Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information for: Redox Behaviour of ([fc(NP^{i}Pr$_2$)$_2$]Fe)$_2$, Formation of an Iron-Iron Bond and Cleavage of Azobenzene

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1 X-ray Crystallographic Analyses

Suitable single crystals were selected in a glovebox, coated in STP motor oil and mounted on a glass loop. X-ray data were collected on a Bruker DUO Apex II diffractometer with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at a temperature of 90 K. Data were collected and integrated using the Bruker SAINT software package.[S1] Absorption corrections were performed using the multiscan technique (SADABS).[S2] The structures were solved by direct methods and refined using all reflections with the SHELX-2013[S3] program package. All non-hydrogen atoms were refined anisotropically. All structures were solved and refined using the Olex2 (version 1.2.5)[S4] software package.

Table S1: Crystal data and refinement details for **2**, **3** and **4**

Compound	**2**	**3**	**4**
empirical formula	$C_{22}H_{36}Fe_2I_4N_2P_2$	$C_{68}H_{120}Fe_4N_4P_4O_6K$	$C_{34}H_{46}Fe_2N_4P_2$
formula weight	1009.72	1475.24	684.35
crystal size [mm]	0.06 x 0.06 x 0.02	0.23 x 0.05 x 0.05	0.12 x 0.11 x 0.08
crystal system	monoclinic	monoclinic	monoclinic
space group	Cc (No. 9)	$P2_1/c$ (No.14)	$P2_1/n$ (No. 14)
a [Å]	14.8284(13)	14.292(3)	13.6777(7)
b [Å]	17.0000(15)	21.153(5)	13.5134(6)
c [Å]	14.5439(13)	24.731(6)	17.7979(8)
α [°]	90.0	90.0	90.0
β [°]	90.654(2)	91.213(5)	94.0140(10)
γ [°]	90.0	90.0	90.0
V [Å^3]	3666.0(6).1(3)	7475(3)	3281.6(3)
ρ [g cm^3]	1.996	1.311	1.385
Z	8	4	2
$F(000)$	2104	3145	1440
μ [mm^{-1}]	4.268 (Mo-Kα)	0.951 (Mo-Kα)	1.011 (Mo-Kα)
T_{min}/T_{max}	0.6248/0.7453	0.6530/0.7456	0.6760/0.7456
hkl range	-18 – 10, ± 20, ± 17	-18 – 17, -26 – 27, ±32	±17, ±17, -23 – 15
θ range [°]	1.82 – 26.10	1.72 – 27.548	1.818 – 27.503
meassured refl.	26127	68997	30760
unique refl.	6304	17128	7523
refined parameters	302	792	563
completeness to θ [%]	99.8	99.5	99.9
goodness-of-fit	1.136	0.985	1.022
$R1$, $wR2$ ($I > 2\sigma(I)$)	0.0243, 0.0572	0.482, 0.0958	0.0279, 0.0638
$R1$, $wR2$ (all data)	0.0252, 0.0575	0.0917, 0.1123	0.0372, 0.0675
res. el. dens. [e- Å^3]	0.564/-0.507	-1.005/0.980	-0.236/0.421

2 Cyclic Voltammetry

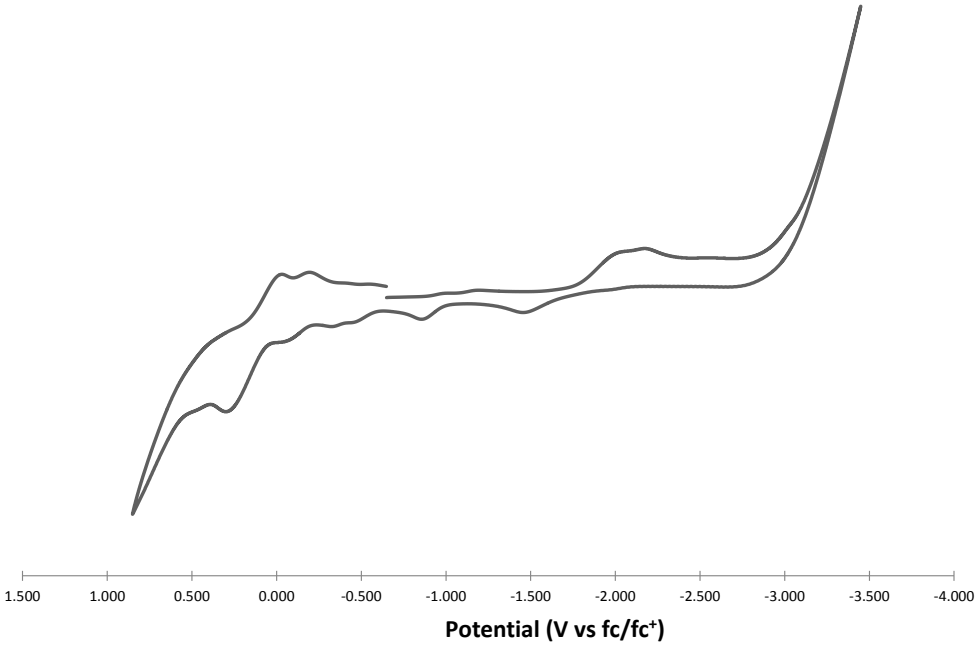

Figure S1: Cyclic voltammograms of complex **1** in 0.1 M $[^{n}Bu_4N][PF_6]$ in THF; scan rate = 100 mv s^{-1}

3 ^{1}H NMR Spectra

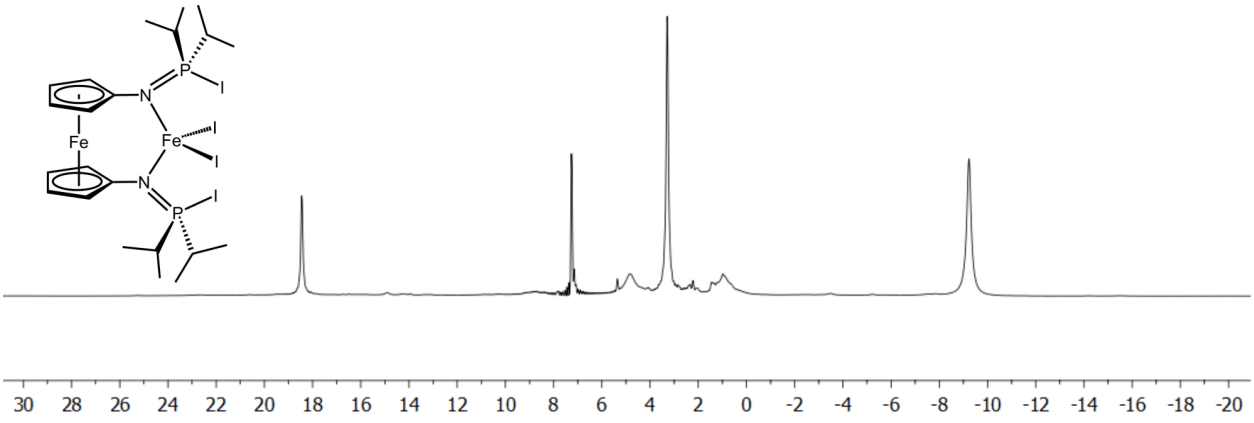

Figure S2: ^{1}H NMR spectrum (400 MHz, 298K) of **2** in C_6D_6

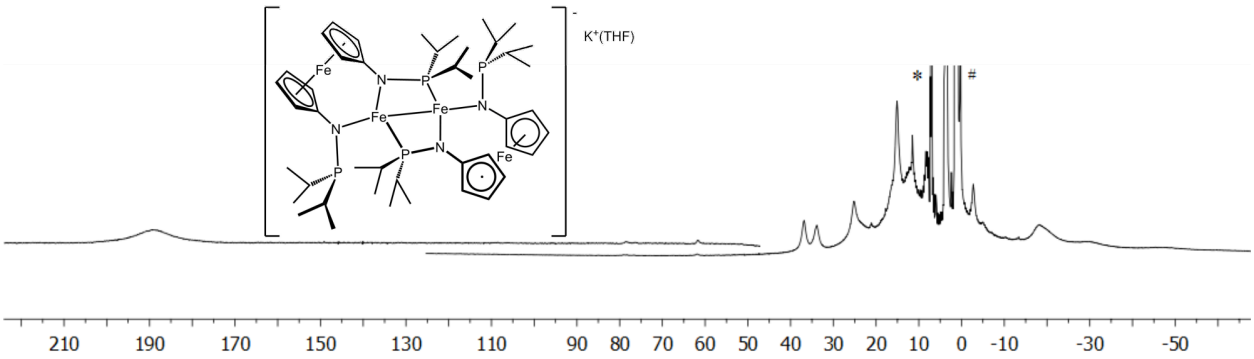

Figure S3: ^{1}H NMR spectrum (400 MHz, 298K) of **3** in C_6D_6. *Residual C_6D_6 $^{\#}$THF needed for solubility.

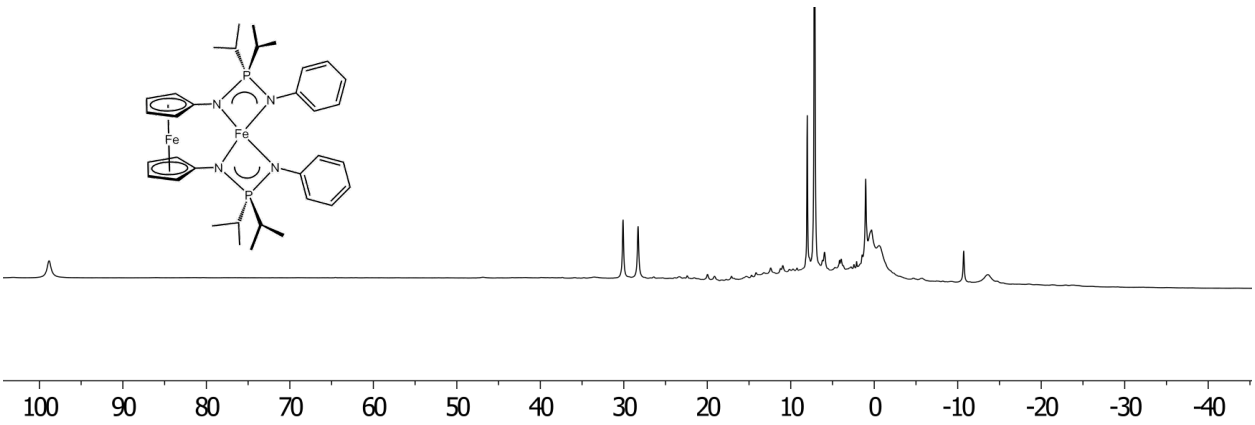

Figure S4: ^{1}H NMR spectrum (400 MHz, 298K) of **4** in C_6D_6

4 Isomerization of Azobenzene

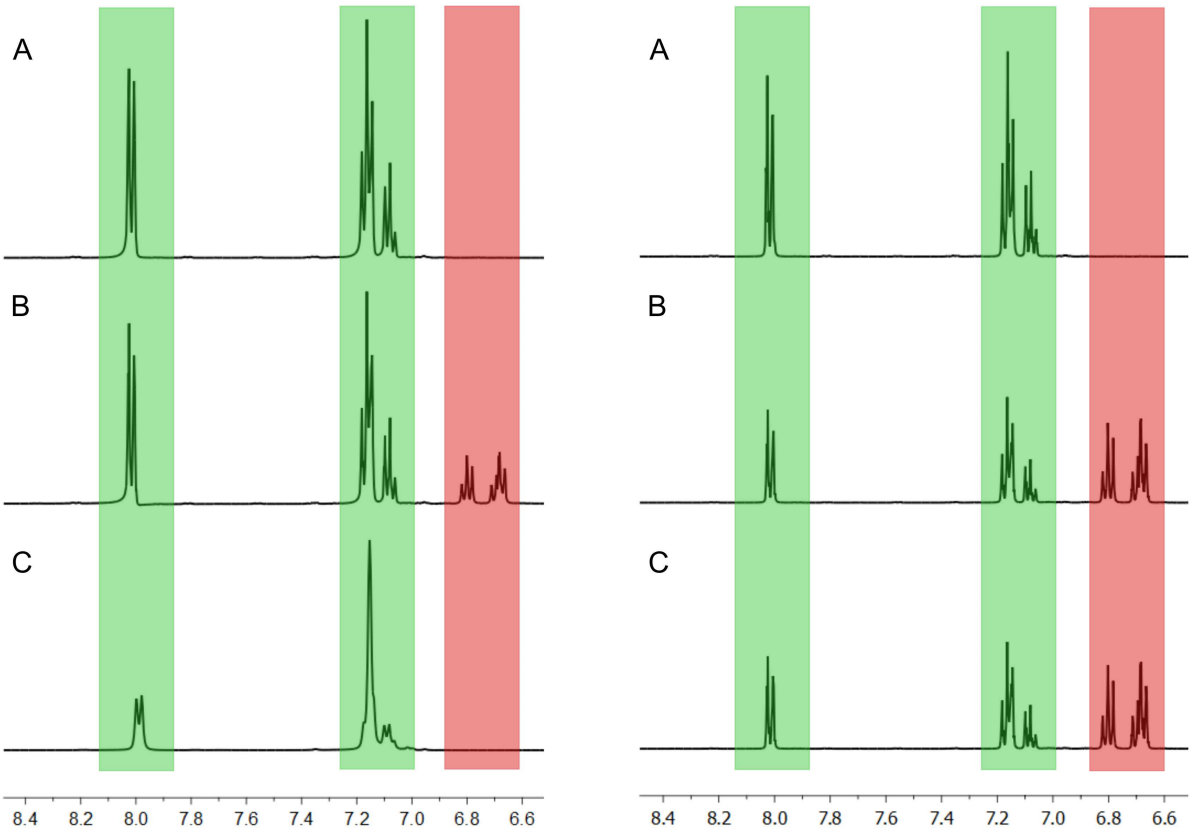

Figure S5: ^{1}H NMR spectra (400 MHz, 298K) of **A** (left and right) Initial solution of *trans*-PhNNPh; **B** (left) Solution after irradiation at 350 nm for 25 min (right) Solution after irradiation at 350 nm for 60 min; **C** 30 minutes after Mixing with (left) and without (right) compound **1**. Green: *trans*-PhNNPh and red:*cis*-PhNNPh

5 Mössbauer Spectra for 3

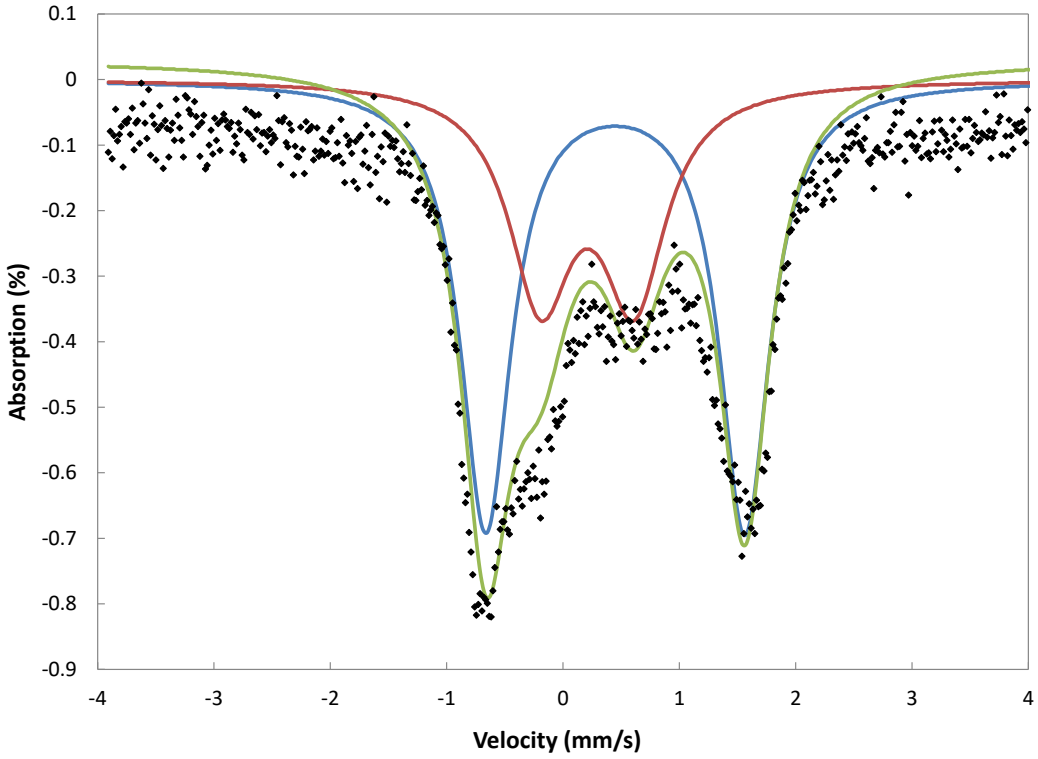

Figure S6: Zero Field Mössbauer Spectra of **3** collected at 298K. Fit 1 (blue) $\delta = 0.458$ mm/s, ΔEq = 2.225 mm/s; Fit 2 (red) $\delta = 0.208$ mm/s; ΔEq = 0.772 mm/s; Fit 3 (green) overall fit.

6 References

References

(S1) SAINT, Version 7.03A. Bruker AXS Inc., Madison, Wisconsin USA, (1997-2003).

(S2) SADABS Bruker Nonius: area detector scaling and absorption correction. Version 2.10. Bruker AXS Inc., Madison, Wisconsin, USA, (2003).

(S3) Sheldrick, G. M. *Acta Cryst. A* **2008**, *A64*, 112.

(S4) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339–341.