 1.38600300 | C     | 1.55105900 | 3.71929700 | -0.43426500 |
| C     | -4.77659400 | -3.29840600 | 1.69879500 | C     | -0.39316700 | 2.59894100 | -0.82905300 |
| H     | -5.24459100 | -4.18230400 | 2.11989200 | C     | 0.09820300 | -1.17860200 | -3.14132300 |
| C     | -3.37754700 | -3.14997900 | 1.76026100 | C     | -5.57310500 | 2.27878200 | -1.17167000 |
| H     | -2.76404200 | -3.89868900 | 2.25121100 | H     | -6.65271700 | 2.39385100 | -1.17625000 |
| C     | 1.71809200 | 1.53630700 | 5.02837000 | C     | -1.27514900 | -1.28921200 | -3.49213100 |
| H     | 0.92273800 | 1.47985200 | 5.78105300 | H     | -1.69999300 | -2.05579900 | -4.12025800 |
| H     | 2.50058900 | 2.20944000 | 5.40076000 | C     | -0.70838900 | 3.76638800 | -0.07676400 |
| H     | 2.15153900 | 0.54002000 | 4.90117500 | H     | -1.70048900 | 4.05361200 | 0.23773800 |
| C     | 3.16427400 | -4.67928200 | 2.04040400 | C     | 1.19197700 | -2.09361100 | -3.66359900 |
| H     | 3.02463600 | -3.85525600 | 2.74565400 | C     | 4.05475100 | 3.11855300 | -0.22704200 |
| H     | 4.17432200 | -5.08468100 | 2.17691700 | H     | 3.96813300 | 2.75978000 | 0.80045900 |
| H     | 2.43903600 | -5.46824900 | 2.27335700 | H     | 5.05083200 | 3.55954200 | -0.35021900 |
| C     | -6.75010700 | 0.57589300 | 1.15122500 | H     | 4.00585000 | 2.27091200 | -0.91101900 |
| H     | -7.39560400 | -0.20527700 | 1.56748700 | C     | -1.96167000 | -0.23072900 | -2.89016300 |
| H     | -7.39355600 | 1.38228700 | 0.78232000 | H     | -3.01633700 | -0.01471500 | -2.96911200 |
| H     | -6.12367100 | 0.97414900 | 1.95765700 | C     | -2.77489100 | 1.99599100 | -1.24811700 |
| C     | 3.23155300 | -5.40529600 | -0.37841400 | C     | 2.99278500 | 4.20015700 | -0.55203200 |
| H     | 2.58712500 | -6.25388800 | -0.12310600 | C     | 0.48765800 | 4.45738500 | 0.15724200 |
| H     | 4.27128300 | -5.73712500 | -0.28051000 | H     | 0.59465500 | 5.38874300 | 0.68944300 |
| H     | 3.05778300 | -5.13617600 | -1.42733300 | C     | -1.31601700 | 1.69760900 | -1.39935500 |
| C     | 2.29743300 | 2.25286300 | 2.65464100 | C     | -4.77829700 | 3.27704500 | -1.76045500 |
| H     | 2.89653500 | 1.34754400 | 2.54292600 | H     | -5.24636900 | 4.15102600 | -2.20170400 |
| H     | 2.97909000 | 3.04210700 | 2.99003100 | C     | -3.37867000 | 3.13043400 | -1.81341800 |
| H     | 1.89188700 | 2.53794400 | 1.68310800 | H     | -2.76526900 | 3.86894600 | -2.31967900 |
| C     | 0.54386700 | 3.49061800 | 3.93531600 | C     | 1.71651400 | -1.51255100 | -5.01151400 |
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| H    | 0.90749200 | -1.46101000 | -5.74988600 |
| H    | 2.50476000 | -2.16610600 | -5.40598700 |
| H    | 2.13381900 | -0.51061500 | -4.87812700 |
| C    | 3.18976800 | 4.69721600  | -2.01806100 |
| H    | 3.04870800 | 3.88392000  | -2.73554500 |
| H    | 4.20711800 | 5.09021000  | -2.13568100 |
| H    | 2.47865600 | 5.49886600  | -2.25089700 |
| C    | -6.78236300 | -0.55492800 | -1.12891600 |
| H    | -7.42719100 | 0.23296700  | -1.53273500 |
| H    | -7.42886500 | -1.35178600 | -0.74540400 |
| H    | -6.17883800 | -0.96240700 | -1.94812000 |
| C    | 3.22489600 | 5.39296300  | 0.41073600  |
| H    | 2.59037400 | 6.24935500  | 0.15712900  |
| H    | 4.26812400 | 5.71879200  | 0.33176600  |
| H    | 3.03377900 | 5.11208000  | 1.45347900  |
| C    | 2.34644200 | -2.24794200 | -2.65570000 |
| H    | 2.91336200 | -1.32555400 | -2.51886300 |
| H    | 3.05403400 | -2.99970200 | -3.02373700 |
| H    | 1.96206200 | -2.57786400 | -1.69032100 |
| C    | 0.60124300 | -3.50510500 | -3.92973500 |
| H    | 0.15988400 | -3.92641700 | -3.01990000 |
| H    | 1.40430000 | -4.17164300 | -4.26553000 |
| H    | -0.16200400 | -3.48814600 | -4.71489400 |
| Fe   | 1.80692300 | 0.86541600  | -1.57188200 |
| Cl   | 3.41077900 | 1.15570300  | -3.14702500 |
| H    | 3.60326900 | 0.03633800  | 0.02003800  |