Supporting Information

Synthesis of pyrazole (hemi)aminals via the cleavage of saturated aliphatic ether C-O bonds in the presence of ferric halides

Evgen V. Govor,[a] Yiannis Sanakis[b] and Raphael G. Raptis*[a]

Synthesis. Anhydrous $FeCl_3$ and $FeBr_3$, 3,5-dimethylpyrazole (3,5-Me_2pzH), ethyl propenyl ether (mixture of *cis*- and *trans*-isomers), $CHCl_3$ and CCl_4 were obtained from commercial sources and used as received. 4-Cl-3,5-dimethylpyrazole (4-Cl-3,5-Me_2pzH), 4-Br-3,5-dimethylpyrazole (4-Br-3,5-Me_2pzH) and 4-I-3,5-dimethylpyrazole (4-I-3,5-Me_2pzH) were prepared from 3,5-Me_2-pzH according to literature procedures.[1] Diethyl ether, hexane and CH_2Cl_2 solvents were purified by standard methods.[2]

[$FeCl_3$(4-Cl-3,5-Me_2-pzH)$_2$(H_2O)] (1a). $FeCl_3$ (50 mg; 0.309 mmol), 4-Cl-3,5-Me_2-pzH (120 mg; 0.926 mmol) and CH_2Cl_2 (10 ml) were mixed together under air. Resulted red solution was stirred overnight, filtered out and the filtrate was layered with hexane, yielfing X-ray quality crystals of **1a** after 4 weeks. Yield 85%. Anal. Found (Calc.) for: C, 27.32 (27.21); H, 3.82 (3.65); N, 12.62 (12.69). **FT**IR-ATR: ν_{max} = 3293 (vs), 3255 (sh), 3167 (m), 2952 (w), 2880 (w), 1569 (vs), 1475 (m), 1426 (w), 1398 (m), 1317 (m), 1298 (m), 1285 (w), 1116 (s), 1193 (w), 1161 (w), 1131 (vs), 1122 (s), 1059 (s), 1055 (s), 1009 (s), 990 (m), 766 (m) 676 (s), 671 (s), 589 (s) cm^{-1}.

[$FeCl_3$(4-Br-3,5-Me_2-pzH)$_2$(H_2O)] (1b). $FeCl_3$ (50 mg; 0.309 mmol), 4-Br-3,5-Me_2-pzH (162 mg; 0.926 mmol) and $CHCl_3$ (10 mL) were mixed together under air. The resulting red solution was stirred overnight, filtered and the filtrate was layered with hexane. A few X-ray quality crystals of the product were obtained in approximately three weeks. Yield 10%.

[{$FeBr_2$(4-Br-3,5-Me_2-pzH)$_2$}$_2$(μ_2-O)]·CCl_4 (2). $FeBr_3$ (91 mg; 0.308 mmol), 4-Br-3,5-Me_2-pzH (162 mg; 0.926 mmol) and CCl_4 (10 mL) were mixed together under air, resulting in a dark-red solution, which was stirred overnight and filtered. Evaporation of the filtrate led to hygroscopic, block-shaped dark-red crystals of complex **2**. Yield 80 %. Anal. Found (Calc) for $C_{20.5}H_{34}Br_8Cl_2Fe_2N_8O_4$ (**2**·3H_2O·0.5CCl_4): C 19.22% (19.26%); H 2.72% (2.68%); N 8.83% (8.74%).

[Fe_2(1-PrO-4-Cl-3,5-Me_2-pz)$_2$$Cl_4$] (3). To a suspension of $FeCl_3$ (50 mg; 0.309 mmol) in CH_2Cl_2 (10 mL) was added 4-Cl-3,5-Me_2-pzH (120 mg; 0.919 mmol), resulting in a red solution, which was stirred over night and then filtered. Ethyl(1-propenyl)ether, Et-O-CH=$CHCH_3$, (0.1 mL) was layered over the filtrate and the flask was sealed. Red crystals of complex **3** appeared after standing for 5 days. Yield 55 %. Anal. Found (Calc.) for $C_{16}H_{24}Cl_6Fe_2N_4O_2$: C, 29.70 (30.56); H, 3.66 (3.85); N, 8.29 (8.91). FTIR-(KBr disk): indistinguishable from the spectrum of

4a (Fig. S1) in the 400 -4000) cm^{-1} range. The crystals of **3** are insoluble in CH_2Cl_2, $CHCl_3$, thf, but dissolve with reaction in alcohols.

[Fe_2(1-EtO-4-I-3,5-Me_2-pz)$_2Cl_4$] (4a). To a suspension of $FeCl_3$ (100 mg; 0.617 mmol) in CH_2Cl_2 (20 mL) were added 4-I-3,5-Me_2-pzH (411 mg; 1.85 mmol), resulting in a red solution, which was stirred overnight and filtered. Block-shaped red crystals of **4a** grew as a result of slow diffusion of Et_2O vapors into the filtrate after approximately one week. Yield 60 %. Anal. Found (Calc.) for $C_{14}H_{20}Cl_4Fe_2I_2N_4O_2$: C, 22.05 (21.46); H, 2.71 (2.57); N, 7.09 (7.15). IR (KBr disk): ν_{max} = 3419 (w), 2979 (w), 2923 (w), 1519 (m), 1470 (s), 1442 (m), 1417 (m), 1380 (s), 1352 (m), 1330 (m), 1247 (s), 1149 (m), 1116 (s), 1104 (s), 1083 (s), 1041 (m), 999 (m), 917 (s), 829 (m), 706 (s), 555 (m), 506 (m) 432 (m) cm^{-1} (Figure S1). The crystals of **4a** are insoluble in CH_2Cl_2, $CHCl_3$, thf and alcohols, but dissolve with reaction in alkaline phenolic solutions.

[Fe_2(1-EtO-4-Br-3,5-Me_2-pz)$_2Br_4$] (4b). Dark red-brown crystals of complex **4b** were obtained similarly to **4a**, using $FeBr_3$ (182 mg; 0.615 mmol) and 4-Br-3,5-Me_2-pzH (324 mg; 1.85 mmol). Yield 65 %. Anal. Found (Calc.) for $C_{14}H_{20}Br_6Fe_2N_4O_2$: C, 19.70 (19.38); H, 2.42 (2.32); N, 6.24 (6.46). IR (KBr disk): indistinguishable from the spectrum of **4a** (Fig. 1) in the 400 -4000) cm^{-1} range. The crystals of **4b** are insoluble in CH_2Cl_2, $CHCl_3$, thf and alcohols, but dissolve with reaction in alcaline phenolic solutions.

[Fe((4-Br-3,5-Me_2-pz)$_2$Et)Cl_2] (5a) and **[Fe((4-Br-3,5-Me_2-pz)$_2$Et)Br_2] (5b).** Almost coloreless crystals with a pale-blue hue of **5a** (or **5b)** were obtained when crystals of **3a** (or **3b)** in their mother-liquors were exposed to diffuse laboratory light for 4-6 weeks.

Physical Measurements. Infrared spectra (KBr pellets) were recorded on Nicolet 750 FTIR spectrophotometer. ^{57}Fe-Mössbauer spectra were recorded with powdered samples of **4a**, **4b** and **5a** with a constant-acceleration conventional spectrometer with a source of ^{57}Co (Rh matrix) using a Janis Cryostat. The spectra were analyzed with the program *WMOSS* (Web Research, Edina, MN). Isomer shift values (δ) are reported relative to iron foil at 293 K.

X-ray diffraction data, taken from a single crystal mounted a top of a glass fiber, were collected on a Bruker AXS SMART 1K CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at room temperature using the program SMART-NT[3] and processed by SAINT-NT.[4] An empirical absorption correction was applied by the program SADABS. The structures were solved by direct method and refined by full-matrix least-squares methods on F^2.[5] All non-hydrogen atoms were refined anisotropically, while H-atoms were placed in calculated positions with their thermal parameters riding on those of their C atoms. Crystallographic details for **1-5** are summarized in Table S1.

Table S1. Crystallographic Data for **1** – **5**.

	1a (CCDC 1521056)	**1b** (CCDC 942440)	**2** (CCDC 942441)	**3** (CCDC 942442)
formula	$C_{10}H_{16}Cl_5FeN_4O$	$C_{10}H_{16}Br_2Cl_3FeN_4O$	$C_{24}H_{28}Br_8Cl_{16}Fe_2N_8O$	$C_{16}H_{24}Cl_6Fe_2N_4O_2$
formula weight	441.37	530.29	1762.72	628.79
temperature (K)	298	296(2)	296(2)	296(2)
crystal system	monoclinic	orthorhombic	tetragonal	monoclinic
space group	*C2/c*	*Pbcn*	$I4_1/a$	*C2/c*
a (Å)	24.487(3)	23.654(6)	19.167(17)	8.5983(15)
b(Å)	8.7651(10)	8.738(2)	19.167(17)	20.475(4)
c(Å)	8.5302(10)	8.595(2)	16.153(15)	14.989(3)
β (°)	110.281(3)	90	90	100.778(2)
V (Å^3)	1717.3(4)	1776.6(8)	5934(9)	2592.2(8)
Z	4	4	4	4
$D_{(calc)}$(g cm^{-3})	1.707	1.983	1.973	1.611
μ (mm^{-1})	1.657	5.800	6.627	1.758
crystal size, mm^3	0.47×0.62×0.70	0.02×0.10×0.13	0.12×0.20×0.25	0.29×0.59×0.64
reflection collected/$2\theta_{max}$	17884 / 55.22	18365 / 54.14	29854 / 52.52	14268 / 54.14
unique reflections / I > 2σ (I)	1975 / 1758	1949 / 1520	2977 / 1796	2841 / 2439
number of parameters / restraints	108 / 0	99 / 0	136 / 0	139 / 0
R_1, wR_2 I > 2r(I)	0.0428 / 0.0848	0.0310 / 0.0820	0.0630 / 0.1668	0.0290 / 0.0693
R_1, wR_2 (all data)	0.0503 / 0.0889	0.0448 / 0.0889	0.1160 / 0.2057	0.0353 / 0.0725
goodness of fit	1.239	1.066	1.004	1.023

	4a (CCDC 942443)	**4b** (CCDC 942444)	**5a** (CCDC 942445)	**5b** (CCDC 942446)
formula	$C_{14}H_{20}Cl_4Fe_2I_2N_4O_2$	$C_{14}H_{20}Br_6Fe_2N_4O_2$	$C_{12}H_{16}Br_2Cl_2FeN_4$	$C_{12}H_{16}Br_4FeN_4$
formula weight	783.64	867.50	502.86	591.78
temperature (K)	296(2)	296(2)	296(2)	296(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	*P2/n*	*P2/n*	$P2_1/n$	$P2_1/n$
a (Å)	8.5950(6)	8.6395(6)	12.1777(13)	12.247(4)
b(Å)	9.6865(7)	9.7711(7)	8.7316(9)	8.932(3)
c(Å)	15.7769(11)	15.8621(11)	17.3452(18)	17.420(5)
β (°)	99.3500(10)	103.6650(10)	92.4070(10)	91.930(3)
V (Å^3)	1296.06(16)	1301.13(16)	1842.7(3)	1904.6(9)
Z	2	2	4	4
$D_{(calc)}$(g cm^{-3})	2.008	2.214	1.813	2.064
μ (mm^{-1})	3.930	10.344	5.443	9.181
crystal size, mm^3	0.08×0.10×0.17	0.06×0.14×0.16	0.28×0.36×0.45	0.21×0.32×0.41
reflection collected/$2\theta_{max}$	14277 / 54.34	14343 / 54.24	19914 / 54.18	18641 / 52.76
unique reflections / I > 2σ (I)	2878 / 2175	2886 / 2155	4050 / 3201	3870 / 3148
number of parameters/ restraints	130 / 0	130 / 0	195 / 0	195 / 0

R_1, wR_2 $I > 2r(I)$	0.0324 / 0.0813	0.0341 / 0.0705	0.0412 / 0.0952	0.0426 / 0.0977
R_1, wR_2 (all data)	0.0481 / 0.0906	0.0556 / 0.0784	0.0565 / 0.1018	0.0564 / 0.1049
goodness of fit	1.026	1.009	1.046	1.036

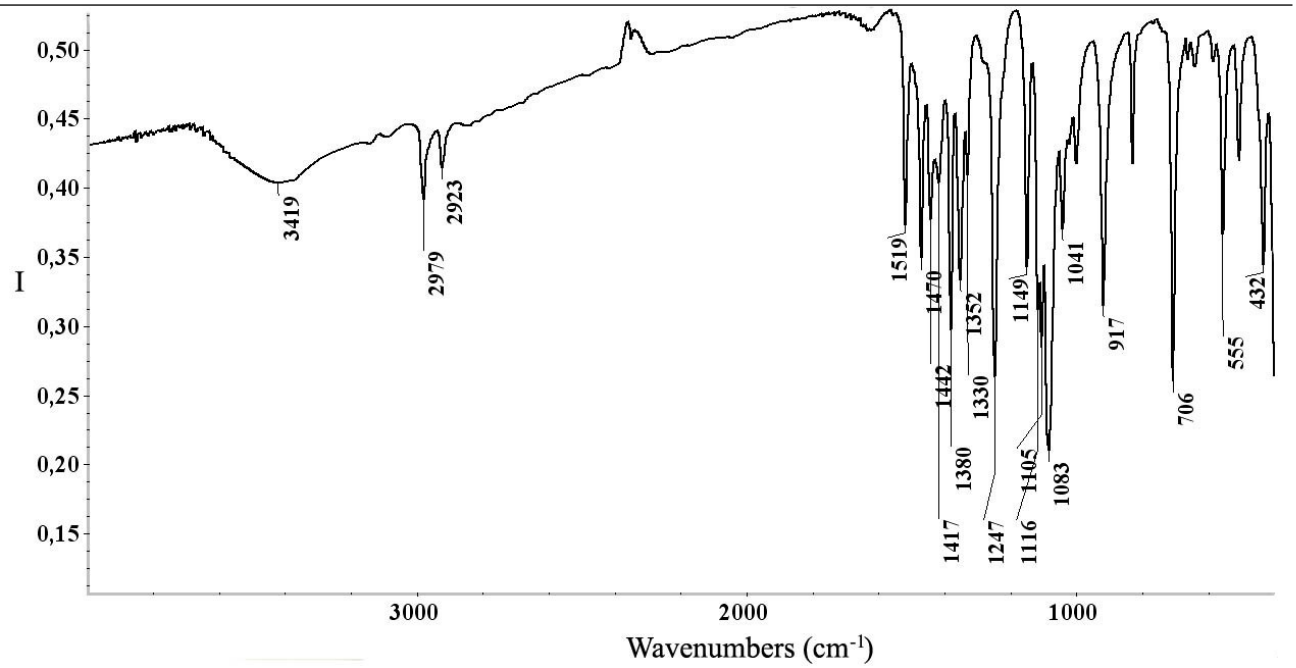

Fig. S1. IR spectrum of compound $[Fe_2(1\text{-EtO-4-I-3,5-Me}_2\text{-pz})_2Cl_4]$ (**4a**).

Table S2. Selected bond lengths (Å) and angles (deg) for **1a** - **2**

	1a	**1b**	**2**
Fe1–Cl1 (Br1)	2.3093(14)	2.362(9)	2.468(2)
Fe1–Cl2 (Br2)	2.348(9)	2.3187(13)	—
Fe1–O1	2.068(4)	2.066(3)	1.770(2)
Fe1–N1	2.158(3)	2.165(3)	2.112(6)
Fe1–O1–Fe1^{i}	—	—	179.99(9)

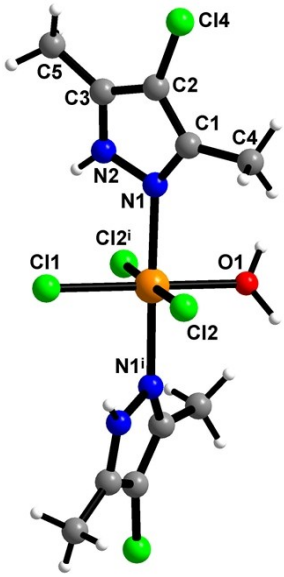

Fig. S2. Ball-and-stick diagram of compound **1a**.

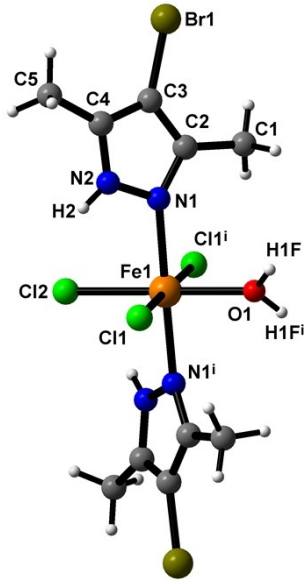

Fig. S3. Ball-and-stick diagram of compound **1b**.

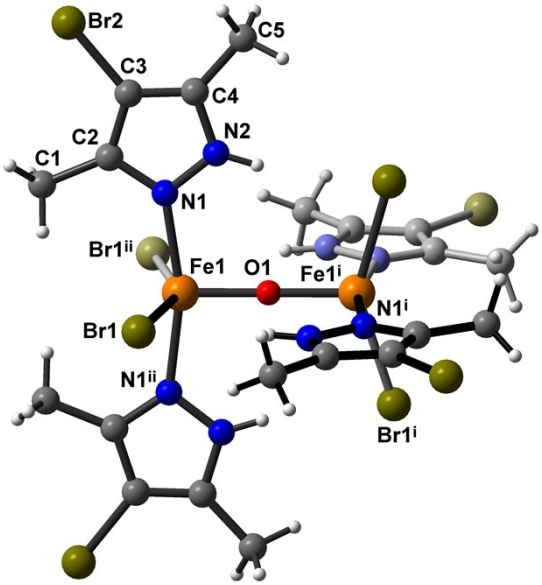

Fig. S4. Ball-and-stick diagram of compound **2**.

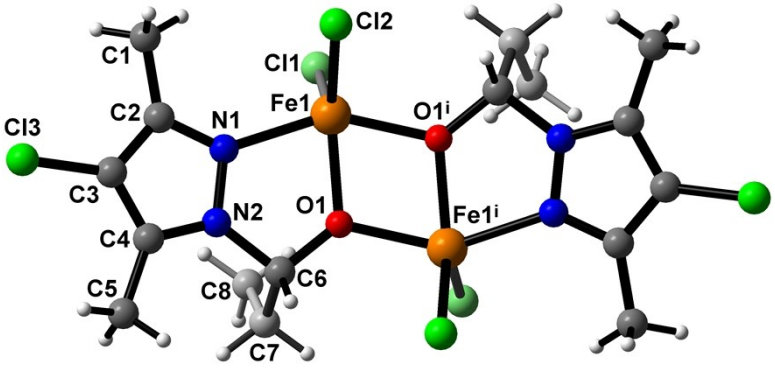

Fig. S5. Ball-and-stick diagram of compound **3**.

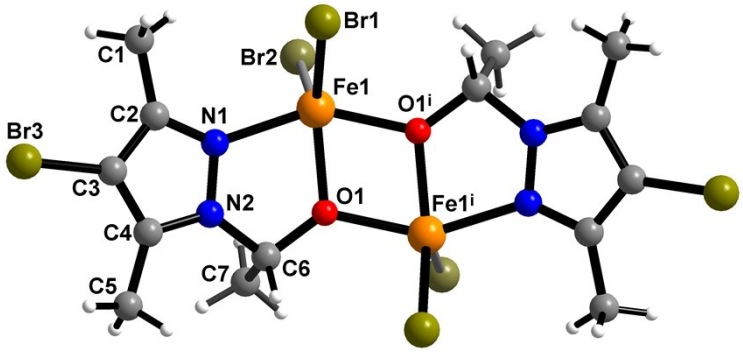

Fig. S6. Ball-and-stick diagram of compound **4b**.

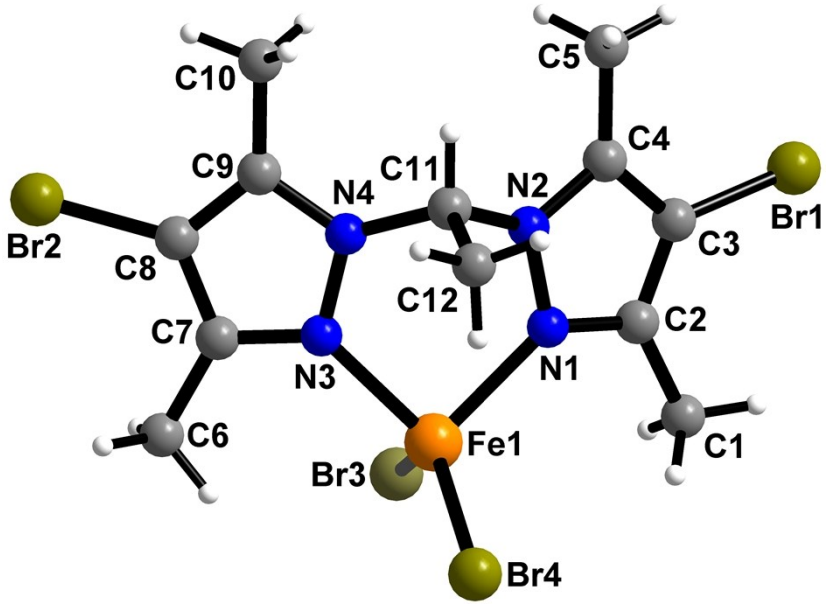

Fig. S7. Ball-and-stick diagram of compound **5b**.

1. M.K. Ehlert, S. J. Rettig, A. Storr, R.C. Thompson and J. Trotte, *Can. J. Chem.* 1991, **69**, 432.
2. D.D. Perrin, W. L. F. Armarego and D.R. Perrin, *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: New York, 1987.
3. *SMART-NT*, version 5.0; Brucker AXS: Madison, WI, 1998.
4. *SAINT-NT*, version 5/6.0; Brucker AXS: Madison, WI, 1999.
5. *SHELXTL-NT*, version 5.1; Brucker AXS: Madison, WI, 1998.