

Synthesis and reactivity of sterically encumbered diazaferrocenes

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1. (VT-) ^1H NMR spectra of **3-Fe**

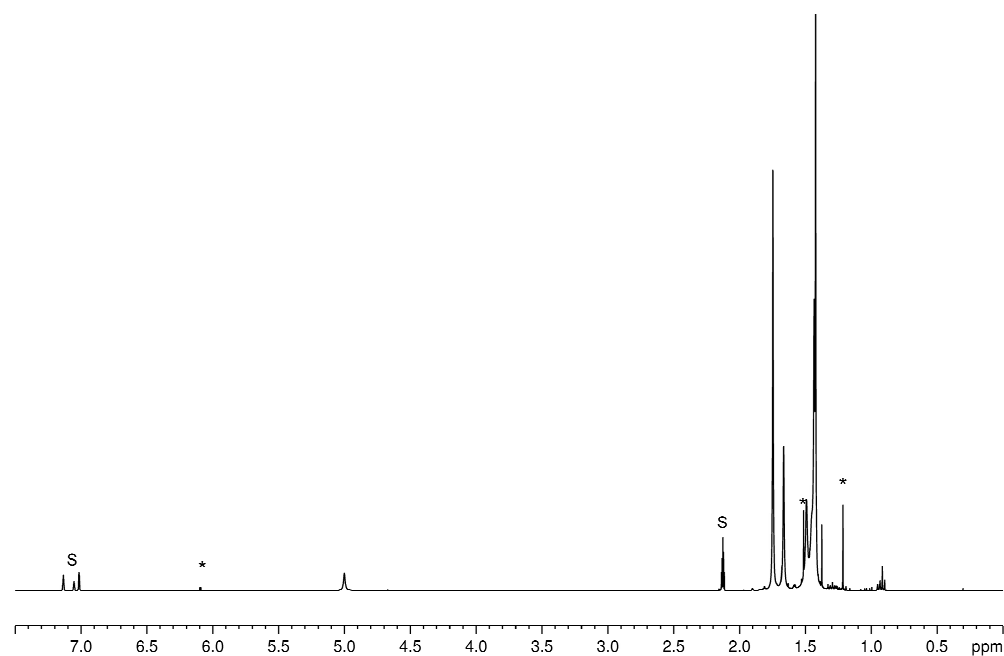


Figure S1. ^1H NMR spectrum of **3-Fe** recorded at 298 K in C_7D_8 . Labels: S = $\text{C}_7\text{D}_7\text{H}$, * free pyrrole (**3-H**)

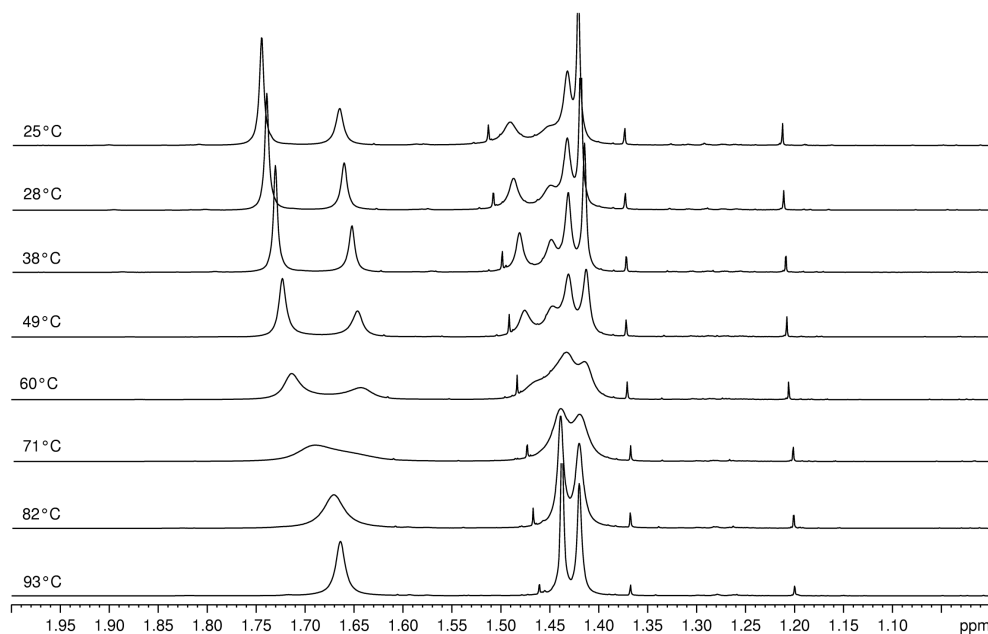


Figure S2. VT ^1H NMR spectrum of **3-Fe** recorded in C_7D_8 . Only the *t*Bu-region is shown.

2. Packing diagram of [5-Fe][SbF₆]

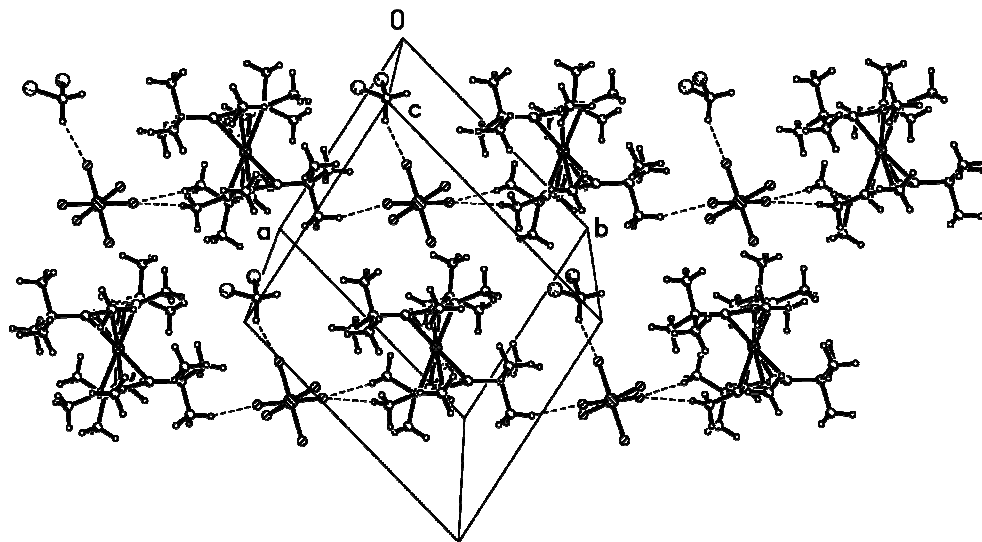


Figure S3. Packing diagram of [5-Fe][SbF₆]CH₂Cl₂ (viewed perpendicular to ab-plane, *z ca.* 0.25).

3. Molecular structure of [4-Fe][SbF₆]

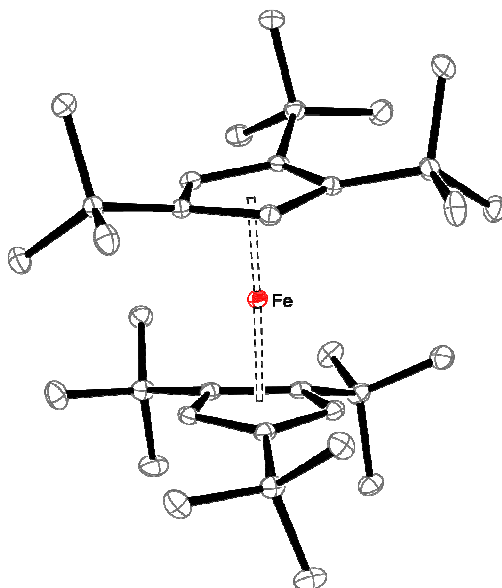


Figure S4. ORTEP diagram of 4-Fe⁺ with thermal displacement parameters drawn at 50% probability. For clarity the H atoms and the counter anion [SbF₆]⁻ are not shown.

3. Synthesis and solid state magnetism of [4-Fe][BF₄]

Synthesis of [4-Fe][BF₄]. AgBF₄ (0.035 mg, 0.18 mmol) was added to a stirred solution of **4-Fe** (0.100g, 0.18 mmol) in CH₂Cl₂. The reaction mixture was stirred overnight and filtered. The filtrate was concentrated and a layer of pentane was carefully added on top of the CH₂Cl₂ solution. Slow pentane diffusion at ambient temperature yielded fine green needles. Yield: 0.084 g (0.13 mmol, 74%). M.p. 262-263 °C (dec.). ¹H NMR (CDCl₃, 19 °C): δ 42.0 (4 H, ring-CH, $\nu_{1/2} \sim 3000$ Hz), $\square$ 8.8 (18 H, s, ring-CMe₃, $\nu_{1/2} = 160$ Hz), $\square$ 9.3 (18H, s, ring-CMe₃, $\nu_{1/2} = 200$ Hz), $\square$ 12.4 (18 H, s, ring-CMe₃, $\nu_{1/2} = 200$ Hz). Anal. calcd. for C₃₄H₅₈FeBF₄·(CH₂Cl₂)_{0.25}: C, 65.14; H, 9.26. Found: C, 65.05; H, 9.40. CH₂Cl₂ was identified in the ¹H NMR spectrum in CDCl₃ (δ 5.31).

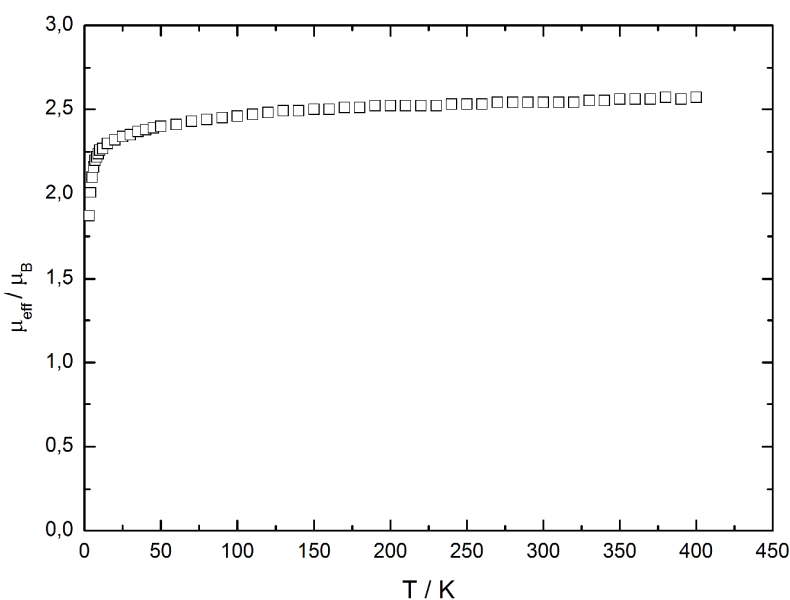


Figure S5. Solid state magnetic susceptibility vs. T data for [4-Fe][BF₄].

4. IR Spectra

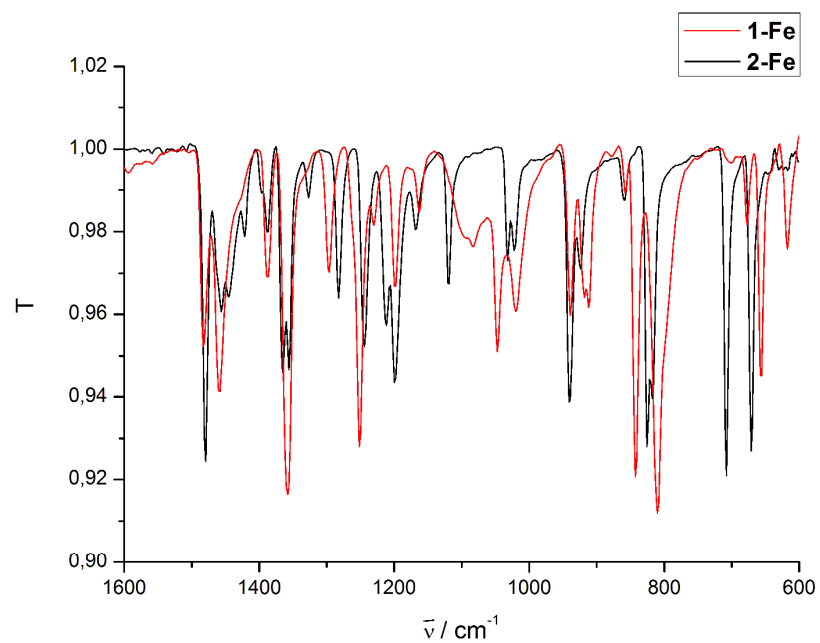


Figure S6. ATR-IR spectra of **1-Fe** and **2-Fe**.

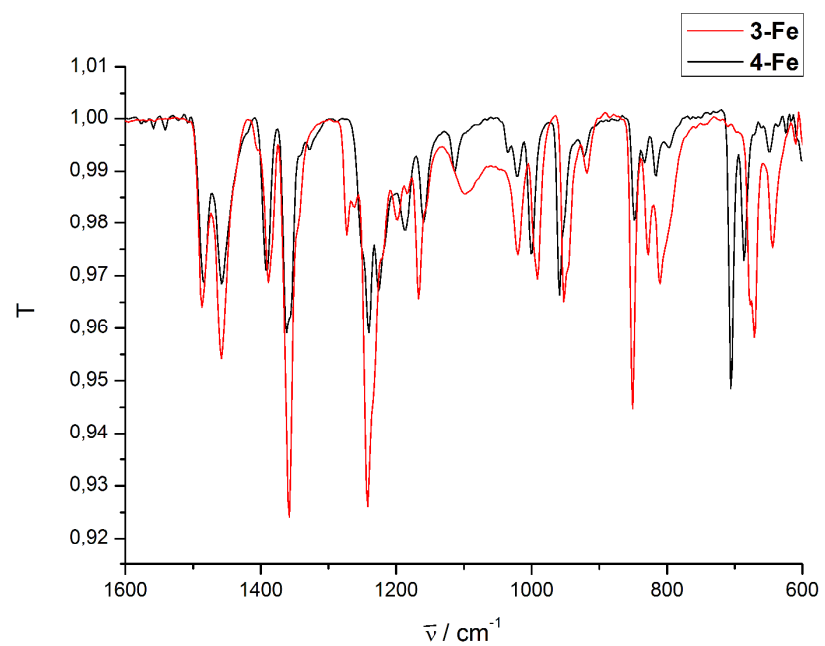


Figure S7. ATR-IR spectra of **3-Fe** and **4-Fe**.

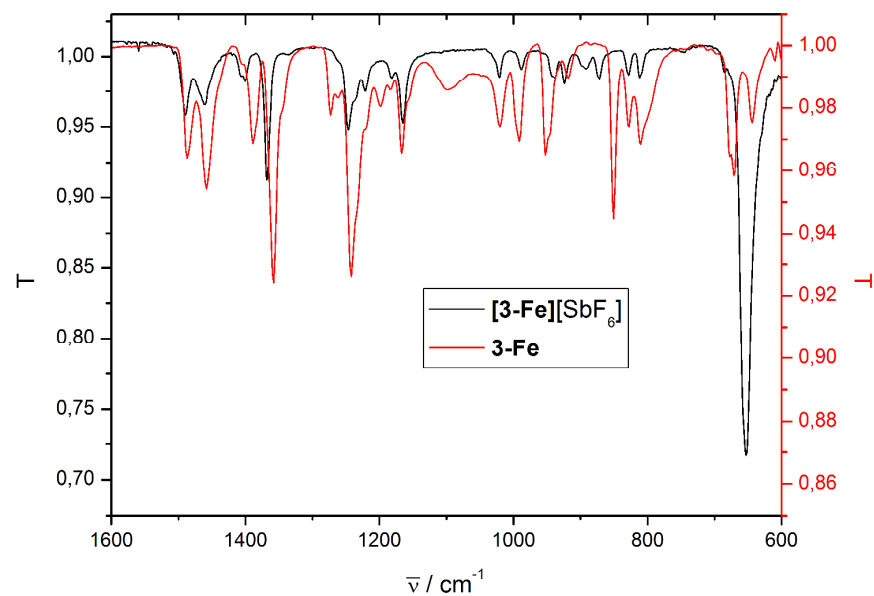


Figure S8. ATR-IR spectra of **3-Fe** and **[3-Fe][SbF₆]**.

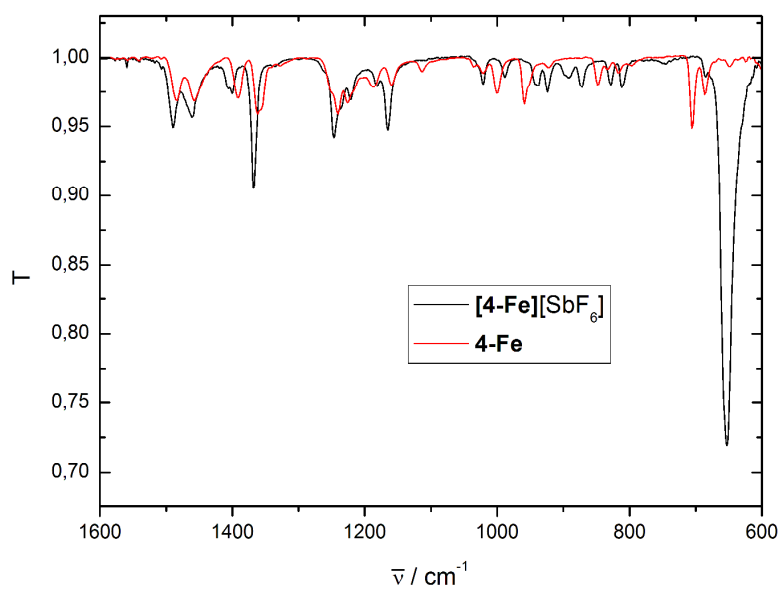


Figure S9. ATR-IR spectra of **4-Fe** and **[4-Fe][SbF₆]**.

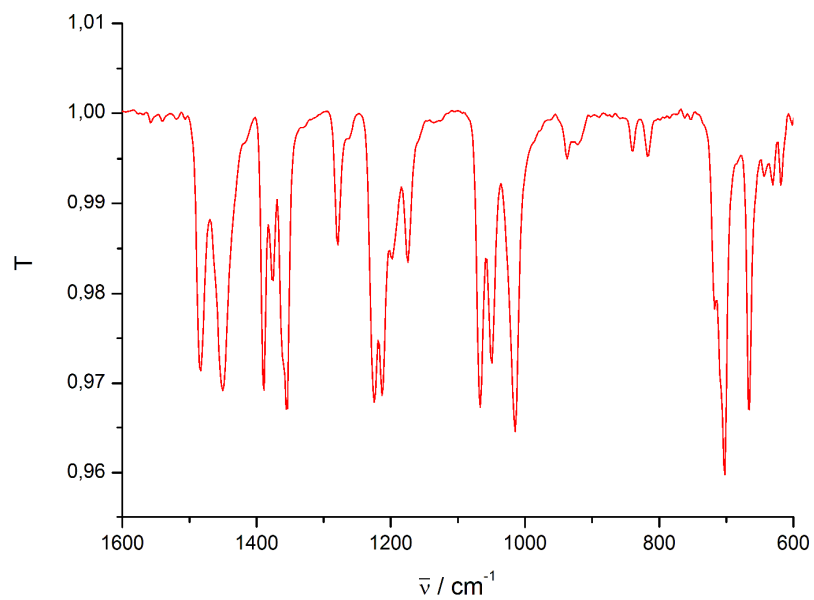


Figure S10. ATR-IR spectrum of **5-Fe**.

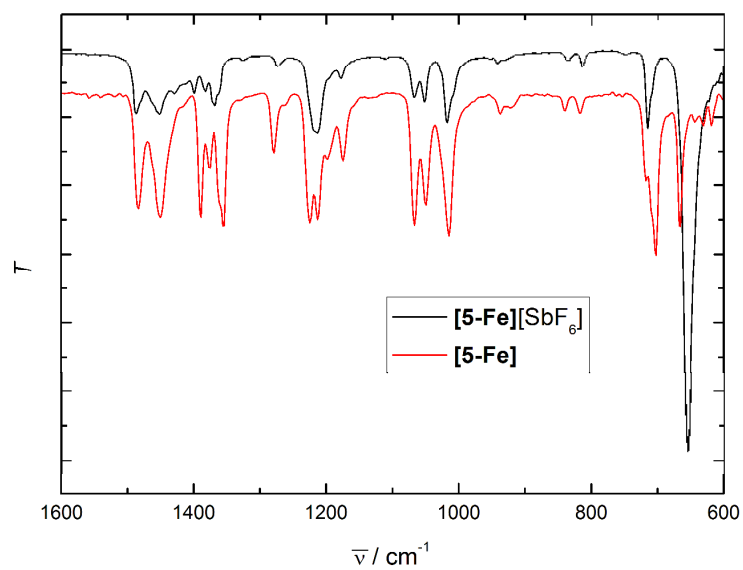


Figure S11. ATR-IR spectra of **5-Fe** and **[5-Fe][SbF₆]**.

5. Electrochemical studies

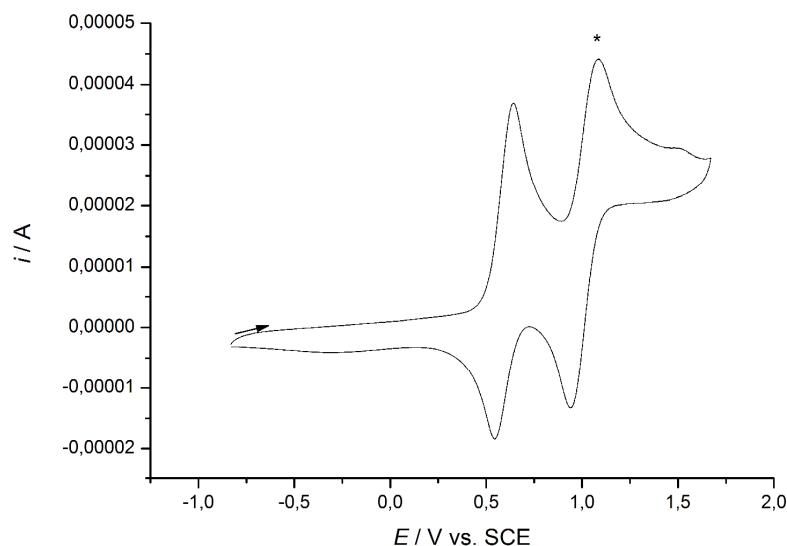


Figure S13a. Cyclic voltammogram (CV) of **3-Fe**. CV recorded at ambient temperature in CH_2Cl_2 with 0.1 M $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ supporting electrolyte. Scan rate: 100 mV/s. Redox-wave indicated with * corresponds to the free pyrrole **3-H**, which is formed during the acquisition of the CV.

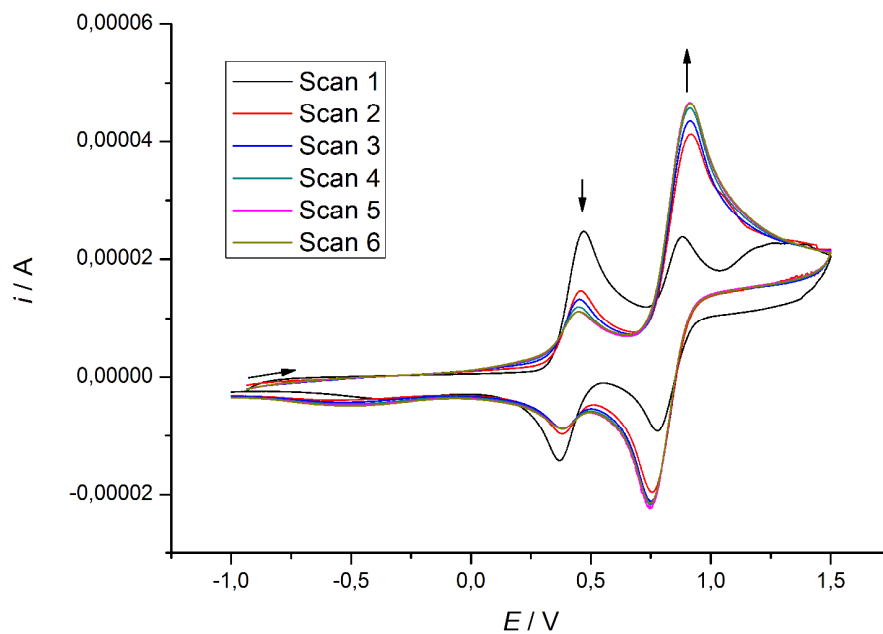


Figure S13b. Cyclic voltammogram (CV) of **3-Fe**. CV recorded in CH_2Cl_2 with 0.1 M $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ supporting electrolyte. Scan rate: 100 mV/s. CV spectra are not calibrated.

6. Mössbauer spectroscopic study on 3-Fe after storage on air for 1 week

In contrast to ferrocene **4-Fe**, which is indefinitely stable on air, diazaferrocene **3-Fe** shows slow decomposition.

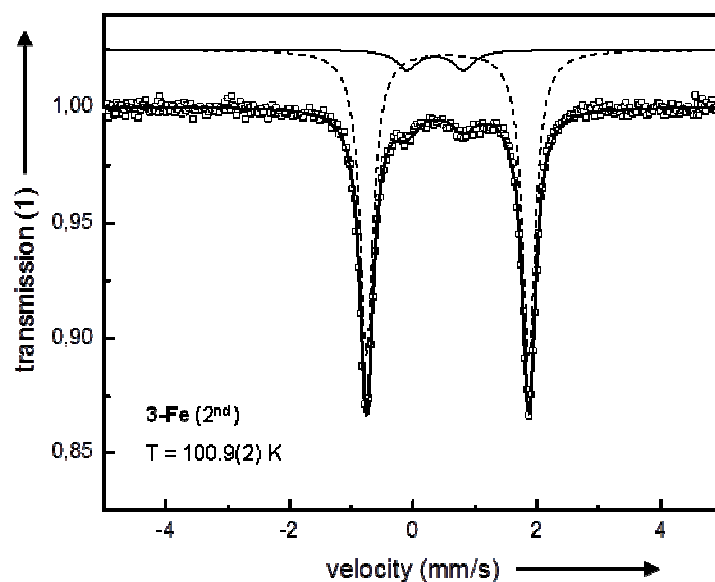


Figure S14. ^{57}Fe Mössbauer spectrum of **3-Fe** recorded on the original ^{57}Fe Mössbauer sample (see manuscript for details) after this sample was exposed (in the closed sample container) to air for 5 days. Two Fe sites can be found: Site 1 (91 %): $\delta = 0.56 \text{ mm s}^{-1}$, $\Delta E_Q = 2.63 \text{ mm s}^{-1}$, $\Gamma_{\text{FWHM}} = 0.26 \text{ mm s}^{-1}$ (corresponding to **3-Fe**); Site 2 (9%): $\delta = 0.47 \text{ mm s}^{-1}$, $\Delta E_Q = 0.91 \text{ mm s}^{-1}$, $\Gamma_{\text{FWHM}} = 0.42 \text{ mm s}^{-1}$.

7. UV-Vis Spectroscopy

Table S1. UV-vis spectra of diazaferrocenes and their ferrocene counterparts

Compound ^a	d → d transitions	
	λ_{max} / nm [ϵ / L mol cm ⁻¹]	
1-Fe	503 [240], 350 [115]	this work
2-Fe	462 [153], 328 [130]	this work
3-Fe	510 [225], 378 [130]	this work
4-Fe	500 [200], 360 [130]	this work
5-Fe	480 [150], 365 [140]	this work

^a UV-vis spectra recorded in pentane solution at ambient temperature.

8. Computational details

All computations were performed using the density functional method B97D as implemented in the Gaussian09 program.¹ For all elements (Fe, C, H and N) the all-electron triple- ζ basis set (6-311G**) was used.²

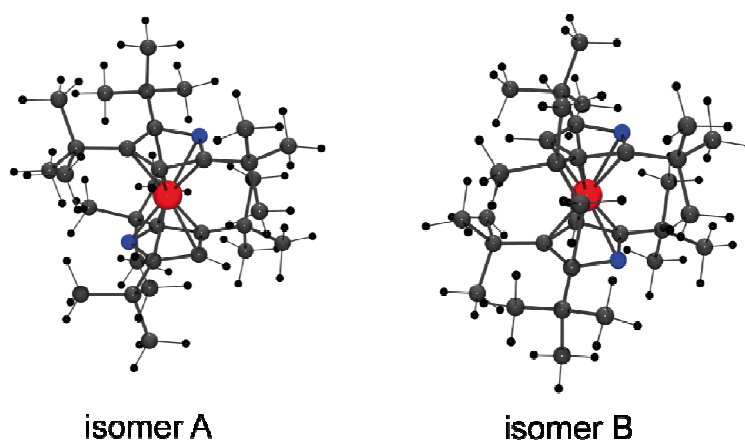


Figure S15. Computed molecular structures of 3-Fe (isomer A and B).

Energies of the optimized structures

Compound	E(0 K) ^a [Ha]	H(298 K) ^b [Ha]	G(298 K) ^b [Ha]
$[(\eta^5\text{-Pyr}^{\text{tBu3}})_2\text{Fe}]$ (3-Fe , A) (isomer A)	-2625.478348	-2625.435949	-2625.542815
$[(\eta^5\text{-Pyr}^{\text{tBu3}})_2\text{Fe}]$ (3-Fe , B) (isomer B)	-2625.476540	-2625.434453	-2625.540736
$[(\eta^5\text{-Pyr}^{\text{tBu3}})_2\text{Fe}]^+$ (3-Fe ⁺)	-2625.256874	-2625.213727	-2625.324446
$[(\eta^5\text{-Cp}^{\text{tBu3}})_2\text{Fe}]$ (4-Fe)	-2593.372704	-2593.330127	-2593.438030
$[(\eta^5\text{-Cp}^{\text{tBu3}})_2\text{Fe}]^+$ (4-Fe ⁺)	-2593.167061	-2593.124170	-2593.233611

^aDFT energy incl. ZPE. ^bstandard conditions T = 298.15 K and p = 1 atm.

9. References

- (1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. J.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, E.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. In *Gaussian 09, Revision A.02*; Gaussian, Inc.: Wallington CT, 2009.
- (2) Cao, X.; Dolg, M. *J. Chem. Phys.* **2001**, *115*, 7348.

