Supporting Information File

Anion-controlled formation of an aminal-(bis)imine Fe(II)-complex

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EXPERIMENTAL SECTION

^{1}H NMR and ^{13}C NMR were measured on a Bruker AV 500 (500 MHz). All the ^{1}H NMR was carried at room temperature mainly in deuterated chloroform unless specified otherwise.

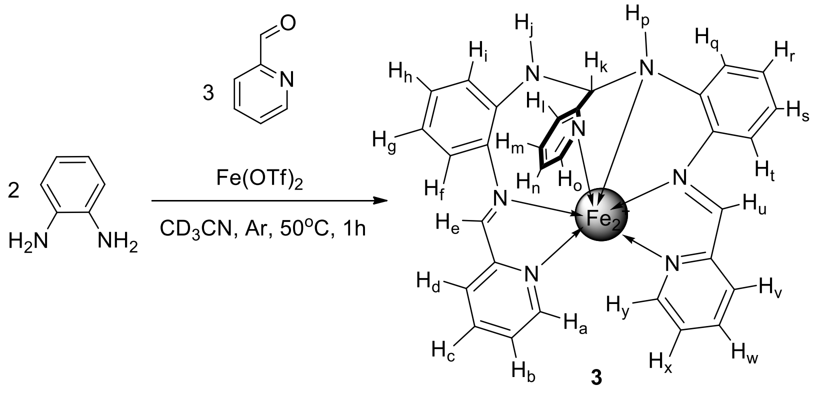
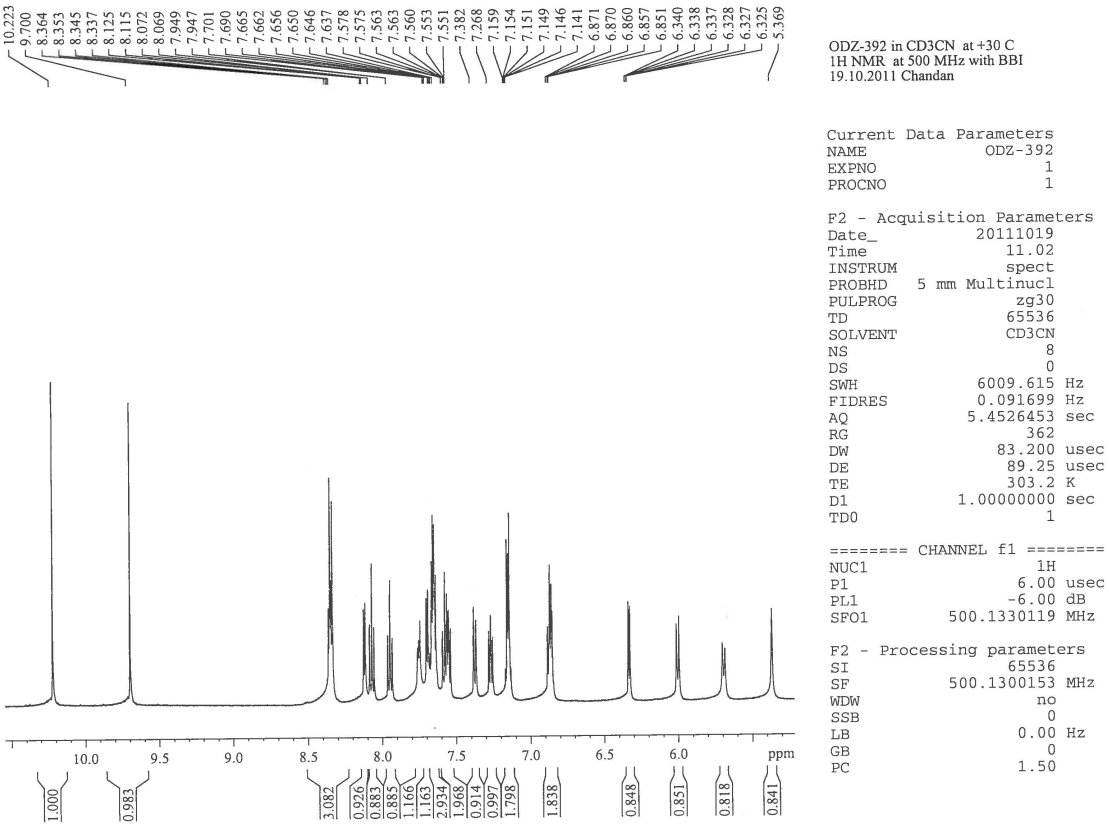


Figure S1. Synthesis of **3** in acetonitrile.

Synthesis of **3**: Into a j-young NMR tube were added 1,2-diaminobenzene (2.0 mg, 18.5 μmol), pyridine-2-carboxaldehyde (2.64 μl, 27.7 μmol), iron(II) triflate (3.27 mg, 9.2 μmol) and CD$_3$CN (0.5 mL). The tube was sealed, and the solution purged off dioxygen by three vacuum/argon fill cycles. All starting materials dissolved in degassed CD$_3$CN giving a dark purple solution. The tube was placed in an oil bath at 323 K for 1 h. ^{1}H NMR: (500 MHz, 303 K, in CD$_3$CN); δ = 10.22(s, 1H, H$_u$), 9.70 (s, 1H, H$_e$), 8.36 (m, 3H, H$_v$, H$_r$, H$_d$), 8.12 (d, J = 5 Hz, H$_y$), 8.07 (td, J_1 = 8 Hz, J_2 = 1.5 Hz H$_w$), 7.95 (td, J_1 = 8 Hz, J_2 = 1.5 Hz H$_c$), 7.75 (m, 1H, H$_q$), 7.70 (d, J = 5.5 Hz, H$_a$), 7.66 (m, 3H, H$_f$, H$_s$, H$_t$), 7.56 (m, 2H, H$_m$, H$_x$), 7.37 (d, J = 8, H$_l$), 7.27 (td, J_1 = 6 Hz, J_2 = 1.5 Hz, H$_b$), 7.15 (m, 2H, H$_g$, H$_h$), 6.87 (m, 2H, H$_i$, H$_n$), 6.33 (dt, J_1 = 6 Hz, J_2 = 1 Hz, H$_o$), 6.00 (d, J = 8.5, H$_k$), 5.69

(d, J = 8.5, H$_j$), 5.37 (s, h$_p$) ppm; ^{13}C NMR(125 MHz, 303K, CD$_3$CN): δ =173.5, 163.5, 161.5, 161.4, 159.8, 155.5, 154.9, 152.9, 149.1, 144.0, 143.5, 139.7, 139.5, 138.8, 138.4, 134.1, 131.4, 131.0, 130.9, 130.2, 129.5, 128.8, 128.0, 128.0, 127.0, 126.2, 126.1, 124.2, 122.0, 84,1 ppm; ESI-MS: m/z: 269.58 $[FeL]^{2+}$, 688.14 $[(FeL)(OTf)]^{+}$. Elemental analysis $[C_{30}H_{25}N_7Fe]^{2+}(CF_3SO_3)^{-}_2$ Observed: C = 45.83, H = 3.31, N = 11.84, Calculated: C = 45.89, H = 3.01, N = 11.71.



ODZ-392 in CD3CN at +30 C
1H NMR at 500 MHz with BBI
19.10.2011 Chandan

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PROCNO                  1

F2 - Acquisition Parameters
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TD                  65536
SOLVENT             CD3CN
NS                      8
DS                      0
SWH              6009.615 Hz
FIDRES           0.091699 Hz
AQ              5.4526453 sec
RG                    362
DW                 83.200 usec
DE                  89.25 usec
TE                  303.2 K
D1             1.00000000 sec
TD0                     1

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NUC1                   1H
P1                   6.00 usec
PL1                 -6.00 dB
SFO1          500.1330119 MHz

F2 - Processing parameters
SI                  65536
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WDW                    no
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GB                      0
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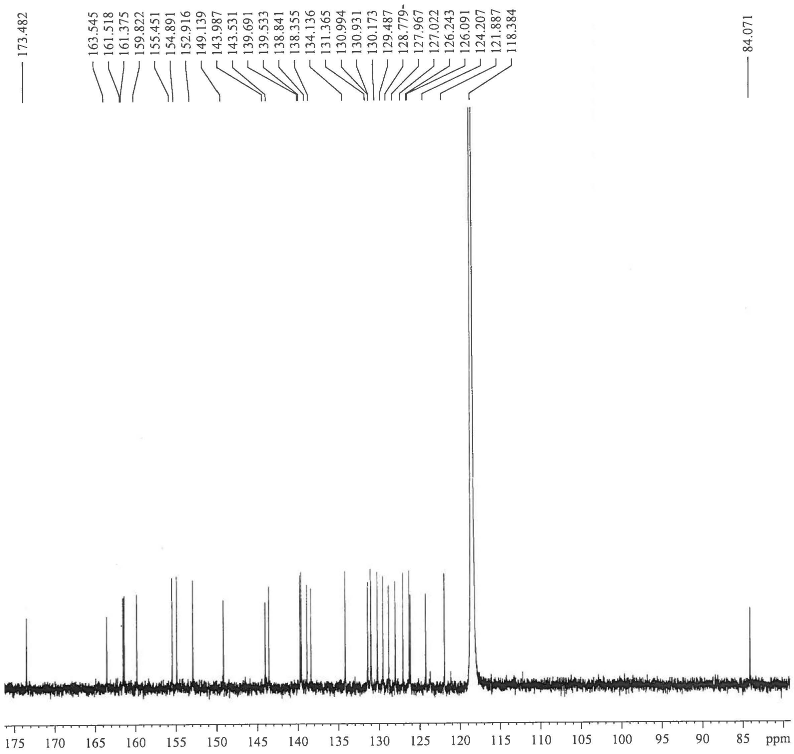
Figure S2. ^{1}H NMR of complex **3** in CD$_3$CN.



ODZ-392 in CD3CN at +30 C
13C NMR at 126 MHz with BBI
19.10.2011 Chandan

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PROCNO                    1

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PULPROG             zgpg30
TD                    65536
SOLVENT               CD3CN
NS                    17447
DS                        0
SWH               30303.031 Hz
FIDRES             0.462388 Hz
AQ                1.0813940 sec
RG                     1024
DW                   16.500 usec
DE                     6.00 usec
TE                    303.2 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                   10240

======== CHANNEL f1 ========
NUC1                    13C
P1                    11.50 usec
PL1                   -4.00 dB
SFO1          125.7716224 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                   -6.00 dB
PL12                  13.47 dB
PL13                 120.00 dB
SFO2          500.1320005 MHz

F2 - Processing parameters
SI                    65536
SF            125.7576501 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
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Figure S3. ^{13}C NMR of complex **3** in CD_3CN.

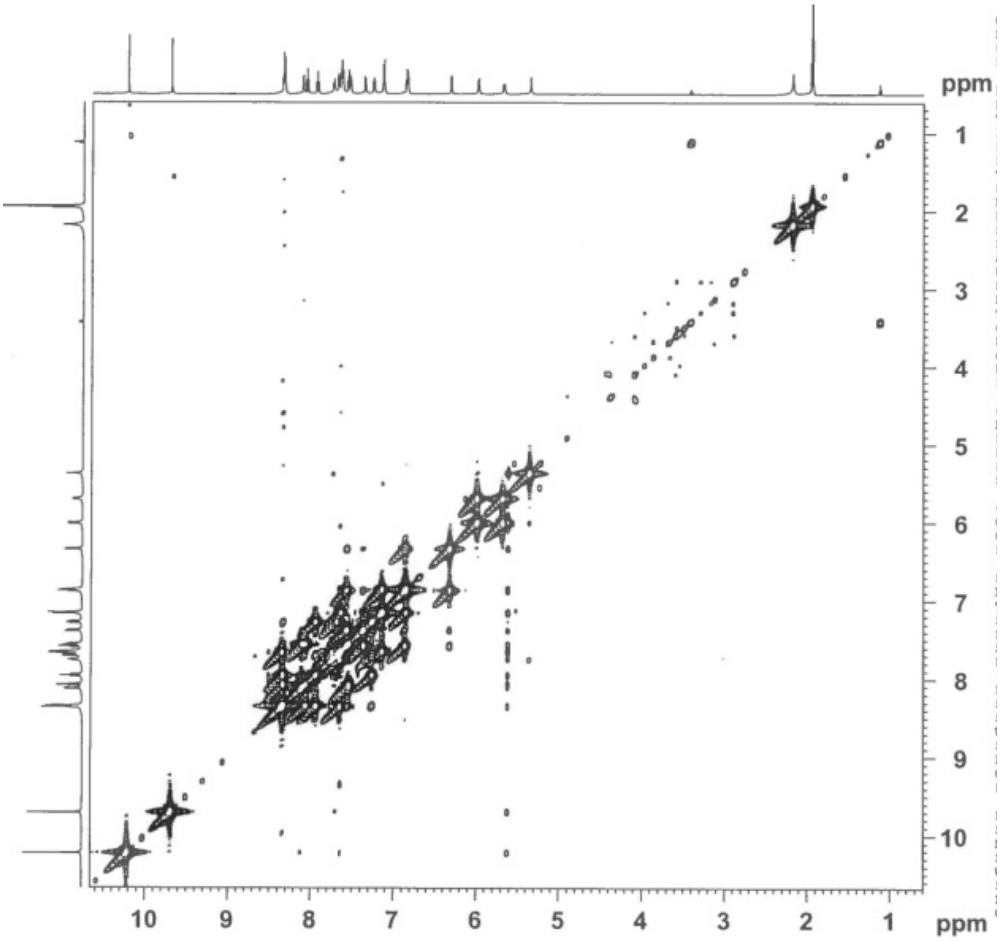
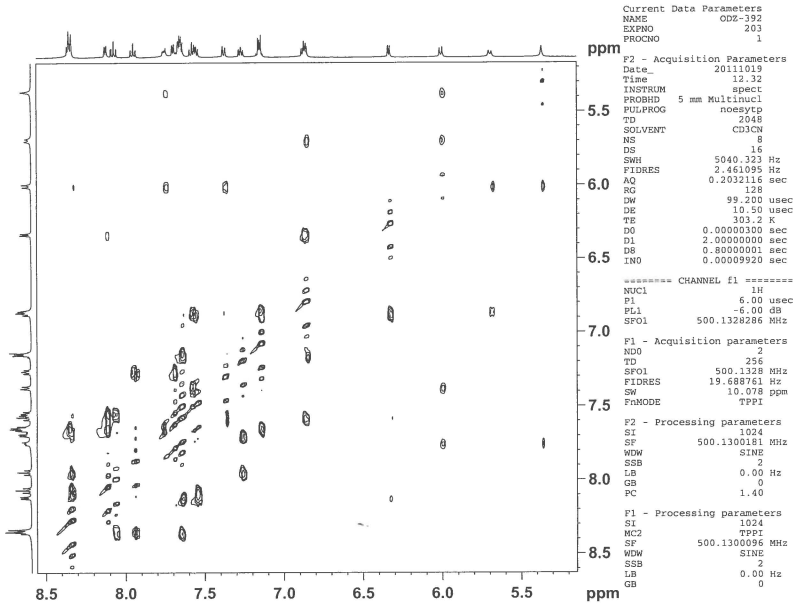


Figure S4. ^1H-^1H COSY NMR of complex **3** in CD_3CN.



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PROCNO                 1

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INSTRUM            spect
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PULPROG          noesytp
TD                  2048
SOLVENT            CD3CN
NS                     8
DS                    16
SWH             5040.323 Hz
FIDRES          2.461095 Hz
AQ             0.2032116 sec
RG                   128
DW                99.200 usec
DE                 10.50 usec
TE                 303.2 K
D0            0.00000300 sec
D1            2.00000000 sec
D8            0.80000001 sec
IN0           0.00009920 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  6.00 usec
PL1                -6.00 dB
SFO1         500.1328286 MHz

F1 - Acquisition parameters
ND0                    2
TD                   256
SFO1            500.1328 MHz
FIDRES         19.688761 Hz
SW                10.078 ppm
FnMODE              TPPI

F2 - Processing parameters
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SF           500.1300181 MHz
WDW                 SINE
SSB                    2
LB                  0.00 Hz
GB                     0
PC                  1.40

F1 - Processing parameters
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SSB                    2
LB                  0.00 Hz
GB                     0
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Figure S5. ^1H-^1H NOESY NMR of complex **3.**

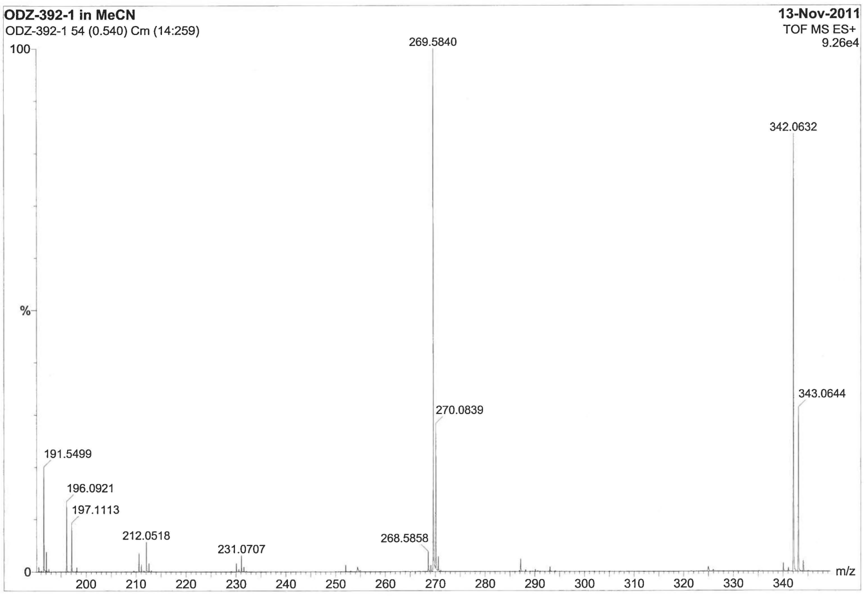

Figure S6. ESI-MS of complex **3.**

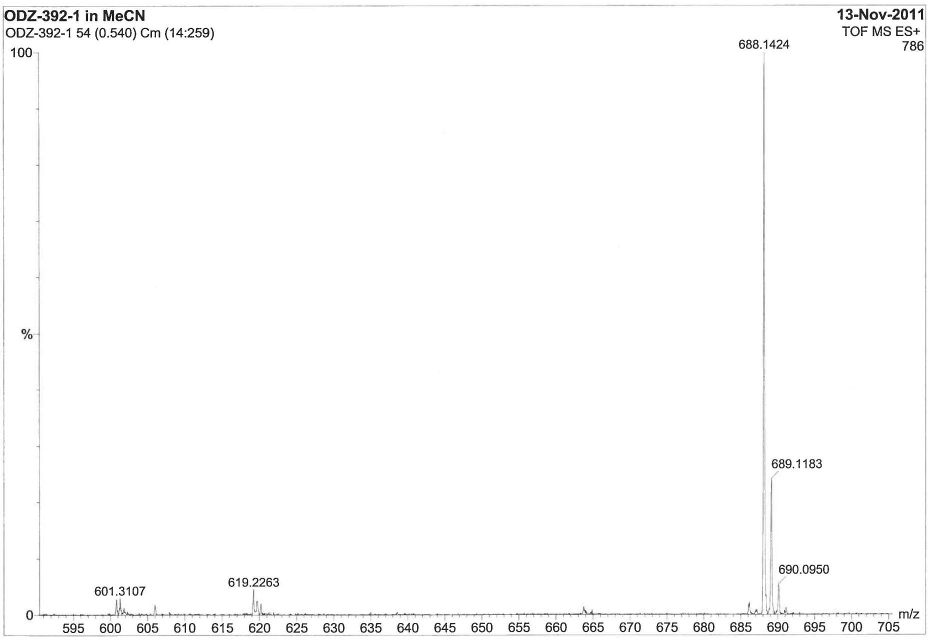

Figure S7. ESI-MS of complex **3.**

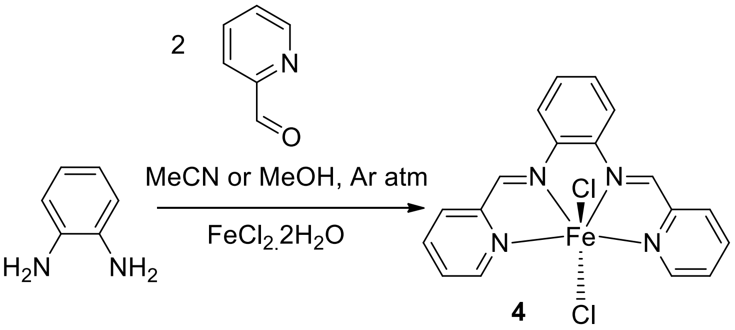

Figure S8. Synthesis of complex **4**.

Synthesis of 4. Into a j-young NMR tube were added 1,2-diaminobenzene (1.5 mg, 13.9 μmol), 2-formyl pyridine (2.64 μl, 27.7 μmol and iron(II) chloride dihydrate (2.24 mg, 13.9 μmol) and CD_3OD (0.5 mL). The tube was sealed, and the solution purged of dioxygen by three vacuum/argon fill cycles. All starting materials dissolved in degassed CD_3OD giving a dark green solution. The tube was placed in an oil bath at 323 K. After 2 h ^1H NMR was checked and only a broad peak was observed. Diffusion of di ethyl-ether to the solution **4** isolated the single crystal.

Molecular modeling

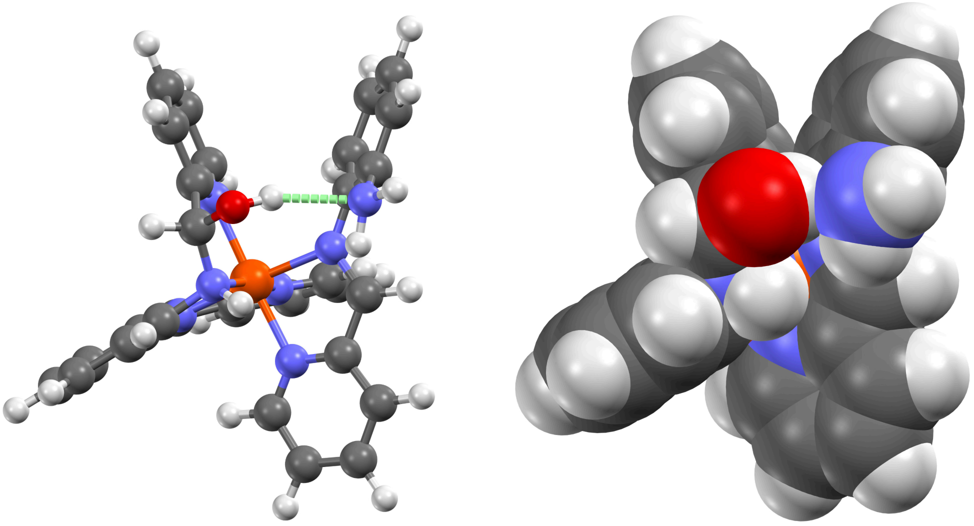

Figure S8. The calculated structure of the hemi-aminal **5**, SPARTAN2014, MM-level (Spartan 2014, Wavefunction Inc., 18401 Von Karman Ave, Irvine, CA 92612, USA.

X-ray crystallography

Experimental data for **3**: Data were collected on a Bruker-Nonius KappaCCD diffractometer with APEX II detector at $T = 123.0(1)$ K using graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å). Collect[1] software was used for data collection, whereas Denzo/Scalepack[2] were used for processing. Semi-empirical absorption correction was applied using SADABS2008.[3]
Crystal dimensions 0.30×0.20×0.20 mm, $C_{32}H_{25}F_6FeN_7O_6S_2$, $M = 837.56$, triclinic, space group $P\bar{1}$, $a = 9.2055(3)$ Å, $b = 11.5244(4)$ Å, $c = 16.9127(5)$ Å, $\alpha = 100.554(2)°$, $\beta = 93.752(2)°$, $\gamma = 100.5206(18)°$, $V = 1725.13(10)$ Å^3, $Z = 2$, $d_c = 1.612$ g cm^{-3}, $\mu = 0.647$ mm^{-1}, $F(000) = 852$, 9519 reflections ($2\theta_{max} = 50.49°$) measured (6216 unique, $R_{\text{int}} = 0.0266$, completeness = 99.7%), Final R indices ($I > 2\sigma(I)$): $R_1 = 0.0505$, $wR_2 = 0.1026$, R indices (all data): $R_1 = 0.0696$, $wR_2 = 0.1146$. $GOF = 1.062$ for 491 parameters and 1 restraint, largest diff. peak and hole 0.789/–0.566 eÅ^{-3}. CCDC-1006930 contains the supplementary data for this structure. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.
Experimental data for **4**: Data were collected on an Agilent SuperNova Dual diffractometer with Atlas detector at $T = 123.0(1)$ K using mirror-monochromated Cu-$K\alpha$ radiation ($\lambda = 1.54184$ Å). CrysAlisPro[4] software was used for data collection, integration and reduction as well as applying the numerical absorption correction.

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[1] R.W.W. Hooft, *COLLECT*, **1998**, Nonius BV, Delft, The Netherlands.

[2] Z. Otwinowski, W. Minor, *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307-326. New York: Academic Press.

[3] G.M. Sheldrick, *SADABS*, Version 2008/2, **1996**, University of Göttingen, Germany.

[4] *CrysAlisPro*, 1.171.36.28 ed., Agilent Technologies, Ltd., Yarton, UK, **2009–2013**.

Crystal dimensions 0.154×0.066×0.018 mm, $C_{18}H_{14}Cl_2FeN_4$, M = 413.08, monoclinic, space group $C2/c$, a = 10.2438(3) Å, b = 19.3127(6) Å, c = 8.8565(2) Å, α = 90°, β = 101.637(3)°, γ = 90°, V = 1716.11(8) Å^3, Z = 4, d_c = 1.599 g cm^{-3}, μ = 9.976 mm^{-1}, $F(000)$ = 840, 2658 reflections ($2\theta_{max}$ = 135.48°) measured (1545 unique, R_{int} = 0.0225, completeness = 98.6%), Final R indices ($I > 2\sigma(I)$): R_1= 0.0343, wR_2 = 0.0897, R indices (all data): R_1= 0.0362, wR_2 = 0.0922. GOF = 1.063 for 114 parameters and 0 restraints, largest diff. peak and hole 0.426/–0.312 eÅ^{-3}. CCDC-1006931 contains the supplementary data for this structure. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

The structures were solved by charge flipping with Superflip[5] and refined by full-matrix least-squares methods using WinGX software,[6] which utilizes the SHELXL-2013 module.[7] The positions of carbon-bound hydrogen atoms were calculated and refined as riding on the parent carbon atoms with U_H = 1.2 U_C. The nitrogen-bound hydrogen atoms in **3** were found in the electron density difference map and refined with U_H = 1.2 U_N, constrained in one (coordinating aminal NH) and restrained in the other case (non-coordinating aminal NH).

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[5] L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* **2007**, *40*, 786–790.

[6] L. J. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849–854.

[7] G. Sheldrick, *Acta Crystallogr. **A*** **2008**, *64*, 112–122.