Supporting information for:

Iron catalyzed oxidation of benzylic alcohols to benzoic acids

B. Stanje,[a] P. Traar,[a] J. A. Schachner,[a]* F. Belaj,[a] N. C. Mösch-Zanetti [a]

Table S 1. Crystal data and structure refinement of complexes **1** and **1a**

	1	**1a**
empirical formula	$C_{20}H_{18}ClFeN_4O_2$	$C_{40}H_{36}Fe_2N_8O_5$
formula weight	437.68	820.47
crystal description	plate, red	block, red
crystal size (mm)	0.30 x 0.25 x 0.11mm	0.28 x 0.21 x 0.17
crystal system, space group	monoclinic, $P2_1/c$	orthorhombic, *P* b c a
Unit cell dimensions, a (Å)	14.1475(6)	18.4514(10)
b (Å)	11.7295(5)	19.5777(11)
c (Å)	11.9893(5)	20.1490(11)
α (°)	90	90
ß (°)	108.0920(10)	90
γ (°)	90	90
volume ($Å^3$)	1891.18(14)	7278.5(7)
Z, Calculated density (gcm^{-3})	4, 1.537	8, 1.497
F(000)	900	3392
linear absorption coefficient μ (mm^{-1})	0.963	0.855
absorption correction	semi-empirical from equivalents	
temperature (K)	100	100
wavelength (MoKα) (Å)	0.71073	0.71073
theta range for data collection (°)	2.30 to 30.00°	2.02 to 30.00
limiting indices	$-19 \le h \le 19$	$-25 \le h \le 19$
	$-14 \le k \le 16$	$-27 \le k \le 14$
	$-12 \le l \le 16$	$-27 \le l \le 28$
reflections collected / unique	25391 / 5517	31306 / 10603
reflections with $I > 2\sigma(I)$	5072	7961
R(int), R(sigma)	0.0255, 0.0179	0.0286, 0.0349
completeness to theta max. (%)	100	99.9
refinement method	full matrix least squares on F^2	
data / restraints / parameters	5517 / 261 / 0	10603 / 512 / 0
goodness-of-fit on F^2	1.038	1.011
final R1[a] *w*R2[b] [I>2σ(I)]	*R*1 = 0.0254, *wR*2 = 0.0721	*R*1 = 0.0355, *wR*2 = 0.0823
R indices (all data)	*R*1 = 0.0284, *wR*2 = 0.0747	*R*1 = 0.0566, *wR*2 = 0.0910
largest diff. peak and hole ($eÅ^{-3}$)	0.543 and -0.337	0.416 and -0.455
CCDC deposition no.	1048055	1048056

[a] $R1=\sum \| F_o \| - | F_c \| / \sum | F_o |$ [b] $wR2=\{\sum[w(F_o^2-F_c^2)^2]^2/\sum[w(F_o^2)^2]\}^{1/2}$

Crystal Structure Determination of 1. All the measurements were performed using graphite-monochromatized Mo K_α radiation at 100K: $C_{20}H_{18}ClFeN_4O_2$, M_r 437.68, monoclinic, space group P $2_1/c$, a = 14.1475(6)Å, b = 11.7295(5)Å, c = 11.9893(5)Å, β = 108.0920(10)°, V = 1891.18(14)Å^3, Z = 4, d_{calc} = 1.537g cm^{-3}, μ = 0.963mm^{-1}. A total of 25391 reflections were collected (Θ_{max} = 30.0°), from which 5517 were unique (R_{int} = 0.0255), with 5072 having I > 2σ(I). The structure was solved by direct methods (SHELXS-97)[1] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2014/6)[1]. The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the pyrazole and of the phenyl rings were put at the external bisectors of the C–C–X angles at C–H distance of 0.95Å and one common isotropic displacement parameter was refined for the H atoms of the same ring. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the N–C bond, and C–H distances of 0.98Å. For 261 parameters final *R* indices of R1 = 0.0254 and wR^2 = 0.0747 (GOF = 1.039) were obtained. The largest peak in a difference Fourier map was 0.543eÅ^{-3}.

Crystal Structure. The crystal structure analysis of **1** confirmed the compound as chloro-bis[2-(1-methyl-*1H*-pyrazol-3-yl)phenolato-N,O]-iron(III). All atoms lie on general positions. The complex shows a trigonal bipyramidal coordination of the iron atom (Figure S 1) with the N atoms in axial positions [N12–Fe1–N32 170.68(4)°] and small deviations from ideal geometry [O41–Fe1–O21 125.49(4)°, O21–Fe1–Cl1 119.59(3)°, O41–Fe1–Cl1 114.91(3)°]. In the two ligands the planar pyrazole rings are rotated by 6.56(6)° and 3.08(6)°, resp., to the phenyl rings.

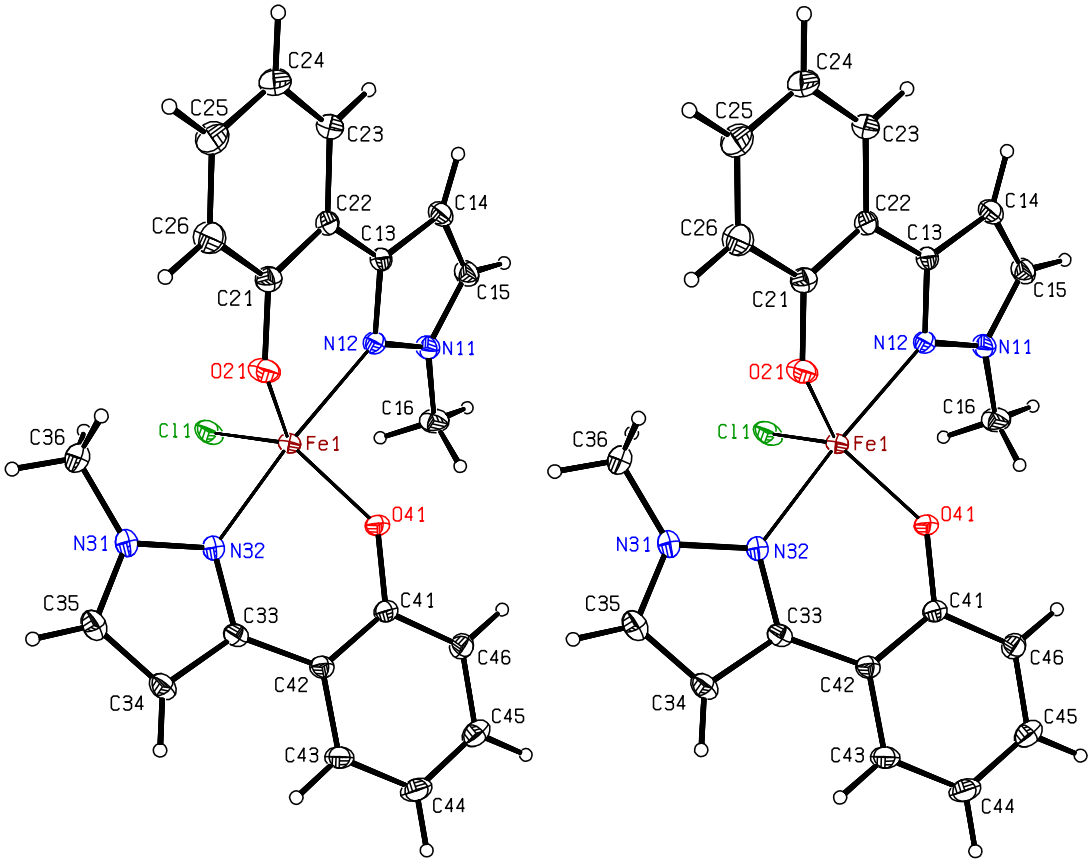

Figure S 1. Stereoscopic ORTEP[2] plot of **1** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms are drawn with arbitrary radii.

Table S 2. Selected bond lengths [Å] and angles [°] for **1**.

Fe(1)-O(21)	1.8630(8)	O(21)-Fe(1)-N(32)	89.41(4)
Fe(1)-O(41)	1.8583(8)	N(12)-Fe(1)-Cl(1)	94.56(3)
Fe(1)-N(12)	2.1201(9)	N(32)-Fe(1)-Cl(1)	94.73(3)
Fe(1)-N(32)	2.1309(9)	C(15)-N(11)-N(12)	111.08(9)
Fe(1)-Cl(1)	2.2703(3)	C(15)-N(11)-C(16)	126.39(10)
N(11)-C(15)	1.3430(14)	N(12)-N(11)-C(16)	122.46(9)
N(11)-N(12)	1.3575(13)	C(13)-N(12)-N(11)	106.01(9)
N(11)-C(16)	1.4523(14)	C(13)-N(12)-Fe(1)	127.15(7)
N(12)-C(13)	1.3545(13)	N(11)-N(12)-Fe(1)	126.73(7)
C(13)-C(14)	1.4069(15)	C(21)-O(21)-Fe(1)	135.11(8)
C(14)-C(15)	1.3750(16)	C(35)-N(31)-N(32)	111.21(10)
O(21)-C(21)	1.3379(13)	C(35)-N(31)-C(36)	126.68(10)
N(31)-C(35)	1.3408(15)	N(32)-N(31)-C(36)	122.10(10)
N(31)-N(32)	1.3584(13)	C(33)-N(32)-N(31)	105.85(9)
N(31)-C(36)	1.4509(16)	C(33)-N(32)-Fe(1)	127.79(7)
N(32)-C(33)	1.3537(14)	N(31)-N(32)-Fe(1)	126.20(7)
C(33)-C(34)	1.4062(15)	C(41)-O(41)-Fe(1)	137.89(7)
C(34)-C(35)	1.3776(17)		
O(41)-C(41)	1.3349(12)	C(15)-N(11)-N(12)-Fe(1)	176.40(8)
		C(16)-N(11)-N(12)-Fe(1)	-0.76(15)
N(12)-Fe(1)-N(32)	170.68(4)	Fe(1)-N(12)-C(13)-C(14)	-176.49(7)
O(41)-Fe(1)-O(21)	125.49(4)	Fe(1)-N(12)-C(13)-C(22)	1.60(15)
O(21)-Fe(1)-Cl(1)	119.59(3)	C(15)-N(11)-N(12)-C(13)	-0.04(12)
O(41)-Fe(1)-Cl(1)	114.91(3)	C(16)-N(11)-N(12)-C(13)	-177.20(10)
O(41)-Fe(1)-N(12)	91.51(4)	N(11)-N(12)-C(13)-C(14)	-0.07(12)
O(21)-Fe(1)-N(12)	85.45(4)	N(12)-C(13)-C(14)-C(15)	0.15(13)
O(41)-Fe(1)-N(32)	85.15(4)	C(13)-C(14)-C(15)-N(11)	-0.16(13)

C(14)-C(15)-N(11)-N(12)0.13(13)

Fe(1)-O(21)-C(21)-C(22)-25.02(18)

Fe(1)-O(21)-C(21)-C(26)155.66(10)

C(35)-N(31)-N(32)-Fe(1)175.59(8)

C(36)-N(31)-N(32)-Fe(1)-3.35(16)

Fe(1)-N(32)-C(33)-C(34)-175.51(8)

Fe(1)-N(32)-C(33)-C(42) 3.27(15)

C(35)-N(31)-N(32)-C(33)-0.16(13)

N(31)-N(32)-C(33)-C(34)0.15(12)

N(32)-C(33)-C(34)-C(35)-0.09(13)

C(33)-C(34)-C(35)-N(31)-0.01(13)

C(34)-C(35)-N(31)-N(32)0.10(14)

Fe(1)-O(41)-C(41)-C(42)-13.71(17)

Fe(1)-O(41)-C(41)-C(46)167.81(8)

Crystal Structure Determination of 1a. All the measurements were performed using graphite-monochromatized Mo K_α radiation at 100K: $C_{40}H_{36}Fe_2N_8O_5$, M_r 820.47, orthorhombic, space group P b c a, a = 18.4514(10)Å, b = 19.5777(11)Å, c = 20.1490(11)Å, V = 7278.5(7)Å^3, Z = 8, d_{calc} = 1.497g cm^{-3}, μ = 0.855mm^{-1}. A total of 31306 reflections were collected (Θ_{max} = 30.0°), from which 10603 were unique (R_{int} = 0.0286), with 7956 having I > 2σ(I). The structure was solved by direct methods (SHELXS-97)[1] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2014/6)[1]. The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the phenyl rings as well as those of the pyrazole rings were put at the external bisectors of the C–C–C angles at C–H distances of 0.95Å and common isotropic displacement parameters were refined for the H atoms of the same ring. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the N–C bond, and C–H distances of 0.98Å. For 512 parameters final *R* indices of R1 = 0.0355 and wR^2 = 0.0910 (GOF = 1.010) were obtained. The largest peak in a difference Fourier map was 0.416eÅ^{-3}.

Crystal Structure. The crystal structure analysis of **1a** confirmed the compound as (μ_2-oxo)-bis(bis[2-(1-methyl-*1H*-pyrazol-3-yl)phenolato-N,O]-iron(III)). The complex shows approx. D_2 symmetry, but all atoms lie on general positions (Figure S 2). The Fe atoms have trigonal-bipyramidal surroundings [N12–Fe1–N32 172.76(5)Å, N52–Fe2–N72 172.41(5)Å] and are connected by a linear O bridge [O1–Fe1 1.7898(11)Å, O1–Fe2 1.7893(11)Å; Fe1–O1–Fe2 179.86(9)°]. In the four ligands the planar pyrazole rings enclose angles of 4.21(9)°-8.54(6)° with the phenyl rings.

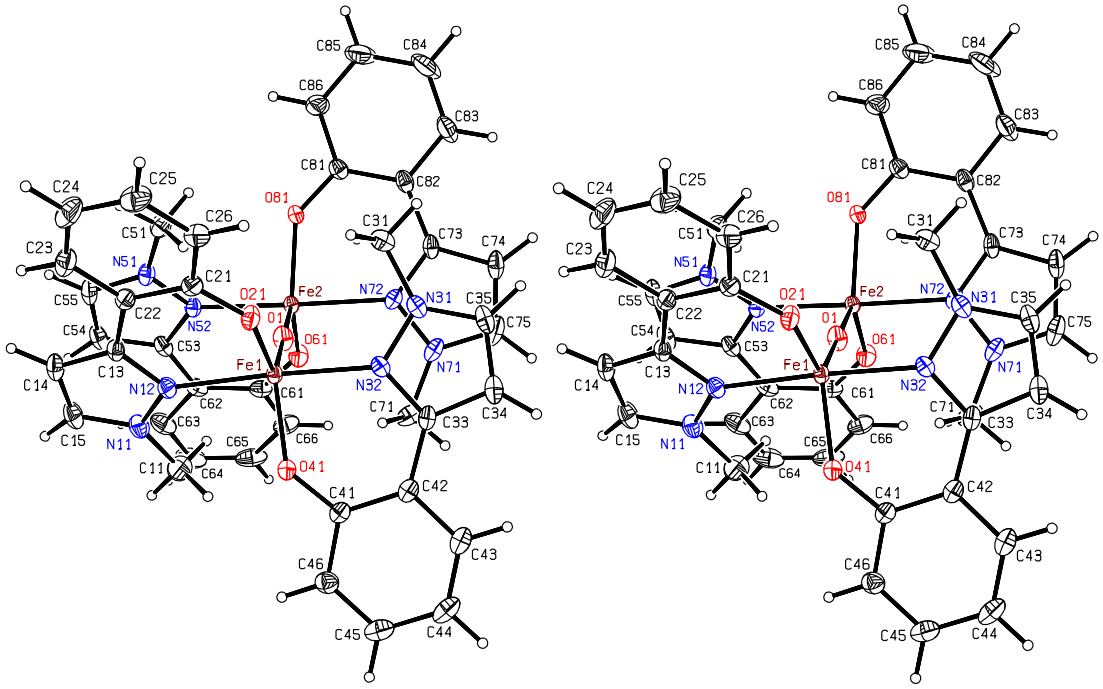

Figure S 2. Stereoscopic ORTEP[2] plot of **1a** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms are drawn with arbitrary radii.

Table S 3. Selected bond lengths [Å] and angles [°] for **1a**.

O(1)-Fe(1)	1.7898(11)	N(32)-N(31)-C(31)	121.13(13)
O(1)-Fe(2)	1.7893(11)	C(33)-N(32)-N(31)	106.24(12)
Fe(1)-O(21)	1.9098(11)	C(33)-N(32)-Fe(1)	127.90(10)
Fe(1)-O(41)	1.8986(11)	N(31)-N(32)-Fe(1)	124.97(10)
Fe(1)-N(12)	2.1531(13)	C(41)-O(41)-Fe(1)	136.10(10)
Fe(1)-N(32)	2.1246(13)	N(52)-Fe(2)-N(72)	172.41(5)
N(11)-C(15)	1.346(2)	O(1)-Fe(2)-O(61)	121.88(5)
N(11)-N(12)	1.3625(18)	O(1)-Fe(2)-O(81)	118.62(5)
N(12)-C(13)	1.3519(19)	O(61)-Fe(2)-O(81)	119.45(5)
C(13)-C(14)	1.411(2)	O(1)-Fe(2)-N(52)	93.61(5)
C(14)-C(15)	1.370(3)	O(61)-Fe(2)-N(52)	85.31(5)
O(21)-C(21)	1.3291(18)	O(81)-Fe(2)-N(52)	93.30(5)
N(31)-C(35)	1.347(2)	O(1)-Fe(2)-N(72)	93.82(5)
N(31)-N(32)	1.3653(17)	O(61)-Fe(2)-N(72)	89.45(5)
N(32)-C(33)	1.351(2)	O(81)-Fe(2)-N(72)	84.48(5)
C(33)-C(34)	1.410(2)	C(55)-N(51)-N(52)	110.81(14)
C(34)-C(35)	1.373(2)	C(55)-N(51)-C(51)	127.38(14)
O(41)-C(41)	1.3354(18)	N(52)-N(51)-C(51)	121.80(13)
Fe(2)-O(61)	1.8993(11)	C(53)-N(52)-N(51)	106.00(12)
Fe(2)-O(81)	1.9094(11)	C(53)-N(52)-Fe(2)	128.13(11)
Fe(2)-N(52)	2.1273(13)	N(51)-N(52)-Fe(2)	125.31(10)
Fe(2)-N(72)	2.1580(13)	C(61)-O(61)-Fe(2)	135.93(10)
N(51)-C(55)	1.344(2)	C(75)-N(71)-N(72)	111.21(14)
N(51)-N(52)	1.3635(17)	C(75)-N(71)-C(71)	127.73(15)
N(52)-C(53)	1.356(2)	N(72)-N(71)-C(71)	120.95(14)
C(53)-C(54)	1.411(2)	C(73)-N(72)-N(71)	105.71(13)
C(54)-C(55)	1.377(2)	C(73)-N(72)-Fe(2)	128.47(10)
O(61)-C(61)	1.3394(19)	N(71)-N(72)-Fe(2)	125.42(10)
N(71)-C(75)	1.342(2)	C(81)-O(81)-Fe(2)	135.69(10)
N(71)-N(72)	1.3626(18)	C(15)-N(11)-N(12)-Fe(1)	-169.00(11)
N(72)-C(73)	1.352(2)	C(11)-N(11)-N(12)-Fe(1)	7.6(2)
C(73)-C(74)	1.411(2)	Fe(1)-N(12)-C(13)-C(14)	168.30(11)
C(74)-C(75)	1.371(3)	Fe(1)-N(12)-C(13)-C(22)	-13.1(2)
O(81)-C(81)	1.3316(18)	Fe(1)-O(21)-C(21)-C(22)	10.9(2)
Fe(2)-O(1)-Fe(1)	179.86(9)	Fe(1)-O(21)-C(21)-C(26)	-171.16(11)
N(32)-Fe(1)-N(12)	172.76(5)	C(35)-N(31)-N(32)-Fe(1)	-170.80(11)
O(1)-Fe(1)-O(41)	118.60(5)	C(31)-N(31)-N(32)-Fe(1)	9.24(19)
O(1)-Fe(1)-O(21)	120.79(5)	Fe(1)-N(32)-C(33)-C(34)	170.25(11)
O(41)-Fe(1)-O(21)	120.59(5)	Fe(1)-N(32)-C(33)-C(42)	-8.5(2)
O(1)-Fe(1)-N(32)	93.62(5)	Fe(1)-O(41)-C(41)-C(42)	13.4(2)
O(41)-Fe(1)-N(32)	85.60(5)	Fe(1)-O(41)-C(41)-C(46)	-167.18(12)
O(21)-Fe(1)-N(32)	91.83(5)	C(55)-N(51)-N(52)-Fe(2)	-173.29(11)
O(1)-Fe(1)-N(12)	93.62(5)	C(51)-N(51)-N(52)-Fe(2)	6.4(2)
O(41)-Fe(1)-N(12)	90.76(5)	Fe(2)-N(52)-C(53)-C(54)	172.62(11)
O(21)-Fe(1)-N(12)	84.63(5)	Fe(2)-N(52)-C(53)-C(62)	-8.1(2)
C(15)-N(11)-N(12)	110.94(14)	Fe(2)-O(61)-C(61)-C(62)	10.3(2)
C(15)-N(11)-C(11)	128.34(15)	Fe(2)-O(61)-C(61)-C(66)	-171.22(12)
N(12)-N(11)-C(11)	120.62(13)	C(75)-N(71)-N(72)-Fe(2)	-173.37(11)
C(13)-N(12)-N(11)	105.89(13)	C(71)-N(71)-N(72)-Fe(2)	3.0(2)
C(13)-N(12)-Fe(1)	127.68(10)	Fe(2)-N(72)-C(73)-C(74)	173.18(11)
N(11)-N(12)-Fe(1)	125.32(10)	Fe(2)-N(72)-C(73)-C(82)	-3.5(2)
C(21)-O(21)-Fe(1)	136.38(10)	Fe(2)-O(81)-C(81)-C(82)	23.4(2)
C(35)-N(31)-N(32)	110.65(13)	Fe(2)-O(81)-C(81)-C(86)	-157.61(13)
C(35)-N(31)-C(31)	128.22(14)		

References.

1. G. M. Sheldrick, *Acta Crystallogr. A, Found. Crystallogr.*, 2008, **64**, 112.
2. Michael N. Burnett and C. K. Johnson, *ORTEP-III: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*, Oak Ridge National Laboratory Report ORNL-6895, Oak Ridge, 1996.