# Spin Transitions in Bis(amidinato)-N-Heterocyclic Carbene Iron(II) and Iron(III) Complexes

Jessica L. Drake,[a] Hilan Z. Kaplan,[a] Matthew J. T. Wilding,[b] Bo Li,[a] and Jeffery A. Byers[a,*]

[a] Eugene F. Merkert Chemistry Center, Department of Chemistry, Boston College, 2609 Beacon Street, Chestnut Hill, Massachusetts, 02467.
[b] Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts, 02138.

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## 1. General Considerations

Unless otherwise stated, all reactions were carried out in oven-dried glassware in a nitrogen atmosphere glovebox or using standard Schlenk line techniques.[1] Solvents were used after passage through a solvent purification system similar to the one reported by Grubbs[2] under a blanket of argon, and then degassed by briefly exposing the solvent to vacuum. Benzene-$d_6$ was purchased from Cambridge Isotope Laboratories and was vacuum distilled from Na/benzophenone. Dichloromethane-$d_2$ and chloroform-*d* were purchased from Cambridge Isotope Laboratories and vacuum distilled from $CaH_2$.

Nuclear Magnetic Resonance (NMR) spectra were recorded at ambient temperature on spectrometers operating at 500 MHz for $^1$H NMR. Resonances for paramagnetic complexes are reported as chemical shift in ppm (peak with at half height). Infrared (IR) spectra were recorded on an ATR infrared spectrometer. Magnetic moments were determined by Evans' method according to the procedure published by Gibson and coworkers.[3] High-resolution mass spectra were obtained at the Boston College Mass Spectrometry Facility using ESI+ or MALDI ionization modes.

Variable temperature (2–300 K) magnetization data were recorded in a 1 T magnetic field on an MPMS-XL Quantum Design SQUID magnetometer. Values for magnetic susceptibility were corrected for the underlying diamagnetic increment by using tabulated Pascal constants. The magnetic data at low temperature (<100 K) were fit using Eckhard Bill's julX program to obtain zero-field splitting parameters.[4] Statistic molar magnetic susceptibilities were calculated using the usual spin Hamiltonian approach for up to four spins with local multiplicities up to $S = {}^5/_2$ based on:

$$H = H_{ex} + H_{ZFS} + H_{Zee} \qquad \text{where}$$

$$H_{ex} = -2\sum_{i=1}^{ns-1}\sum_{j=i=1}^{ns} J_{ij}\bar{S}_i \cdot \bar{S}_j$$

is the exchange Hamiltonian, and

$$H_{ZFS} = \sum_{i=1}^{ns} D_i\left[S_{z,i}^2 - {}^1/_3 S_i(S_i+1) + {}^{E_i}/_{D_i}\left(S_{x,i}^2 - S_{y,i}^2\right)\right]$$

accounts for zero-field splitting, and

$$H_{Zee} = \sum_{i=1}^{ns} g\beta\bar{S}_i \cdot \bar{B}$$

is the Zeeman interaction.

$J_{ij}$ are the exchange *coupling constants* of spins i and j, ns is the number of spins (max. four), $D_i$, $E/D_i$ and $g_i$ are the local axial and rhombic zero field splitting parameters and g-values (isotropic average). At temperatures >100 K, the data was modeled using Sorai's model[5] as described in the text.

EPR samples were prepared in 4 mM OD suprasil quartz air-tight EPR tubes from Wilmad Labglass. All samples for EPR spectroscopy were run of pure solid powder or diluted in silica. X-band EPR spectra were recorded on a Bruker EMXplus spectrometer equipped with a 4119HS cavity and an Oxford ESR-900 helium flow cryostat operating at 10 K. The instrumental parameters employed for all samples were as follows: 1 mW power; time constant 41 ms; modulation amplitude 8 G; 9.40 GHz (10K spectra); modulation frequency 100 kHz. The approximate g-values are represented in Figures S1.

Selected single crystals suitable for X-ray crystallographic analysis were used for structural determination. Unless otherwise stated, the X-ray intensity data were measured at 100(2) K (Oxford Cryostream 700) on a Bruker Kappa APEX Duo diffractometer system equipped with a sealed Mo-target X-ray tube ($\lambda$ = 0.71073 Å) and a high brightness I$\mu$S copper source ($\lambda$ = 1.54178 Å). The crystals were mounted on a goniometer head with paratone oil. The detector was placed at a distance of 5.000 cm from the crystal. For each experiment, data collection strategy was determined by APEX software package and all frames were collected with a scan width of 0.5° in $\omega$ and $\phi$ with an exposure time of 10 or 20 s/frame. The frames were integrated with the Bruker SAINT Software package using a narrow- frame integration algorithm to a maximum $2\theta$ angle of 56.54° (0.75 Å resolution) for Mo data and 136.50° (0.83 Å resolution) for Cu data. The final cell constants are based upon the refinement of the XYZ-centroids of several thousand reflections above 20 $\sigma(I)$. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the empirical method (SADABS). The structures were solved and refined by full-matrix least squares procedures on $|F^2|$ using the Bruker SHELXTL (version 6.12) software package. All hydrogen atoms were included in idealized positions for structure factor calculations. Anisotropic displacement parameters were assigned to all non-hydrogen atoms, except those disordered. SQUEEZE (PLATON, A.Spek) was used in crystal structure of **3** to treat disordered solvent molecules (THF and/or $CH_2Cl_2$), which could not be satisfactorily modeled.

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[1] B. J. Burger and J. E. Bercaw. *New Developments in the Synthesis, Manipulation and Characterization of Organometallic Compounds*; A. L. Wayda and M. Y. Darensbourg, eds.; American Chemical Society: Washington, D.C., 1987.

[2] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rose and F. J. Timmers, *Organometallics* 1996**, 15***,* 1518.

[3] G. J. P. Britsovsek, V. C. Gibson, S. K. Spitzmesser, K. P. Tellmann, A. J. P. White, and D. J. Williams, *J. Chem. Soc., Dalton Trans.* 2002, 1159.

[4] E. Bill, julX version 1.5, MPI for Chemical Energy Conversion, Germany, 2013.

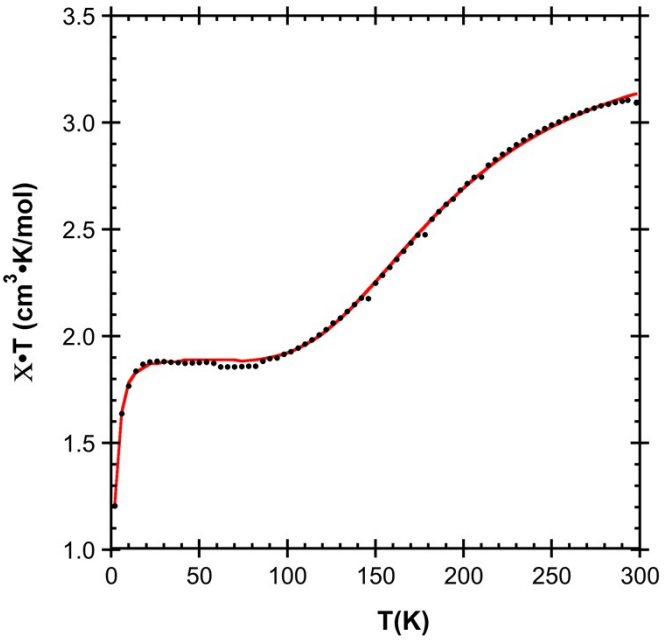
[5] O. Kahn, *Moclecular Magnetism*, VCH Publishers, Inc.: New York, N. Y., 1993.

The chlorine atoms of some $CH_2Cl_2$ molecules in the structure of **2a** and chlorine ligands in structure of **3** appeared to be disordered over two orientations, and the disorder was modeled as such.

$^{57}$Fe Mössbauer spectra were measured on liquid nitrogen cooled samples at zero magnetic field with a constant acceleration spectrometer (SEE Co., Edina, MN). Solid or crystalline samples were prepared as Paratone-N mulls in an inert atmosphere glovebox and frozen in liquid nitrogen prior to handling in air. Isomer shifts are quoted relative to Fe foil at room temperature. Data was processed, simulated, and analyzed using a package written by E.R.K. for IGOR Pro 6 (Wavemetrics, Lake Oswego, OR).

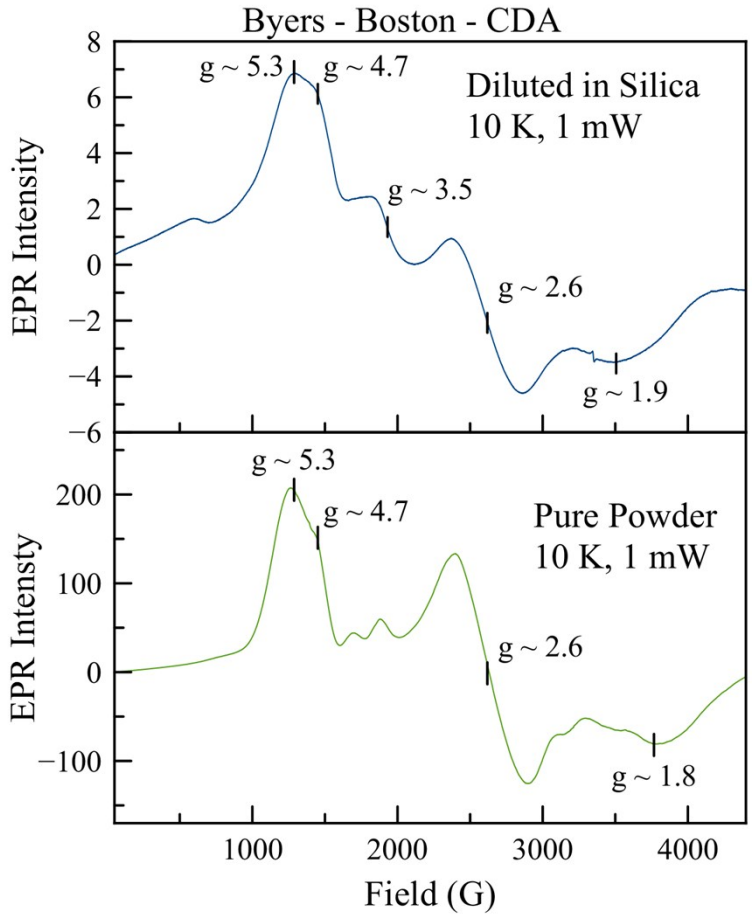
## 2. Sorai model for SQUID data for $[(CDA^{iPr})FeCl_2]BF_4 \bullet 0.5CH_2Cl_2$ (**3**)

**Figure S1**. Variable temperature solid-state dc-magnetization data for **3** using SQUID magnetometry. Filled symbols represent experimental data, and the solid line represents the simulation obtained by combining two models: below 100 K, the data were fit to intermediate spin iron complexes with significant contributions from zero-field splitting (for S = 3/2: $g_{iso} = 2.01$, $|D| = 3.4$ cm$^{-1}$, $|E| = 2.0$ cm$^{-1}$) and above 100 K, the data were fit using $x = 1/[1 + \exp\{(\Delta H/R)(1/T - 1/T_c)\}]$ ($T_c = 201$ K; $\Delta H = 503$ cm$^{-1}$).[17]



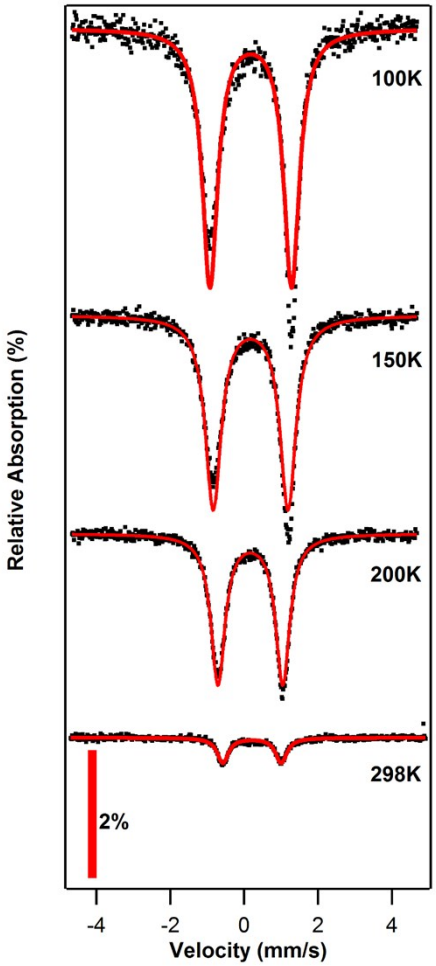
## 3. X-Band EPR Spectra for $[(CDA^{iPr})FeCl_2]BF_4 \bullet 0.5CH_2Cl_2$ (3)

**Figure S2.** X-Band EPR spectra at 3 K of $[(CDA^{iPr})FeCl_2]BF_4$ (**3**).



## 4. $^{57}$Fe Mössbauer Spectra for $[(CDA^{iPr})FeCl_2]BF_4 \cdot 0.5CH_2Cl_2$ (3)

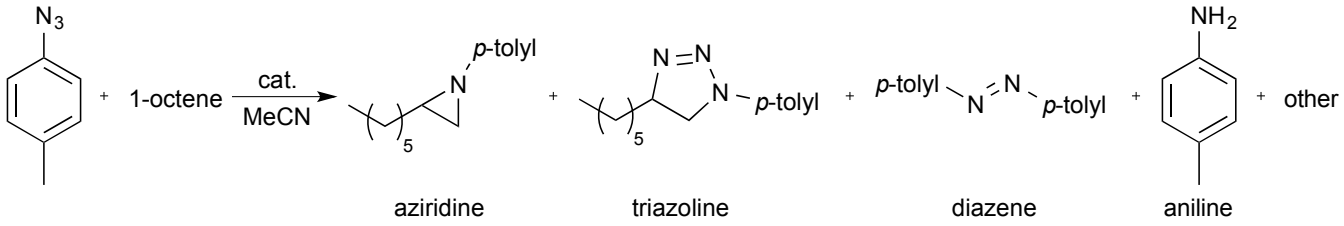
**Figure S3.** Zero-field $^{57}$Fe Mössbauer spectra of $[(CDA^{iPr})FeCl_2]BF_4$ (**3**). Simulation yields the following parameters: δ, $|\Delta E_Q|$(mm/s) at 100 K: 0.18, 2.21 (Γ) = 0.25 mm/s; at 150 K: 0.18, 2.02 (Γ) = 0.26 mm/s); at 200 K: 0.17, 1.75 (Γ) = 0.22 mm/s; at 298 K: 0.21, 1.59 (Γ) = 0.1 mm/s where Γ = half width at half height. The asymmetry of the recorded spectrum at low temperatures may be related to vibrational anisotropy with regard to the crystal lattice.[6]




[6] V. I. Goldanskii, E. F. Makarov, I. P. Suzdalev and I. A. Vinogradov, *Phys. Rev. Lett.* 1968, **20**, 137.

## 5. Iron Catalyzed Aziridination Results

**Table S1.** Catalytic aziridination of 1-octene with *p*-tolylazide.




| entry | cat. | temp. (ºC) | conv. (%) | aziridine (%) | triazoline (%) | diazene (%) | aniline (%) | others (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | N/A | 50 | 0 | - | - | - | - | - |
| 2 | $FeCl_2$ | 50 | 0 | - | - | - | - | - |
| 3 | $(PDI^{iPr})FeCl_2$ (**1a**) | 50 | 0 | - | - | - | - | - |
| 4 | $(CDA^{iPr})FeCl_2$ (**2a**) | 50 | 0 | - | - | - | - | - |
| 5 | N/A | 90 | 44 | 23 | 13 | 0 | 0 | 8 |
| 6 | $FeCl_2$ | 90 | 79 | 26 | 28 | 2 | 11 | 11 |
| 7 | $(PDI^{iPr})FeCl_2$ (**1a**) | 90 | 78 | 18 | 31 | 3 | 14 | 12 |
| 8 | $(CDA^{iPr})FeCl_2$ (**2a**) | 90 | 80 | 25 | 27 | 6 | 20 | 3 |
| 9 | $(PDI^{Me})FeCl_2$ (**1b**) | 50 | 11 | 0 | 0 | 0 | 11 | 0 |
| 10 | $(CDA^{Me})FeCl_2$ (**2b**) | 50 | 75 | 28 | 0 | 5 | 19 | 23 |
| 11 | hν | 50 | 73 | 10 | 2 | 29 | 20 | 11 |

## 6. Computational Methods

All DFT calculations were carried out in an analogous fashion as described by Wieghardt, Chirik, and coworkers for the related bis(imino)pyridine complexes[7] using the ORCA open access software package.[8] Spin unrestricted Kohn-Sham geometry optimizations were carried out starting from coordinates obtained from the crystal structures of compounds **2a** and **3**. Calculations were carried out using the B3LYP functional. The triple-d quality basis sets def2-TZVP developed by Ahlrichs[9] with one set of polarization functions were used on the metal, on the nitrogen atoms, and on all atoms attached to the metal. For all remaining carbon and hydrogen atoms, a double-ζ quality def2-SV(P) basis set also developed by Ahlrichs[10] was used that also included a polarizing set of d-functions on the carbon atoms. Appropriate auxiliary basis sets were chosen to match the orbital basis sets.[11] The RIJCOSX[12] approximation was used to accelerate the calculations. Nonrelativistic single-point calculations were carried out on the optimized geometry to predict Mössbauer isomer shifts (δ) and quadropole splittings ($\Delta E_Q$). The ORCA "CoreProp" basis set CP(PPP) was used for iron.[13] This basis set is based on the TruboMole DZ basis set developed by Ahlrichs and coworkers and obtained from the basis set library under ftp.chemi.uni-karlsruhe.de/pub/basen. The Ahlrichs (2d2fg,3p2df) polarization functions used were obtained from the TurboMole basis set library under ftp.chemie.uni-karlsuhe.de/pub/basen. All other basis sets were the same as those used in the geometry optimization calculations. Output files for these calculations are available upon request.

**Table S2.** Coordinates from ORCA for ($CDA^{iPr}$)$FeCl_2$ (**2a**).

| **S = 2** | | | | **S = 1** | | | |
|---|---|---|---|---|---|---|---|
| ZPE = -3648.072220660154 H | | | | ZPE = -3648.063584850536 H | | | |
| Fe | -0.141248 | 0.010487 | -0.172481 | Fe | -0.068459 | -0.041262 | 0.093672 |
| Cl | -1.270947 | 0.255670 | -2.119733 | Cl | -0.780495 | 0.110796 | -2.061290 |
| Cl | 2.221212 | -0.023715 | -0.082547 | Cl | 2.302117 | -0.058591 | 0.176698 |
| N | -0.418120 | 2.120793 | 0.661453 | N | -0.410082 | 1.920464 | 0.671305 |
| N | -0.437956 | -2.199216 | 0.313596 | N | -0.456477 | -2.051279 | 0.392584 |
| N | 0.093755 | 0.960613 | 2.586860 | N | 0.158267 | 0.967136 | 2.654169 |
| N | 0.062093 | -1.372474 | 2.403645 | N | 0.091218 | -1.394349 | 2.498322 |
| C | -0.095914 | -0.151550 | 1.843804 | C | 0.045138 | -0.167166 | 1.908838 |
| C | 0.576032 | 0.920625 | 3.980171 | C | 0.525831 | 0.937748 | 4.076520 |
| H | -0.280622 | 0.956356 | 4.679602 | H | -0.381083 | 1.020506 | 4.704899 |
| H | 1.206546 | 1.797829 | 4.177910 | H | 1.172599 | 1.796606 | 4.306572 |
| C | 1.387246 | -0.354824 | 4.177979 | C | 1.269063 | -0.366326 | 4.363635 |
| H | 2.297738 | -0.305688 | 3.555847 | H | 2.235577 | -0.355828 | 3.831076 |
| H | 1.695611 | -0.446177 | 5.232613 | H | 1.473258 | -0.445858 | 5.444239 |
| C | 0.566875 | -1.573342 | 3.775696 | C | 0.459182 | -1.578794 | 3.908790 |
| H | 1.196132 | -2.473510 | 3.806423 | H | 1.062069 | -2.492550 | 4.013179 |
| H | -0.276713 | -1.728767 | 4.474044 | H | -0.450065 | -1.701726 | 4.527210 |
| C | -0.195838 | -2.468594 | 1.541758 | C | -0.178203 | -2.427525 | 1.604662 |
| C | -0.181813 | -3.842157 | 2.157690 | C | -0.137391 | -3.836109 | 2.122733 |
| H | -0.611292 | -4.567456 | 1.452653 | H | -0.546906 | -4.527293 | 1.374088 |
| H | -0.760698 | -3.867741 | 3.096219 | H | -0.718590 | -3.933818 | 3.055814 |
| H | 0.847899 | -4.169069 | 2.389399 | H | 0.900723 | -4.147887 | 2.340439 |
| C | -0.714039 | -3.212694 | -0.660221 | C | -0.734924 | -3.025735 | -0.632252 |
| C | 0.354739 | -3.936822 | -1.244399 | C | 0.326097 | -3.744494 | -1.234937 |
| C | 0.041886 | -4.881120 | -2.235647 | C | 0.000443 | -4.692249 | -2.218482 |

[7] Bart, S.; Krzystof, C.; Eckhard, B.; Boukamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901-13912.

[8] Neese, F., Orca: an ab initio, DFT and Semiempirical Electronic Structure Package, Version 2.8, Revision 2287; Institut für Physikalische und Theoretische Chemie, Universität Bonn: Bonn, Germany, 2010.

[9] a) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571. b) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

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[13] Neese, F. *Inorg. Chim. Acta* **2002**, *337*, 181.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 0.852503 | -5.445176 | -2.705601 | H | 0.804870 | -5.253691 | -2.701510 |
| C | -1.272871 | -5.108458 | -2.639205 | C | -1.319890 | -4.924962 | -2.600082 |
| H | -1.493412 | -5.849424 | -3.414616 | H | -1.551445 | -5.672440 | -3.366086 |
| C | -2.307575 | -4.372344 | -2.060285 | C | -2.345354 | -4.181923 | -2.015525 |
| H | -3.336108 | -4.545510 | -2.391203 | H | -3.377853 | -4.352202 | -2.335859 |
| C | -2.055348 | -3.403582 | -1.079131 | C | -2.077483 | -3.208865 | -1.042273 |
| C | 1.818809 | -3.709553 | -0.865648 | C | 1.795501 | -3.490216 | -0.904815 |
| H | 1.865273 | -2.954839 | -0.065137 | H | 1.856610 | -2.775310 | -0.071098 |
| C | 2.484339 | -4.997194 | -0.336580 | C | 2.537096 | -4.770332 | -0.472116 |
| H | 3.493311 | -4.776689 | 0.059374 | H | 3.548710 | -4.517514 | -0.103154 |
| H | 2.600017 | -5.754266 | -1.134469 | H | 2.660352 | -5.482482 | -1.309578 |
| H | 1.892941 | -5.461350 | 0.473871 | H | 2.001919 | -5.302069 | 0.336632 |
| C | 2.614183 | -3.111622 | -2.042937 | C | 2.500902 | -2.800490 | -2.090395 |
| H | 3.640157 | -2.860348 | -1.717963 | H | 3.523544 | -2.500185 | -1.800321 |
| H | 2.145272 | -2.179224 | -2.397130 | H | 1.957533 | -1.887429 | -2.385710 |
| H | 2.680857 | -3.819289 | -2.890777 | H | 2.565024 | -3.472642 | -2.967043 |
| C | -3.211961 | -2.605800 | -0.476871 | C | -3.224715 | -2.387665 | -0.458456 |
| H | -2.772497 | -1.773192 | 0.094926 | H | -2.777964 | -1.573676 | 0.134120 |
| C | -4.037188 | -3.461054 | 0.505403 | C | -4.102589 | -3.225406 | 0.491433 |
| H | -3.407818 | -3.900734 | 1.300804 | H | -3.506674 | -3.685950 | 1.301059 |
| H | -4.538192 | -4.295705 | -0.019215 | H | -4.611482 | -4.043608 | -0.051263 |
| H | -4.820833 | -2.848111 | 0.990025 | H | -4.882941 | -2.594699 | 0.958585 |
| C | -4.121757 | -1.974714 | -1.546342 | C | -4.072911 | -1.721298 | -1.556309 |
| H | -3.531928 | -1.357113 | -2.242919 | H | -3.433337 | -1.110287 | -2.215799 |
| H | -4.872403 | -1.320058 | -1.063994 | H | -4.832457 | -1.059176 | -1.099828 |
| H | -4.674416 | -2.737791 | -2.125666 | H | -4.611981 | -2.463533 | -2.174041 |
| C | -0.161347 | 2.185326 | 1.915007 | C | -0.091135 | 2.120379 | 1.914046 |
| C | -0.125916 | 3.441200 | 2.744897 | C | 0.007118 | 3.444569 | 2.615786 |
| H | -0.489278 | 4.290441 | 2.150160 | H | -0.307437 | 4.254222 | 1.943444 |
| H | 0.904789 | 3.669977 | 3.071568 | H | 1.048271 | 3.641106 | 2.932093 |
| H | -0.748729 | 3.347647 | 3.650940 | H | -0.623620 | 3.468546 | 3.521577 |
| C | -0.856991 | 3.256744 | -0.093296 | C | -0.864698 | 3.005532 | -0.161054 |
| C | -2.221484 | 3.637478 | -0.025559 | C | -2.233452 | 3.364999 | -0.094290 |
| C | -2.640554 | 4.731107 | -0.796991 | C | -2.682608 | 4.417627 | -0.904809 |
| H | -3.689302 | 5.042908 | -0.759538 | H | -3.735477 | 4.715051 | -0.865446 |
| C | -1.754155 | 5.422933 | -1.621482 | C | -1.816647 | 5.089521 | -1.766249 |
| H | -2.103326 | 6.276104 | -2.212130 | H | -2.186775 | 5.910618 | -2.388995 |
| C | -0.426267 | 5.005901 | -1.702078 | C | -0.481267 | 4.696584 | -1.839760 |
| H | 0.261406 | 5.533861 | -2.369554 | H | 0.191268 | 5.212746 | -2.531270 |
| C | 0.049483 | 3.914438 | -0.959488 | C | 0.024103 | 3.647709 | -1.055436 |
| C | -3.256356 | 2.863449 | 0.791735 | C | -3.238310 | 2.625676 | 0.788792 |
| H | -2.732353 | 2.073822 | 1.352977 | H | -2.700231 | 1.826655 | 1.322656 |
| C | -4.256217 | 2.148265 | -0.139166 | C | -4.313811 | 1.931832 | -0.067468 |
| H | -3.723660 | 1.498494 | -0.855302 | H | -3.844829 | 1.267146 | -0.812886 |
| H | -4.857795 | 2.874315 | -0.717150 | H | -4.938226 | 2.666059 | -0.609552 |
| H | -4.956234 | 1.525029 | 0.449468 | H | -4.986281 | 1.325955 | 0.569426 |
| C | -3.984580 | 3.748229 | 1.821669 | C | -3.873761 | 3.540251 | 1.853427 |
| H | -4.676224 | 3.137906 | 2.433133 | H | -4.549080 | 2.958820 | 2.509803 |
| H | -4.585036 | 4.536725 | 1.332026 | H | -4.472144 | 4.346936 | 1.391628 |
| H | -3.276105 | 4.249818 | 2.506968 | H | -3.109118 | 4.021364 | 2.491280 |
| C | 1.488683 | 3.444607 | -1.152016 | C | 1.484852 | 3.237228 | -1.215358 |
| H | 1.683373 | 2.616583 | -0.454214 | H | 1.683580 | 2.382436 | -0.552679 |
| C | 1.690216 | 2.874399 | -2.571449 | C | 1.777084 | 2.752654 | -2.649739 |
| H | 0.946292 | 2.090476 | -2.790562 | H | 1.073587 | 1.954961 | -2.938324 |
| H | 2.695221 | 2.422970 | -2.658488 | H | 2.801011 | 2.339091 | -2.704228 |
| H | 1.595287 | 3.665624 | -3.339810 | H | 1.700012 | 3.577732 | -3.383652 |
| C | 2.524710 | 4.542420 | -0.852683 | C | 2.454134 | 4.362059 | -0.807799 |
| H | 2.425604 | 4.937330 | 0.176285 | H | 2.285941 | 4.696848 | 0.233550 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 2.435098 | 5.400710 | -1.544292 | H | 2.358153 | 5.251026 | -1.459162 |
| H | 3.544413 | 4.128124 | -0.964333 | H | 3.496492 | 3.999378 | -0.884104 |

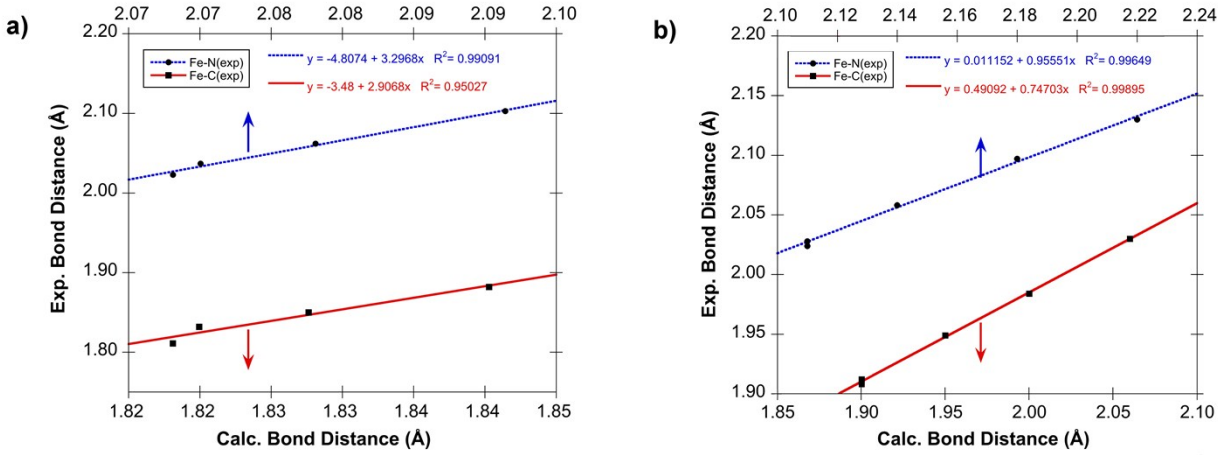
**Table S3.** Coordinates from ORCA for [(CDA$^{i\text{Pr}}$)$FeCl_2$]$BF_4$ (**3**).

| $S = 5/2$ | | | | $S = 3/2$ | | | |
|---|---|---|---|---|---|---|---|
| ZPE = -3647.863481162823 H | | | | ZPE = -3647.856704256630H | | | |
| Fe | 0.084974 | 0.025918 | -0.246556 | Fe | 0.050143 | 0.061154 | -0.030500 |
| Cl | -1.204901 | -1.769138 | -0.327716 | Cl | -1.313583 | -1.794116 | 0.265453 |
| Cl | 0.925052 | 0.838214 | -2.095624 | Cl | 0.388919 | 0.391815 | -2.156461 |
| N | 0.758051 | -0.687640 | 2.548274 | N | 0.727259 | -0.769580 | 2.562462 |
| N | -0.983380 | 0.848774 | 2.411329 | N | -1.079326 | 0.718633 | 2.464342 |
| N | 1.927040 | -0.978538 | 0.577311 | N | 1.850341 | -0.820897 | 0.583175 |
| N | -1.441955 | 1.620110 | 0.277586 | N | -1.336088 | 1.593396 | 0.379918 |
| C | 0.003984 | 0.158791 | 1.852878 | C | -0.121122 | -0.000067 | 1.864739 |
| C | 0.494202 | -1.013684 | 3.970085 | C | 0.489514 | -1.113444 | 3.983122 |
| H | 1.162629 | -0.415088 | 4.613049 | H | 1.141772 | -0.495971 | 4.625036 |
| H | 0.716930 | -2.075645 | 4.140897 | H | 0.752302 | -2.169706 | 4.136766 |
| C | -0.971330 | -0.724040 | 4.275822 | C | -0.984297 | -0.880202 | 4.300484 |
| H | -1.153677 | -0.841235 | 5.356421 | H | -1.157119 | -1.024214 | 5.379154 |
| H | -1.612827 | -1.452483 | 3.750613 | H | -1.600984 | -1.616805 | 3.758497 |
| C | -1.346618 | 0.690039 | 3.840454 | C | -1.407516 | 0.529751 | 3.895466 |
| H | -2.425654 | 0.851474 | 3.959506 | H | -2.490270 | 0.658861 | 4.028114 |
| H | -0.818459 | 1.451746 | 4.439556 | H | -0.891959 | 1.298921 | 4.496298 |
| C | -1.697996 | 1.724382 | 1.525177 | C | -1.741774 | 1.609797 | 1.604313 |
| C | -2.660253 | 2.679356 | 2.163316 | C | -2.795207 | 2.495952 | 2.188264 |
| H | -3.014295 | 3.408922 | 1.422534 | H | -3.122632 | 3.236253 | 1.445898 |
| H | -2.177486 | 3.215534 | 2.999507 | H | -2.402199 | 3.024973 | 3.075273 |
| H | -3.542153 | 2.147726 | 2.563284 | H | -3.677104 | 1.909639 | 2.503263 |
| C | -2.141947 | 2.410028 | -0.711373 | C | -1.981392 | 2.382871 | -0.643223 |
| C | -3.407142 | 1.959624 | -1.166326 | C | -3.223305 | 1.948769 | -1.170207 |
| C | -4.038874 | 2.710705 | -2.169511 | C | -3.773063 | 2.700151 | -2.219928 |
| H | -5.013091 | 2.385231 | -2.543116 | H | -4.722806 | 2.384290 | -2.659086 |
| C | -3.451215 | 3.856010 | -2.701766 | C | -3.135464 | 3.835171 | -2.717479 |
| H | -3.964184 | 4.424018 | -3.483706 | H | -3.586820 | 4.402919 | -3.536706 |
| C | -2.210611 | 4.281976 | -2.228446 | C | -1.925565 | 4.252388 | -2.162464 |
| H | -1.763581 | 5.187763 | -2.644662 | H | -1.442838 | 5.153502 | -2.548833 |
| C | -1.521200 | 3.572323 | -1.235209 | C | -1.314736 | 3.534928 | -1.125886 |
| C | -4.119277 | 0.718748 | -0.622609 | C | -3.984748 | 0.721867 | -0.667374 |
| H | -3.469485 | 0.239243 | 0.126105 | H | -3.422086 | 0.269227 | 0.162951 |
| C | -5.446646 | 1.089356 | 0.078430 | C | -5.382831 | 1.105221 | -0.129602 |
| H | -5.296519 | 1.830005 | 0.884599 | H | -5.327737 | 1.890056 | 0.646969 |
| H | -5.918404 | 0.192470 | 0.520495 | H | -5.884821 | 0.223499 | 0.309231 |
| H | -6.170413 | 1.527006 | -0.632094 | H | -6.036990 | 1.491840 | -0.931653 |
| C | -4.358570 | -0.332064 | -1.723999 | C | -4.080280 | -0.367839 | -1.752637 |
| H | -3.416407 | -0.616755 | -2.222550 | H | -3.081215 | -0.648412 | -2.126918 |
| H | -5.055894 | 0.040134 | -2.495252 | H | -4.688286 | -0.032044 | -2.611626 |
| H | -4.800003 | -1.245382 | -1.286079 | H | -4.551747 | -1.275940 | -1.336854 |
| C | -0.185742 | 4.114111 | -0.722726 | C | -0.012168 | 4.052771 | -0.519917 |
| H | 0.314817 | 3.309393 | -0.156959 | H | 0.410026 | 3.256985 | 0.119635 |
| C | -0.408292 | 5.300645 | 0.240159 | C | -0.282672 | 5.274733 | 0.384382 |
| H | -1.043369 | 5.025304 | 1.100997 | H | -0.997086 | 5.036110 | 1.192776 |
| H | -0.905976 | 6.138087 | -0.281190 | H | -0.713068 | 6.108671 | -0.198905 |
| H | 0.554311 | 5.676332 | 0.633421 | H | 0.651976 | 5.638822 | 0.849971 |
| C | 0.769767 | 4.525123 | -1.857435 | C | 1.045777 | 4.382590 | -1.586346 |
| H | 0.939666 | 3.694638 | -2.561786 | H | 1.263121 | 3.505020 | -2.219725 |
| H | 1.746356 | 4.825283 | -1.436983 | H | 1.984056 | 4.703900 | -1.100962 |
| H | 0.384282 | 5.388916 | -2.427521 | H | 0.723134 | 5.207376 | -2.245435 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 1.861031 | -1.251690 | 1.822971 | C | 1.829791 | -1.210807 | 1.813525 |
| C | 2.823847 | -2.094734 | 2.602430 | C | 2.858759 | -2.042586 | 2.510366 |
| H | 2.364835 | -3.074666 | 2.832780 | H | 2.463455 | -3.058904 | 2.696159 |
| H | 3.108643 | -1.621643 | 3.556333 | H | 3.133555 | -1.601771 | 3.483422 |
| H | 3.728483 | -2.278258 | 2.006188 | H | 3.760072 | -2.135326 | 1.889614 |
| C | 3.098372 | -1.265313 | -0.215630 | C | 2.965620 | -1.113021 | -0.284726 |
| C | 4.037279 | -0.208585 | -0.344986 | C | 3.863453 | -0.046316 | -0.550152 |
| C | 5.179393 | -0.447200 | -1.118991 | C | 4.967069 | -0.316422 | -1.368469 |
| H | 5.924382 | 0.342579 | -1.244720 | H | 5.679740 | 0.477718 | -1.600176 |
| C | 5.377491 | -1.678399 | -1.749692 | C | 5.172274 | -1.591292 | -1.902775 |
| H | 6.277622 | -1.849752 | -2.347806 | H | 6.044994 | -1.787137 | -2.533205 |
| C | 4.421452 | -2.684006 | -1.632542 | C | 4.257017 | -2.610026 | -1.650534 |
| H | 4.582841 | -3.632908 | -2.151029 | H | 4.420720 | -3.593135 | -2.099531 |
| C | 3.252677 | -2.505840 | -0.872281 | C | 3.122963 | -2.400471 | -0.848094 |
| C | 3.808068 | 1.141956 | 0.339276 | C | 3.638023 | 1.338270 | 0.058731 |
| H | 2.714222 | 1.278468 | 0.415171 | H | 2.543697 | 1.499701 | 0.084854 |
| C | 4.331236 | 2.343597 | -0.464203 | C | 4.224572 | 2.490655 | -0.768333 |
| H | 3.949470 | 2.329088 | -1.498903 | H | 3.867781 | 2.461834 | -1.811912 |
| H | 5.434740 | 2.374325 | -0.499635 | H | 5.328963 | 2.477607 | -0.776537 |
| H | 3.994131 | 3.283846 | 0.009857 | H | 3.914567 | 3.455880 | -0.330116 |
| C | 4.377478 | 1.169843 | 1.772687 | C | 4.156198 | 1.418361 | 1.511103 |
| H | 4.160004 | 2.139744 | 2.258884 | H | 3.903525 | 2.397011 | 1.961159 |
| H | 5.474361 | 1.032926 | 1.765792 | H | 5.255369 | 1.304699 | 1.542547 |
| H | 3.954866 | 0.374572 | 2.410652 | H | 3.727593 | 0.634180 | 2.158625 |
| C | 2.201182 | -3.615152 | -0.830405 | C | 2.103966 | -3.526926 | -0.679137 |
| H | 1.415072 | -3.316741 | -0.117611 | H | 1.353344 | -3.212124 | 0.062723 |
| C | 1.516048 | -3.782115 | -2.204319 | C | 1.335175 | -3.768530 | -1.996614 |
| H | 1.099992 | -2.827146 | -2.568213 | H | 0.862850 | -2.841353 | -2.362113 |
| H | 0.685829 | -4.507445 | -2.132738 | H | 0.538143 | -4.516340 | -1.838331 |
| H | 2.228752 | -4.156786 | -2.960896 | H | 2.008163 | -4.149875 | -2.785877 |
| C | 2.775615 | -4.963938 | -0.351664 | C | 2.739184 | -4.838297 | -0.174009 |
| H | 3.257449 | -4.885167 | 0.640772 | H | 3.303390 | -4.697491 | 0.766562 |
| H | 3.530913 | -5.358701 | -1.054245 | H | 3.437312 | -5.267692 | -0.914573 |
| H | 1.969513 | -5.716305 | -0.283061 | H | 1.954791 | -5.593436 | 0.009429 |

## 7. Comparison of Semi-empirical (DFT + SQUID) and Experimental Bond Distances

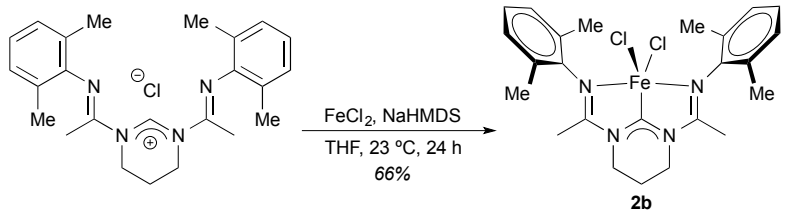
**Figure S4.** Semi-empirical (DFT + SQUID) vs. experimental bond distances in a) (CDA$^{i\text{Pr}}$)$FeCl_2$ (**2a**) and b) for [(CDA$^{i\text{Pr}}$)$FeCl_2$]$BF_4$ (**3**).




By using the magnetic data and the bond metrics from the DFT calculations as the limit for the high and intermediate spin electronic configurations, a theoretical bond distance at various temperatures can be predicted. While the absolute value for these semi-empirically determined bond distances do not match experimentally determined bond distances, they do reproduce how the bond distances respond to temperature. To illustrate this correlation, the semi-empirical metal-ligand bond distances are plotted versus the experimental metal-ligand bond distances at different temperatures in Figure S2. The nearly linear correlation observed for all bond lengths suggest that the same phenomenon that is responsible for the magnetic behavior is also responsible for the changes in bond distances. Since an equilibrium mixture of two spin states was used to model the magnetic behavior, we interpret the positive correlation between the magnetic and crystallographic data to be evidence for the existence of spin equilibrium between an intermediate and high spin state for both **2a** and **3**. Nevertheless, we cannot definitively rule out other possibilities such as significant inter-particle magnetic cooperativity or admixed quantum states to explain the solid state magnetic behavior that we observe.

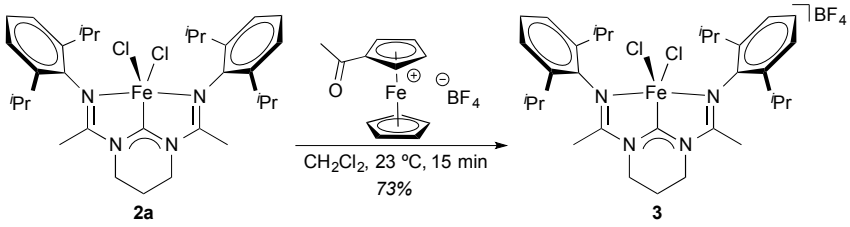
## 8. Experimental Procedures

**Synthesis of {N,N-1,3-bis[1-(2,6-dimethylphenylimino)ethyl]4,5,6-trihydropyrimid-2-ylidene}iron dichloride (2b).**




In an inert atmosphere glovebox, anhydrous iron(II) chloride (133 mg, 1.05 mmol, 1.05 equiv) was suspended in THF (15 mL) and cooled to −40 ºC. To the cold suspension was then added dropwise to a precooled (−40 ºC) solution of sodium bis(trimethylsilyl)amide (195 mg, 1.05 mmol, 1.05 equiv) in THF (10 mL) and the mixture was held at −40 ºC and agitated occasionally for twelve hours. The mixture was then warmed to 23 ºC for twenty minutes, during which time most of the remaining solid dissolved. The orange/brown solution was recooled to −40 ºC, filtered through Celite, and added to a precooled (−40 ºC) suspension of 1,3-bis[1-(2,6-dimethylphenylimino)ethyl]-4,5,6-trihydropyrimidinium chloride[14] (414 mg, 1.00 mmol, 1.00 eq) in THF (10 mL). The suspension was allowed to gradually warm to 23 ºC, during which time it turned bright pink in color. The reaction mixture was allowed to stir at 23 ºC for twenty-four hours and was then concentrated *in vacuo*. The crude solid was dissolved in $CH_2Cl_2$, filtered through Celite, and was washed with THF. The crude residue was recrystallized from a mixture of $CH_2Cl_2$ and pentane at −40 ºC to deliver the title compound **2b** as a bright pink red solid (331 mg, 66%). $^1$H NMR ($CD_2Cl_2$, 500 MHz) δ 22.82 (262.7 Hz), 18.93 (225.9 Hz), 10.51 (319.4 Hz), 7.02 (94.3 Hz), 6.86 (73.3 Hz), 6.65 (40.2 Hz), 6.58 (60.3 Hz), 4.13 (78.1 Hz), 3.80 (214.5 Hz), 2.03 (65.7 Hz), 1.66 (112.4 Hz), 1.28 (50.0 Hz), 0.99 (130.1 Hz), 0.87 (42.9 Hz), 0.45 (427.2 Hz), 0.39 (162.2 Hz), −13.16 (240.3 Hz), −31.05 (526.2 Hz), −39.52 (462.1 Hz). IR (neat) 1631, 1590, 1473, 1377, 1291, 1203, 1092, 1060, 1033, 1010, 817, 768 cm$^{-1}$. HRMS (ESI+) for $C_{24}H_{30}ClFeN_4$ $[M]^+$: Calcd. 465.15084; Found 465.15202.

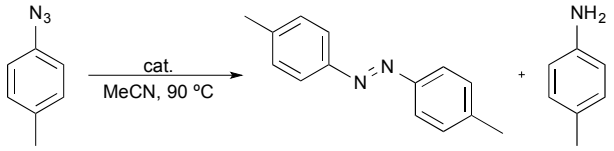
**Synthesis of {N,N-1,3-bis[1-(2,6-diisopropylphenylimino)ethyl]4,5,6-trihydropyrimid-2-ylidene}iron dichloride tetrafluoroborate (3)•0.5$CH_2Cl_2$.**




In an inert atmosphere glovebox, **2a** (50.0 mg, 0.0815 mmol, 1.00 equiv) was suspended in $CH_2Cl_2$ (2.0 mL) and a solution of acetylferrocenium tetrafluoroborate (25.7 mg, 0.0815 mmol, 1.0 equiv) in $CH_2Cl_2$ (2.0 mL) was added dropwise. Immediately upon addition, the reaction mixture changed from dark blue to a deep red. The solution was allowed to stir for 15 minutes at 25 ºC and was the concentrated *in vacuo*. The crude solid was washed with pentane (5 x 10 mL) and was again dried *in vacuo*. The crude residue was recrystallized from 2:3:2 $Et_2O/CH_2Cl_2$/THF v/v at −40 ºC to deliver the title compound **3** as dark red crystals suitable for X-ray crystallography (41.9 mg, 73%). $^1$H NMR ($CD_2Cl_2$, 500 MHz) δ 77.58 (745.4 Hz), 60.25 (768.5 Hz), 39.06 (269.0 Hz), 7.52 (2853.2 Hz), 5.70 (358.3 Hz), 3.72 (95.9 Hz), 3.41 (11.7 Hz), 1.83 (13.9 Hz), 1.26 (14.8 Hz), 1.13 (9.4 Hz), 0.86 (14.5 Hz), −34.50 (216.3 Hz). IR (neat) 1627, 1517, 1264, 1204, 1043, 1026, 1008, 816, 803 cm$^{-1}$. $\mu_{eff}$ = 5.0 $\mu_B$ at 25 ˚C (Evans' method). HRMS (MALDI) for $C_{32}H_{46}Cl_2FeN_4$ $[M]^+$: Calcd. 612.2449; Found 612.2450. Elemental analysis revealed that 0.5 equivalents of $CH_2Cl_2$ crystallized with **3**: $C_{32.5}H_{47}BCl_3F_4FeN_4$; calc'd: 52.55% C, 6.38% H, 7.54% N; found: 52.11% C, 6.78% H, 7.31% N. This resulted in a molecular weight of 742.85 g/mol, which was used as the molecular weight for the complex in magnetic moment measurements.

[14] J. A. Thagfi and G. G. Lavoie, *Organometallics* 2012, **31**, 7351.

**General procedure for the catalytic homocoupling of *p*-tolylazide.**




In an inert atmosphere glovebox, *p*-tolylazide (20 mg, 0.15 mmol, 1.00 equiv), cat. (0.008 mmol, 0.05 equiv), and MeCN (1 mL) were added to a Schlenk tube. The tube was removed from the glovebox and heated to 90 ºC for 14 hours (or less), during which time the solution turned black. The solution was brought back into the glovebox and the mixture was extracted with pentane (3 x 1 mL). The combined pentane layers were concentrated *in vacuo* and analyzed by $^{1}$H NMR spectroscopy.

## 9. $^{1}$H NMR Spectra

**Figure S5.** $^{1}$H NMR for spectrum {N,N-1,3-bis[1-(2,6-dimethylphenylimino)ethyl]4,5,6-trihydropyrimid-2-ylidene}iron dichloride (**2b**) in $CD_2Cl_2$.

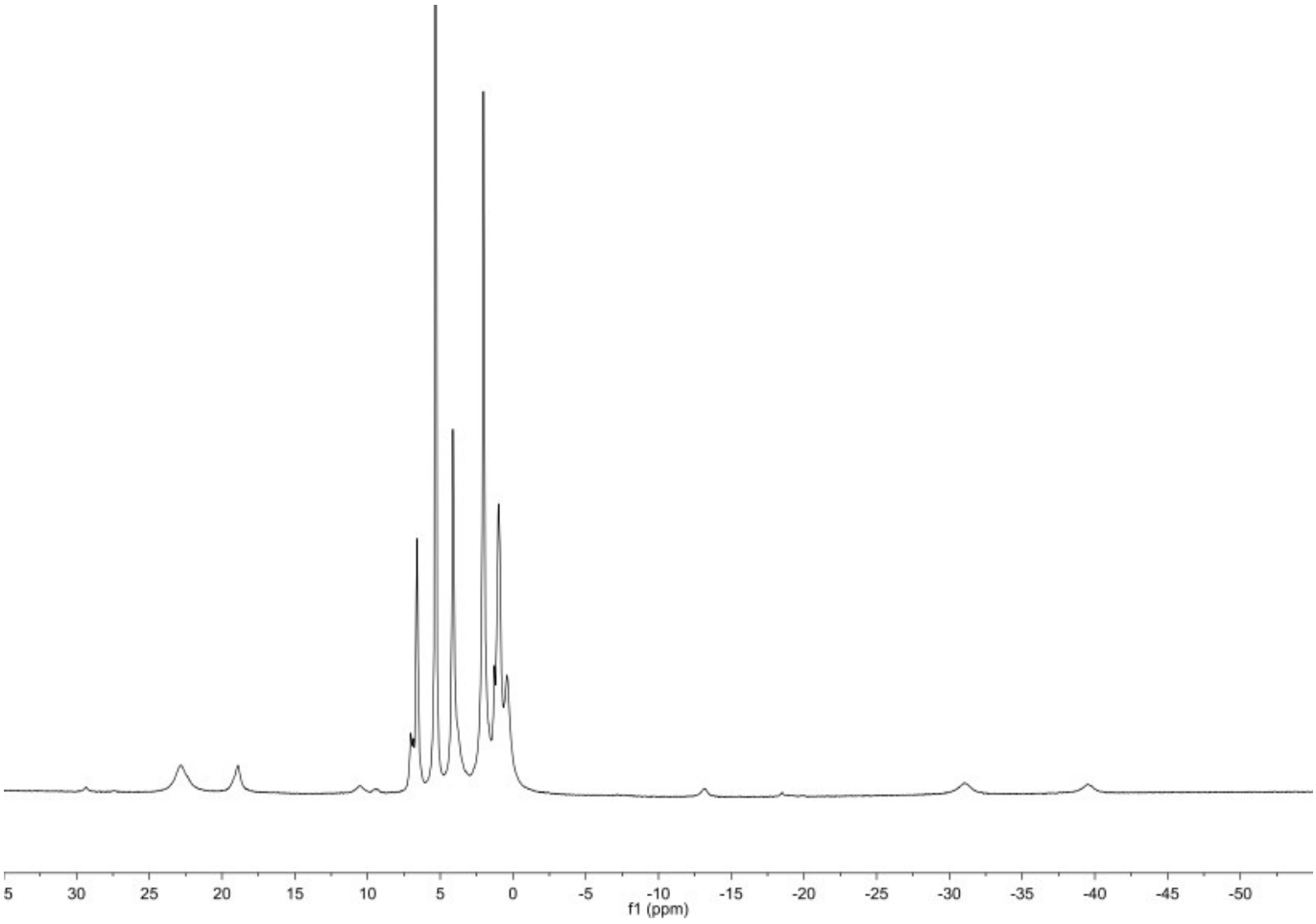


**Figure S6.** $^{1}$H NMR spectrum for {N,N-1,3-bis[1-(2,6-diisopropylphenylimino)ethyl]4,5,6-trihydropyrimid-2-ylidene}iron dichloride tetrafluoroborate (**3**) in $CD_2Cl_2$.

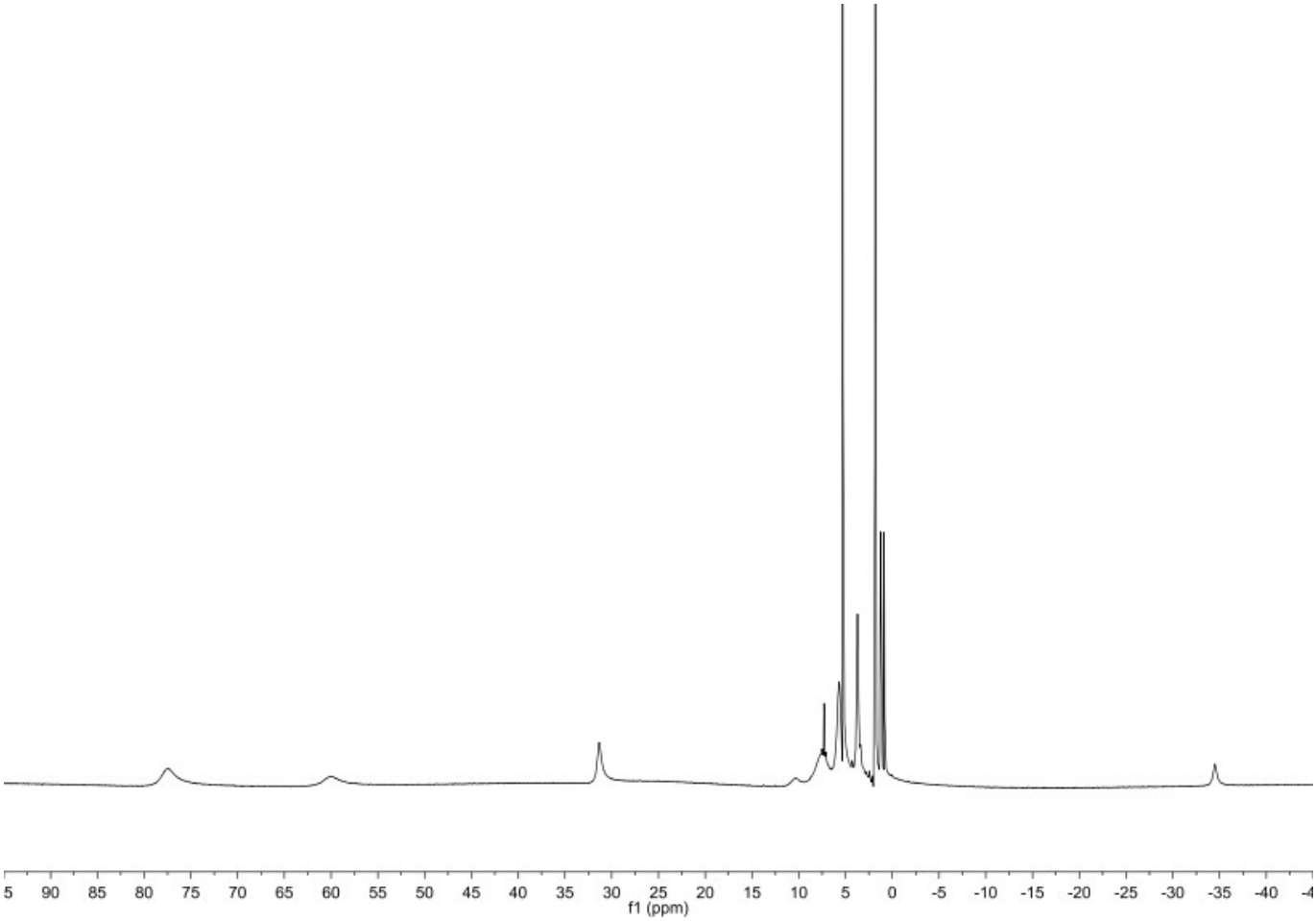
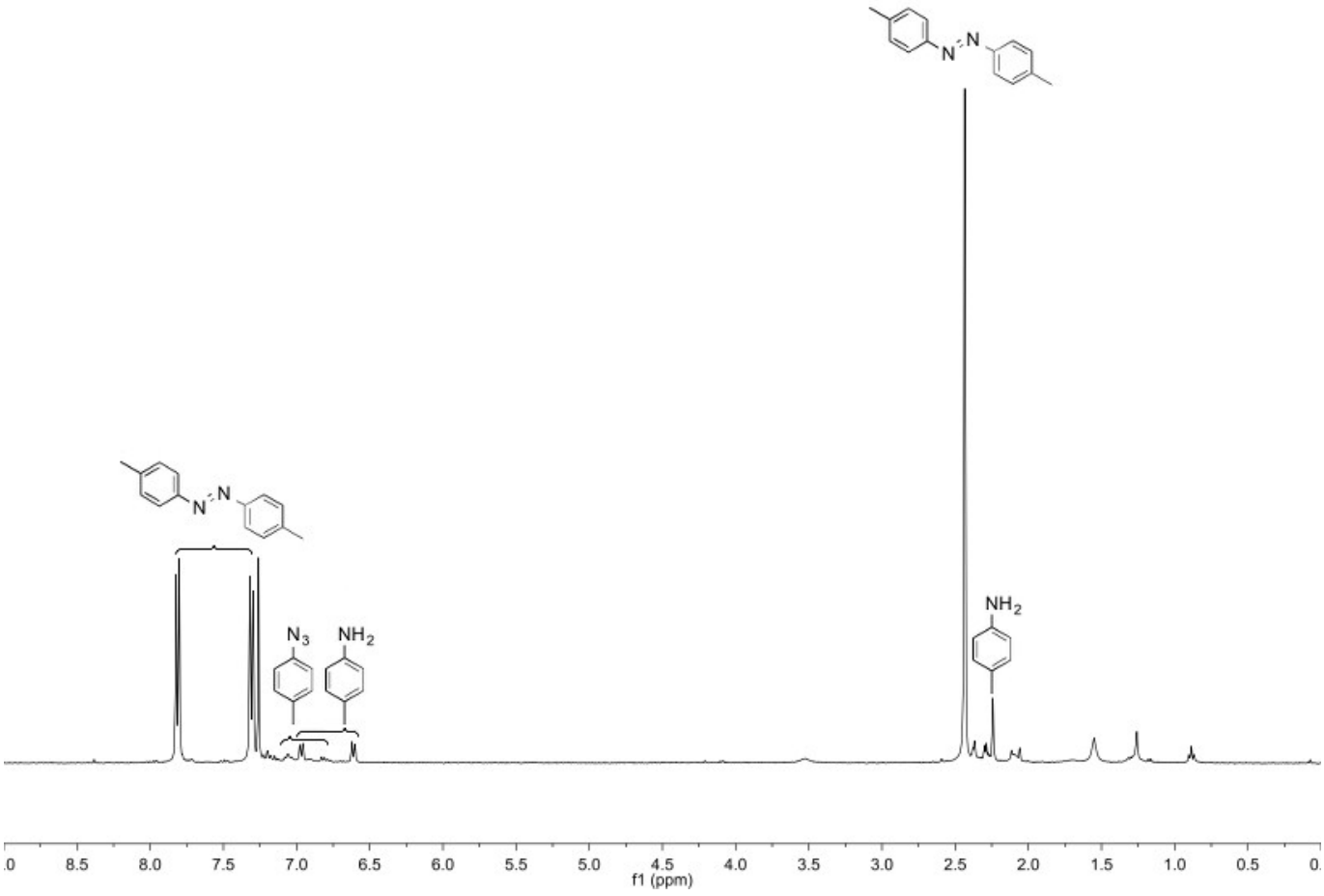


**Figure S7.** Representative $^{1}H$ NMR spectrum for the catalytic homocoupling of *p*-tolylazide in $CDCl_3$.



## 10. Variable Temperature X-ray Crystallography Data for ($CDA^{iPr}$)$FeCl_2$ (2a)

**Table S4.** Variable temperature X-ray data for ($CDA^{iPr}$)$FeCl_2$ (**2a**).

| | 100 K | 150 K | 200 K | 250 K |
|---|---|---|---|---|
| Identification code/CCDC | C32H46Cl2FeN4/900881 | C32H46Cl2FeN4_150K/927786 | C32H46Cl2FeN4_200K/927787 | C32H46Cl2FeN4_250K/927788 |
| Empirical formula | $C_{34.25}H_{50.50}Cl_{6.50}FeN_4$ | $C_{34}H_{50}Cl_6FeN_4$ | $C_{34}H_{50}Cl_6FeN_4$ | $C_{34}H_{50}Cl_6FeN_4$ |
| Formula weight | 804.56 | 783.33 | 783.33 | 783.33 |
| Temperature | 100(2) K | 150(2) K | 200(2) K | 250(2) K |
| Wavelength | 0.71073 Å | 1.54178 Å | 1.54178 Å | 0.54178 Å |
| Crystal system | Tetragonal | Tetragonal | Tetragonal | Tetragonal |
| Space group | I 4(1)/a | I 4(1)/a | I 4(1)/a | I 4(1)/a |
| Unit cell dimensions | a = 21.4058(9) Å α = 90°<br>b = 21.4058(9) Å β = 90°<br>c = 35.1534(16) Å γ = 90° | a = 21.3621(4) Å α = 90°<br>b = 21.3621(4) Å β = 90°<br>c = 35.3633(7) Å γ = 90° | a = 21.4369(4) Å α = 90°<br>b = 21.4369(4) Å β = 90°<br>c = 35.4666(8) Å γ = 90° | a = 21.5767(7) Å α = 90°<br>b = 21.5767(7) Å β = 90°<br>c = 35.5041(14) Å γ = 90° |
| Volume | 16107.6(12) $Å^3$ | 16137.7(5) $Å^3$ | 16298.3(6) $Å^3$ | 16529.1(10) $Å^3$ |
| Z | 16 | 16 | 16 | 16 |
| Density (calculated) | 1.327 $Mg/m^3$ | 1.290 $Mg/m^3$ | 1.277 $Mg/m^3$ | 1.259 $Mg/m^3$ |
| Absorption coefficient | 0.834 $mm^{-1}$ | 6.863 $mm^{-1}$ | 6.795 $mm^{-1}$ | 6.701 $mm^{-1}$ |
| F(000) | 6728 | 6560 | 6560 | 6560 |
| Crystal size | 0.15 x 0.14 x 0.14 $mm^3$ | 0.38 x 0.25 x 0.12 $mm^3$ | 0.38 x 0.25 x 0.12 $mm^3$ | 0.38 x 0.25 x 0.12 $mm^3$ |
| Theta range for data collection | 1.35 to 32.15° | 2.42 to 68.25° | 2.41 to 68.40° | 2.40 to 66.36° |
| Index ranges | $-28\le h\le 32$, $-31\le k\le 32$, $-52\le l\le 52$ | $-25\le h\le 24$, $-25\le k\le 18$, $-42\le l\le 41$ | $-25\le h\le 24$, $-25\le k\le 18$, $-42\le l\le 41$ | $-25\le h\le 24$, $-25\le k\le 18$, $-42\le l\le 41$ |
| Reflections collected | 147766 | 78662 | 79314 | 79058 |
| Independent reflections | 14118 [$R_{int}$ = 0.04331] | 7133 [$R_{int}$ = 0.0460] | 7212 [$R_{int}$ = 0.0472] | 7169 [$R_{int}$ = 0.0597] |
| Completeness to θ = 32.15/66.36° | 99.8 % | 96.6 % | 96.4 % | 98.7 % |
| Max. and min. transmission | 0.8921 and 0.8850 | 0.4931 and 0.1801 | 0.4960 and 0.1822 | 0.5002 and 0.1851 |
| Data / restraints / parameters | 14118 / 1 / 417 | 7133 / 2 / 425 | 7212 / 2 / 425 | 7169 / 2 / 425 |
| Goodness-of-fit on $F^2$ | 1.078 | 1.029 | 1.027 | 1.020 |
| Final R indices [I>2σ(I)] | $R_1$ = 0.0433, $\omega R_2$ = 0.1152 | R1 = 0.0415, $\omega R_2$ = 0.1133 | R1 = 0.0425, $\omega R_2$ = 0.1148 | R1 = 0.0520, $\omega R_2$ = 0.1450 |
| R indices (all data) | $R_1$ = 0.0559, $\omega R_2$ = 0.1253 | R1 = 0.0455, $\omega R_2$ = 0.1170 | R1 = 0.0484, $\omega R_2$ = 0.1198 | R1 = 0.0639, $\omega R_2$ = 0.1557 |
| Largest diff. peak and hole | 1.195 and −1.056 e.Å-3 | 0.615 and −0.356 e.Å-3 | 0.528 and −0.371 e.Å-3 | 0.556 and −0.415 e.Å-3 |

**Figure S8.** ORTEP plot of (CDA$^{i\text{Pr}}$)$FeCl_2$ (**2a**) at 100 K at 50% probability level. Hydrogen atoms and solvent molecules were excluded for clarity.

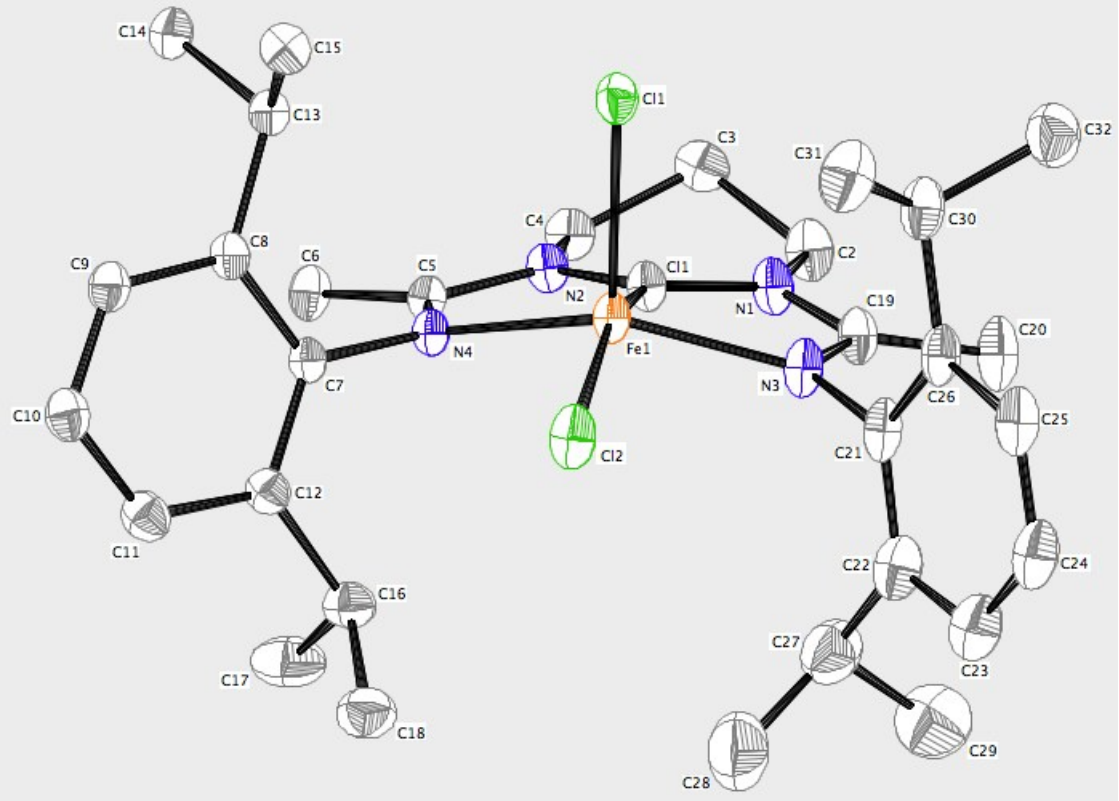


**Table S5.** Bond lengths (Å) and angles (º) for (CDA$^{iPr}$)$FeCl_2$ (**2a**) at 100 K.

| | | | | | |
|---|---|---|---|---|---|
| Fe(1)-C(1) | 1.8116(18) | C(11)-C(12) | 1.400(3) | C(26)-C(30) | 1.511(4) |
| Fe(1)-N(1) | 2.0234(18) | C(11)-H(11A) | 0.9500 | C(27)-C(28) | 1.516(6) |
| Fe(1)-N(2) | 2.0283(17) | C(12)-C(16) | 1.517(3) | C(27)-C(29) | 1.543(5) |
| Fe(1)-Cl(1) | 2.2803(6) | C(13)-C(14) | 1.526(3) | C(27)-H(27A) | 1.0000 |
| Fe(1)-Cl(2) | 2.3250(6) | C(13)-C(15) | 1.531(3) | C(28)-H(28A) | 0.9800 |
| N(1)-C(19) | 1.305(3) | C(13)-H(13A) | 1.0000 | C(28)-H(28B) | 0.9800 |
| N(1)-C(21) | 1.436(3) | C(14)-H(14A) | 0.9800 | C(28)-H(28C) | 0.9800 |
| N(2)-C(5) | 1.306(2) | C(14)-H(14B) | 0.9800 | C(29)-H(29A) | 0.9800 |
| N(2)-C(7) | 1.442(2) | C(14)-H(14C) | 0.9800 | C(29)-H(29B) | 0.9800 |
| N(3)-C(1) | 1.360(3) | C(15)-H(15A) | 0.9800 | C(29)-H(29C) | 0.9800 |
| N(3)-C(19) | 1.372(3) | C(15)-H(15B) | 0.9800 | C(30)-C(32) | 1.528(4) |
| N(3)-C(2) | 1.470(3) | C(15)-H(15C) | 0.9800 | C(30)-C(31) | 1.535(4) |
| N(4)-C(1) | 1.360(3) | C(16)-C(17) | 1.529(4) | C(30)-H(30A) | 1.0000 |
| N(4)-C(5) | 1.374(3) | C(16)-C(18) | 1.529(4) | C(31)-H(31A) | 0.9800 |
| N(4)-C(4) | 1.477(3) | C(16)-H(16A) | 1.0000 | C(31)-H(31B) | 0.9800 |
| C(2)-C(3) | 1.513(4) | C(17)-H(17A) | 0.9800 | C(31)-H(31C) | 0.9800 |
| C(2)-H(2A) | 0.9900 | C(17)-H(17B) | 0.9800 | C(32)-H(32A) | 0.9800 |
| C(2)-H(2B) | 0.9900 | C(17)-H(17C) | 0.9800 | C(32)-H(32B) | 0.9800 |
| C(3)-C(4) | 1.518(3) | C(18)-H(18A) | 0.9800 | C(32)-H(32C) | 0.9800 |
| C(3)-H(3A) | 0.9900 | C(18)-H(18B) | 0.9800 | C(1S)-Cl(4S) | 1.758(4) |
| C(3)-H(3B) | 0.9900 | C(18)-H(18C) | 0.9800 | C(1S)-Cl(3S) | 1.777(4) |
| C(4)-H(4A) | 0.9900 | C(19)-C(20) | 1.488(3) | C(1S)-H(1SA) | 0.9900 |
| C(4)-H(4B) | 0.9900 | C(20)-H(20A) | 0.9800 | C(1S)-H(1SB) | 0.9900 |
| C(5)-C(6) | 1.486(3) | C(20)-H(20B) | 0.9800 | C(2S)-Cl(5S) | 1.733(3) |
| C(6)-H(6A) | 0.9800 | C(20)-H(20C) | 0.9800 | C(2S)-Cl(6S) | 1.756(3) |
| C(6)-H(6B) | 0.9800 | C(21)-C(26) | 1.399(3) | C(2S)-H(2SA) | 0.9900 |
| C(6)-H(6C) | 0.9800 | C(21)-C(22) | 1.415(4) | C(2S)-H(2SB) | 0.9900 |
| C(7)-C(8) | 1.406(3) | C(22)-C(23) | 1.391(4) | C(3S)-Cl(8S) | 1.711(17) |
| C(7)-C(12) | 1.406(3) | C(22)-C(27) | 1.518(4) | C(3S)-Cl(7S) | 1.733(17) |
| C(8)-C(9) | 1.402(3) | C(23)-C(24) | 1.387(4) | C(3S)-H(3S1) | 0.9900 |
| C(8)-C(13) | 1.520(3) | C(23)-H(23A) | 0.9500 | C(3S)-H(3S2) | 0.9900 |
| C(9)-C(10) | 1.379(3) | C(24)-C(25) | 1.369(4) | C(1)-Fe(1)-N(1) | 78.42(8) |
| C(9)-H(9A) | 0.9500 | C(24)-H(24A) | 0.9500 | C(1)-Fe(1)-N(2) | 78.25(8) |
| C(10)-C(11) | 1.380(3) | C(25)-C(26) | 1.405(3) | N(1)-Fe(1)-N(2) | 146.60(7) |
| C(10)-H(10A) | 0.9500 | C(25)-H(25A) | 0.9500 | C(1)-Fe(1)-Cl(1) | 158.02(7) |

| | | | | | |
|---|---|---|---|---|---|
| N(1)-Fe(1)-Cl(1) | 94.66(6) | C(3)-C(4)-H(4B) | 110.1 | H(14A)-C(14)-H(14B) | 109.5 |
| N(2)-Fe(1)-Cl(1) | 98.13(5) | H(4A)-C(4)-H(4B) | 108.4 | C(13)-C(14)-H(14C) | 109.5 |
| C(1)-Fe(1)-Cl(2) | 95.53(7) | N(2)-C(5)-N(4) | 114.61(17) | H(14A)-C(14)-H(14C) | 109.5 |
| N(1)-Fe(1)-Cl(2) | 103.71(6) | N(2)-C(5)-C(6) | 126.88(18) | H(14B)-C(14)-H(14C) | 109.5 |
| N(2)-Fe(1)-Cl(2) | 102.02(5) | N(4)-C(5)-C(6) | 118.48(17) | C(13)-C(15)-H(15A) | 109.5 |
| Cl(1)-Fe(1)-Cl(2) | 106.40(2) | C(5)-C(6)-H(6A) | 109.5 | C(13)-C(15)-H(15B) | 109.5 |
| C(19)-N(1)-C(21) | 118.58(18) | C(5)-C(6)-H(6B) | 109.5 | H(15A)-C(15)-H(15B) | 109.5 |
| C(19)-N(1)-Fe(1) | 113.43(15) | H(6A)-C(6)-H(6B) | 109.5 | C(13)-C(15)-H(15C) | 109.5 |
| C(21)-N(1)-Fe(1) | 127.98(14) | C(5)-C(6)-H(6C) | 109.5 | H(15A)-C(15)-H(15C) | 109.5 |
| C(5)-N(2)-C(7) | 117.66(16) | H(6A)-C(6)-H(6C) | 109.5 | H(15B)-C(15)-H(15C) | 109.5 |
| C(5)-N(2)-Fe(1) | 113.63(13) | H(6B)-C(6)-H(6C) | 109.5 | C(12)-C(16)-C(17) | 110.7(2) |
| C(7)-N(2)-Fe(1) | 128.22(12) | C(8)-C(7)-C(12) | 121.52(18) | C(12)-C(16)-C(18) | 112.1(2) |
| C(1)-N(3)-C(19) | 112.02(17) | C(8)-C(7)-N(2) | 119.56(18) | C(17)-C(16)-C(18) | 110.1(2) |
| C(1)-N(3)-C(2) | 122.95(18) | C(12)-C(7)-N(2) | 118.90(18) | C(12)-C(16)-H(16A) | 107.9 |
| C(19)-N(3)-C(2) | 124.73(18) | C(9)-C(8)-C(7) | 117.7(2) | C(17)-C(16)-H(16A) | 107.9 |
| C(1)-N(4)-C(5) | 112.00(16) | C(9)-C(8)-C(13) | 118.97(19) | C(18)-C(16)-H(16A) | 107.9 |
| C(1)-N(4)-C(4) | 122.85(17) | C(7)-C(8)-C(13) | 123.33(18) | C(16)-C(17)-H(17A) | 109.5 |
| C(5)-N(4)-C(4) | 124.80(17) | C(10)-C(9)-C(8) | 121.5(2) | C(16)-C(17)-H(17B) | 109.5 |
| N(3)-C(1)-N(4) | 119.51(16) | C(10)-C(9)-H(9A) | 119.3 | H(17A)-C(17)-H(17B) | 109.5 |
| N(3)-C(1)-Fe(1) | 119.98(15) | C(8)-C(9)-H(9A) | 119.3 | C(16)-C(17)-H(17C) | 109.5 |
| N(4)-C(1)-Fe(1) | 120.44(14) | C(9)-C(10)-C(11) | 120.1(2) | H(17A)-C(17)-H(17C) | 109.5 |
| N(3)-C(2)-C(3) | 108.73(18) | C(9)-C(10)-H(10A) | 120.0 | H(17B)-C(17)-H(17C) | 109.5 |
| N(3)-C(2)-H(2A) | 109.9 | C(11)-C(10)-H(10A) | 120.0 | C(16)-C(18)-H(18A) | 109.5 |
| C(3)-C(2)-H(2A) | 109.9 | C(10)-C(11)-C(12) | 121.1(2) | C(16)-C(18)-H(18B) | 109.5 |
| N(3)-C(2)-H(2B) | 109.9 | C(10)-C(11)-H(11A) | 119.5 | H(18A)-C(18)-H(18B) | 109.5 |
| C(3)-C(2)-H(2B) | 109.9 | C(12)-C(11)-H(11A) | 119.5 | C(16)-C(18)-H(18C) | 109.5 |
| H(2A)-C(2)-H(2B) | 108.3 | C(11)-C(12)-C(7) | 118.2(2) | H(18A)-C(18)-H(18C) | 109.5 |
| C(2)-C(3)-C(4) | 111.02(19) | C(11)-C(12)-C(16) | 119.6(2) | H(18B)-C(18)-H(18C) | 109.5 |
| C(2)-C(3)-H(3A) | 109.4 | C(7)-C(12)-C(16) | 122.17(18) | N(1)-C(19)-N(3) | 114.72(19) |
| C(4)-C(3)-H(3A) | 109.4 | C(8)-C(13)-C(14) | 112.35(18) | N(1)-C(19)-C(20) | 126.8(2) |
| C(2)-C(3)-H(3B) | 109.4 | C(8)-C(13)-C(15) | 111.15(18) | N(3)-C(19)-C(20) | 118.44(19) |
| C(4)-C(3)-H(3B) | 109.4 | C(14)-C(13)-C(15) | 109.46(19) | C(19)-C(20)-H(20A) | 109.5 |
| H(3A)-C(3)-H(3B) | 108.0 | C(8)-C(13)-H(13A) | 107.9 | C(19)-C(20)-H(20B) | 109.5 |
| N(4)-C(4)-C(3) | 107.86(17) | C(14)-C(13)-H(13A) | 107.9 | H(20A)-C(20)-H(20B) | 109.5 |
| N(4)-C(4)-H(4A) | 110.1 | C(15)-C(13)-H(13A) | 107.9 | C(19)-C(20)-H(20C) | 109.5 |
| C(3)-C(4)-H(4A) | 110.1 | C(13)-C(14)-H(14A) | 109.5 | H(20A)-C(20)-H(20C) | 109.5 |
| N(4)-C(4)-H(4B) | 110.1 | C(13)-C(14)-H(14B) | 109.5 | H(20B)-C(20)-H(20C) | 109.5 |

| | | | |
|---|---|---|---|
| C(26)-C(21)-C(22) | 121.6(2) | C(26)-C(30)-C(31) | 110.3(2) |
| C(26)-C(21)-N(1) | 120.2(2) | C(32)-C(30)-C(31) | 111.1(2) |
| C(22)-C(21)-N(1) | 118.1(2) | C(26)-C(30)-H(30A) | 107.8 |
| C(23)-C(22)-C(21) | 117.9(3) | C(32)-C(30)-H(30A) | 107.8 |
| C(23)-C(22)-C(27) | 119.5(3) | C(31)-C(30)-H(30A) | 107.8 |
| C(21)-C(22)-C(27) | 122.6(2) | C(30)-C(31)-H(31A) | 109.5 |
| C(24)-C(23)-C(22) | 121.2(3) | C(30)-C(31)-H(31B) | 109.5 |
| C(24)-C(23)-H(23A) | 119.4 | H(31A)-C(31)-H(31B) | 109.5 |
| C(22)-C(23)-H(23A) | 119.4 | C(30)-C(31)-H(31C) | 109.5 |
| C(25)-C(24)-C(23) | 119.8(3) | H(31A)-C(31)-H(31C) | 109.5 |
| C(25)-C(24)-H(24A) | 120.1 | H(31B)-C(31)-H(31C) | 109.5 |
| C(23)-C(24)-H(24A) | 120.1 | C(30)-C(32)-H(32A) | 109.5 |
| C(24)-C(25)-C(26) | 121.9(2) | C(30)-C(32)-H(32B) | 109.5 |
| C(24)-C(25)-H(25A) | 119.1 | H(32A)-C(32)-H(32B) | 109.5 |
| C(26)-C(25)-H(25A) | 119.1 | C(30)-C(32)-H(32C) | 109.5 |
| C(21)-C(26)-C(25) | 117.5(3) | H(32A)-C(32)-H(32C) | 109.5 |
| C(21)-C(26)-C(30) | 123.4(2) | H(32B)-C(32)-H(32C) | 109.5 |
| C(25)-C(26)-C(30) | 119.1(2) | Cl(4S)-C(1S)-Cl(3S) | 111.22(16) |
| C(28)-C(27)-C(22) | 112.1(3) | Cl(4S)-C(1S)-H(1SA) | 109.4 |
| C(28)-C(27)-C(29) | 110.3(3) | Cl(3S)-C(1S)-H(1SA) | 109.4 |
| C(22)-C(27)-C(29) | 111.2(3) | Cl(4S)-C(1S)-H(1SB) | 109.4 |
| C(28)-C(27)-H(27A) | 107.7 | Cl(3S)-C(1S)-H(1SB) | 109.4 |
| C(22)-C(27)-H(27A) | 107.7 | H(1SA)-C(1S)-H(1SB) | 108.0 |
| C(29)-C(27)-H(27A) | 107.7 | Cl(5S)-C(2S)-Cl(6S) | 110.51(17) |
| C(27)-C(28)-H(28A) | 109.5 | Cl(5S)-C(2S)-H(2SA) | 109.5 |
| C(27)-C(28)-H(28B) | 109.5 | Cl(6S)-C(2S)-H(2SA) | 109.5 |
| H(28A)-C(28)-H(28B) | 109.5 | Cl(5S)-C(2S)-H(2SB) | 109.5 |
| C(27)-C(28)-H(28C) | 109.5 | Cl(6S)-C(2S)-H(2SB) | 109.5 |
| H(28A)-C(28)-H(28C) | 109.5 | H(2SA)-C(2S)-H(2SB) | 108.1 |
| H(28B)-C(28)-H(28C) | 109.5 | Cl(8S)-C(3S)-Cl(7S) | 112.2(13) |
| C(27)-C(29)-H(29A) | 109.5 | Cl(8S)-C(3S)-H(3S1) | 109.2 |
| C(27)-C(29)-H(29B) | 109.5 | Cl(7S)-C(3S)-H(3S1) | 109.2 |
| H(29A)-C(29)-H(29B) | 109.5 | Cl(8S)-C(3S)-H(3S2) | 109.2 |
| C(27)-C(29)-H(29C) | 109.5 | Cl(7S)-C(3S)-H(3S2) | 109.2 |
| H(29A)-C(29)-H(29C) | 109.5 | H(3S1)-C(3S)-H(3S2) | 107.9 |
| H(29B)-C(29)-H(29C) | 109.5 | | |
| C(26)-C(30)-C(32) | 111.8(2) | | |

**Table S6.** Anisotropic displacement parameters ($Å^2$ x $10^3$) for ($CDA^{iPr}$)$FeCl_2$ (**2a**) at 100 K. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11}+...+2hka^*b^*U^{12}]$.

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 29(1) | 15(1) | 11(1) | 0(1) | 1(1) | -2(1) |
| Cl(1) | 47(1) | 24(1) | 13(1) | 0(1) | -5(1) | 2(1) |
| Cl(2) | 28(1) | 19(1) | 26(1) | 1(1) | 4(1) | -4(1) |
| N(1) | 38(1) | 16(1) | 16(1) | 0(1) | 2(1) | -1(1) |
| N(2) | 23(1) | 16(1) | 12(1) | -1(1) | 0(1) | -1(1) |
| N(3) | 36(1) | 19(1) | 12(1) | -2(1) | 0(1) | -6(1) |
| N(4) | 26(1) | 20(1) | 10(1) | 2(1) | -1(1) | -4(1) |
| C(1) | 28(1) | 17(1) | 11(1) | 0(1) | -1(1) | -5(1) |
| C(2) | 42(1) | 27(1) | 11(1) | -4(1) | 1(1) | -7(1) |
| C(3) | 28(1) | 36(1) | 13(1) | -2(1) | -1(1) | -4(1) |
| C(4) | 30(1) | 27(1) | 10(1) | 2(1) | 0(1) | 0(1) |
| C(5) | 22(1) | 16(1) | 14(1) | 1(1) | 0(1) | 1(1) |
| C(6) | 34(1) | 18(1) | 18(1) | 4(1) | 4(1) | -1(1) |
| C(7) | 22(1) | 16(1) | 13(1) | -1(1) | 0(1) | -2(1) |
| C(8) | 25(1) | 18(1) | 14(1) | -1(1) | 1(1) | -2(1) |
| C(9) | 28(1) | 21(1) | 21(1) | -6(1) | 3(1) | 0(1) |
| C(10) | 31(1) | 24(1) | 23(1) | -7(1) | 1(1) | -5(1) |
| C(11) | 27(1) | 29(1) | 22(1) | -6(1) | -1(1) | -7(1) |
| C(12) | 22(1) | 23(1) | 18(1) | -3(1) | 0(1) | -2(1) |
| C(13) | 24(1) | 18(1) | 17(1) | 0(1) | 2(1) | -2(1) |
| C(14) | 30(1) | 19(1) | 24(1) | 1(1) | 0(1) | 1(1) |
| C(15) | 28(1) | 29(1) | 22(1) | 2(1) | 2(1) | -5(1) |
| C(16) | 24(1) | 33(1) | 22(1) | -5(1) | -1(1) | 1(1) |
| C(17) | 28(1) | 64(2) | 32(1) | 1(1) | 8(1) | 4(1) |
| C(18) | 29(1) | 41(1) | 35(1) | -5(1) | -9(1) | 5(1) |
| C(19) | 36(1) | 18(1) | 18(1) | -3(1) | 2(1) | -6(1) |
| C(20) | 62(2) | 20(1) | 25(1) | -8(1) | -2(1) | -7(1) |
| C(21) | 46(1) | 16(1) | 17(1) | -1(1) | 1(1) | 0(1) |
| C(22) | 47(2) | 25(1) | 31(1) | 1(1) | 6(1) | 4(1) |
| C(23) | 50(2) | 30(1) | 43(2) | 0(1) | -1(1) | 9(1) |
| C(24) | 56(2) | 22(1) | 27(1) | 1(1) | -3(1) | 7(1) |
| C(25) | 53(2) | 20(1) | 18(1) | 1(1) | -1(1) | -3(1) |
| C(26) | 43(1) | 17(1) | 17(1) | 0(1) | -1(1) | -1(1) |
| C(27) | 46(2) | 36(1) | 57(2) | 13(1) | 17(2) | 8(1) |
| C(28) | 67(2) | 40(2) | 81(3) | -12(2) | 22(2) | -10(2) |
| C(29) | 59(2) | 66(2) | 51(2) | -1(2) | 17(2) | -1(2) |
| C(30) | 44(1) | 20(1) | 26(1) | 4(1) | 4(1) | -2(1) |
| C(31) | 58(2) | 33(1) | 36(1) | 1(1) | 17(1) | 6(1) |
| C(32) | 45(2) | 29(1) | 46(2) | 6(1) | -3(1) | -4(1) |
| C(1S) | 55(2) | 27(1) | 56(2) | 4(1) | -20(2) | -9(1) |
| C(2S) | 46(2) | 42(2) | 29(1) | -5(1) | 1(1) | -4(1) |
| Cl(4S) | 39(1) | 54(1) | 43(1) | 1(1) | 5(1) | 0(1) |
| Cl(3S) | 47(1) | 100(1) | 45(1) | -1(1) | 8(1) | -30(1) |
| Cl(6S) | 80(1) | 60(1) | 37(1) | -9(1) | 10(1) | 14(1) |
| Cl(5S) | 48(1) | 161(1) | 45(1) | -12(1) | 2(1) | -24(1) |

**Figure S9.** ORTEP plot of (CDA$^{i\text{Pr}}$)$FeCl_2$ (**2a**) at 150 K at 50% probability level. Hydrogen atoms and solvent molecules were excluded for clarity.

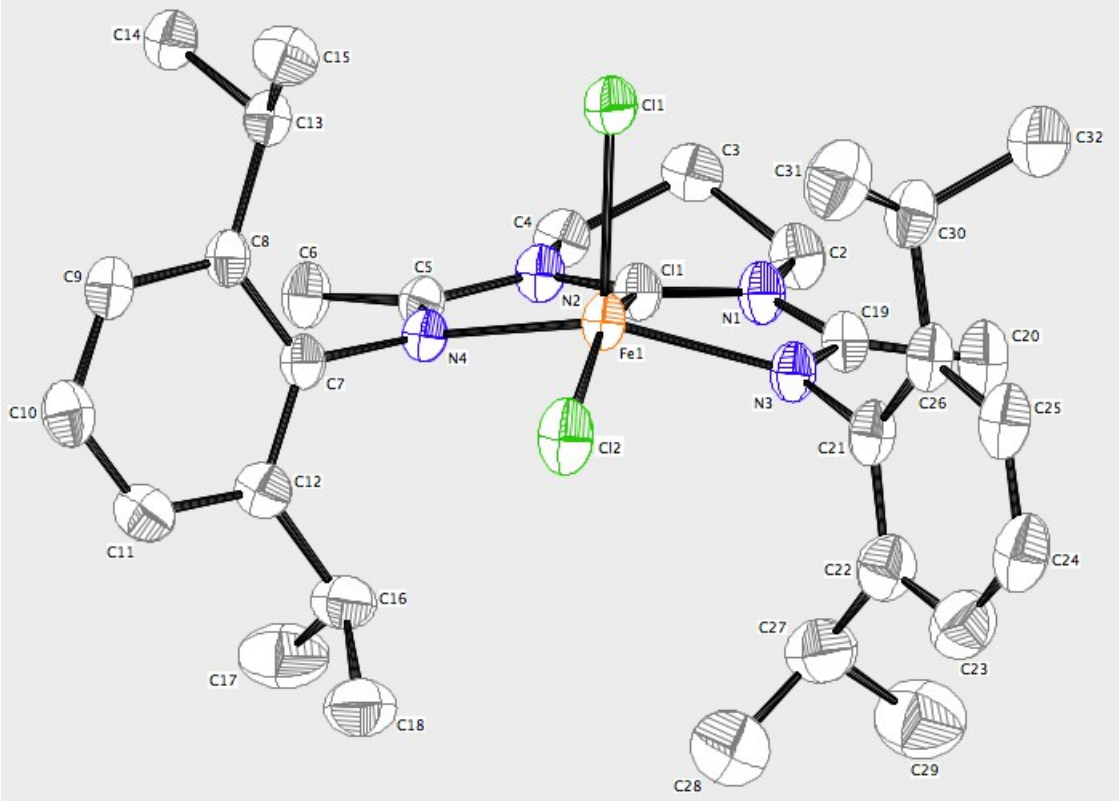


**Table S7.** Bond lengths (Å) and angles (º) for (CDA$^{iPr}$)$FeCl_2$ (**2a**) at 150 K.

| | | | | | |
|---|---|---|---|---|---|
| Fe(1)-C(1) | 1.832(2) | C(11)-H(11A) | 0.9500 | C(27)-C(29) | 1.535(6) |
| Fe(1)-N(3) | 2.037(2) | C(12)-C(16) | 1.523(4) | C(27)-H(27A) | 1.0000 |
| Fe(1)-N(4) | 2.041(2) | C(13)-C(15) | 1.527(4) | C(28)-H(28A) | 0.9800 |
| Fe(1)-Cl(2) | 2.2697(7) | C(13)-C(14) | 1.531(4) | C(28)-H(28B) | 0.9800 |
| Fe(1)-Cl(1) | 2.3210(8) | C(13)-H(13A) | 1.0000 | C(28)-H(28C) | 0.9800 |
| N(1)-C(1) | 1.358(3) | C(14)-H(14A) | 0.9800 | C(29)-H(29A) | 0.9800 |
| N(1)-C(19) | 1.372(3) | C(14)-H(14B) | 0.9800 | C(29)-H(29B) | 0.9800 |
| N(1)-C(2) | 1.472(3) | C(14)-H(14C) | 0.9800 | C(29)-H(29C) | 0.9800 |
| N(2)-C(1) | 1.351(3) | C(15)-H(15A) | 0.9800 | C(30)-C(32) | 1.525(5) |
| N(2)-C(5) | 1.374(3) | C(15)-H(15B) | 0.9800 | C(30)-C(31) | 1.537(4) |
| N(2)-C(4) | 1.478(3) | C(15)-H(15C) | 0.9800 | C(30)-H(30A) | 1.0000 |
| N(3)-C(19) | 1.298(3) | C(16)-C(17) | 1.520(5) | C(31)-H(31A) | 0.9800 |
| N(3)-C(21) | 1.445(3) | C(16)-C(18) | 1.522(4) | C(31)-H(31B) | 0.9800 |
| N(4)-C(5) | 1.300(3) | C(16)-H(16A) | 1.0000 | C(31)-H(31C) | 0.9800 |
| N(4)-C(7) | 1.452(3) | C(17)-H(17A) | 0.9800 | C(32)-H(32A) | 0.9800 |
| C(2)-C(3) | 1.505(4) | C(17)-H(17B) | 0.9800 | C(32)-H(32B) | 0.9800 |
| C(2)-H(2A) | 0.9900 | C(17)-H(17C) | 0.9800 | C(32)-H(32C) | 0.9800 |
| C(2)-H(2B) | 0.9900 | C(18)-H(18A) | 0.9800 | C(1S)-Cl(3S) | 1.685(6) |
| C(3)-C(4) | 1.517(4) | C(18)-H(18B) | 0.9800 | C(1S)-Cl(4S) | 1.821(5) |
| C(3)-H(3A) | 0.9900 | C(18)-H(18C) | 0.9800 | C(1S)-H(1S1) | 0.9900 |
| C(3)-H(3B) | 0.9900 | C(19)-C(20) | 1.490(4) | C(1S)-H(1S2) | 0.9900 |
| C(4)-H(4A) | 0.9900 | C(20)-H(20A) | 0.9800 | C(2S)-Cl(5S) | 1.714(4) |
| C(4)-H(4B) | 0.9900 | C(20)-H(20B) | 0.9800 | C(2S)-Cl(6S) | 1.777(4) |
| C(5)-C(6) | 1.486(3) | C(20)-H(20C) | 0.9800 | C(2S)-H(2S1) | 0.9900 |
| C(6)-H(6A) | 0.9800 | C(21)-C(22) | 1.402(4) | C(2S)-H(2S2) | 0.9900 |
| C(6)-H(6B) | 0.9800 | C(21)-C(26) | 1.404(4) | C(1)-Fe(1)-N(3) | 78.02(10) |
| C(6)-H(6C) | 0.9800 | C(22)-C(23) | 1.389(5) | C(1)-Fe(1)-N(4) | 77.76(9) |
| C(7)-C(12) | 1.401(4) | C(22)-C(27) | 1.521(5) | N(3)-Fe(1)-N(4) | 146.12(8) |
| C(7)-C(8) | 1.401(4) | C(23)-C(24) | 1.374(5) | C(1)-Fe(1)-Cl(2) | 157.99(9) |
| C(8)-C(9) | 1.404(4) | C(23)-H(23A) | 0.9500 | N(3)-Fe(1)-Cl(2) | 95.08(6) |
| C(8)-C(13) | 1.513(4) | C(24)-C(25) | 1.376(5) | N(4)-Fe(1)-Cl(2) | 98.58(6) |
| C(9)-C(10) | 1.376(4) | C(24)-H(24A) | 0.9500 | C(1)-Fe(1)-Cl(1) | 94.79(9) |
| C(9)-H(9A) | 0.9500 | C(25)-C(26) | 1.399(4) | N(3)-Fe(1)-Cl(1) | 103.63(7) |
| C(10)-C(11) | 1.374(4) | C(25)-H(25A) | 0.9500 | N(4)-Fe(1)-Cl(1) | 101.68(6) |
| C(10)-H(10A) | 0.9500 | C(26)-C(30) | 1.504(4) | Cl(2)-Fe(1)-Cl(1) | 107.18(3) |
| C(11)-C(12) | 1.391(4) | C(27)-C(28) | 1.515(6) | C(1)-N(1)-C(19) | 112.3(2) |

| | | | | | |
|---|---|---|---|---|---|
| C(1)-N(1)-C(2) | 122.6(2) | H(6A)-C(6)-H(6B) | 109.5 | C(13)-C(15)-H(15C) | 109.5 |
| C(19)-N(1)-C(2) | 124.9(2) | C(5)-C(6)-H(6C) | 109.5 | H(15A)-C(15)-H(15C) | 109.5 |
| C(1)-N(2)-C(5) | 112.2(2) | H(6A)-C(6)-H(6C) | 109.5 | H(15B)-C(15)-H(15C) | 109.5 |
| C(1)-N(2)-C(4) | 122.5(2) | H(6B)-C(6)-H(6C) | 109.5 | C(17)-C(16)-C(18) | 110.8(3) |
| C(5)-N(2)-C(4) | 125.1(2) | C(12)-C(7)-C(8) | 122.1(2) | C(17)-C(16)-C(12) | 110.3(3) |
| C(19)-N(3)-C(21) | 119.0(2) | C(12)-C(7)-N(4) | 118.6(2) | C(18)-C(16)-C(12) | 111.8(2) |
| C(19)-N(3)-Fe(1) | 113.44(17) | C(8)-C(7)-N(4) | 119.3(2) | C(17)-C(16)-H(16A) | 107.9 |
| C(21)-N(3)-Fe(1) | 127.53(16) | C(7)-C(8)-C(9) | 117.5(2) | C(18)-C(16)-H(16A) | 107.9 |
| C(5)-N(4)-C(7) | 118.0(2) | C(7)-C(8)-C(13) | 123.7(2) | C(12)-C(16)-H(16A) | 107.9 |
| C(5)-N(4)-Fe(1) | 113.51(16) | C(9)-C(8)-C(13) | 118.9(2) | C(16)-C(17)-H(17A) | 109.5 |
| C(7)-N(4)-Fe(1) | 127.96(15) | C(10)-C(9)-C(8) | 121.1(3) | C(16)-C(17)-H(17B) | 109.5 |
| N(2)-C(1)-N(1) | 120.0(2) | C(10)-C(9)-H(9A) | 119.5 | H(17A)-C(17)-H(17B) | 109.5 |
| N(2)-C(1)-Fe(1) | 120.33(18) | C(8)-C(9)-H(9A) | 119.5 | C(16)-C(17)-H(17C) | 109.5 |
| N(1)-C(1)-Fe(1) | 119.59(18) | C(11)-C(10)-C(9) | 120.1(2) | H(17A)-C(17)-H(17C) | 109.5 |
| N(1)-C(2)-C(3) | 108.7(2) | C(11)-C(10)-H(10A) | 119.9 | H(17B)-C(17)-H(17C) | 109.5 |
| N(1)-C(2)-H(2A) | 109.9 | C(9)-C(10)-H(10A) | 119.9 | C(16)-C(18)-H(18A) | 109.5 |
| C(3)-C(2)-H(2A) | 109.9 | C(10)-C(11)-C(12) | 121.6(3) | C(16)-C(18)-H(18B) | 109.5 |
| N(1)-C(2)-H(2B) | 109.9 | C(10)-C(11)-H(11A) | 119.2 | H(18A)-C(18)-H(18B) | 109.5 |
| C(3)-C(2)-H(2B) | 109.9 | C(12)-C(11)-H(11A) | 119.2 | C(16)-C(18)-H(18C) | 109.5 |
| H(2A)-C(2)-H(2B) | 108.3 | C(11)-C(12)-C(7) | 117.6(3) | H(18A)-C(18)-H(18C) | 109.5 |
| C(2)-C(3)-C(4) | 111.1(2) | C(11)-C(12)-C(16) | 120.5(3) | H(18B)-C(18)-H(18C) | 109.5 |
| C(2)-C(3)-H(3A) | 109.4 | C(7)-C(12)-C(16) | 121.9(2) | N(3)-C(19)-N(1) | 115.1(2) |
| C(4)-C(3)-H(3A) | 109.4 | C(8)-C(13)-C(15) | 111.4(2) | N(3)-C(19)-C(20) | 126.6(2) |
| C(2)-C(3)-H(3B) | 109.4 | C(8)-C(13)-C(14) | 112.2(2) | N(1)-C(19)-C(20) | 118.2(2) |
| C(4)-C(3)-H(3B) | 109.4 | C(15)-C(13)-C(14) | 109.5(2) | C(19)-C(20)-H(20A) | 109.5 |
| H(3A)-C(3)-H(3B) | 108.0 | C(8)-C(13)-H(13A) | 107.9 | C(19)-C(20)-H(20B) | 109.5 |
| N(2)-C(4)-C(3) | 108.0(2) | C(15)-C(13)-H(13A) | 107.9 | H(20A)-C(20)-H(20B) | 109.5 |
| N(2)-C(4)-H(4A) | 110.1 | C(14)-C(13)-H(13A) | 107.9 | C(19)-C(20)-H(20C) | 109.5 |
| C(3)-C(4)-H(4A) | 110.1 | C(13)-C(14)-H(14A) | 109.5 | H(20A)-C(20)-H(20C) | 109.5 |
| N(2)-C(4)-H(4B) | 110.1 | C(13)-C(14)-H(14B) | 109.5 | H(20B)-C(20)-H(20C) | 109.5 |
| C(3)-C(4)-H(4B) | 110.1 | H(14A)-C(14)-H(14B) | 109.5 | C(22)-C(21)-C(26) | 121.9(3) |
| H(4A)-C(4)-H(4B) | 108.4 | C(13)-C(14)-H(14C) | 109.5 | C(22)-C(21)-N(3) | 118.5(3) |
| N(4)-C(5)-N(2) | 115.1(2) | H(14A)-C(14)-H(14C) | 109.5 | C(26)-C(21)-N(3) | 119.6(3) |
| N(4)-C(5)-C(6) | 126.8(2) | H(14B)-C(14)-H(14C) | 109.5 | C(23)-C(22)-C(21) | 117.7(3) |
| N(2)-C(5)-C(6) | 118.1(2) | C(13)-C(15)-H(15A) | 109.5 | C(23)-C(22)-C(27) | 119.9(3) |
| C(5)-C(6)-H(6A) | 109.5 | C(13)-C(15)-H(15B) | 109.5 | C(21)-C(22)-C(27) | 122.4(3) |
| C(5)-C(6)-H(6B) | 109.5 | H(15A)-C(15)-H(15B) | 109.5 | C(24)-C(23)-C(22) | 121.7(3) |

| | | | |
|---|---|---|---|
| C(24)-C(23)-H(23A) | 119.1 | C(30)-C(31)-H(31B) | 109.5 |
| C(22)-C(23)-H(23A) | 119.1 | H(31A)-C(31)-H(31B) | 109.5 |
| C(23)-C(24)-C(25) | 119.8(3) | C(30)-C(31)-H(31C) | 109.5 |
| C(23)-C(24)-H(24A) | 120.1 | H(31A)-C(31)-H(31C) | 109.5 |
| C(25)-C(24)-H(24A) | 120.1 | H(31B)-C(31)-H(31C) | 109.5 |
| C(24)-C(25)-C(26) | 121.5(3) | C(30)-C(32)-H(32A) | 109.5 |
| C(24)-C(25)-H(25A) | 119.3 | C(30)-C(32)-H(32B) | 109.5 |
| C(26)-C(25)-H(25A) | 119.3 | H(32A)-C(32)-H(32B) | 109.5 |
| C(25)-C(26)-C(21) | 117.4(3) | C(30)-C(32)-H(32C) | 109.5 |
| C(25)-C(26)-C(30) | 119.2(3) | H(32A)-C(32)-H(32C) | 109.5 |
| C(21)-C(26)-C(30) | 123.4(2) | H(32B)-C(32)-H(32C) | 109.5 |
| C(28)-C(27)-C(22) | 111.4(3) | Cl(3S)-C(1S)-Cl(4S) | 111.4(2) |
| C(28)-C(27)-C(29) | 110.8(3) | Cl(3S)-C(1S)-H(1S1) | 109.3 |
| C(22)-C(27)-C(29) | 111.6(3) | Cl(4S)-C(1S)-H(1S1) | 109.3 |
| C(28)-C(27)-H(27A) | 107.6 | Cl(3S)-C(1S)-H(1S2) | 109.3 |
| C(22)-C(27)-H(27A) | 107.6 | Cl(4S)-C(1S)-H(1S2) | 109.3 |
| C(29)-C(27)-H(27A) | 107.6 | H(1S1)-C(1S)-H(1S2) | 108.0 |
| C(27)-C(28)-H(28A) | 109.5 | Cl(5S)-C(2S)-Cl(6S) | 110.7(2) |
| C(27)-C(28)-H(28B) | 109.5 | Cl(5S)-C(2S)-H(2S1) | 109.5 |
| H(28A)-C(28)-H(28B) | 109.5 | Cl(6S)-C(2S)-H(2S1) | 109.5 |
| C(27)-C(28)-H(28C) | 109.5 | Cl(5S)-C(2S)-H(2S2) | 109.5 |
| H(28A)-C(28)-H(28C) | 109.5 | Cl(6S)-C(2S)-H(2S2) | 109.5 |
| H(28B)-C(28)-H(28C) | 109.5 | H(2S1)-C(2S)-H(2S2) | 108.1 |
| C(27)-C(29)-H(29A) | 109.5 | | |
| C(27)-C(29)-H(29B) | 109.5 | | |
| H(29A)-C(29)-H(29B) | 109.5 | | |
| C(27)-C(29)-H(29C) | 109.5 | | |
| H(29A)-C(29)-H(29C) | 109.5 | | |
| H(29B)-C(29)-H(29C) | 109.5 | | |
| C(26)-C(30)-C(32) | 112.1(3) | | |
| C(26)-C(30)-C(31) | 110.4(3) | | |
| C(32)-C(30)-C(31) | 110.8(3) | | |
| C(26)-C(30)-H(30A) | 107.8 | | |
| C(32)-C(30)-H(30A) | 107.8 | | |
| C(31)-C(30)-H(30A) | 107.8 | | |
| C(30)-C(31)-H(31A) | 109.5 | | |

**Table S8.** Anisotropic displacement parameters ($Å^2$ x $10^3$) for ($CDA^{iPr}$)$FeCl_2$ (**2a**) at 150 K. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11}+...+2hka^*b^*U^{12}]$.

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 37(1) | 21(1) | 24(1) | -1(1) | 2(1) | -1(1) |
| Cl(1) | 38(1) | 30(1) | 52(1) | 1(1) | 4(1) | -2(1) |
| Cl(2) | 67(1) | 35(1) | 24(1) | -1(1) | -9(1) | 1(1) |
| N(1) | 44(1) | 25(1) | 22(1) | -3(1) | -1(1) | -4(1) |
| N(2) | 37(1) | 27(1) | 18(1) | 1(1) | 0(1) | 0(1) |
| N(3) | 41(1) | 24(1) | 23(1) | -2(1) | -1(1) | 0(1) |
| N(4) | 31(1) | 22(1) | 21(1) | 0(1) | 2(1) | 1(1) |
| C(1) | 37(1) | 26(1) | 24(1) | -1(1) | 0(1) | -3(1) |
| C(2) | 49(2) | 38(2) | 20(1) | -5(1) | -3(1) | -8(1) |
| C(3) | 37(1) | 45(2) | 21(1) | -1(1) | -2(1) | -2(1) |
| C(4) | 39(1) | 36(1) | 19(1) | 3(1) | 1(1) | 2(1) |
| C(5) | 30(1) | 23(1) | 23(1) | 0(1) | 4(1) | 3(1) |
| C(6) | 49(2) | 26(1) | 28(1) | 4(1) | 2(1) | -1(1) |
| C(7) | 34(1) | 23(1) | 22(1) | 0(1) | 0(1) | -3(1) |
| C(8) | 36(1) | 22(1) | 24(1) | 1(1) | 2(1) | -3(1) |
| C(9) | 44(2) | 26(1) | 33(1) | -5(1) | 5(1) | 0(1) |
| C(10) | 49(2) | 35(2) | 34(1) | -11(1) | -1(1) | -11(1) |
| C(11) | 36(2) | 44(2) | 37(2) | -4(1) | -2(1) | -11(1) |
| C(12) | 34(1) | 38(1) | 26(1) | -1(1) | 0(1) | -2(1) |
| C(13) | 34(1) | 26(1) | 27(1) | -2(1) | 3(1) | 0(1) |
| C(14) | 40(2) | 32(1) | 39(2) | 1(1) | 0(1) | 2(1) |
| C(15) | 39(2) | 49(2) | 36(1) | 5(1) | 5(1) | -7(1) |
| C(16) | 32(2) | 52(2) | 40(2) | -10(1) | -2(1) | 1(1) |
| C(17) | 47(2) | 96(3) | 52(2) | 0(2) | 13(2) | 7(2) |
| C(18) | 39(2) | 61(2) | 60(2) | -7(2) | -10(2) | 9(2) |
| C(19) | 41(2) | 24(1) | 29(1) | -2(1) | 2(1) | -5(1) |
| C(20) | 69(2) | 30(1) | 38(2) | -8(1) | -7(1) | -2(1) |
| C(21) | 50(2) | 25(1) | 26(1) | -4(1) | -2(1) | 2(1) |
| C(22) | 51(2) | 40(2) | 40(2) | -4(1) | -3(1) | 6(1) |
| C(23) | 56(2) | 50(2) | 50(2) | -6(2) | -12(2) | 16(2) |
| C(24) | 74(2) | 35(2) | 38(2) | -2(1) | -12(2) | 15(2) |
| C(25) | 67(2) | 29(1) | 30(1) | 0(1) | -1(1) | 4(1) |
| C(26) | 54(2) | 25(1) | 26(1) | -2(1) | -2(1) | 2(1) |
| C(27) | 46(2) | 56(2) | 68(2) | 5(2) | 5(2) | 6(2) |
| C(28) | 63(3) | 74(3) | 100(3) | -17(3) | 6(2) | -10(2) |
| C(29) | 69(3) | 100(3) | 71(3) | -8(2) | 18(2) | -5(2) |
| C(30) | 54(2) | 28(1) | 40(2) | 6(1) | 8(1) | 2(1) |
| C(31) | 74(2) | 49(2) | 53(2) | 1(2) | 21(2) | 11(2) |
| C(32) | 56(2) | 41(2) | 71(2) | 4(2) | 0(2) | -2(2) |
| C(1S) | 71(2) | 38(2) | 98(3) | -1(2) | -30(2) | -5(2) |
| Cl(3S) | 67(1) | 154(3) | 85(1) | -15(2) | 22(1) | -39(2) |
| Cl(4S) | 50(1) | 56(1) | 67(1) | 4(1) | 10(1) | -3(1) |
| C(2S) | 74(2) | 52(2) | 41(2) | -4(2) | -2(2) | -6(2) |
| Cl(5S) | 61(1) | 147(4) | 68(1) | -3(1) | -2(1) | -20(1) |
| Cl(6S) | 96(2) | 84(1) | 56(1) | -13(1) | 18(1) | 12(1) |

**Figure S10.** ORTEP plot of (CDA$^{i\text{Pr}}$)$FeCl_2$ (**2a**) at 200 K at 50% probability level. Hydrogen atoms and solvent molecules were excluded for clarity.

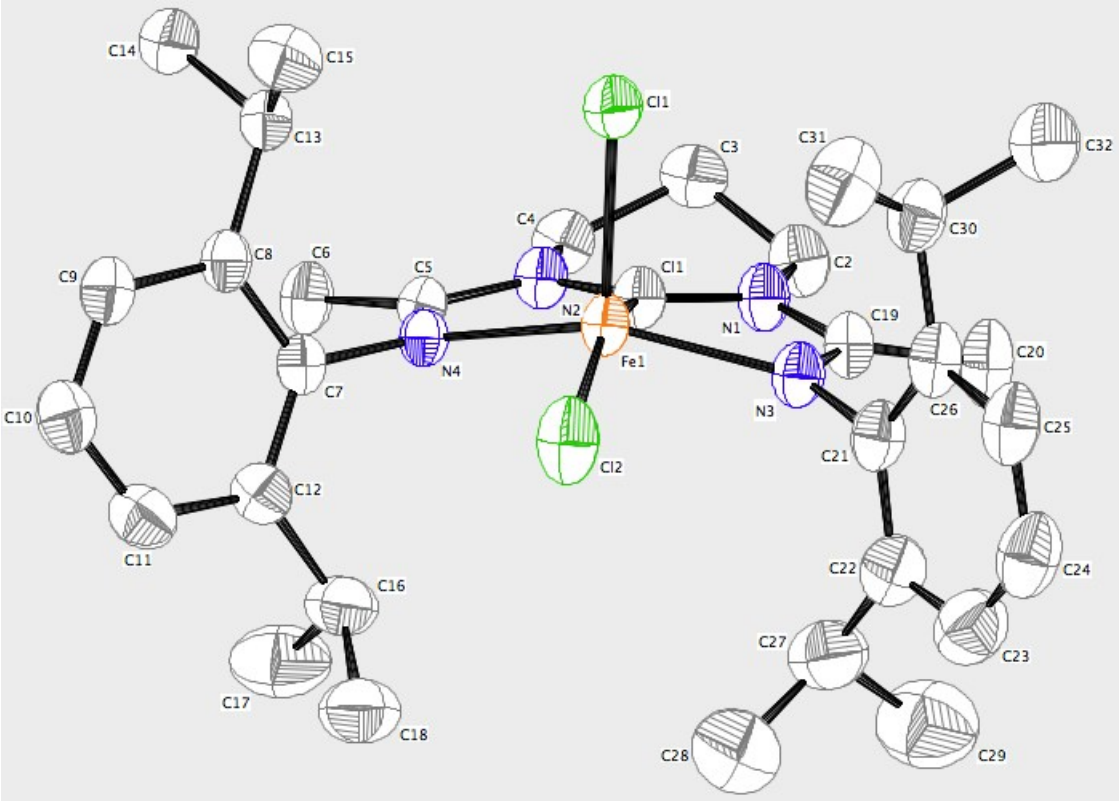


**Table S9.** Bond lengths (Å) and angles (º) for (CDA$^{iPr}$)$FeCl_2$ (**2a**) at 200 K.

| | | | | | |
|---|---|---|---|---|---|
| Fe(1)-C(1) | 1.850(2) | C(11)-C(12) | 1.391(4) | C(26)-C(30) | 1.501(5) |
| Fe(1)-N(3) | 2.062(2) | C(11)-H(11A) | 0.9500 | C(27)-C(28) | 1.512(6) |
| Fe(1)-N(4) | 2.065(2) | C(12)-C(16) | 1.520(4) | C(27)-C(29) | 1.532(6) |
| Fe(1)-Cl(2) | 2.2648(8) | C(13)-C(15) | 1.526(4) | C(27)-H(27A) | 1.0000 |
| Fe(1)-Cl(1) | 2.3216(8) | C(13)-C(14) | 1.528(4) | C(28)-H(28A) | 0.9800 |
| N(1)-C(1) | 1.354(3) | C(13)-H(13A) | 1.0000 | C(28)-H(28B) | 0.9800 |
| N(1)-C(19) | 1.378(3) | C(14)-H(14A) | 0.9800 | C(28)-H(28C) | 0.9800 |
| N(1)-C(2) | 1.470(3) | C(14)-H(14B) | 0.9800 | C(29)-H(29A) | 0.9800 |
| N(2)-C(1) | 1.351(3) | C(14)-H(14C) | 0.9800 | C(29)-H(29B) | 0.9800 |
| N(2)-C(5) | 1.374(3) | C(15)-H(15A) | 0.9800 | C(29)-H(29C) | 0.9800 |
| N(2)-C(4) | 1.478(3) | C(15)-H(15B) | 0.9800 | C(30)-C(32) | 1.526(5) |
| N(3)-C(19) | 1.293(3) | C(15)-H(15C) | 0.9800 | C(30)-C(31) | 1.533(5) |
| N(3)-C(21) | 1.444(3) | C(16)-C(17) | 1.518(5) | C(30)-H(30A) | 1.0000 |
| N(4)-C(5) | 1.299(3) | C(16)-C(18) | 1.523(5) | C(31)-H(31A) | 0.9800 |
| N(4)-C(7) | 1.450(3) | C(16)-H(16A) | 1.0000 | C(31)-H(31B) | 0.9800 |
| C(2)-C(3) | 1.503(4) | C(17)-H(17A) | 0.9800 | C(31)-H(31C) | 0.9800 |
| C(2)-H(2A) | 0.9900 | C(17)-H(17B) | 0.9800 | C(32)-H(32A) | 0.9800 |
| C(2)-H(2B) | 0.9900 | C(17)-H(17C) | 0.9800 | C(32)-H(32B) | 0.9800 |
| C(3)-C(4) | 1.515(4) | C(18)-H(18A) | 0.9800 | C(32)-H(32C) | 0.9800 |
| C(3)-H(3A) | 0.9900 | C(18)-H(18B) | 0.9800 | C(1S)-Cl(3S) | 1.665(7) |
| C(3)-H(3B) | 0.9900 | C(18)-H(18C) | 0.9800 | C(1S)-Cl(4S) | 1.834(5) |
| C(4)-H(4A) | 0.9900 | C(19)-C(20) | 1.492(4) | C(1S)-H(1S1) | 0.9900 |
| C(4)-H(4B) | 0.9900 | C(20)-H(20A) | 0.9800 | C(1S)-H(1S2) | 0.9900 |
| C(5)-C(6) | 1.485(3) | C(20)-H(20B) | 0.9800 | C(2S)-Cl(5S) | 1.693(5) |
| C(6)-H(6A) | 0.9800 | C(20)-H(20C) | 0.9800 | C(2S)-Cl(6S) | 1.775(5) |
| C(6)-H(6B) | 0.9800 | C(21)-C(22) | 1.400(5) | C(2S)-H(2S1) | 0.9900 |
| C(6)-H(6C) | 0.9800 | C(21)-C(26) | 1.401(4) | C(2S)-H(2S2) | 0.9900 |
| C(7)-C(8) | 1.400(4) | C(22)-C(23) | 1.390(5) | C(1)-Fe(1)-N(3) | 77.34(10) |
| C(7)-C(12) | 1.401(4) | C(22)-C(27) | 1.520(5) | C(1)-Fe(1)-N(4) | 77.27(9) |
| C(8)-C(9) | 1.401(4) | C(23)-C(24) | 1.374(5) | N(3)-Fe(1)-N(4) | 145.88(8) |
| C(8)-C(13) | 1.513(4) | C(23)-H(23A) | 0.9500 | C(1)-Fe(1)-Cl(2) | 156.89(9) |
| C(9)-C(10) | 1.374(4) | C(24)-C(25) | 1.365(5) | N(3)-Fe(1)-Cl(2) | 95.44(6) |
| C(9)-H(9A) | 0.9500 | C(24)-H(24A) | 0.9500 | N(4)-Fe(1)-Cl(2) | 99.05(6) |
| C(10)-C(11) | 1.374(5) | C(25)-C(26) | 1.400(4) | C(1)-Fe(1)-Cl(1) | 94.76(9) |
| C(10)-H(10A) | 0.9500 | C(25)-H(25A) | 0.9500 | N(3)-Fe(1)-Cl(1) | 103.17(7) |

| | | | | | |
|---|---|---|---|---|---|
| N(4)-Fe(1)-Cl(1) | 101.31(6) | N(2)-C(5)-C(6) | 118.2(2) | C(13)-C(15)-H(15A) | 109.5 |
| Cl(2)-Fe(1)-Cl(1) | 108.30(3) | C(5)-C(6)-H(6A) | 109.5 | C(13)-C(15)-H(15B) | 109.5 |
| C(1)-N(1)-C(19) | 112.3(2) | C(5)-C(6)-H(6B) | 109.5 | H(15A)-C(15)-H(15B) | 109.5 |
| C(1)-N(1)-C(2) | 122.8(2) | H(6A)-C(6)-H(6B) | 109.5 | C(13)-C(15)-H(15C) | 109.5 |
| C(19)-N(1)-C(2) | 124.7(2) | C(5)-C(6)-H(6C) | 109.5 | H(15A)-C(15)-H(15C) | 109.5 |
| C(1)-N(2)-C(5) | 112.5(2) | H(6A)-C(6)-H(6C) | 109.5 | H(15B)-C(15)-H(15C) | 109.5 |
| C(1)-N(2)-C(4) | 122.5(2) | H(6B)-C(6)-H(6C) | 109.5 | C(17)-C(16)-C(12) | 110.6(3) |
| C(5)-N(2)-C(4) | 124.8(2) | C(8)-C(7)-C(12) | 122.0(2) | C(17)-C(16)-C(18) | 110.9(3) |
| C(19)-N(3)-C(21) | 119.2(2) | C(8)-C(7)-N(4) | 119.5(2) | C(12)-C(16)-C(18) | 111.7(3) |
| C(19)-N(3)-Fe(1) | 113.38(17) | C(12)-C(7)-N(4) | 118.6(2) | C(17)-C(16)-H(16A) | 107.8 |
| C(21)-N(3)-Fe(1) | 127.42(16) | C(7)-C(8)-C(9) | 117.5(2) | C(12)-C(16)-H(16A) | 107.8 |
| C(5)-N(4)-C(7) | 118.4(2) | C(7)-C(8)-C(13) | 123.5(2) | C(18)-C(16)-H(16A) | 107.8 |
| C(5)-N(4)-Fe(1) | 113.30(16) | C(9)-C(8)-C(13) | 119.0(2) | C(16)-C(17)-H(17A) | 109.5 |
| C(7)-N(4)-Fe(1) | 127.86(15) | C(10)-C(9)-C(8) | 121.3(3) | C(16)-C(17)-H(17B) | 109.5 |
| N(2)-C(1)-N(1) | 120.0(2) | C(10)-C(9)-H(9A) | 119.4 | H(17A)-C(17)-H(17B) | 109.5 |
| N(2)-C(1)-Fe(1) | 120.20(18) | C(8)-C(9)-H(9A) | 119.4 | C(16)-C(17)-H(17C) | 109.5 |
| N(1)-C(1)-Fe(1) | 119.85(18) | C(11)-C(10)-C(9) | 120.0(3) | H(17A)-C(17)-H(17C) | 109.5 |
| N(1)-C(2)-C(3) | 108.7(2) | C(11)-C(10)-H(10A) | 120.0 | H(17B)-C(17)-H(17C) | 109.5 |
| N(1)-C(2)-H(2A) | 110.0 | C(9)-C(10)-H(10A) | 120.0 | C(16)-C(18)-H(18A) | 109.5 |
| C(3)-C(2)-H(2A) | 110.0 | C(10)-C(11)-C(12) | 121.6(3) | C(16)-C(18)-H(18B) | 109.5 |
| N(1)-C(2)-H(2B) | 110.0 | C(10)-C(11)-H(11A) | 119.2 | H(18A)-C(18)-H(18B) | 109.5 |
| C(3)-C(2)-H(2B) | 110.0 | C(12)-C(11)-H(11A) | 119.2 | C(16)-C(18)-H(18C) | 109.5 |
| H(2A)-C(2)-H(2B) | 108.3 | C(11)-C(12)-C(7) | 117.7(3) | H(18A)-C(18)-H(18C) | 109.5 |
| C(2)-C(3)-C(4) | 111.1(2) | C(11)-C(12)-C(16) | 120.1(3) | H(18B)-C(18)-H(18C) | 109.5 |
| C(2)-C(3)-H(3A) | 109.4 | C(7)-C(12)-C(16) | 122.2(2) | N(3)-C(19)-N(1) | 115.4(2) |
| C(4)-C(3)-H(3A) | 109.4 | C(8)-C(13)-C(15) | 111.3(2) | N(3)-C(19)-C(20) | 126.4(2) |
| C(2)-C(3)-H(3B) | 109.4 | C(8)-C(13)-C(14) | 112.3(2) | N(1)-C(19)-C(20) | 118.1(2) |
| C(4)-C(3)-H(3B) | 109.4 | C(15)-C(13)-C(14) | 109.7(2) | C(19)-C(20)-H(20A) | 109.5 |
| H(3A)-C(3)-H(3B) | 108.0 | C(8)-C(13)-H(13A) | 107.8 | C(19)-C(20)-H(20B) | 109.5 |
| N(2)-C(4)-C(3) | 108.1(2) | C(15)-C(13)-H(13A) | 107.8 | H(20A)-C(20)-H(20B) | 109.5 |
| N(2)-C(4)-H(4A) | 110.1 | C(14)-C(13)-H(13A) | 107.8 | C(19)-C(20)-H(20C) | 109.5 |
| C(3)-C(4)-H(4A) | 110.1 | C(13)-C(14)-H(14A) | 109.5 | H(20A)-C(20)-H(20C) | 109.5 |
| N(2)-C(4)-H(4B) | 110.1 | C(13)-C(14)-H(14B) | 109.5 | H(20B)-C(20)-H(20C) | 109.5 |
| C(3)-C(4)-H(4B) | 110.1 | H(14A)-C(14)-H(14B) | 109.5 | C(22)-C(21)-C(26) | 121.9(3) |
| H(4A)-C(4)-H(4B) | 108.4 | C(13)-C(14)-H(14C) | 109.5 | C(22)-C(21)-N(3) | 118.5(3) |
| N(4)-C(5)-N(2) | 115.4(2) | H(14A)-C(14)-H(14C) | 109.5 | C(26)-C(21)-N(3) | 119.5(3) |
| N(4)-C(5)-C(6) | 126.4(2) | H(14B)-C(14)-H(14C) | 109.5 | C(23)-C(22)-C(21) | 117.6(3) |

| | | | |
|---|---|---|---|
| C(23)-C(22)-C(27) | 119.7(3) | C(31)-C(30)-H(30A) | 107.7 |
| C(21)-C(22)-C(27) | 122.7(3) | C(30)-C(31)-H(31A) | 109.5 |
| C(24)-C(23)-C(22) | 121.7(3) | C(30)-C(31)-H(31B) | 109.5 |
| C(24)-C(23)-H(23A) | 119.2 | H(31A)-C(31)-H(31B) | 109.5 |
| C(22)-C(23)-H(23A) | 119.2 | C(30)-C(31)-H(31C) | 109.5 |
| C(25)-C(24)-C(23) | 119.8(3) | H(31A)-C(31)-H(31C) | 109.5 |
| C(25)-C(24)-H(24A) | 120.1 | H(31B)-C(31)-H(31C) | 109.5 |
| C(23)-C(24)-H(24A) | 120.1 | C(30)-C(32)-H(32A) | 109.5 |
| C(24)-C(25)-C(26) | 121.7(3) | C(30)-C(32)-H(32B) | 109.5 |
| C(24)-C(25)-H(25A) | 119.1 | H(32A)-C(32)-H(32B) | 109.5 |
| C(26)-C(25)-H(25A) | 119.1 | C(30)-C(32)-H(32C) | 109.5 |
| C(25)-C(26)-C(21) | 117.2(3) | H(32A)-C(32)-H(32C) | 109.5 |
| C(25)-C(26)-C(30) | 119.4(3) | H(32B)-C(32)-H(32C) | 109.5 |
| C(21)-C(26)-C(30) | 123.3(3) | Cl(3S)-C(1S)-Cl(4S) | 111.2(3) |
| C(28)-C(27)-C(22) | 111.4(4) | Cl(3S)-C(1S)-H(1S1) | 109.4 |
| C(28)-C(27)-C(29) | 110.8(4) | Cl(4S)-C(1S)-H(1S1) | 109.4 |
| C(22)-C(27)-C(29) | 111.8(4) | Cl(3S)-C(1S)-H(1S2) | 109.4 |
| C(28)-C(27)-H(27A) | 107.6 | Cl(4S)-C(1S)-H(1S2) | 109.4 |
| C(22)-C(27)-H(27A) | 107.6 | H(1S1)-C(1S)-H(1S2) | 108.0 |
| C(29)-C(27)-H(27A) | 107.6 | Cl(5S)-C(2S)-Cl(6S) | 111.5(3) |
| C(27)-C(28)-H(28A) | 109.5 | Cl(5S)-C(2S)-H(2S1) | 109.3 |
| C(27)-C(28)-H(28B) | 109.5 | Cl(6S)-C(2S)-H(2S1) | 109.3 |
| H(28A)-C(28)-H(28B) | 109.5 | Cl(5S)-C(2S)-H(2S2) | 109.3 |
| C(27)-C(28)-H(28C) | 109.5 | Cl(6S)-C(2S)-H(2S2) | 109.3 |
| H(28A)-C(28)-H(28C) | 109.5 | H(2S1)-C(2S)-H(2S2) | 108.0 |
| H(28B)-C(28)-H(28C) | 109.5 | | |
| C(27)-C(29)-H(29A) | 109.5 | | |
| C(27)-C(29)-H(29B) | 109.5 | | |
| H(29A)-C(29)-H(29B) | 109.5 | | |
| C(27)-C(29)-H(29C) | 109.5 | | |
| H(29A)-C(29)-H(29C) | 109.5 | | |
| H(29B)-C(29)-H(29C) | 109.5 | | |
| C(26)-C(30)-C(32) | 112.1(3) | | |
| C(26)-C(30)-C(31) | 110.5(3) | | |
| C(32)-C(30)-C(31) | 110.9(3) | | |
| C(26)-C(30)-H(30A) | 107.7 | | |
| C(32)-C(30)-H(30A) | 107.7 | | |

**Table S10.** Anisotropic displacement parameters ($Å^2$ x $10^3$) for ($CDA^{iPr}$)$FeCl_2$ (**2a**) at 200 K. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11}+...+2hka^*b^*U^{12}]$.

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 44(1) | 25(1) | 32(1) | -2(1) | 1(1) | 0(1) |
| Cl(1) | 45(1) | 36(1) | 68(1) | 2(1) | 5(1) | -2(1) |
| Cl(2) | 89(1) | 44(1) | 29(1) | -2(1) | -12(1) | -1(1) |
| N(1) | 52(1) | 31(1) | 27(1) | -4(1) | -1(1) | -4(1) |
| N(2) | 44(1) | 32(1) | 23(1) | 1(1) | 1(1) | 0(1) |
| N(3) | 49(1) | 32(1) | 29(1) | -3(1) | -2(1) | 1(1) |
| N(4) | 37(1) | 27(1) | 27(1) | 0(1) | 2(1) | -1(1) |
| C(1) | 45(1) | 31(1) | 28(1) | 0(1) | 1(1) | -2(1) |
| C(2) | 59(2) | 45(2) | 25(1) | -6(1) | -3(1) | -9(1) |
| C(3) | 45(2) | 55(2) | 26(1) | -1(1) | -3(1) | -1(1) |
| C(4) | 49(2) | 44(2) | 23(1) | 3(1) | 1(1) | 3(1) |
| C(5) | 37(1) | 27(1) | 28(1) | 0(1) | 3(1) | 3(1) |
| C(6) | 62(2) | 29(1) | 38(1) | 6(1) | 1(1) | 0(1) |
| C(7) | 42(1) | 28(1) | 28(1) | 0(1) | -1(1) | -3(1) |
| C(8) | 44(1) | 28(1) | 31(1) | 2(1) | 3(1) | -3(1) |
| C(9) | 53(2) | 36(1) | 41(1) | -8(1) | 5(1) | -1(1) |
| C(10) | 60(2) | 45(2) | 45(2) | -14(1) | -2(1) | -13(1) |
| C(11) | 45(2) | 57(2) | 47(2) | -7(1) | -4(1) | -12(1) |
| C(12) | 42(2) | 44(2) | 34(1) | -1(1) | -1(1) | -5(1) |
| C(13) | 41(1) | 31(1) | 36(1) | -2(1) | 3(1) | -2(1) |
| C(14) | 49(2) | 40(2) | 51(2) | 1(1) | 0(1) | 2(1) |
| C(15) | 50(2) | 64(2) | 44(2) | 6(1) | 7(1) | -9(2) |
| C(16) | 39(2) | 66(2) | 53(2) | -13(2) | -4(1) | 0(1) |
| C(17) | 59(2) | 119(4) | 66(2) | 1(2) | 18(2) | 9(2) |
| C(18) | 48(2) | 79(2) | 77(2) | -9(2) | -12(2) | 10(2) |
| C(19) | 49(2) | 28(1) | 34(1) | -3(1) | 3(1) | -5(1) |
| C(20) | 88(2) | 33(2) | 51(2) | -12(1) | -10(2) | -1(2) |
| C(21) | 58(2) | 34(1) | 34(1) | -3(1) | -2(1) | 4(1) |
| C(22) | 59(2) | 50(2) | 50(2) | -3(1) | -4(1) | 8(2) |
| C(23) | 68(2) | 63(2) | 64(2) | -7(2) | -15(2) | 21(2) |
| C(24) | 88(3) | 46(2) | 46(2) | 0(1) | -13(2) | 19(2) |
| C(25) | 80(2) | 37(2) | 40(2) | 1(1) | -1(2) | 4(2) |
| C(26) | 66(2) | 31(1) | 34(1) | -2(1) | -2(1) | 3(1) |
| C(27) | 55(2) | 70(2) | 88(3) | 8(2) | 7(2) | 9(2) |
| C(28) | 77(3) | 95(3) | 123(4) | -20(3) | 7(3) | -17(3) |
| C(29) | 86(3) | 127(4) | 90(3) | -10(3) | 26(3) | -4(3) |
| C(30) | 62(2) | 36(2) | 52(2) | 8(1) | 8(2) | 2(1) |
| C(31) | 91(3) | 62(2) | 70(2) | 2(2) | 26(2) | 14(2) |
| C(32) | 69(2) | 53(2) | 90(3) | 3(2) | 0(2) | -4(2) |
| C(1S) | 87(3) | 46(2) | 121(4) | 1(2) | -35(3) | -5(2) |
| Cl(3S) | 85(2) | 185(3) | 111(2) | -23(2) | 30(1) | -45(2) |
| Cl(4S) | 64(1) | 71(2) | 89(1) | 6(1) | 15(1) | -3(1) |
| C(2S) | 96(3) | 68(2) | 56(2) | -2(2) | -6(2) | -8(2) |
| Cl(5S) | 78(1) | 167(5) | 90(1) | 1(1) | -5(1) | -21(2) |
| Cl(6S) | 117(2) | 121(2) | 77(1) | -19(1) | 26(1) | 12(2) |

**Figure S11.** ORTEP plot of (CDA$^{i\text{Pr}}$)$FeCl_2$ (**2a**) at 250 K at 50% probability level. Hydrogen atoms and solvent molecules were excluded for clarity.

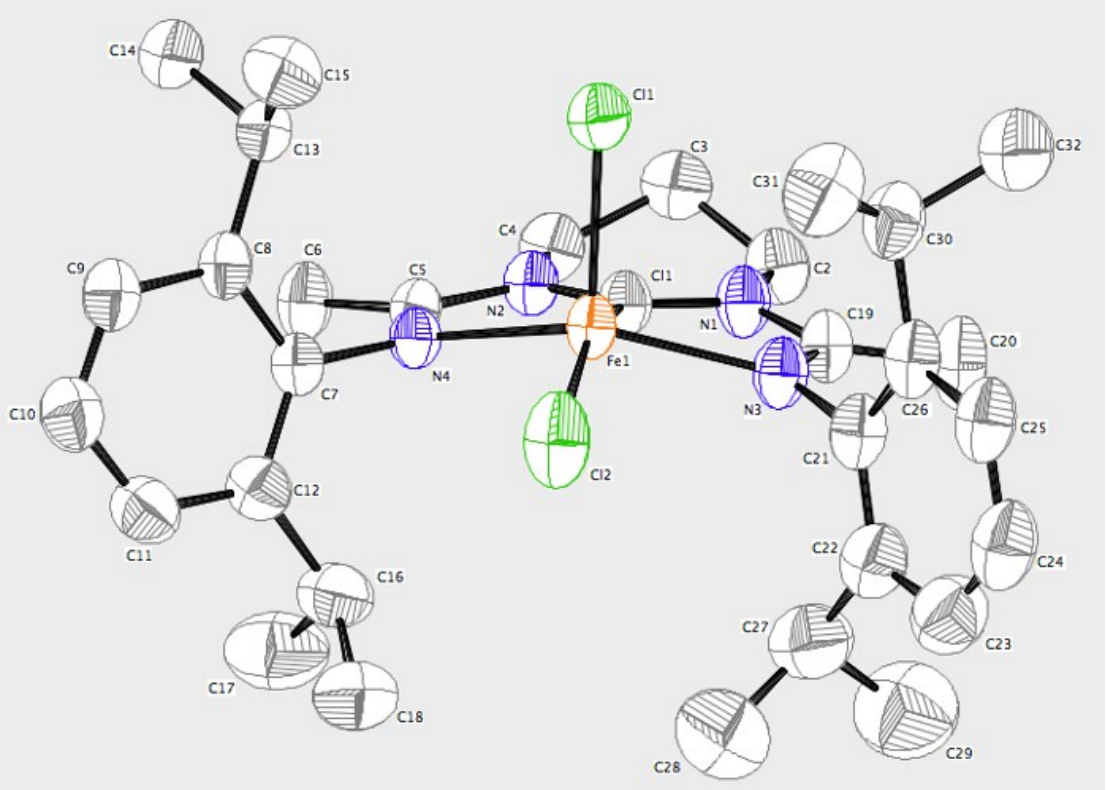


**Table S11.** Bond lengths (Å) and angles (º) for (CDA$^{iPr}$)$FeCl_2$ (**2a**) at 250 K.

| | | | | | |
|---|---|---|---|---|---|
| Fe(1)-C(1) | 1.882(3) | C(11)-H(11A) | 0.9400 | C(27)-C(29) | 1.532(8) |
| Fe(1)-N(3) | 2.103(3) | C(12)-C(16) | 1.510(6) | C(27)-H(27A) | 0.9900 |
| Fe(1)-N(4) | 2.104(2) | C(13)-C(15) | 1.525(5) | C(28)-H(28A) | 0.9700 |
| Fe(1)-Cl(2) | 2.2574(11) | C(13)-C(14) | 1.526(5) | C(28)-H(28B) | 0.9700 |
| Fe(1)-Cl(1) | 2.3214(11) | C(13)-H(13A) | 0.9900 | C(28)-H(28C) | 0.9700 |
| N(1)-C(1) | 1.347(4) | C(14)-H(14A) | 0.9700 | C(29)-H(29A) | 0.9700 |
| N(1)-C(19) | 1.385(4) | C(14)-H(14B) | 0.9700 | C(29)-H(29B) | 0.9700 |
| N(1)-C(2) | 1.470(4) | C(14)-H(14C) | 0.9700 | C(29)-H(29C) | 0.9700 |
| N(2)-C(1) | 1.353(4) | C(15)-H(15A) | 0.9700 | C(30)-C(31) | 1.521(6) |
| N(2)-C(5) | 1.382(4) | C(15)-H(15B) | 0.9700 | C(30)-C(32) | 1.523(7) |
| N(2)-C(4) | 1.474(4) | C(15)-H(15C) | 0.9700 | C(30)-H(30A) | 0.9900 |
| N(3)-C(19) | 1.287(4) | C(16)-C(17) | 1.514(7) | C(31)-H(31A) | 0.9700 |
| N(3)-C(21) | 1.445(5) | C(16)-C(18) | 1.529(6) | C(31)-H(31B) | 0.9700 |
| N(4)-C(5) | 1.289(4) | C(16)-H(16A) | 0.9900 | C(31)-H(31C) | 0.9700 |
| N(4)-C(7) | 1.451(4) | C(17)-H(17A) | 0.9700 | C(32)-H(32A) | 0.9700 |
| C(2)-C(3) | 1.507(5) | C(17)-H(17B) | 0.9700 | C(32)-H(32B) | 0.9700 |
| C(2)-H(2A) | 0.9800 | C(17)-H(17C) | 0.9700 | C(32)-H(32C) | 0.9700 |
| C(2)-H(2B) | 0.9800 | C(18)-H(18A) | 0.9700 | C(1S)-Cl(3S) | 1.659(9) |
| C(3)-C(4) | 1.512(5) | C(18)-H(18B) | 0.9700 | C(1S)-Cl(4S) | 1.843(7) |
| C(3)-H(3A) | 0.9800 | C(18)-H(18C) | 0.9700 | C(1S)-H(1S1) | 0.9800 |
| C(3)-H(3B) | 0.9800 | C(19)-C(20) | 1.496(5) | C(1S)-H(1S2) | 0.9800 |
| C(4)-H(4A) | 0.9800 | C(20)-H(20A) | 0.9700 | C(2S)-Cl(5S) | 1.689(7) |
| C(4)-H(4B) | 0.9800 | C(20)-H(20B) | 0.9700 | C(2S)-Cl(6S) | 1.761(7) |
| C(5)-C(6) | 1.492(4) | C(20)-H(20C) | 0.9700 | C(2S)-H(2S1) | 0.9800 |
| C(6)-H(6A) | 0.9700 | C(21)-C(26) | 1.398(6) | C(2S)-H(2S2) | 0.9800 |
| C(6)-H(6B) | 0.9700 | C(21)-C(22) | 1.401(6) | C(1)-Fe(1)-N(3) | 76.21(12) |
| C(6)-H(6C) | 0.9700 | C(22)-C(23) | 1.391(6) | C(1)-Fe(1)-N(4) | 76.34(11) |
| C(7)-C(8) | 1.398(5) | C(22)-C(27) | 1.524(7) | N(3)-Fe(1)-N(4) | 145.23(10) |
| C(7)-C(12) | 1.400(5) | C(23)-C(24) | 1.373(7) | C(1)-Fe(1)-Cl(2) | 154.88(11) |
| C(8)-C(9) | 1.405(5) | C(23)-H(23A) | 0.9400 | N(3)-Fe(1)-Cl(2) | 95.90(8) |
| C(8)-C(13) | 1.514(5) | C(24)-C(25) | 1.359(7) | N(4)-Fe(1)-Cl(2) | 99.97(8) |
| C(9)-C(10) | 1.355(6) | C(24)-H(24A) | 0.9400 | C(1)-Fe(1)-Cl(1) | 94.92(11) |
| C(9)-H(9A) | 0.9400 | C(25)-C(26) | 1.394(5) | N(3)-Fe(1)-Cl(1) | 102.46(9) |
| C(10)-C(11) | 1.381(6) | C(25)-H(25A) | 0.9400 | N(4)-Fe(1)-Cl(1) | 100.77(8) |
| C(10)-H(10A) | 0.9400 | C(26)-C(30) | 1.508(6) | Cl(2)-Fe(1)-Cl(1) | 110.13(5) |
| C(11)-C(12) | 1.387(5) | C(27)-C(28) | 1.518(9) | C(1)-N(1)-C(19) | 112.7(3) |

| | | | | | |
|---|---|---|---|---|---|
| C(1)-N(1)-C(2) | 123.2(3) | H(6A)-C(6)-H(6B) | 109.5 | C(13)-C(15)-H(15C) | 109.5 |
| C(19)-N(1)-C(2) | 123.9(3) | C(5)-C(6)-H(6C) | 109.5 | H(15A)-C(15)-H(15C) | 109.5 |
| C(1)-N(2)-C(5) | 112.6(2) | H(6A)-C(6)-H(6C) | 109.5 | H(15B)-C(15)-H(15C) | 109.5 |
| C(1)-N(2)-C(4) | 122.9(3) | H(6B)-C(6)-H(6C) | 109.5 | C(12)-C(16)-C(17) | 110.9(4) |
| C(5)-N(2)-C(4) | 124.4(3) | C(8)-C(7)-C(12) | 122.0(3) | C(12)-C(16)-C(18) | 112.0(4) |
| C(19)-N(3)-C(21) | 119.3(3) | C(8)-C(7)-N(4) | 119.2(3) | C(17)-C(16)-C(18) | 110.6(4) |
| C(19)-N(3)-Fe(1) | 113.5(2) | C(12)-C(7)-N(4) | 118.8(3) | C(12)-C(16)-H(16A) | 107.7 |
| C(21)-N(3)-Fe(1) | 127.1(2) | C(7)-C(8)-C(9) | 117.2(3) | C(17)-C(16)-H(16A) | 107.7 |
| C(5)-N(4)-C(7) | 118.9(3) | C(7)-C(8)-C(13) | 123.6(3) | C(18)-C(16)-H(16A) | 107.7 |
| C(5)-N(4)-Fe(1) | 113.4(2) | C(9)-C(8)-C(13) | 119.2(3) | C(16)-C(17)-H(17A) | 109.5 |
| C(7)-N(4)-Fe(1) | 127.45(19) | C(10)-C(9)-C(8) | 121.8(4) | C(16)-C(17)-H(17B) | 109.5 |
| N(1)-C(1)-N(2) | 119.6(3) | C(10)-C(9)-H(9A) | 119.1 | H(17A)-C(17)-H(17B) | 109.5 |
| N(1)-C(1)-Fe(1) | 120.1(2) | C(8)-C(9)-H(9A) | 119.1 | C(16)-C(17)-H(17C) | 109.5 |
| N(2)-C(1)-Fe(1) | 120.2(2) | C(9)-C(10)-C(11) | 119.8(3) | H(17A)-C(17)-H(17C) | 109.5 |
| N(1)-C(2)-C(3) | 108.7(3) | C(9)-C(10)-H(10A) | 120.1 | H(17B)-C(17)-H(17C) | 109.5 |
| N(1)-C(2)-H(2A) | 110.0 | C(11)-C(10)-H(10A) | 120.1 | C(16)-C(18)-H(18A) | 109.5 |
| C(3)-C(2)-H(2A) | 110.0 | C(10)-C(11)-C(12) | 121.7(4) | C(16)-C(18)-H(18B) | 109.5 |
| N(1)-C(2)-H(2B) | 110.0 | C(10)-C(11)-H(11A) | 119.2 | H(18A)-C(18)-H(18B) | 109.5 |
| C(3)-C(2)-H(2B) | 110.0 | C(12)-C(11)-H(11A) | 119.2 | C(16)-C(18)-H(18C) | 109.5 |
| H(2A)-C(2)-H(2B) | 108.3 | C(11)-C(12)-C(7) | 117.5(3) | H(18A)-C(18)-H(18C) | 109.5 |
| C(2)-C(3)-C(4) | 111.0(3) | C(11)-C(12)-C(16) | 120.1(3) | H(18B)-C(18)-H(18C) | 109.5 |
| C(2)-C(3)-H(3A) | 109.4 | C(7)-C(12)-C(16) | 122.4(3) | N(3)-C(19)-N(1) | 115.6(3) |
| C(4)-C(3)-H(3A) | 109.4 | C(8)-C(13)-C(15) | 111.3(3) | N(3)-C(19)-C(20) | 126.5(3) |
| C(2)-C(3)-H(3B) | 109.4 | C(8)-C(13)-C(14) | 112.2(3) | N(1)-C(19)-C(20) | 117.9(3) |
| C(4)-C(3)-H(3B) | 109.4 | C(15)-C(13)-C(14) | 110.1(3) | C(19)-C(20)-H(20A) | 109.5 |
| H(3A)-C(3)-H(3B) | 108.0 | C(8)-C(13)-H(13A) | 107.7 | C(19)-C(20)-H(20B) | 109.5 |
| N(2)-C(4)-C(3) | 108.3(3) | C(15)-C(13)-H(13A) | 107.7 | H(20A)-C(20)-H(20B) | 109.5 |
| N(2)-C(4)-H(4A) | 110.0 | C(14)-C(13)-H(13A) | 107.7 | C(19)-C(20)-H(20C) | 109.5 |
| C(3)-C(4)-H(4A) | 110.0 | C(13)-C(14)-H(14A) | 109.5 | H(20A)-C(20)-H(20C) | 109.5 |
| N(2)-C(4)-H(4B) | 110.0 | C(13)-C(14)-H(14B) | 109.5 | H(20B)-C(20)-H(20C) | 109.5 |
| C(3)-C(4)-H(4B) | 110.0 | H(14A)-C(14)-H(14B) | 109.5 | C(26)-C(21)-C(22) | 121.9(4) |
| H(4A)-C(4)-H(4B) | 108.4 | C(13)-C(14)-H(14C) | 109.5 | C(26)-C(21)-N(3) | 119.6(4) |
| N(4)-C(5)-N(2) | 116.0(3) | H(14A)-C(14)-H(14C) | 109.5 | C(22)-C(21)-N(3) | 118.5(3) |
| N(4)-C(5)-C(6) | 126.2(3) | H(14B)-C(14)-H(14C) | 109.5 | C(23)-C(22)-C(21) | 117.1(4) |
| N(2)-C(5)-C(6) | 117.8(3) | C(13)-C(15)-H(15A) | 109.5 | C(23)-C(22)-C(27) | 120.4(5) |
| C(5)-C(6)-H(6A) | 109.5 | C(13)-C(15)-H(15B) | 109.5 | C(21)-C(22)-C(27) | 122.5(4) |
| C(5)-C(6)-H(6B) | 109.5 | H(15A)-C(15)-H(15B) | 109.5 | C(24)-C(23)-C(22) | 121.9(5) |

| | | | |
|---|---|---|---|
| C(24)-C(23)-H(23A) | 119.0 | H(31A)-C(31)-H(31B) | 109.5 |
| C(22)-C(23)-H(23A) | 119.0 | C(30)-C(31)-H(31C) | 109.5 |
| C(25)-C(24)-C(23) | 119.8(4) | H(31A)-C(31)-H(31C) | 109.5 |
| C(25)-C(24)-H(24A) | 120.1 | H(31B)-C(31)-H(31C) | 109.5 |
| C(23)-C(24)-H(24A) | 120.1 | C(30)-C(32)-H(32A) | 109.5 |
| C(24)-C(25)-C(26) | 121.7(4) | C(30)-C(32)-H(32B) | 109.5 |
| C(24)-C(25)-H(25A) | 119.1 | H(32A)-C(32)-H(32B) | 109.5 |
| C(26)-C(25)-H(25A) | 119.1 | C(30)-C(32)-H(32C) | 109.5 |
| C(25)-C(26)-C(21) | 117.6(4) | H(32A)-C(32)-H(32C) | 109.5 |
| C(25)-C(26)-C(30) | 119.2(4) | H(32B)-C(32)-H(32C) | 109.5 |
| C(21)-C(26)-C(30) | 123.3(3) | Cl(3S)-C(1S)-Cl(4S) | 110.3(3) |
| C(28)-C(27)-C(22) | 111.2(5) | Cl(3S)-C(1S)-H(1S1) | 109.6 |
| C(28)-C(27)-C(29) | 109.9(5) | Cl(4S)-C(1S)-H(1S1) | 109.6 |
| C(22)-C(27)-C(29) | 111.8(5) | Cl(3S)-C(1S)-H(1S2) | 109.6 |
| C(28)-C(27)-H(27A) | 107.9 | Cl(4S)-C(1S)-H(1S2) | 109.6 |
| C(22)-C(27)-H(27A) | 107.9 | H(1S1)-C(1S)-H(1S2) | 108.1 |
| C(29)-C(27)-H(27A) | 107.9 | Cl(5S)-C(2S)-Cl(6S) | 113.8(4) |
| C(27)-C(28)-H(28A) | 109.5 | Cl(5S)-C(2S)-H(2S1) | 108.8 |
| C(27)-C(28)-H(28B) | 109.5 | Cl(6S)-C(2S)-H(2S1) | 108.8 |
| H(28A)-C(28)-H(28B) | 109.5 | Cl(5S)-C(2S)-H(2S2) | 108.8 |
| C(27)-C(28)-H(28C) | 109.5 | Cl(6S)-C(2S)-H(2S2) | 108.8 |
| H(28A)-C(28)-H(28C) | 109.5 | H(2S1)-C(2S)-H(2S2) | 107.7 |
| H(28B)-C(28)-H(28C) | 109.5 | | |
| C(27)-C(29)-H(29A) | 109.5 | | |
| C(27)-C(29)-H(29B) | 109.5 | | |
| H(29A)-C(29)-H(29B) | 109.5 | | |
| C(27)-C(29)-H(29C) | 109.5 | | |
| H(29A)-C(29)-H(29C) | 109.5 | | |
| H(29B)-C(29)-H(29C) | 109.5 | | |
| C(26)-C(30)-C(31) | 110.0(4) | | |
| C(26)-C(30)-C(32) | 112.1(4) | | |
| C(31)-C(30)-C(32) | 112.2(4) | | |
| C(26)-C(30)-H(30A) | 107.4 | | |
| C(31)-C(30)-H(30A) | 107.4 | | |
| C(32)-C(30)-H(30A) | 107.4 | | |
| C(30)-C(31)-H(31A) | 109.5 | | |
| C(30)-C(31)-H(31B) | 109.5 | | |

**Table S12.** Anisotropic displacement parameters ($Å^2$ x $10^3$) for ($CDA^{iPr}$)$FeCl_2$ (**2a**) at 250 K. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11}+...+2hka^*b^*U^{12}]$.

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 55(1) | 30(1) | 42(1) | -2(1) | 1(1) | -1(1) |
| Cl(1) | 56(1) | 45(1) | 89(1) | 2(1) | 8(1) | -4(1) |
| Cl(2) | 118(1) | 56(1) | 38(1) | -2(1) | -15(1) | -2(1) |
| N(1) | 64(2) | 38(1) | 34(1) | -5(1) | 0(1) | -5(1) |
| N(2) | 52(2) | 38(1) | 30(1) | 0(1) | 0(1) | -1(1) |
| N(3) | 65(2) | 39(1) | 37(1) | -5(1) | 0(1) | 0(1) |
| N(4) | 46(2) | 33(1) | 34(1) | 2(1) | 1(1) | -2(1) |
| C(1) | 54(2) | 36(2) | 35(2) | -2(1) | -1(1) | -3(1) |
| C(2) | 72(2) | 56(2) | 32(2) | -8(2) | -4(2) | -10(2) |
| C(3) | 59(2) | 66(2) | 31(2) | 0(2) | -3(2) | -1(2) |
| C(4) | 62(2) | 53(2) | 30(2) | 6(1) | 2(1) | 3(2) |
| C(5) | 45(2) | 32(2) | 37(2) | 2(1) | 4(1) | 2(1) |
| C(6) | 80(3) | 36(2) | 46(2) | 6(1) | 2(2) | -2(2) |
| C(7) | 50(2) | 35(2) | 37(2) | -1(1) | 1(1) | -4(1) |
| C(8) | 57(2) | 35(2) | 40(2) | 1(1) | 4(2) | -4(1) |
| C(9) | 66(2) | 45(2) | 51(2) | -11(2) | 5(2) | -3(2) |
| C(10) | 70(3) | 56(2) | 60(2) | -17(2) | 0(2) | -12(2) |
| C(11) | 55(2) | 66(2) | 61(2) | -10(2) | -4(2) | -14(2) |
| C(12) | 52(2) | 56(2) | 44(2) | -4(2) | -1(2) | -6(2) |
| C(13) | 50(2) | 40(2) | 43(2) | -3(1) | 4(2) | 0(1) |
| C(14) | 61(2) | 50(2) | 67(2) | 0(2) | 0(2) | 3(2) |
| C(15) | 64(3) | 81(3) | 56(2) | 8(2) | 10(2) | -14(2) |
| C(16) | 52(2) | 80(3) | 65(2) | -15(2) | -3(2) | -3(2) |
| C(17) | 75(3) | 142(5) | 82(3) | -1(3) | 21(3) | 9(3) |
| C(18) | 62(3) | 94(4) | 104(4) | -10(3) | -18(3) | 14(2) |
| C(19) | 65(2) | 35(2) | 41(2) | -5(1) | 3(2) | -8(2) |
| C(20) | 111(4) | 39(2) | 67(3) | -15(2) | -12(2) | -4(2) |
| C(21) | 74(3) | 41(2) | 43(2) | -3(1) | -4(2) | 3(2) |
| C(22) | 74(3) | 57(2) | 64(2) | -1(2) | -5(2) | 9(2) |
| C(23) | 83(3) | 74(3) | 84(3) | -4(3) | -16(3) | 20(3) |
| C(24) | 107(4) | 54(2) | 62(3) | 1(2) | -15(3) | 19(2) |
| C(25) | 95(3) | 44(2) | 53(2) | 3(2) | -1(2) | 6(2) |
| C(26) | 80(3) | 38(2) | 47(2) | -2(2) | -1(2) | 0(2) |
| C(27) | 71(3) | 85(3) | 113(4) | 8(3) | 14(3) | 8(3) |
| C(28) | 99(5) | 118(5) | 152(6) | -21(5) | 12(4) | -28(4) |
| C(29) | 116(5) | 145(6) | 112(5) | -10(4) | 36(4) | -1(4) |
| C(30) | 77(3) | 44(2) | 65(2) | 11(2) | 14(2) | 1(2) |
| C(31) | 113(4) | 79(3) | 91(4) | 2(3) | 32(3) | 19(3) |
| C(32) | 85(3) | 67(3) | 112(4) | 3(3) | 3(3) | -3(3) |
| C(1S) | 107(4) | 61(3) | 148(5) | 2(3) | -41(4) | -11(3) |
| Cl(3S) | 101(2) | 218(5) | 139(2) | -30(3) | 39(2) | -45(2) |
| Cl(4S) | 82(1) | 94(2) | 114(2) | 9(1) | 20(1) | -2(1) |
| C(2S) | 128(5) | 93(4) | 76(3) | -8(3) | -12(3) | -7(3) |
| Cl(5S) | 96(2) | 178(6) | 116(2) | 6(2) | -11(1) | -23(2) |
| Cl(6S) | 159(4) | 219(5) | 116(2) | -42(3) | 47(3) | -4(4) |

## 11. Variable Temperature X-ray Crystallography Data for [(CDA$^{i\text{Pr}}$)$FeCl_2$]$BF_4$ (3)

**Table S13.** Variable temperature X-ray data for [(CDA$^{i\text{Pr}}$)$FeCl_2$]$BF_4$ (**3**).

| | 80 K | 150 K | 200 K | 298 K |
|---|---|---|---|---|
| Identification code<br>CCDC | C32H46BCl2F4FeN4_80K<br>927790 | C32H46BCl2F4FeN4_150K<br>927792 | C32H46BCl2F4FeN4_200K<br>927793 | C32H46BCl2F4FeN4_298K<br>927794 |
| Empirical formula | $C_{32}H_{46}BCl_2F_4FeN_4$ | $C_{32}H_{46}BCl_2F_4FeN_4$ | $C_{32}H_{46}BCl_2F_4FeN_4$ | $C_{32}H_{46}BCl_2F_4FeN_4$ |
| Formula weight | 700.29 | 700.29 | 700.29 | 700.29 |
| Temperature | 80(2) K | 150(2) K | 200(2) K | 298(2) K |
| Wavelength | 0.71073 Å | 1.54178 Å | 0.71073 Å | 1.54178 Å |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | P 2(1)/c | P 2(1)/c | P 2(1)/c | P 2(1)/c |
| Unit cell dimensions | a = 18.6409(8) Å α = 90°<br>b = 13.2744(6) Å β = 115.405(2)°<br>c = 18.8709(8) Å γ = 90° | a = 18.8421(7) Å α = 90°<br>b = 13.3315(5) Å β = 115.841(2)°<br>c = 18.9846(7) Å γ = 90° | a = 19.0241(11) Å α = 90°<br>b = 13.3780(9) Å β = 116.142(3)°<br>c = 19.0251(12) Å γ = 90° | a = 19.2475(3) Å α = 90°<br>b = 13.5333(2) Å β = 116.9130(10)°<br>c = 19.2087(2) Å γ = 90° |
| Volume | 4218.0(3) Å$^3$ | 4292.0(3) Å$^3$ | 4346.7(5) Å$^3$ | 4461.62(11) Å$^3$ |
| Z | 4 | 4 | 4 | 4 |
| Density (calculated) | 1.103 Mg/m$^3$ | 1.084 Mg/m$^3$ | 1.070 Mg/m$^3$ | 1.043 Mg/m$^3$ |
| Absorption coefficient | 0.525 mm$^{-1}$ | 4.298 mm$^{-1}$ | 0.509 mm$^{-1}$ | 4.134 mm$^{-1}$ |
| F(000) | 1468 | 1468 | 1468 | 1468 |
| Crystal size | 0.18 x 0.12 x 0.10 mm$^3$ | 0.20 x 0.14 x 0.10 mm$^3$ | 0.18 x 0.12 x 0.10 mm$^3$ | 0.18 x 0.12 x 0.10 mm$^3$ |
| Theta range for data collection | 1.94 to 28.33° | 2.61 to 66.40° | 1.93 to 28.37° | 2.57 to 66.38° |
| Index ranges | $-24\le h\le 22$, $0\le k\le 17$, $0\le l\le 25$ | $-22\le h\le 19$, $0\le k\le 15$, $0\le l\le 22$ | $-25\le h\le 22$, $0\le k\le 17$, $0\le l\le 25$ | $-22\le h\le 20$, $0\le k\le 15$, $0\le l\le 22$ |
| Reflections collected | 10497 | 7441 | 10806 | 7616 |
| Independent reflections | 10497 [$R_{int}$ = 0.0000] | 7441 [$R_{int}$ = 0.0000] | 10806 [$R_{int}$ = 0.0000] | 7616 [$R_{int}$ = 0.0000] |
| Completeness to θ = 32.15/66.36° | 99.8 % | 98.3 % | 99.4 % | 97.1 % |
| Max. and min. transmission | 0.9494 and 0.9115 | 0.6732 and 0.4803 | 0.9508 and 0.9139 | 0.6826 and 0.5232 |
| Data / restraints / parameters | 10497 / 1 / 418 | 7441 / 1 / 418 | 10806 / 1 / 418 | 7616 / 41 / 425 |
| Goodness-of-fit on $F^2$ | 1.014 | 1.046 | 0.940 | 0.961 |
| Final R indices [I>2σ(I)] | R1 = 0.0450, ω$R_2$= 0.1036 | R1 = 0.0389, ω$R_2$= 0.1027 | R1 = 0.0523, ω$R_2$= 0.1285 | R1 = 0.0473, ω$R_2$= 0.1236 |
| R indices (all data) | R1 = 0.0771, ω$R_2$= 0.1120 | R1 = 0.0452, ω$R_2$= 0.1062 | R1 = 0.1027, ω$R_2$= 0.1419 | R1 = 0.0821, ω$R_2$= 0.1352 |
| Largest diff. peak and hole | 0.598 and −0.364 e.Å$^{-3}$ | 0.525 and −0.236 e.Å$^{-3}$ | 0.480 and −0.319 e.Å$^{-3}$ | 0.238 and −0.260 e.Å$^{-3}$ |

**Figure S12.** ORTEP plot of [(CDA$^{i\text{Pr}}$)$FeCl_2$]$BF_4$ (**3**) at 80 K at 50% probability level. Hydrogen atoms, solvent molecules, and counterion were excluded for clarity.

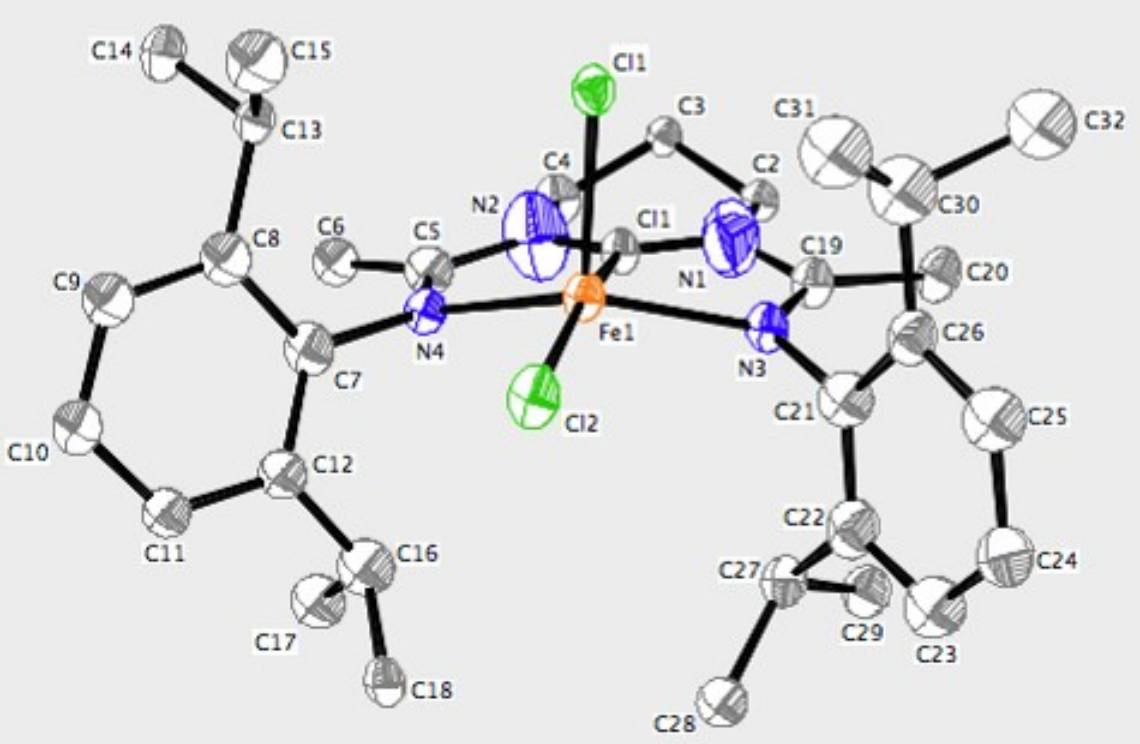



**Table S14.** Bond lengths (Å) and angles (º) for [(CDA$^{i\text{Pr}}$)$FeCl_2$]$BF_4$ (**3**) at 80 K.

| | | | | | |
|---|---|---|---|---|---|
| Fe(1)-C(1) | 1.9081(19) | C(10)-H(10) | 0.9500 | C(26)-C(30) | 1.503(3) |
| Fe(1)-N(3) | 2.0242(15) | C(11)-C(12) | 1.392(3) | C(27)-C(28) | 1.512(3) |
| Fe(1)-N(4) | 2.0388(16) | C(11)-H(11) | 0.9500 | C(27)-C(29) | 1.519(3) |
| Fe(1)-Cl(2) | 2.168(4) | C(12)-C(16) | 1.514(3) | C(27)-H(27) | 1.0000 |
| Fe(1)-Cl(2X) | 2.211(12) | C(13)-C(15) | 1.524(3) | C(28)-H(28A) | 0.9800 |
| Fe(1)-Cl(1X) | 2.254(9) | C(13)-C(14) | 1.532(3) | C(28)-H(28B) | 0.9800 |
| Fe(1)-Cl(1) | 2.264(2) | C(13)-H(13) | 1.0000 | C(28)-H(28C) | 0.9800 |
| N(1)-C(1) | 1.341(2) | C(14)-H(14A) | 0.9800 | C(29)-H(29A) | 0.9800 |
| N(1)-C(19) | 1.390(2) | C(14)-H(14B) | 0.9800 | C(29)-H(29B) | 0.9800 |
| N(1)-C(2) | 1.482(2) | C(14)-H(14C) | 0.9800 | C(29)-H(29C) | 0.9800 |
| N(2)-C(1) | 1.327(2) | C(15)-H(15A) | 0.9800 | C(30)-C(31) | 1.527(3) |
| N(2)-C(5) | 1.386(2) | C(15)-H(15B) | 0.9800 | C(30)-C(32) | 1.537(3) |
| N(2)-C(4) | 1.480(2) | C(15)-H(15C) | 0.9800 | C(30)-H(30) | 1.0000 |
| N(3)-C(19) | 1.289(2) | C(16)-C(17) | 1.527(3) | C(31)-H(31A) | 0.9800 |
| N(3)-C(21) | 1.448(2) | C(16)-C(18) | 1.528(3) | C(31)-H(31B) | 0.9800 |
| N(4)-C(5) | 1.292(2) | C(16)-H(16) | 1.0000 | C(31)-H(31C) | 0.9800 |
| N(4)-C(7) | 1.450(2) | C(17)-H(17A) | 0.9800 | C(32)-H(32A) | 0.9800 |
| C(2)-C(3) | 1.512(3) | C(17)-H(17B) | 0.9800 | C(32)-H(32B) | 0.9800 |
| C(2)-H(2A) | 0.9900 | C(17)-H(17C) | 0.9800 | C(32)-H(32C) | 0.9800 |
| C(2)-H(2B) | 0.9900 | C(18)-H(18A) | 0.9800 | B(1)-F(3) | 1.376(3) |
| C(3)-C(4) | 1.514(3) | C(18)-H(18B) | 0.9800 | B(1)-F(1) | 1.387(3) |
| C(3)-H(3A) | 0.9900 | C(18)-H(18C) | 0.9800 | B(1)-F(4) | 1.396(3) |
| C(3)-H(3B) | 0.9900 | C(19)-C(20) | 1.478(3) | B(1)-F(2) | 1.399(3) |
| C(4)-H(4A) | 0.9900 | C(20)-H(20A) | 0.9800 | C(1)-Fe(1)-N(3) | 76.69(7) |
| C(4)-H(4B) | 0.9900 | C(20)-H(20B) | 0.9800 | C(1)-Fe(1)-N(4) | 76.40(7) |
| C(5)-C(6) | 1.480(3) | C(20)-H(20C) | 0.9800 | N(3)-Fe(1)-N(4) | 144.71(7) |
| C(6)-H(6A) | 0.9800 | C(21)-C(22) | 1.400(3) | C(1)-Fe(1)-Cl(2) | 167.61(10) |
| C(6)-H(6B) | 0.9800 | C(21)-C(26) | 1.404(3) | N(3)-Fe(1)-Cl(2) | 101.98(11) |
| C(6)-H(6C) | 0.9800 | C(22)-C(23) | 1.394(3) | N(4)-Fe(1)-Cl(2) | 99.46(12) |
| C(7)-C(12) | 1.403(3) | C(22)-C(27) | 1.519(3) | C(1)-Fe(1)-Cl(2X) | 158.5(6) |
| C(7)-C(8) | 1.406(3) | C(23)-C(24) | 1.387(3) | N(3)-Fe(1)-Cl(2X) | 101.2(3) |
| C(8)-C(9) | 1.391(3) | C(23)-H(23) | 0.9500 | N(4)-Fe(1)-Cl(2X) | 95.6(4) |
| C(8)-C(13) | 1.519(3) | C(24)-C(25) | 1.382(3) | Cl(2)-Fe(1)-Cl(2X) | 9.2(6) |
| C(9)-C(10) | 1.378(3) | C(24)-H(24) | 0.9500 | C(1)-Fe(1)-Cl(1X) | 94.8(6) |
| C(9)-H(9) | 0.9500 | C(25)-C(26) | 1.396(3) | N(3)-Fe(1)-Cl(1X) | 101.6(3) |
| C(10)-C(11) | 1.384(3) | C(25)-H(25) | 0.9500 | N(4)-Fe(1)-Cl(1X) | 103.0(2) |

| | | | | | |
|---|---|---|---|---|---|
| Cl(2)-Fe(1)-Cl(1X) | 97.5(6) | C(3)-C(4)-H(4A) | 110.0 | C(13)-C(14)-H(14A) | 109.5 |
| Cl(2X)-Fe(1)-Cl(1X) | 106.5(3) | N(2)-C(4)-H(4B) | 110.0 | C(13)-C(14)-H(14B) | 109.5 |
| C(1)-Fe(1)-Cl(1) | 86.65(8) | C(3)-C(4)-H(4B) | 110.0 | H(14A)-C(14)-H(14B) | 109.5 |
| N(3)-Fe(1)-Cl(1) | 97.62(8) | H(4A)-C(4)-H(4B) | 108.4 | C(13)-C(14)-H(14C) | 109.5 |
| N(4)-Fe(1)-Cl(1) | 103.15(8) | N(4)-C(5)-N(2) | 114.46(16) | H(14A)-C(14)-H(14C) | 109.5 |
| Cl(2)-Fe(1)-Cl(1) | 105.70(9) | N(4)-C(5)-C(6) | 127.45(18) | H(14B)-C(14)-H(14C) | 109.5 |
| Cl(2X)-Fe(1)-Cl(1) | 114.8(6) | N(2)-C(5)-C(6) | 118.08(16) | C(13)-C(15)-H(15A) | 109.5 |
| Cl(1X)-Fe(1)-Cl(1) | 8.4(6) | C(5)-C(6)-H(6A) | 109.5 | C(13)-C(15)-H(15B) | 109.5 |
| C(1)-N(1)-C(19) | 112.70(15) | C(5)-C(6)-H(6B) | 109.5 | H(15A)-C(15)-H(15B) | 109.5 |
| C(1)-N(1)-C(2) | 122.05(16) | H(6A)-C(6)-H(6B) | 109.5 | C(13)-C(15)-H(15C) | 109.5 |
| C(19)-N(1)-C(2) | 124.39(16) | C(5)-C(6)-H(6C) | 109.5 | H(15A)-C(15)-H(15C) | 109.5 |
| C(1)-N(2)-C(5) | 113.12(15) | H(6A)-C(6)-H(6C) | 109.5 | H(15B)-C(15)-H(15C) | 109.5 |
| C(1)-N(2)-C(4) | 122.08(15) | H(6B)-C(6)-H(6C) | 109.5 | C(12)-C(16)-C(17) | 110.07(18) |
| C(5)-N(2)-C(4) | 124.56(15) | C(12)-C(7)-C(8) | 122.66(18) | C(12)-C(16)-C(18) | 112.27(19) |
| C(19)-N(3)-C(21) | 120.08(16) | C(12)-C(7)-N(4) | 118.05(18) | C(17)-C(16)-C(18) | 110.5(2) |
| C(19)-N(3)-Fe(1) | 115.67(13) | C(8)-C(7)-N(4) | 119.23(18) | C(12)-C(16)-H(16) | 107.9 |
| C(21)-N(3)-Fe(1) | 124.26(12) | C(9)-C(8)-C(7) | 117.06(19) | C(17)-C(16)-H(16) | 107.9 |
| C(5)-N(4)-C(7) | 119.98(16) | C(9)-C(8)-C(13) | 119.26(19) | C(18)-C(16)-H(16) | 107.9 |
| C(5)-N(4)-Fe(1) | 115.48(13) | C(7)-C(8)-C(13) | 123.67(18) | C(16)-C(17)-H(17A) | 109.5 |
| C(7)-N(4)-Fe(1) | 123.85(12) | C(10)-C(9)-C(8) | 121.9(2) | C(16)-C(17)-H(17B) | 109.5 |
| N(2)-C(1)-N(1) | 122.32(16) | C(10)-C(9)-H(9) | 119.1 | H(17A)-C(17)-H(17B) | 109.5 |
| N(2)-C(1)-Fe(1) | 119.39(13) | C(8)-C(9)-H(9) | 119.1 | C(16)-C(17)-H(17C) | 109.5 |
| N(1)-C(1)-Fe(1) | 118.29(13) | C(9)-C(10)-C(11) | 119.5(2) | H(17A)-C(17)-H(17C) | 109.5 |
| N(1)-C(2)-C(3) | 107.81(16) | C(9)-C(10)-H(10) | 120.2 | H(17B)-C(17)-H(17C) | 109.5 |
| N(1)-C(2)-H(2A) | 110.1 | C(11)-C(10)-H(10) | 120.2 | C(16)-C(18)-H(18A) | 109.5 |
| C(3)-C(2)-H(2A) | 110.1 | C(10)-C(11)-C(12) | 121.8(2) | C(16)-C(18)-H(18B) | 109.5 |
| N(1)-C(2)-H(2B) | 110.1 | C(10)-C(11)-H(11) | 119.1 | H(18A)-C(18)-H(18B) | 109.5 |
| C(3)-C(2)-H(2B) | 110.1 | C(12)-C(11)-H(11) | 119.1 | C(16)-C(18)-H(18C) | 109.5 |
| H(2A)-C(2)-H(2B) | 108.5 | C(11)-C(12)-C(7) | 117.0(2) | H(18A)-C(18)-H(18C) | 109.5 |
| C(2)-C(3)-C(4) | 111.84(17) | C(11)-C(12)-C(16) | 119.0(2) | H(18B)-C(18)-H(18C) | 109.5 |
| C(2)-C(3)-H(3A) | 109.2 | C(7)-C(12)-C(16) | 123.97(18) | N(3)-C(19)-N(1) | 114.37(17) |
| C(4)-C(3)-H(3A) | 109.2 | C(8)-C(13)-C(15) | 109.80(18) | N(3)-C(19)-C(20) | 127.25(18) |
| C(2)-C(3)-H(3B) | 109.2 | C(8)-C(13)-C(14) | 111.33(17) | N(1)-C(19)-C(20) | 118.37(16) |
| C(4)-C(3)-H(3B) | 109.2 | C(15)-C(13)-C(14) | 110.80(18) | C(19)-C(20)-H(20A) | 109.5 |
| H(3A)-C(3)-H(3B) | 107.9 | C(8)-C(13)-H(13) | 108.3 | C(19)-C(20)-H(20B) | 109.5 |
| N(2)-C(4)-C(3) | 108.29(16) | C(15)-C(13)-H(13) | 108.3 | H(20A)-C(20)-H(20B) | 109.5 |
| N(2)-C(4)-H(4A) | 110.0 | C(14)-C(13)-H(13) | 108.3 | C(19)-C(20)-H(20C) | 109.5 |

| | | | |
|---|---|---|---|
| H(20A)-C(20)-H(20C) | 109.5 | H(29A)-C(29)-H(29C) | 109.5 |
| H(20B)-C(20)-H(20C) | 109.5 | H(29B)-C(29)-H(29C) | 109.5 |
| C(22)-C(21)-C(26) | 123.40(18) | C(26)-C(30)-C(31) | 111.15(18) |
| C(22)-C(21)-N(3) | 116.61(18) | C(26)-C(30)-C(32) | 110.99(18) |
| C(26)-C(21)-N(3) | 119.96(18) | C(31)-C(30)-C(32) | 110.78(19) |
| C(23)-C(22)-C(21) | 117.45(19) | C(26)-C(30)-H(30) | 107.9 |
| C(23)-C(22)-C(27) | 120.82(19) | C(31)-C(30)-H(30) | 107.9 |
| C(21)-C(22)-C(27) | 121.68(18) | C(32)-C(30)-H(30) | 107.9 |
| C(24)-C(23)-C(22) | 120.5(2) | C(30)-C(31)-H(31A) | 109.5 |
| C(24)-C(23)-H(23) | 119.8 | C(30)-C(31)-H(31B) | 109.5 |
| C(22)-C(23)-H(23) | 119.8 | H(31A)-C(31)-H(31B) | 109.5 |
| C(25)-C(24)-C(23) | 120.6(2) | C(30)-C(31)-H(31C) | 109.5 |
| C(25)-C(24)-H(24) | 119.7 | H(31A)-C(31)-H(31C) | 109.5 |
| C(23)-C(24)-H(24) | 119.7 | H(31B)-C(31)-H(31C) | 109.5 |
| C(24)-C(25)-C(26) | 121.4(2) | C(30)-C(32)-H(32A) | 109.5 |
| C(24)-C(25)-H(25) | 119.3 | C(30)-C(32)-H(32B) | 109.5 |
| C(26)-C(25)-H(25) | 119.3 | H(32A)-C(32)-H(32B) | 109.5 |
| C(25)-C(26)-C(21) | 116.5(2) | C(30)-C(32)-H(32C) | 109.5 |
| C(25)-C(26)-C(30) | 120.56(19) | H(32A)-C(32)-H(32C) | 109.5 |
| C(21)-C(26)-C(30) | 122.91(18) | H(32B)-C(32)-H(32C) | 109.5 |
| C(28)-C(27)-C(29) | 111.78(18) | F(3)-B(1)-F(1) | 110.0(2) |
| C(28)-C(27)-C(22) | 112.00(17) | F(3)-B(1)-F(4) | 109.7(2) |
| C(29)-C(27)-C(22) | 110.85(17) | F(1)-B(1)-F(4) | 109.27(19) |
| C(28)-C(27)-H(27) | 107.3 | F(3)-B(1)-F(2) | 110.24(19) |
| C(29)-C(27)-H(27) | 107.3 | F(1)-B(1)-F(2) | 109.32(19) |
| C(22)-C(27)-H(27) | 107.3 | F(4)-B(1)-F(2) | 108.21(19) |
| C(27)-C(28)-H(28A) | 109.5 | | |
| C(27)-C(28)-H(28B) | 109.5 | | |
| H(28A)-C(28)-H(28B) | 109.5 | | |
| C(27)-C(28)-H(28C) | 109.5 | | |
| H(28A)-C(28)-H(28C) | 109.5 | | |
| H(28B)-C(28)-H(28C) | 109.5 | | |
| C(27)-C(29)-H(29A) | 109.5 | | |
| C(27)-C(29)-H(29B) | 109.5 | | |
| H(29A)-C(29)-H(29B) | 109.5 | | |
| C(27)-C(29)-H(29C) | 109.5 | | |

**Table S15.** Anisotropic displacement parameters ($Å^2$ x $10^3$) for [(CDA$^{iPr}$)$FeCl_2$]$BF_4$ (**3**) at 80 K. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11}+...+2hka^*b^*U^{12}]$.

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 19(1) | 29(1) | 14(1) | 1(1) | 8(1) | 7(1) |
| Cl(1) | 21(1) | 26(1) | 24(1) | -1(1) | 10(1) | 4(1) |
| Cl(2) | 27(1) | 47(1) | 12(1) | 4(1) | 8(1) | 13(1) |
| Cl(1X) | 42(3) | 48(3) | 153(7) | -30(4) | 38(5) | -4(2) |
| Cl(2X) | 83(6) | 96(8) | 23(3) | 18(4) | 29(4) | 60(4) |
| N(1) | 21(1) | 29(1) | 12(1) | 2(1) | 6(1) | 7(1) |
| N(2) | 20(1) | 29(1) | 10(1) | -2(1) | 7(1) | 2(1) |
| N(3) | 21(1) | 27(1) | 13(1) | 0(1) | 7(1) | 7(1) |
| N(4) | 20(1) | 26(1) | 14(1) | 0(1) | 7(1) | 2(1) |
| C(1) | 18(1) | 25(1) | 15(1) | 2(1) | 8(1) | 3(1) |
| C(2) | 31(1) | 37(1) | 12(1) | 3(1) | 6(1) | 7(1) |
| C(3) | 30(1) | 40(1) | 15(1) | 5(1) | 10(1) | 4(1) |
| C(4) | 27(1) | 40(1) | 10(1) | -2(1) | 10(1) | 3(1) |
| C(5) | 18(1) | 26(1) | 17(1) | -2(1) | 8(1) | 1(1) |
| C(6) | 26(1) | 39(1) | 22(1) | -4(1) | 11(1) | 6(1) |
| C(7) | 24(1) | 29(1) | 15(1) | 4(1) | 8(1) | 10(1) |
| C(8) | 24(1) | 31(1) | 18(1) | -1(1) | 10(1) | 6(1) |
| C(9) | 20(1) | 44(1) | 24(1) | 1(1) | 7(1) | 8(1) |
| C(10) | 28(1) | 48(2) | 29(1) | 15(1) | 11(1) | 13(1) |
| C(11) | 30(1) | 42(1) | 31(1) | 16(1) | 13(1) | 8(1) |
| C(12) | 24(1) | 37(1) | 25(1) | 7(1) | 12(1) | 7(1) |
| C(13) | 22(1) | 33(1) | 24(1) | -2(1) | 8(1) | 1(1) |
| C(14) | 27(1) | 39(1) | 36(1) | 4(1) | 14(1) | 2(1) |
| C(15) | 34(1) | 42(2) | 28(1) | -9(1) | 4(1) | 1(1) |
| C(16) | 23(1) | 33(1) | 33(1) | 12(1) | 8(1) | 6(1) |
| C(17) | 32(1) | 40(2) | 49(2) | 6(1) | 12(1) | 1(1) |
| C(18) | 28(1) | 66(2) | 45(2) | 20(1) | 17(1) | 6(1) |
| C(19) | 21(1) | 23(1) | 19(1) | -1(1) | 7(1) | 4(1) |
| C(20) | 25(1) | 38(1) | 18(1) | 5(1) | 5(1) | 14(1) |
| C(21) | 18(1) | 33(1) | 12(1) | 2(1) | 4(1) | 9(1) |
| C(22) | 24(1) | 33(1) | 17(1) | 1(1) | 8(1) | 8(1) |
| C(23) | 27(1) | 38(1) | 18(1) | 4(1) | 9(1) | 8(1) |
| C(24) | 29(1) | 43(1) | 17(1) | 4(1) | 11(1) | 16(1) |
| C(25) | 25(1) | 39(1) | 15(1) | -2(1) | 3(1) | 15(1) |
| C(26) | 20(1) | 34(1) | 15(1) | 0(1) | 3(1) | 12(1) |
| C(27) | 28(1) | 32(1) | 24(1) | -4(1) | 15(1) | 1(1) |
| C(28) | 26(1) | 34(1) | 24(1) | -1(1) | 5(1) | 2(1) |
| C(29) | 50(2) | 37(1) | 22(1) | 0(1) | 10(1) | 5(1) |
| C(30) | 28(1) | 34(1) | 24(1) | -7(1) | 9(1) | 6(1) |
| C(31) | 29(1) | 53(2) | 38(1) | -9(1) | 5(1) | 2(1) |
| C(32) | 39(1) | 33(1) | 39(1) | -2(1) | 13(1) | 10(1) |
| B(1) | 28(1) | 42(2) | 20(1) | 4(1) | 8(1) | 2(1) |
| F(1) | 47(1) | 46(1) | 29(1) | -3(1) | 13(1) | -7(1) |
| F(2) | 43(1) | 57(1) | 47(1) | 11(1) | 28(1) | 7(1) |
| F(3) | 38(1) | 67(1) | 27(1) | 14(1) | 17(1) | 7(1) |
| F(4) | 50(1) | 41(1) | 40(1) | -5(1) | 24(1) | 0(1) |

**Figure S13.** ORTEP plot of [(CDA$^{iPr}$)$FeCl_2$]$BF_4$ (**3**) at 150 K at 50% probability level. Hydrogen atoms, solvent molecules, and counterion were excluded for clarity.

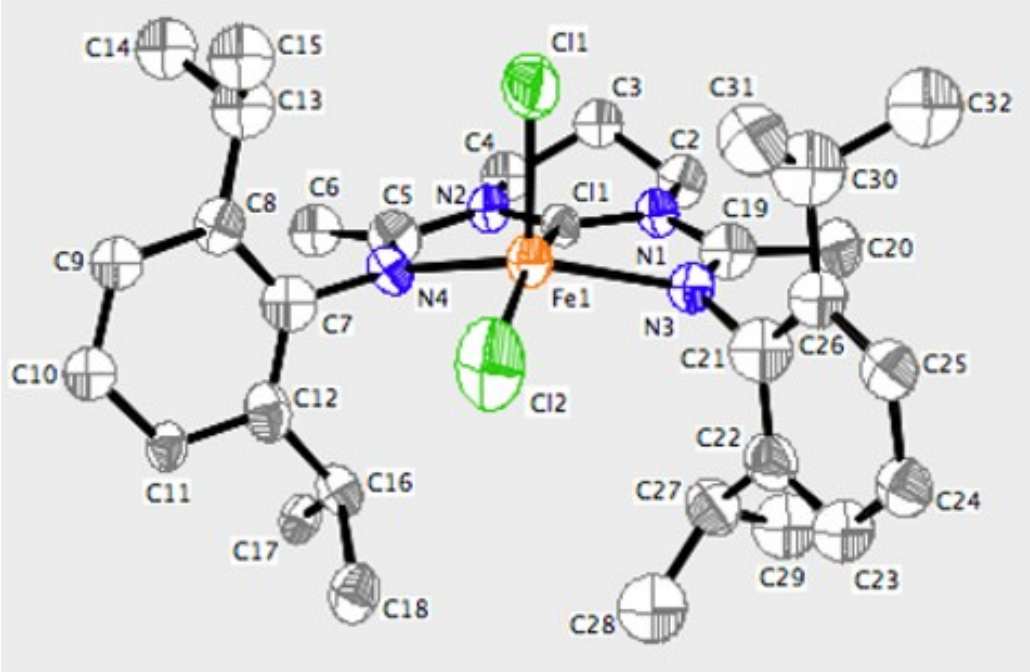


**Table S16.** Bond lengths (Å) and angles (°) for [(CDA$^{i\text{Pr}}$)$FeCl_2$]$BF_4$ (**3**) at 150 K.

| | | | | | |
|---|---|---|---|---|---|
| Fe(1)-C(1) | 1.9488(18) | C(10)-H(10) | 0.9500 | C(26)-C(30) | 1.506(3) |
| Fe(1)-N(3) | 2.0586(15) | C(11)-C(12) | 1.395(3) | C(27)-C(29) | 1.506(3) |
| Fe(1)-N(4) | 2.0758(15) | C(11)-H(11) | 0.9500 | C(27)-C(28) | 1.514(3) |
| Fe(1)-Cl(2) | 2.149(2) | C(12)-C(16) | 1.516(3) | C(27)-H(27) | 1.0000 |
| Fe(1)-Cl(1X) | 2.232(5) | C(13)-C(15) | 1.524(3) | C(28)-H(28A) | 0.9800 |
| Fe(1)-Cl(1) | 2.2516(14) | C(13)-C(14) | 1.527(3) | C(28)-H(28B) | 0.9800 |
| Fe(1)-Cl(2X) | 2.273(7) | C(13)-H(13) | 1.0000 | C(28)-H(28C) | 0.9800 |
| N(1)-C(1) | 1.336(2) | C(14)-H(14A) | 0.9800 | C(29)-H(29A) | 0.9800 |
| N(1)-C(19) | 1.395(2) | C(14)-H(14B) | 0.9800 | C(29)-H(29B) | 0.9800 |
| N(1)-C(2) | 1.486(2) | C(14)-H(14C) | 0.9800 | C(29)-H(29C) | 0.9800 |
| N(2)-C(1) | 1.326(3) | C(15)-H(15A) | 0.9800 | C(30)-C(31) | 1.530(3) |
| N(2)-C(5) | 1.394(2) | C(15)-H(15B) | 0.9800 | C(30)-C(32) | 1.530(3) |
| N(2)-C(4) | 1.484(2) | C(15)-H(15C) | 0.9800 | C(30)-H(30) | 1.0000 |
| N(3)-C(19) | 1.289(2) | C(16)-C(17) | 1.525(4) | C(31)-H(31A) | 0.9800 |
| N(3)-C(21) | 1.449(2) | C(16)-C(18) | 1.527(4) | C(31)-H(31B) | 0.9800 |
| N(4)-C(5) | 1.289(2) | C(16)-H(16) | 1.0000 | C(31)-H(31C) | 0.9800 |
| N(4)-C(7) | 1.448(2) | C(17)-H(17A) | 0.9800 | C(32)-H(32A) | 0.9800 |
| C(2)-C(3) | 1.513(3) | C(17)-H(17B) | 0.9800 | C(32)-H(32B) | 0.9800 |
| C(2)-H(2A) | 0.9900 | C(17)-H(17C) | 0.9800 | C(32)-H(32C) | 0.9800 |
| C(2)-H(2B) | 0.9900 | C(18)-H(18A) | 0.9800 | B(1)-F(1) | 1.360(3) |
| C(3)-C(4) | 1.516(3) | C(18)-H(18B) | 0.9800 | B(1)-F(3) | 1.369(3) |
| C(3)-H(3A) | 0.9900 | C(18)-H(18C) | 0.9800 | B(1)-F(4) | 1.390(4) |
| C(3)-H(3B) | 0.9900 | C(19)-C(20) | 1.477(3) | B(1)-F(2) | 1.403(3) |
| C(4)-H(4A) | 0.9900 | C(20)-H(20A) | 0.9800 | C(1)-Fe(1)-N(3) | 75.80(7) |
| C(4)-H(4B) | 0.9900 | C(20)-H(20B) | 0.9800 | C(1)-Fe(1)-N(4) | 75.53(7) |
| C(5)-C(6) | 1.482(3) | C(20)-H(20C) | 0.9800 | N(3)-Fe(1)-N(4) | 144.06(6) |
| C(6)-H(6A) | 0.9800 | C(21)-C(22) | 1.398(3) | C(1)-Fe(1)-Cl(2) | 164.3(2) |
| C(6)-H(6B) | 0.9800 | C(21)-C(26) | 1.400(3) | N(3)-Fe(1)-Cl(2) | 101.98(8) |
| C(6)-H(6C) | 0.9800 | C(22)-C(23) | 1.397(3) | N(4)-Fe(1)-Cl(2) | 99.80(8) |
| C(7)-C(8) | 1.400(3) | C(22)-C(27) | 1.519(3) | C(1)-Fe(1)-Cl(1X) | 103.2(5) |
| C(7)-C(12) | 1.403(3) | C(23)-C(24) | 1.375(3) | N(3)-Fe(1)-Cl(1X) | 103.6(2) |
| C(8)-C(9) | 1.391(3) | C(23)-H(23) | 0.9500 | N(4)-Fe(1)-Cl(1X) | 103.65(13) |
| C(8)-C(13) | 1.525(3) | C(24)-C(25) | 1.381(3) | Cl(2)-Fe(1)-Cl(1X) | 92.4(3) |
| C(9)-C(10) | 1.377(3) | C(24)-H(24) | 0.9500 | C(1)-Fe(1)-Cl(1) | 87.90(18) |
| C(9)-H(9) | 0.9500 | C(25)-C(26) | 1.399(3) | N(3)-Fe(1)-Cl(1) | 98.00(9) |
| C(10)-C(11) | 1.375(3) | C(25)-H(25) | 0.9500 | N(4)-Fe(1)-Cl(1) | 102.15(6) |

| | | | | | |
|---|---|---|---|---|---|
| Cl(2)-Fe(1)-Cl(1) | 107.74(6) | C(3)-C(4)-H(4A) | 110.1 | C(13)-C(14)-H(14A) | 109.5 |
| Cl(1X)-Fe(1)-Cl(1) | 15.4(3) | N(2)-C(4)-H(4B) | 110.1 | C(13)-C(14)-H(14B) | 109.5 |
| C(1)-Fe(1)-Cl(2X) | 149.4(4) | C(3)-C(4)-H(4B) | 110.1 | H(14A)-C(14)-H(14B) | 109.5 |
| N(3)-Fe(1)-Cl(2X) | 98.26(17) | H(4A)-C(4)-H(4B) | 108.4 | C(13)-C(14)-H(14C) | 109.5 |
| N(4)-Fe(1)-Cl(2X) | 95.5(2) | N(4)-C(5)-N(2) | 115.15(16) | H(14A)-C(14)-H(14C) | 109.5 |
| Cl(2)-Fe(1)-Cl(2X) | 14.9(2) | N(4)-C(5)-C(6) | 127.04(18) | H(14B)-C(14)-H(14C) | 109.5 |
| Cl(1X)-Fe(1)-Cl(2X) | 107.33(18) | N(2)-C(5)-C(6) | 117.81(16) | C(13)-C(15)-H(15A) | 109.5 |
| Cl(1)-Fe(1)-Cl(2X) | 122.7(3) | C(5)-C(6)-H(6A) | 109.5 | C(13)-C(15)-H(15B) | 109.5 |
| C(1)-N(1)-C(19) | 113.00(15) | C(5)-C(6)-H(6B) | 109.5 | H(15A)-C(15)-H(15B) | 109.5 |
| C(1)-N(1)-C(2) | 122.31(16) | H(6A)-C(6)-H(6B) | 109.5 | C(13)-C(15)-H(15C) | 109.5 |
| C(19)-N(1)-C(2) | 123.94(15) | C(5)-C(6)-H(6C) | 109.5 | H(15A)-C(15)-H(15C) | 109.5 |
| C(1)-N(2)-C(5) | 113.29(15) | H(6A)-C(6)-H(6C) | 109.5 | H(15B)-C(15)-H(15C) | 109.5 |
| C(1)-N(2)-C(4) | 122.19(16) | H(6B)-C(6)-H(6C) | 109.5 | C(12)-C(16)-C(17) | 110.1(2) |
| C(5)-N(2)-C(4) | 124.25(15) | C(8)-C(7)-C(12) | 122.28(18) | C(12)-C(16)-C(18) | 112.1(2) |
| C(19)-N(3)-C(21) | 120.20(16) | C(8)-C(7)-N(4) | 119.09(18) | C(17)-C(16)-C(18) | 110.6(2) |
| C(19)-N(3)-Fe(1) | 115.62(13) | C(12)-C(7)-N(4) | 118.57(18) | C(12)-C(16)-H(16) | 108.0 |
| C(21)-N(3)-Fe(1) | 124.15(11) | C(9)-C(8)-C(7) | 117.4(2) | C(17)-C(16)-H(16) | 108.0 |
| C(5)-N(4)-C(7) | 120.38(16) | C(9)-C(8)-C(13) | 118.98(19) | C(18)-C(16)-H(16) | 108.0 |
| C(5)-N(4)-Fe(1) | 115.43(13) | C(7)-C(8)-C(13) | 123.62(18) | C(16)-C(17)-H(17A) | 109.5 |
| C(7)-N(4)-Fe(1) | 123.80(12) | C(10)-C(9)-C(8) | 121.7(2) | C(16)-C(17)-H(17B) | 109.5 |
| N(2)-C(1)-N(1) | 122.33(16) | C(10)-C(9)-H(9) | 119.1 | H(17A)-C(17)-H(17B) | 109.5 |
| N(2)-C(1)-Fe(1) | 119.29(13) | C(8)-C(9)-H(9) | 119.1 | C(16)-C(17)-H(17C) | 109.5 |
| N(1)-C(1)-Fe(1) | 118.33(13) | C(11)-C(10)-C(9) | 119.7(2) | H(17A)-C(17)-H(17C) | 109.5 |
| N(1)-C(2)-C(3) | 107.53(16) | C(11)-C(10)-H(10) | 120.1 | H(17B)-C(17)-H(17C) | 109.5 |
| N(1)-C(2)-H(2A) | 110.2 | C(9)-C(10)-H(10) | 120.1 | C(16)-C(18)-H(18A) | 109.5 |
| C(3)-C(2)-H(2A) | 110.2 | C(10)-C(11)-C(12) | 121.7(2) | C(16)-C(18)-H(18B) | 109.5 |
| N(1)-C(2)-H(2B) | 110.2 | C(10)-C(11)-H(11) | 119.2 | H(18A)-C(18)-H(18B) | 109.5 |
| C(3)-C(2)-H(2B) | 110.2 | C(12)-C(11)-H(11) | 119.2 | C(16)-C(18)-H(18C) | 109.5 |
| H(2A)-C(2)-H(2B) | 108.5 | C(11)-C(12)-C(7) | 117.2(2) | H(18A)-C(18)-H(18C) | 109.5 |
| C(2)-C(3)-C(4) | 111.95(18) | C(11)-C(12)-C(16) | 119.1(2) | H(18B)-C(18)-H(18C) | 109.5 |
| C(2)-C(3)-H(3A) | 109.2 | C(7)-C(12)-C(16) | 123.65(18) | N(3)-C(19)-N(1) | 114.98(16) |
| C(4)-C(3)-H(3A) | 109.2 | C(15)-C(13)-C(8) | 110.0(2) | N(3)-C(19)-C(20) | 126.90(18) |
| C(2)-C(3)-H(3B) | 109.2 | C(15)-C(13)-C(14) | 110.8(2) | N(1)-C(19)-C(20) | 118.12(16) |
| C(4)-C(3)-H(3B) | 109.2 | C(8)-C(13)-C(14) | 111.29(18) | C(19)-C(20)-H(20A) | 109.5 |
| H(3A)-C(3)-H(3B) | 107.9 | C(15)-C(13)-H(13) | 108.2 | C(19)-C(20)-H(20B) | 109.5 |
| N(2)-C(4)-C(3) | 108.11(16) | C(8)-C(13)-H(13) | 108.2 | H(20A)-C(20)-H(20B) | 109.5 |
| N(2)-C(4)-H(4A) | 110.1 | C(14)-C(13)-H(13) | 108.2 | C(19)-C(20)-H(20C) | 109.5 |

| | | | |
|---|---|---|---|
| H(20A)-C(20)-H(20C) | 109.5 | H(29B)-C(29)-H(29C) | 109.5 |
| H(20B)-C(20)-H(20C) | 109.5 | C(26)-C(30)-C(31) | 110.7(2) |
| C(22)-C(21)-C(26) | 123.27(18) | C(26)-C(30)-C(32) | 111.66(19) |
| C(22)-C(21)-N(3) | 116.64(17) | C(31)-C(30)-C(32) | 110.3(2) |
| C(26)-C(21)-N(3) | 120.05(18) | C(26)-C(30)-H(30) | 108.0 |
| C(23)-C(22)-C(21) | 117.3(2) | C(31)-C(30)-H(30) | 108.0 |
| C(23)-C(22)-C(27) | 120.6(2) | C(32)-C(30)-H(30) | 108.0 |
| C(21)-C(22)-C(27) | 122.11(18) | C(30)-C(31)-H(31A) | 109.5 |
| C(24)-C(23)-C(22) | 121.0(2) | C(30)-C(31)-H(31B) | 109.5 |
| C(24)-C(23)-H(23) | 119.5 | H(31A)-C(31)-H(31B) | 109.5 |
| C(22)-C(23)-H(23) | 119.5 | C(30)-C(31)-H(31C) | 109.5 |
| C(23)-C(24)-C(25) | 120.4(2) | H(31A)-C(31)-H(31C) | 109.5 |
| C(23)-C(24)-H(24) | 119.8 | H(31B)-C(31)-H(31C) | 109.5 |
| C(25)-C(24)-H(24) | 119.8 | C(30)-C(32)-H(32A) | 109.5 |
| C(24)-C(25)-C(26) | 121.4(2) | C(30)-C(32)-H(32B) | 109.5 |
| C(24)-C(25)-H(25) | 119.3 | H(32A)-C(32)-H(32B) | 109.5 |
| C(26)-C(25)-H(25) | 119.3 | C(30)-C(32)-H(32C) | 109.5 |
| C(25)-C(26)-C(21) | 116.6(2) | H(32A)-C(32)-H(32C) | 109.5 |
| C(25)-C(26)-C(30) | 120.56(19) | H(32B)-C(32)-H(32C) | 109.5 |
| C(21)-C(26)-C(30) | 122.87(18) | F(1)-B(1)-F(3) | 110.7(2) |
| C(29)-C(27)-C(28) | 111.2(2) | F(1)-B(1)-F(4) | 109.4(2) |
| C(29)-C(27)-C(22) | 111.07(19) | F(3)-B(1)-F(4) | 110.3(2) |
| C(28)-C(27)-C(22) | 112.39(18) | F(1)-B(1)-F(2) | 109.0(2) |
| C(29)-C(27)-H(27) | 107.3 | F(3)-B(1)-F(2) | 110.3(2) |
| C(28)-C(27)-H(27) | 107.3 | F(4)-B(1)-F(2) | 107.0(2) |
| C(22)-C(27)-H(27) | 107.3 | | |
| C(27)-C(28)-H(28A) | 109.5 | | |
| C(27)-C(28)-H(28B) | 109.5 | | |
| H(28A)-C(28)-H(28B) | 109.5 | | |
| C(27)-C(28)-H(28C) | 109.5 | | |
| H(28A)-C(28)-H(28C) | 109.5 | | |
| H(28B)-C(28)-H(28C) | 109.5 | | |
| C(27)-C(29)-H(29A) | 109.5 | | |
| C(27)-C(29)-H(29B) | 109.5 | | |
| H(29A)-C(29)-H(29B) | 109.5 | | |
| C(27)-C(29)-H(29C) | 109.5 | | |
| H(29A)-C(29)-H(29C) | 109.5 | | |

**Table S17.** Anisotropic displacement parameters ($Å^2$ x $10^3$) for [(CDA$^{iPr}$)$FeCl_2$]$BF_4$ (**3**) at 150 K. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11}+...+2hka^*b^*U^{12}]$.

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 30(1) | 40(1) | 23(1) | 1(1) | 11(1) | 8(1) |
| Cl(1) | 39(1) | 42(1) | 58(2) | -4(1) | 21(1) | 1(1) |
| Cl(2) | 52(1) | 81(2) | 21(1) | 8(1) | 16(1) | 25(1) |
| Cl(1X) | 31(2) | 51(2) | 47(5) | -16(2) | 7(2) | -1(1) |
| Cl(2X) | 39(3) | 64(4) | 24(2) | 8(2) | 16(2) | 14(2) |
| N(1) | 32(1) | 40(1) | 20(1) | 2(1) | 8(1) | 6(1) |
| N(2) | 31(1) | 39(1) | 19(1) | -2(1) | 10(1) | 3(1) |
| N(3) | 28(1) | 39(1) | 21(1) | -2(1) | 8(1) | 5(1) |
| N(4) | 32(1) | 34(1) | 24(1) | 0(1) | 10(1) | 4(1) |
| C(1) | 30(1) | 38(1) | 20(1) | 1(1) | 9(1) | 4(1) |
| C(2) | 42(1) | 54(1) | 20(1) | 6(1) | 8(1) | 9(1) |
| C(3) | 47(1) | 59(1) | 22(1) | 6(1) | 15(1) | 5(1) |
| C(4) | 39(1) | 56(1) | 20(1) | -2(1) | 14(1) | 3(1) |
| C(5) | 30(1) | 35(1) | 27(1) | -2(1) | 12(1) | 1(1) |
| C(6) | 41(1) | 52(1) | 34(1) | -4(1) | 17(1) | 11(1) |
| C(7) | 36(1) | 42(1) | 22(1) | 2(1) | 11(1) | 9(1) |
| C(8) | 37(1) | 46(1) | 28(1) | -2(1) | 14(1) | 6(1) |
| C(9) | 35(1) | 60(2) | 35(1) | 2(1) | 10(1) | 8(1) |
| C(10) | 40(1) | 68(2) | 43(1) | 18(1) | 12(1) | 14(1) |
| C(11) | 46(1) | 59(2) | 46(1) | 22(1) | 18(1) | 11(1) |
| C(12) | 40(1) | 50(1) | 35(1) | 11(1) | 16(1) | 9(1) |
| C(13) | 38(1) | 45(1) | 40(1) | -2(1) | 12(1) | 3(1) |
| C(14) | 47(1) | 58(2) | 56(1) | 6(1) | 25(1) | 2(1) |
| C(15) | 59(2) | 57(2) | 56(2) | -13(1) | 12(1) | -4(1) |
| C(16) | 40(1) | 47(1) | 51(1) | 17(1) | 13(1) | 6(1) |
| C(17) | 55(2) | 58(2) | 79(2) | 6(1) | 17(1) | 1(1) |
| C(18) | 48(1) | 82(2) | 78(2) | 31(2) | 29(1) | 6(1) |
| C(19) | 31(1) | 35(1) | 23(1) | 0(1) | 8(1) | 3(1) |
| C(20) | 39(1) | 56(1) | 32(1) | 9(1) | 11(1) | 19(1) |
| C(21) | 29(1) | 43(1) | 21(1) | 0(1) | 8(1) | 10(1) |
| C(22) | 34(1) | 47(1) | 28(1) | -2(1) | 13(1) | 4(1) |
| C(23) | 40(1) | 56(1) | 31(1) | 5(1) | 16(1) | 8(1) |
| C(24) | 43(1) | 60(1) | 26(1) | 6(1) | 16(1) | 18(1) |
| C(25) | 39(1) | 52(1) | 24(1) | -2(1) | 6(1) | 18(1) |
| C(26) | 30(1) | 46(1) | 20(1) | -1(1) | 3(1) | 10(1) |
| C(27) | 45(1) | 48(1) | 41(1) | -5(1) | 23(1) | -1(1) |
| C(28) | 44(1) | 48(1) | 43(1) | -2(1) | 8(1) | 3(1) |
| C(29) | 78(2) | 52(2) | 34(1) | -1(1) | 6(1) | 2(1) |
| C(30) | 40(1) | 46(1) | 36(1) | -8(1) | 10(1) | 5(1) |
| C(31) | 47(1) | 78(2) | 54(2) | -15(1) | 2(1) | -9(1) |
| C(32) | 61(2) | 46(1) | 67(2) | -1(1) | 22(1) | 3(1) |
| B(1) | 54(2) | 67(2) | 32(1) | 5(1) | 20(1) | 4(1) |
| F(1) | 83(1) | 86(1) | 42(1) | -3(1) | 14(1) | -21(1) |
| F(2) | 67(1) | 104(1) | 80(1) | 26(1) | 45(1) | 13(1) |
| F(3) | 65(1) | 124(2) | 44(1) | 28(1) | 29(1) | 13(1) |
| F(4) | 96(1) | 68(1) | 76(1) | -11(1) | 46(1) | -9(1) |

**Figure S14.** ORTEP plot of [(CDA$^{iPr}$)$FeCl_2$]$BF_4$ (**3**) at 200 K at 50% probability level. Hydrogen atoms, solvent molecules, and counterion were excluded for clarity.

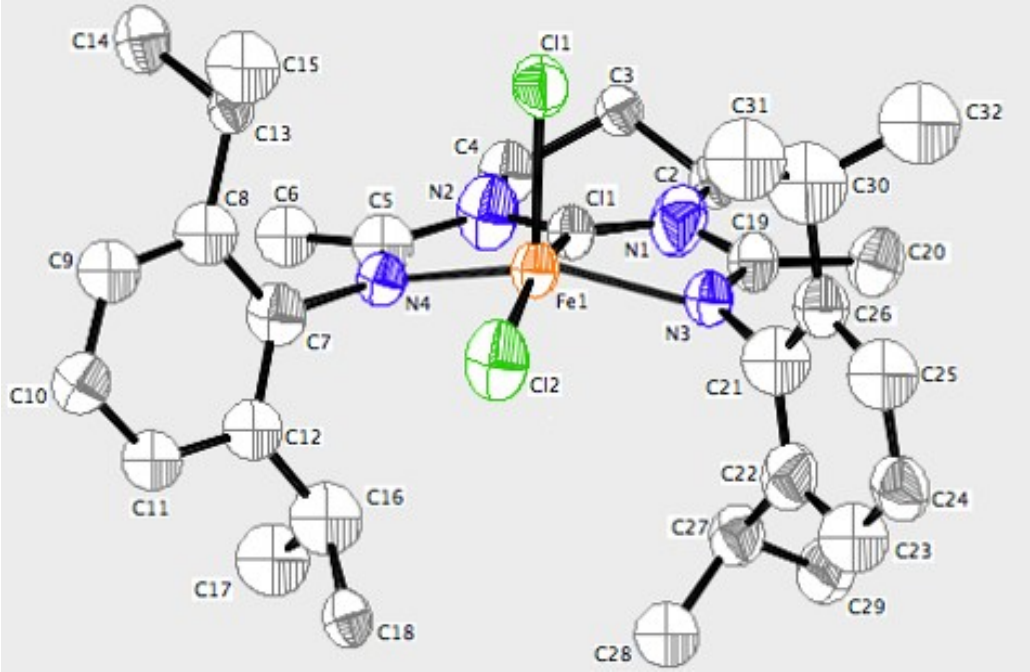


**Table S18.** Bond lengths (Å) and angles (°) for $[(CDA^{iPr})FeCl_2]BF_4$ (**3**) at 200 K.

| | | | | | |
|---|---|---|---|---|---|
| Fe(1)-C(1) | 1.984(2) | C(10)-H(10) | 0.9500 | C(26)-C(30) | 1.496(4) |
| Fe(1)-N(3) | 2.0974(18) | C(11)-C(12) | 1.401(4) | C(27)-C(29) | 1.512(4) |
| Fe(1)-N(4) | 2.1096(18) | C(11)-H(11) | 0.9500 | C(27)-C(28) | 1.513(4) |
| Fe(1)-Cl(2) | 2.113(8) | C(12)-C(16) | 1.507(4) | C(27)-H(27) | 1.0000 |
| Fe(1)-Cl(1X) | 2.218(7) | C(13)-C(14) | 1.523(4) | C(28)-H(28A) | 0.9800 |
| Fe(1)-Cl(2X) | 2.227(8) | C(13)-C(15) | 1.531(4) | C(28)-H(28B) | 0.9800 |
| Fe(1)-Cl(1) | 2.234(6) | C(13)-H(13) | 1.0000 | C(28)-H(28C) | 0.9800 |
| N(1)-C(1) | 1.336(3) | C(14)-H(14A) | 0.9800 | C(29)-H(29A) | 0.9800 |
| N(1)-C(19) | 1.392(3) | C(14)-H(14B) | 0.9800 | C(29)-H(29B) | 0.9800 |
| N(1)-C(2) | 1.484(3) | C(14)-H(14C) | 0.9800 | C(29)-H(29C) | 0.9800 |
| N(2)-C(1) | 1.327(3) | C(15)-H(15A) | 0.9800 | C(30)-C(31) | 1.519(4) |
| N(2)-C(5) | 1.396(3) | C(15)-H(15B) | 0.9800 | C(30)-C(32) | 1.530(4) |
| N(2)-C(4) | 1.478(3) | C(15)-H(15C) | 0.9800 | C(30)-H(30) | 1.0000 |
| N(3)-C(19) | 1.286(3) | C(16)-C(17) | 1.533(4) | C(31)-H(31A) | 0.9800 |
| N(3)-C(21) | 1.442(3) | C(16)-C(18) | 1.541(4) | C(31)-H(31B) | 0.9800 |
| N(4)-C(5) | 1.287(3) | C(16)-H(16) | 1.0000 | C(31)-H(31C) | 0.9800 |
| N(4)-C(7) | 1.453(3) | C(17)-H(17A) | 0.9800 | C(32)-H(32A) | 0.9800 |
| C(2)-C(3) | 1.503(3) | C(17)-H(17B) | 0.9800 | C(32)-H(32B) | 0.9800 |
| C(2)-H(2A) | 0.9900 | C(17)-H(17C) | 0.9800 | C(32)-H(32C) | 0.9800 |
| C(2)-H(2B) | 0.9900 | C(18)-H(18A) | 0.9800 | B(1)-F(1) | 1.337(4) |
| C(3)-C(4) | 1.519(4) | C(18)-H(18B) | 0.9800 | B(1)-F(3) | 1.360(4) |
| C(3)-H(3A) | 0.9900 | C(18)-H(18C) | 0.9800 | B(1)-F(4) | 1.378(5) |
| C(3)-H(3B) | 0.9900 | C(19)-C(20) | 1.488(3) | B(1)-F(2) | 1.381(4) |
| C(4)-H(4A) | 0.9900 | C(20)-H(20A) | 0.9800 | C(1)-Fe(1)-N(3) | 74.80(8) |
| C(4)-H(4B) | 0.9900 | C(20)-H(20B) | 0.9800 | C(1)-Fe(1)-N(4) | 74.45(8) |
| C(5)-C(6) | 1.477(3) | C(20)-H(20C) | 0.9800 | N(3)-Fe(1)-N(4) | 143.07(7) |
| C(6)-H(6A) | 0.9800 | C(21)-C(26) | 1.395(3) | C(1)-Fe(1)-Cl(2) | 162.0(5) |
| C(6)-H(6B) | 0.9800 | C(21)-C(22) | 1.397(4) | N(3)-Fe(1)-Cl(2) | 102.0(3) |
| C(6)-H(6C) | 0.9800 | C(22)-C(23) | 1.389(3) | N(4)-Fe(1)-Cl(2) | 100.9(3) |
| C(7)-C(8) | 1.393(3) | C(22)-C(27) | 1.527(4) | C(1)-Fe(1)-Cl(1X) | 101.7(5) |
| C(7)-C(12) | 1.403(4) | C(23)-C(24) | 1.379(4) | N(3)-Fe(1)-Cl(1X) | 102.5(2) |
| C(8)-C(9) | 1.389(4) | C(23)-H(23) | 0.9500 | N(4)-Fe(1)-Cl(1X) | 103.35(18) |
| C(8)-C(13) | 1.520(4) | C(24)-C(25) | 1.373(4) | Cl(2)-Fe(1)-Cl(1X) | 96.27(16) |
| C(9)-C(10) | 1.377(4) | C(24)-H(24) | 0.9500 | C(1)-Fe(1)-Cl(2X) | 148.6(4) |
| C(9)-H(9) | 0.9500 | C(25)-C(26) | 1.406(4) | N(3)-Fe(1)-Cl(2X) | 99.0(2) |
| C(10)-C(11) | 1.359(4) | C(25)-H(25) | 0.9500 | N(4)-Fe(1)-Cl(2X) | 96.7(3) |

| | | | | | |
|---|---|---|---|---|---|
| Cl(2)-Fe(1)-Cl(2X) | 13.4(2) | C(3)-C(4)-H(4A) | 110.1 | C(13)-C(14)-H(14A) | 109.5 |
| Cl(1X)-Fe(1)-Cl(2X) | 109.64(18) | N(2)-C(4)-H(4B) | 110.1 | C(13)-C(14)-H(14B) | 109.5 |
| C(1)-Fe(1)-Cl(1) | 88.5(4) | C(3)-C(4)-H(4B) | 110.1 | H(14A)-C(14)-H(14B) | 109.5 |
| N(3)-Fe(1)-Cl(1) | 98.1(2) | H(4A)-C(4)-H(4B) | 108.4 | C(13)-C(14)-H(14C) | 109.5 |
| N(4)-Fe(1)-Cl(1) | 101.08(19) | N(4)-C(5)-N(2) | 115.54(19) | H(14A)-C(14)-H(14C) | 109.5 |
| Cl(2)-Fe(1)-Cl(1) | 109.45(18) | N(4)-C(5)-C(6) | 126.8(2) | H(14B)-C(14)-H(14C) | 109.5 |
| Cl(1X)-Fe(1)-Cl(1) | 13.22(17) | N(2)-C(5)-C(6) | 117.6(2) | C(13)-C(15)-H(15A) | 109.5 |
| Cl(2X)-Fe(1)-Cl(1) | 122.83(16) | C(5)-C(6)-H(6A) | 109.5 | C(13)-C(15)-H(15B) | 109.5 |
| C(1)-N(1)-C(19) | 113.29(18) | C(5)-C(6)-H(6B) | 109.5 | H(15A)-C(15)-H(15B) | 109.5 |
| C(1)-N(1)-C(2) | 122.45(19) | H(6A)-C(6)-H(6B) | 109.5 | C(13)-C(15)-H(15C) | 109.5 |
| C(19)-N(1)-C(2) | 123.78(18) | C(5)-C(6)-H(6C) | 109.5 | H(15A)-C(15)-H(15C) | 109.5 |
| C(1)-N(2)-C(5) | 113.31(18) | H(6A)-C(6)-H(6C) | 109.5 | H(15B)-C(15)-H(15C) | 109.5 |
| C(1)-N(2)-C(4) | 122.42(18) | H(6B)-C(6)-H(6C) | 109.5 | C(12)-C(16)-C(17) | 110.7(2) |
| C(5)-N(2)-C(4) | 123.91(18) | C(8)-C(7)-C(12) | 122.6(2) | C(12)-C(16)-C(18) | 111.4(3) |
| C(19)-N(3)-C(21) | 120.03(19) | C(8)-C(7)-N(4) | 119.2(2) | C(17)-C(16)-C(18) | 109.9(3) |
| C(19)-N(3)-Fe(1) | 115.55(15) | C(12)-C(7)-N(4) | 118.1(2) | C(12)-C(16)-H(16) | 108.2 |
| C(21)-N(3)-Fe(1) | 124.30(14) | C(9)-C(8)-C(7) | 117.2(2) | C(17)-C(16)-H(16) | 108.2 |
| C(5)-N(4)-C(7) | 120.17(19) | C(9)-C(8)-C(13) | 119.1(2) | C(18)-C(16)-H(16) | 108.2 |
| C(5)-N(4)-Fe(1) | 115.68(15) | C(7)-C(8)-C(13) | 123.6(2) | C(16)-C(17)-H(17A) | 109.5 |
| C(7)-N(4)-Fe(1) | 123.97(14) | C(10)-C(9)-C(8) | 121.9(3) | C(16)-C(17)-H(17B) | 109.5 |
| N(2)-C(1)-N(1) | 121.95(19) | C(10)-C(9)-H(9) | 119.1 | H(17A)-C(17)-H(17B) | 109.5 |
| N(2)-C(1)-Fe(1) | 119.40(15) | C(8)-C(9)-H(9) | 119.1 | C(16)-C(17)-H(17C) | 109.5 |
| N(1)-C(1)-Fe(1) | 118.49(16) | C(11)-C(10)-C(9) | 119.5(3) | H(17A)-C(17)-H(17C) | 109.5 |
| N(1)-C(2)-C(3) | 107.79(19) | C(11)-C(10)-H(10) | 120.2 | H(17B)-C(17)-H(17C) | 109.5 |
| N(1)-C(2)-H(2A) | 110.1 | C(9)-C(10)-H(10) | 120.2 | C(16)-C(18)-H(18A) | 109.5 |
| C(3)-C(2)-H(2A) | 110.1 | C(10)-C(11)-C(12) | 122.3(3) | C(16)-C(18)-H(18B) | 109.5 |
| N(1)-C(2)-H(2B) | 110.1 | C(10)-C(11)-H(11) | 118.9 | H(18A)-C(18)-H(18B) | 109.5 |
| C(3)-C(2)-H(2B) | 110.1 | C(12)-C(11)-H(11) | 118.9 | C(16)-C(18)-H(18C) | 109.5 |
| H(2A)-C(2)-H(2B) | 108.5 | C(11)-C(12)-C(7) | 116.5(2) | H(18A)-C(18)-H(18C) | 109.5 |
| C(2)-C(3)-C(4) | 112.0(2) | C(11)-C(12)-C(16) | 119.8(3) | H(18B)-C(18)-H(18C) | 109.5 |
| C(2)-C(3)-H(3A) | 109.2 | C(7)-C(12)-C(16) | 123.7(2) | N(3)-C(19)-N(1) | 115.71(19) |
| C(4)-C(3)-H(3A) | 109.2 | C(8)-C(13)-C(14) | 111.4(2) | N(3)-C(19)-C(20) | 126.4(2) |
| C(2)-C(3)-H(3B) | 109.2 | C(8)-C(13)-C(15) | 110.1(3) | N(1)-C(19)-C(20) | 117.92(19) |
| C(4)-C(3)-H(3B) | 109.2 | C(14)-C(13)-C(15) | 110.8(2) | C(19)-C(20)-H(20A) | 109.5 |
| H(3A)-C(3)-H(3B) | 107.9 | C(8)-C(13)-H(13) | 108.1 | C(19)-C(20)-H(20B) | 109.5 |
| N(2)-C(4)-C(3) | 108.08(19) | C(14)-C(13)-H(13) | 108.1 | H(20A)-C(20)-H(20B) | 109.5 |
| N(2)-C(4)-H(4A) | 110.1 | C(15)-C(13)-H(13) | 108.1 | C(19)-C(20)-H(20C) | 109.5 |

| | | | |
|---|---|---|---|
| H(20A)-C(20)-H(20C) | 109.5 | H(29B)-C(29)-H(29C) | 109.5 |
| H(20B)-C(20)-H(20C) | 109.5 | C(26)-C(30)-C(31) | 111.7(2) |
| C(26)-C(21)-C(22) | 123.1(2) | C(26)-C(30)-C(32) | 111.2(2) |
| C(26)-C(21)-N(3) | 120.1(2) | C(31)-C(30)-C(32) | 110.0(3) |
| C(22)-C(21)-N(3) | 116.8(2) | C(26)-C(30)-H(30) | 107.9 |
| C(23)-C(22)-C(21) | 117.7(2) | C(31)-C(30)-H(30) | 107.9 |
| C(23)-C(22)-C(27) | 119.7(2) | C(32)-C(30)-H(30) | 107.9 |
| C(21)-C(22)-C(27) | 122.6(2) | C(30)-C(31)-H(31A) | 109.5 |
| C(24)-C(23)-C(22) | 121.3(3) | C(30)-C(31)-H(31B) | 109.5 |
| C(24)-C(23)-H(23) | 119.3 | H(31A)-C(31)-H(31B) | 109.5 |
| C(22)-C(23)-H(23) | 119.3 | C(30)-C(31)-H(31C) | 109.5 |
| C(25)-C(24)-C(23) | 119.4(2) | H(31A)-C(31)-H(31C) | 109.5 |
| C(25)-C(24)-H(24) | 120.3 | H(31B)-C(31)-H(31C) | 109.5 |
| C(23)-C(24)-H(24) | 120.3 | C(30)-C(32)-H(32A) | 109.5 |
| C(24)-C(25)-C(26) | 122.4(2) | C(30)-C(32)-H(32B) | 109.5 |
| C(24)-C(25)-H(25) | 118.8 | H(32A)-C(32)-H(32B) | 109.5 |
| C(26)-C(25)-H(25) | 118.8 | C(30)-C(32)-H(32C) | 109.5 |
| C(21)-C(26)-C(25) | 116.0(2) | H(32A)-C(32)-H(32C) | 109.5 |
| C(21)-C(26)-C(30) | 122.8(2) | H(32B)-C(32)-H(32C) | 109.5 |
| C(25)-C(26)-C(30) | 121.2(2) | F(1)-B(1)-F(3) | 110.0(3) |
| C(29)-C(27)-C(28) | 110.9(2) | F(1)-B(1)-F(4) | 108.4(3) |
| C(29)-C(27)-C(22) | 111.0(2) | F(3)-B(1)-F(4) | 110.5(3) |
| C(28)-C(27)-C(22) | 112.3(2) | F(1)-B(1)-F(2) | 109.2(3) |
| C(29)-C(27)-H(27) | 107.4 | F(3)-B(1)-F(2) | 111.4(3) |
| C(28)-C(27)-H(27) | 107.4 | F(4)-B(1)-F(2) | 107.2(3) |
| C(22)-C(27)-H(27) | 107.4 | | |
| C(27)-C(28)-H(28A) | 109.5 | | |
| C(27)-C(28)-H(28B) | 109.5 | | |
| H(28A)-C(28)-H(28B) | 109.5 | | |
| C(27)-C(28)-H(28C) | 109.5 | | |
| H(28A)-C(28)-H(28C) | 109.5 | | |
| H(28B)-C(28)-H(28C) | 109.5 | | |
| C(27)-C(29)-H(29A) | 109.5 | | |
| C(27)-C(29)-H(29B) | 109.5 | | |
| H(29A)-C(29)-H(29B) | 109.5 | | |
| C(27)-C(29)-H(29C) | 109.5 | | |
| H(29A)-C(29)-H(29C) | 109.5 | | |

**Table S19.** Anisotropic displacement parameters ($Å^2$ x $10^3$) for $[(CDA^{iPr})FeCl_2]BF_4$ (**3**) at 200 K. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11}+...+2hka^*b^*U^{12}]$.

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 34(1) | 46(1) | 29(1) | 0(1) | 14(1) | 9(1) |
| Cl(1) | 46(2) | 44(1) | 81(4) | -7(2) | 30(2) | -1(1) |
| Cl(2) | 66(3) | 97(4) | 27(1) | 8(2) | 20(2) | 35(3) |
| Cl(1X) | 40(2) | 61(2) | 84(4) | -27(2) | 22(2) | -3(1) |
| Cl(2X) | 60(3) | 89(4) | 32(2) | 16(2) | 25(2) | 32(2) |
| N(1) | 34(1) | 46(1) | 22(1) | 2(1) | 9(1) | 6(1) |
| N(2) | 34(1) | 45(1) | 24(1) | -1(1) | 14(1) | 3(1) |
| N(3) | 33(1) | 42(1) | 26(1) | -2(1) | 13(1) | 5(1) |
| N(4) | 35(1) | 40(1) | 28(1) | -1(1) | 12(1) | 5(1) |
| C(1) | 33(1) | 38(1) | 28(1) | 2(1) | 14(1) | 4(1) |
| C(2) | 48(2) | 62(2) | 21(1) | 3(1) | 12(1) | 9(1) |
| C(3) | 53(2) | 64(2) | 25(1) | 8(1) | 16(1) | 7(1) |
| C(4) | 47(2) | 63(2) | 26(1) | -3(1) | 19(1) | 1(1) |
| C(5) | 30(1) | 37(1) | 32(1) | -4(1) | 14(1) | 1(1) |
| C(6) | 52(2) | 58(2) | 43(2) | -7(1) | 22(1) | 14(1) |
| C(7) | 41(1) | 45(2) | 30(1) | 0(1) | 13(1) | 10(1) |
| C(8) | 39(1) | 51(2) | 36(1) | -2(1) | 18(1) | 9(1) |
| C(9) | 42(2) | 75(2) | 44(2) | -1(1) | 14(1) | 10(1) |
| C(10) | 46(2) | 77(2) | 47(2) | 25(2) | 17(1) | 20(2) |
| C(11) | 56(2) | 64(2) | 54(2) | 24(1) | 22(2) | 16(1) |
| C(12) | 46(2) | 59(2) | 42(2) | 11(1) | 21(1) | 11(1) |
| C(13) | 41(2) | 54(2) | 52(2) | -6(1) | 18(1) | 0(1) |
| C(14) | 48(2) | 67(2) | 83(2) | 9(2) | 34(2) | 3(1) |
| C(15) | 69(2) | 68(2) | 81(2) | -29(2) | 17(2) | -8(2) |
| C(16) | 48(2) | 53(2) | 63(2) | 21(1) | 19(1) | 9(1) |
| C(17) | 71(2) | 66(2) | 90(3) | 2(2) | 24(2) | 1(2) |
| C(18) | 62(2) | 93(3) | 99(3) | 35(2) | 39(2) | 6(2) |
| C(19) | 33(1) | 36(1) | 32(1) | 2(1) | 12(1) | 5(1) |
| C(20) | 48(2) | 72(2) | 40(2) | 16(1) | 18(1) | 25(1) |
| C(21) | 32(1) | 51(2) | 26(1) | -2(1) | 10(1) | 10(1) |
| C(22) | 36(1) | 54(2) | 36(1) | -2(1) | 15(1) | 7(1) |
| C(23) | 47(2) | 61(2) | 40(2) | 7(1) | 23(1) | 8(1) |
| C(24) | 48(2) | 74(2) | 34(1) | 10(1) | 20(1) | 22(1) |
| C(25) | 44(2) | 60(2) | 30(1) | -7(1) | 7(1) | 20(1) |
| C(26) | 33(1) | 48(2) | 29(1) | -2(1) | 7(1) | 9(1) |
| C(27) | 51(2) | 53(2) | 53(2) | -10(1) | 30(1) | -5(1) |
| C(28) | 60(2) | 58(2) | 58(2) | -1(2) | 14(2) | 0(1) |
| C(29) | 93(2) | 65(2) | 49(2) | -3(2) | 4(2) | 3(2) |
| C(30) | 48(2) | 53(2) | 46(2) | -13(1) | 12(1) | 4(1) |
| C(31) | 51(2) | 109(3) | 64(2) | -13(2) | 5(2) | -11(2) |
| C(32) | 75(2) | 57(2) | 92(3) | 0(2) | 26(2) | 12(2) |
| B(1) | 59(2) | 87(3) | 47(2) | 15(2) | 26(2) | 6(2) |
| F(1) | 122(2) | 141(2) | 57(1) | -14(1) | 18(1) | -47(2) |
| F(2) | 104(2) | 142(2) | 114(2) | 42(2) | 71(2) | 17(1) |
| F(3) | 94(2) | 169(2) | 68(1) | 44(1) | 46(1) | 23(1) |
| F(4) | 159(2) | 91(2) | 127(2) | -17(1) | 89(2) | -17(2) |

**Figure S15.** ORTEP plot of [(CDA$^{iPr}$)$FeCl_2$]$BF_4$ (**3**) at 298 K at 50% probability level. Hydrogen atoms, solvent molecules, and counterion were excluded for clarity.

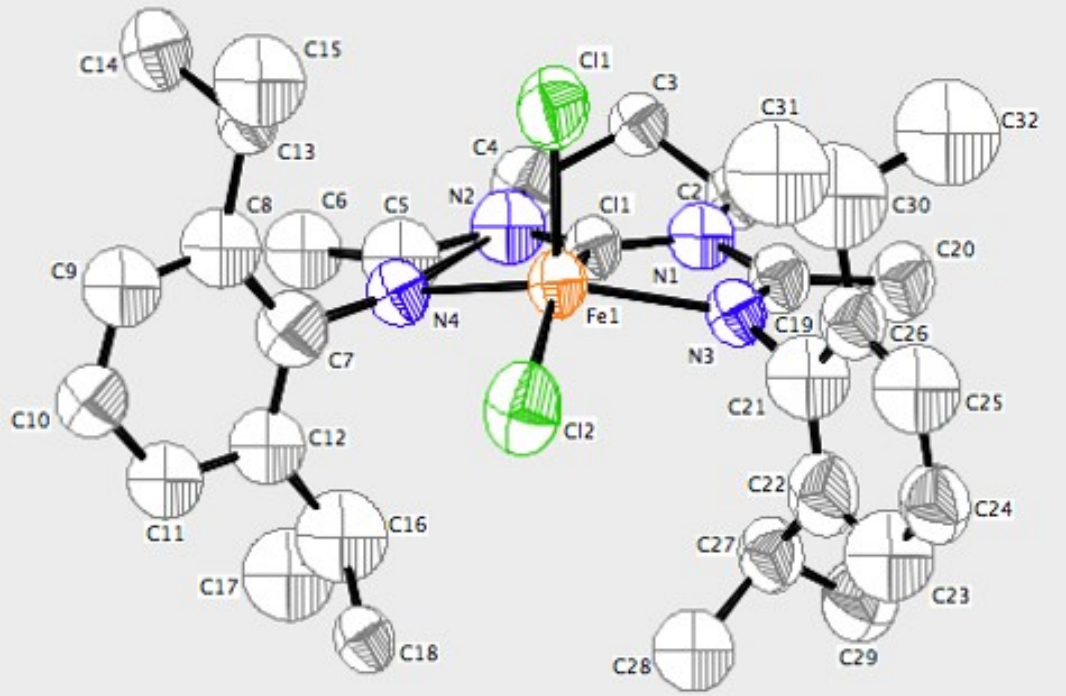


**Table S20.** Bond lengths (Å) and angles (°) for $[(CDA^{iPr})FeCl_2]BF_4$ (**3**) at 298 K.

| | | | | | |
|---|---|---|---|---|---|
| Fe(1)-Cl(2X) | 2.009(14) | C(10)-H(10) | 0.9300 | C(26)-C(30) | 1.501(5) |
| Fe(1)-C(1) | 2.033(2) | C(11)-C(12) | 1.402(4) | C(27)-C(29) | 1.506(5) |
| Fe(1)-N(3) | 2.132(2) | C(11)-H(11) | 0.9300 | C(27)-C(28) | 1.522(5) |
| Fe(1)-N(4) | 2.152(2) | C(12)-C(16) | 1.519(5) | C(27)-H(27) | 0.9800 |
| Fe(1)-Cl(1X) | 2.162(13) | C(13)-C(14) | 1.536(5) | C(28)-H(28A) | 0.9600 |
| Fe(1)-Cl(2) | 2.1798(16) | C(13)-C(15) | 1.556(5) | C(28)-H(28B) | 0.9600 |
| Fe(1)-Cl(1) | 2.1980(14) | C(13)-H(13) | 0.9800 | C(28)-H(28C) | 0.9600 |
| N(1)-C(1) | 1.325(3) | C(14)-H(14A) | 0.9600 | C(29)-H(29A) | 0.9600 |
| N(1)-C(19) | 1.401(3) | C(14)-H(14B) | 0.9600 | C(29)-H(29B) | 0.9600 |
| N(1)-C(2) | 1.496(3) | C(14)-H(14C) | 0.9600 | C(29)-H(29C) | 0.9600 |
| N(2)-C(1) | 1.317(3) | C(15)-H(15A) | 0.9600 | C(30)-C(32) | 1.524(5) |
| N(2)-C(5) | 1.402(3) | C(15)-H(15B) | 0.9600 | C(30)-C(31) | 1.527(4) |
| N(2)-C(4) | 1.486(3) | C(15)-H(15C) | 0.9600 | C(30)-H(30) | 0.9800 |
| N(3)-C(19) | 1.286(3) | C(16)-C(17) | 1.532(6) | C(31)-H(31A) | 0.9600 |
| N(3)-C(21) | 1.453(3) | C(16)-C(18) | 1.536(5) | C(31)-H(31B) | 0.9600 |
| N(4)-C(5) | 1.301(3) | C(16)-H(16) | 0.9800 | C(31)-H(31C) | 0.9600 |
| N(4)-C(7) | 1.443(3) | C(17)-H(17A) | 0.9600 | C(32)-H(32A) | 0.9600 |
| C(2)-C(3) | 1.508(4) | C(17)-H(17B) | 0.9600 | C(32)-H(32B) | 0.9600 |
| C(2)-H(2A) | 0.9700 | C(17)-H(17C) | 0.9600 | C(32)-H(32C) | 0.9600 |
| C(2)-H(2B) | 0.9700 | C(18)-H(18A) | 0.9600 | B(1)-F(3X) | 1.214(16) |
| C(3)-C(4) | 1.503(4) | C(18)-H(18B) | 0.9600 | B(1)-F(1) | 1.282(6) |
| C(3)-H(3A) | 0.9700 | C(18)-H(18C) | 0.9600 | B(1)-F(4X) | 1.299(17) |
| C(3)-H(3B) | 0.9700 | C(19)-C(20) | 1.476(4) | B(1)-F(3) | 1.339(6) |
| C(4)-H(4A) | 0.9700 | C(20)-H(20A) | 0.9600 | B(1)-F(4) | 1.357(7) |
| C(4)-H(4B) | 0.9700 | C(20)-H(20B) | 0.9600 | B(1)-F(1X) | 1.361(18) |
| C(5)-C(6) | 1.468(4) | C(20)-H(20C) | 0.9600 | B(1)-F(2) | 1.396(6) |
| C(6)-H(6A) | 0.9600 | C(21)-C(22) | 1.392(4) | B(1)-F(2X) | 1.41(2) |
| C(6)-H(6B) | 0.9600 | C(21)-C(26) | 1.402(4) | Cl(2X)-Fe(1)-C(1) | 169.2(5) |
| C(6)-H(6C) | 0.9600 | C(22)-C(23) | 1.393(4) | Cl(2X)-Fe(1)-N(3) | 104.0(4) |
| C(7)-C(8) | 1.396(4) | C(22)-C(27) | 1.512(5) | C(1)-Fe(1)-N(3) | 73.91(10) |
| C(7)-C(12) | 1.400(5) | C(23)-C(24) | 1.383(5) | Cl(2X)-Fe(1)-N(4) | 103.8(4) |
| C(8)-C(9) | 1.381(4) | C(23)-H(23) | 0.9300 | C(1)-Fe(1)-N(4) | 73.97(10) |
| C(8)-C(13) | 1.501(5) | C(24)-C(25) | 1.367(5) | N(3)-Fe(1)-N(4) | 142.44(8) |
| C(9)-C(10) | 1.374(5) | C(24)-H(24) | 0.9300 | Cl(2X)-Fe(1)-Cl(1X) | 108.3(4) |
| C(9)-H(9) | 0.9300 | C(25)-C(26) | 1.389(4) | C(1)-Fe(1)-Cl(1X) | 82.5(4) |
| C(10)-C(11) | 1.385(5) | C(25)-H(25) | 0.9300 | N(3)-Fe(1)-Cl(1X) | 96.8(3) |

| | | | | | |
|---|---|---|---|---|---|
| N(4)-Fe(1)-Cl(1X) | 97.8(3) | C(2)-C(3)-H(3B) | 109.1 | C(14)-C(13)-C(15) | 110.1(3) |
| Cl(2X)-Fe(1)-Cl(2) | 19.3(4) | H(3A)-C(3)-H(3B) | 107.8 | C(8)-C(13)-H(13) | 107.9 |
| C(1)-Fe(1)-Cl(2) | 149.86(15) | N(2)-C(4)-C(3) | 108.1(2) | C(14)-C(13)-H(13) | 107.9 |
| N(3)-Fe(1)-Cl(2) | 99.56(7) | N(2)-C(4)-H(4A) | 110.1 | C(15)-C(13)-H(13) | 107.9 |
| N(4)-Fe(1)-Cl(2) | 98.46(8) | C(3)-C(4)-H(4A) | 110.1 | C(13)-C(14)-H(14A) | 109.5 |
| Cl(1X)-Fe(1)-Cl(2) | 127.6(3) | N(2)-C(4)-H(4B) | 110.1 | C(13)-C(14)-H(14B) | 109.5 |
| Cl(2X)-Fe(1)-Cl(1) | 91.9(4) | C(3)-C(4)-H(4B) | 110.1 | H(14A)-C(14)-H(14B) | 109.5 |
| C(1)-Fe(1)-Cl(1) | 98.91(14) | H(4A)-C(4)-H(4B) | 108.4 | C(13)-C(14)-H(14C) | 109.5 |
| N(3)-Fe(1)-Cl(1) | 101.43(8) | N(4)-C(5)-N(2) | 115.8(2) | H(14A)-C(14)-H(14C) | 109.5 |
| N(4)-Fe(1)-Cl(1) | 102.29(8) | N(4)-C(5)-C(6) | 125.9(3) | H(14B)-C(14)-H(14C) | 109.5 |
| Cl(1X)-Fe(1)-Cl(1) | 16.4(3) | N(2)-C(5)-C(6) | 118.3(2) | C(13)-C(15)-H(15A) | 109.5 |
| Cl(2)-Fe(1)-Cl(1) | 111.22(7) | C(5)-C(6)-H(6A) | 109.5 | C(13)-C(15)-H(15B) | 109.5 |
| C(1)-N(1)-C(19) | 114.4(2) | C(5)-C(6)-H(6B) | 109.5 | H(15A)-C(15)-H(15B) | 109.5 |
| C(1)-N(1)-C(2) | 121.7(2) | H(6A)-C(6)-H(6B) | 109.5 | C(13)-C(15)-H(15C) | 109.5 |
| C(19)-N(1)-C(2) | 123.3(2) | C(5)-C(6)-H(6C) | 109.5 | H(15A)-C(15)-H(15C) | 109.5 |
| C(1)-N(2)-C(5) | 114.6(2) | H(6A)-C(6)-H(6C) | 109.5 | H(15B)-C(15)-H(15C) | 109.5 |
| C(1)-N(2)-C(4) | 122.3(2) | H(6B)-C(6)-H(6C) | 109.5 | C(12)-C(16)-C(17) | 110.5(3) |
| C(5)-N(2)-C(4) | 122.8(2) | C(8)-C(7)-C(12) | 122.5(3) | C(12)-C(16)-C(18) | 111.8(3) |
| C(19)-N(3)-C(21) | 119.0(2) | C(8)-C(7)-N(4) | 119.3(3) | C(17)-C(16)-C(18) | 111.1(4) |
| C(19)-N(3)-Fe(1) | 116.04(18) | C(12)-C(7)-N(4) | 118.2(3) | C(12)-C(16)-H(16) | 107.8 |
| C(21)-N(3)-Fe(1) | 124.66(15) | C(9)-C(8)-C(7) | 117.0(3) | C(17)-C(16)-H(16) | 107.8 |
| C(5)-N(4)-C(7) | 120.1(2) | C(9)-C(8)-C(13) | 119.6(3) | C(18)-C(16)-H(16) | 107.8 |
| C(5)-N(4)-Fe(1) | 115.01(18) | C(7)-C(8)-C(13) | 123.4(3) | C(16)-C(17)-H(17A) | 109.5 |
| C(7)-N(4)-Fe(1) | 124.86(16) | C(10)-C(9)-C(8) | 122.6(3) | C(16)-C(17)-H(17B) | 109.5 |
| N(2)-C(1)-N(1) | 122.9(2) | C(10)-C(9)-H(9) | 118.7 | H(17A)-C(17)-H(17B) | 109.5 |
| N(2)-C(1)-Fe(1) | 118.75(18) | C(8)-C(9)-H(9) | 118.7 | C(16)-C(17)-H(17C) | 109.5 |
| N(1)-C(1)-Fe(1) | 117.95(19) | C(9)-C(10)-C(11) | 119.7(3) | H(17A)-C(17)-H(17C) | 109.5 |
| N(1)-C(2)-C(3) | 107.4(2) | C(9)-C(10)-H(10) | 120.2 | H(17B)-C(17)-H(17C) | 109.5 |
| N(1)-C(2)-H(2A) | 110.2 | C(11)-C(10)-H(10) | 120.2 | C(16)-C(18)-H(18A) | 109.5 |
| C(3)-C(2)-H(2A) | 110.2 | C(10)-C(11)-C(12) | 120.4(4) | C(16)-C(18)-H(18B) | 109.5 |
| N(1)-C(2)-H(2B) | 110.2 | C(10)-C(11)-H(11) | 119.8 | H(18A)-C(18)-H(18B) | 109.5 |
| C(3)-C(2)-H(2B) | 110.2 | C(12)-C(11)-H(11) | 119.8 | C(16)-C(18)-H(18C) | 109.5 |
| H(2A)-C(2)-H(2B) | 108.5 | C(7)-C(12)-C(11) | 117.8(3) | H(18A)-C(18)-H(18C) | 109.5 |
| C(4)-C(3)-C(2) | 112.6(3) | C(7)-C(12)-C(16) | 123.9(3) | H(18B)-C(18)-H(18C) | 109.5 |
| C(4)-C(3)-H(3A) | 109.1 | C(11)-C(12)-C(16) | 118.3(3) | N(3)-C(19)-N(1) | 115.4(2) |
| C(2)-C(3)-H(3A) | 109.1 | C(8)-C(13)-C(14) | 111.7(3) | N(3)-C(19)-C(20) | 126.6(3) |
| C(4)-C(3)-H(3B) | 109.1 | C(8)-C(13)-C(15) | 111.2(3) | N(1)-C(19)-C(20) | 118.0(2) |

| | | | | | |
|---|---|---|---|---|---|
| C(19)-C(20)-H(20A) | 109.5 | C(27)-C(29)-H(29B) | 109.5 | F(4)-B(1)-F(1X) | 58.2(13) |
| C(19)-C(20)-H(20B) | 109.5 | H(29A)-C(29)-H(29B) | 109.5 | F(3X)-B(1)-F(2) | 81.0(9) |
| H(20A)-C(20)-H(20B) | 109.5 | C(27)-C(29)-H(29C) | 109.5 | F(1)-B(1)-F(2) | 109.1(5) |
| C(19)-C(20)-H(20C) | 109.5 | H(29A)-C(29)-H(29C) | 109.5 | F(4X)-B(1)-F(2) | 44.5(10) |
| H(20A)-C(20)-H(20C) | 109.5 | H(29B)-C(29)-H(29C) | 109.5 | F(3)-B(1)-F(2) | 112.2(5) |
| H(20B)-C(20)-H(20C) | 109.5 | C(26)-C(30)-C(32) | 111.4(3) | F(4)-B(1)-F(2) | 103.0(5) |
| C(22)-C(21)-C(26) | 122.8(3) | C(26)-C(30)-C(31) | 112.1(3) | F(1X)-B(1)-F(2) | 131.1(10) |
| C(22)-C(21)-N(3) | 117.5(3) | C(32)-C(30)-C(31) | 108.8(3) | F(3X)-B(1)-F(2X) | 110.6(13) |
| C(26)-C(21)-N(3) | 119.6(3) | C(26)-C(30)-H(30) | 108.2 | F(1)-B(1)-F(2X) | 72.0(11) |
| C(21)-C(22)-C(23) | 117.5(3) | C(32)-C(30)-H(30) | 108.2 | F(4X)-B(1)-F(2X) | 96.2(14) |
| C(21)-C(22)-C(27) | 122.9(3) | C(31)-C(30)-H(30) | 108.2 | F(3)-B(1)-F(2X) | 40.6(10) |
| C(23)-C(22)-C(27) | 119.6(3) | C(30)-C(31)-H(31A) | 109.5 | F(4)-B(1)-F(2X) | 134.1(11) |
| C(24)-C(23)-C(22) | 120.9(4) | C(30)-C(31)-H(31B) | 109.5 | F(1X)-B(1)-F(2X) | 97.9(13) |
| C(24)-C(23)-H(23) | 119.5 | H(31A)-C(31)-H(31B) | 109.5 | F(2)-B(1)-F(2X) | 120.4(11) |
| C(22)-C(23)-H(23) | 119.5 | C(30)-C(31)-H(31C) | 109.5 | | |
| C(25)-C(24)-C(23) | 120.1(3) | H(31A)-C(31)-H(31C) | 109.5 | | |
| C(25)-C(24)-H(24) | 120.0 | H(31B)-C(31)-H(31C) | 109.5 | | |
| C(23)-C(24)-H(24) | 120.0 | C(30)-C(32)-H(32A) | 109.5 | | |
| C(24)-C(25)-C(26) | 121.9(3) | C(30)-C(32)-H(32B) | 109.5 | | |
| C(24)-C(25)-H(25) | 119.0 | H(32A)-C(32)-H(32B) | 109.5 | | |
| C(26)-C(25)-H(25) | 119.0 | C(30)-C(32)-H(32C) | 109.5 | | |
| C(25)-C(26)-C(21) | 116.8(3) | H(32A)-C(32)-H(32C) | 109.5 | | |
| C(25)-C(26)-C(30) | 121.0(3) | H(32B)-C(32)-H(32C) | 109.5 | | |
| C(21)-C(26)-C(30) | 122.1(3) | F(3X)-B(1)-F(1) | 166.9(11) | | |
| C(29)-C(27)-C(22) | 112.6(3) | F(3X)-B(1)-F(4X) | 125.3(14) | | |
| C(29)-C(27)-C(28) | 109.9(3) | F(1)-B(1)-F(4X) | 65.9(10) | | |
| C(22)-C(27)-C(28) | 111.7(3) | F(3X)-B(1)-F(3) | 70.0(10) | | |
| C(29)-C(27)-H(27) | 107.5 | F(1)-B(1)-F(3) | 111.9(6) | | |
| C(22)-C(27)-H(27) | 107.5 | F(4X)-B(1)-F(3) | 119.4(10) | | |
| C(28)-C(27)-H(27) | 107.5 | F(3X)-B(1)-F(4) | 59.8(10) | | |
| C(27)-C(28)-H(28A) | 109.5 | F(1)-B(1)-F(4) | 108.7(6) | | |
| C(27)-C(28)-H(28B) | 109.5 | F(4X)-B(1)-F(4) | 126.9(10) | | |
| H(28A)-C(28)-H(28B) | 109.5 | F(3)-B(1)-F(4) | 111.5(5) | | |
| C(27)-C(28)-H(28C) | 109.5 | F(3X)-B(1)-F(1X) | 114.6(16) | | |
| H(28A)-C(28)-H(28C) | 109.5 | F(1)-B(1)-F(1X) | 52.5(11) | | |
| H(28B)-C(28)-H(28C) | 109.5 | F(4X)-B(1)-F(1X) | 107.3(12) | | |
| C(27)-C(29)-H(29A) | 109.5 | F(3)-B(1)-F(1X) | 116.7(10) | | |

**Table S21.** Anisotropic displacement parameters ($Å^2$ x $10^3$) for $[(CDA^{iPr})FeCl_2]BF_4$ (**3**) at 298 K. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11}+...+2hka^*b^*U^{12}]$.

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 52(1) | 66(1) | 43(1) | -1(1) | 20(1) | 10(1) |
| Cl(1) | 71(1) | 78(1) | 139(2) | -31(1) | 46(1) | -8(1) |
| Cl(2) | 95(1) | 145(2) | 52(1) | 28(1) | 42(1) | 49(1) |
| N(1) | 54(1) | 62(2) | 39(1) | 4(1) | 17(1) | 8(1) |
| N(2) | 58(1) | 61(2) | 38(1) | -5(1) | 24(1) | 3(1) |
| N(3) | 46(1) | 60(2) | 42(1) | 0(1) | 16(1) | 6(1) |
| N(4) | 54(1) | 54(2) | 47(1) | -3(1) | 21(1) | 4(1) |
| C(1) | 49(2) | 61(2) | 40(1) | -2(1) | 18(1) | 0(1) |
| C(2) | 67(2) | 95(3) | 39(1) | 11(1) | 16(1) | 11(2) |
| C(3) | 76(2) | 98(3) | 46(2) | 12(2) | 30(2) | 6(2) |
| C(4) | 70(2) | 93(3) | 41(1) | -2(2) | 30(1) | -2(2) |
| C(5) | 52(2) | 59(2) | 51(1) | -3(1) | 24(1) | 0(2) |
| C(6) | 85(2) | 87(3) | 67(2) | -8(2) | 41(2) | 22(2) |
| C(7) | 61(2) | 62(2) | 48(1) | 5(1) | 22(1) | 11(2) |
| C(8) | 57(2) | 66(2) | 60(2) | -3(2) | 25(1) | 7(2) |
| C(9) | 61(2) | 96(3) | 72(2) | 6(2) | 18(2) | 13(2) |
| C(10) | 80(3) | 108(4) | 81(2) | 34(2) | 26(2) | 31(2) |
| C(11) | 80(3) | 93(3) | 96(2) | 33(2) | 38(2) | 20(2) |
| C(12) | 69(2) | 81(3) | 68(2) | 15(2) | 29(2) | 13(2) |
| C(13) | 64(2) | 74(3) | 84(2) | -4(2) | 27(2) | 7(2) |
| C(14) | 88(3) | 105(4) | 134(3) | 14(3) | 67(3) | 7(3) |
| C(15) | 100(3) | 112(4) | 115(3) | -37(3) | 25(3) | -7(3) |
| C(16) | 76(2) | 75(3) | 111(3) | 28(2) | 36(2) | 11(2) |
| C(17) | 98(3) | 107(4) | 154(4) | -21(3) | 43(3) | -19(3) |
| C(18) | 107(3) | 132(4) | 156(4) | 41(3) | 76(3) | 1(3) |
| C(19) | 54(2) | 55(2) | 47(1) | 1(1) | 20(1) | 8(1) |
| C(20) | 64(2) | 108(3) | 58(2) | 18(2) | 23(2) | 31(2) |
| C(21) | 48(2) | 70(2) | 42(1) | 0(1) | 17(1) | 11(2) |
| C(22) | 58(2) | 72(2) | 54(2) | 3(1) | 27(1) | 9(2) |
| C(23) | 66(2) | 82(3) | 67(2) | 8(2) | 32(2) | 13(2) |
| C(24) | 79(2) | 98(3) | 56(2) | 7(2) | 34(2) | 27(2) |
| C(25) | 75(2) | 80(3) | 52(2) | -6(2) | 23(2) | 30(2) |
| C(26) | 54(2) | 69(2) | 46(1) | -2(1) | 12(1) | 15(2) |
| C(27) | 81(2) | 74(3) | 73(2) | -13(2) | 45(2) | -13(2) |
| C(28) | 93(3) | 77(3) | 105(3) | 1(2) | 22(2) | 0(2) |
| C(29) | 133(4) | 89(4) | 83(2) | -7(2) | 10(2) | -5(3) |
| C(30) | 68(2) | 65(2) | 71(2) | -15(2) | 21(2) | 6(2) |
| C(31) | 79(3) | 149(5) | 98(3) | -26(3) | 5(2) | -17(3) |
| C(32) | 117(3) | 82(4) | 155(4) | 25(3) | 48(3) | 11(3) |
| B(1) | 120(5) | 131(6) | 84(3) | 1(3) | 52(3) | -12(4) |
| F(1) | 227(6) | 232(7) | 80(2) | -31(3) | 13(3) | -110(5) |
| F(2) | 142(4) | 233(6) | 173(4) | 48(4) | 103(3) | -6(4) |
| F(3) | 142(3) | 245(6) | 96(2) | 62(3) | 69(2) | 9(3) |
| F(4) | 290(7) | 130(5) | 227(6) | -49(4) | 171(6) | -68(5) |