Supplementary Information

Synthesis and characterization of μ-nitrido, μ-carbido and μ-oxo dimers of iron octapropylporphyrazine

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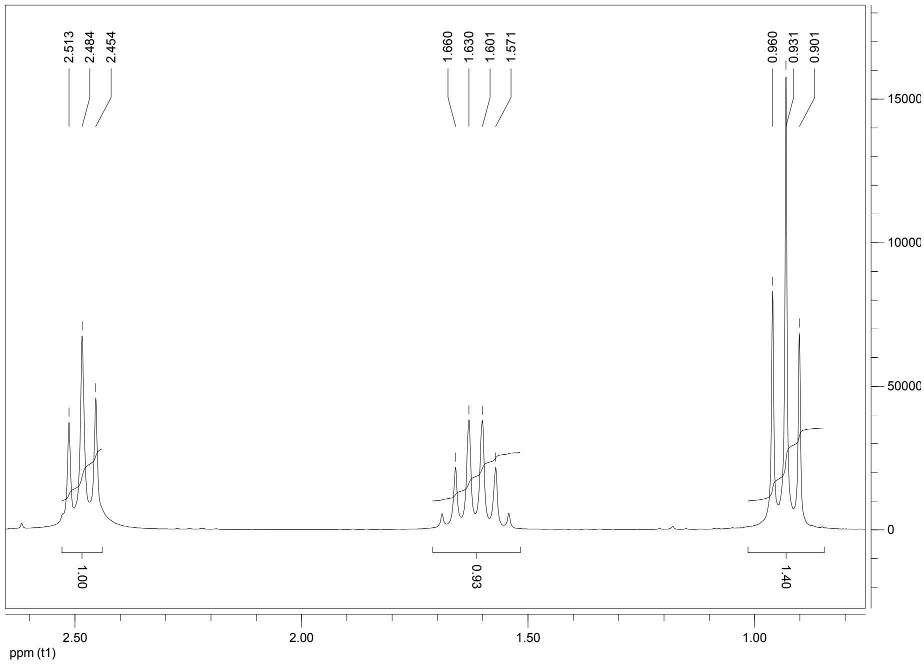

Figure S1. [1]H NMR spectrum of dipropylfumaronitrile **(3).**

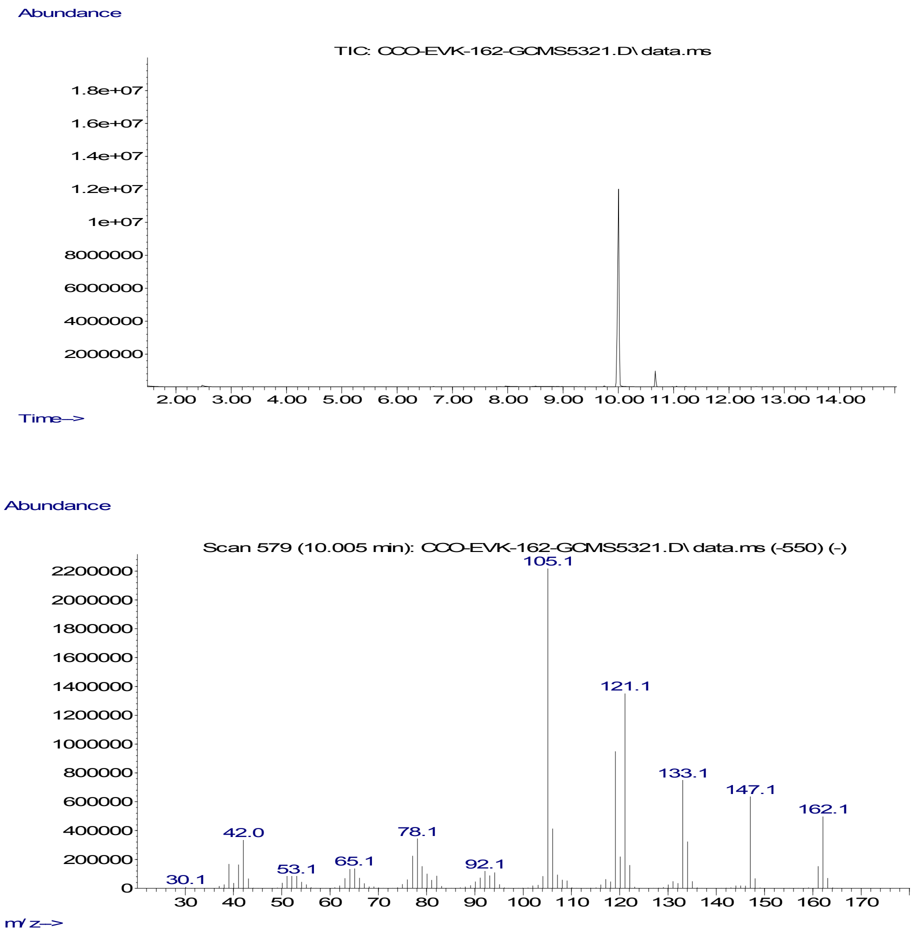

Figure S2. GC and mass spectrum of dipropylfumaronitrile (**3**)

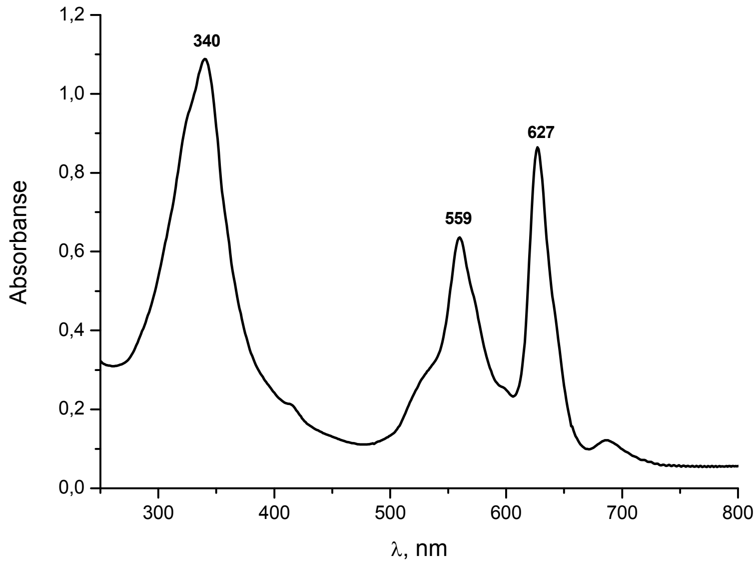

Figure S3. UV-Vis spectrum of $H_2TAP(C_3H_7)_8$ (**4**) in CH_2Cl_2.

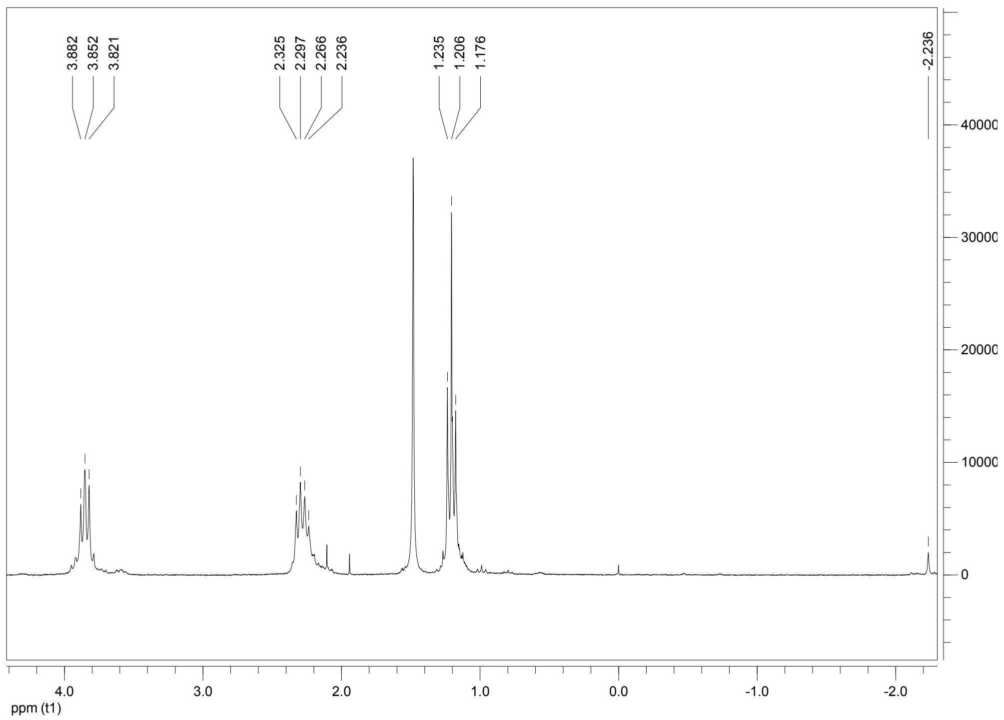

Figure S4. ^{1}H NMR spectrum of $H_2TAP(C_3H_7)_8$ (**4**).

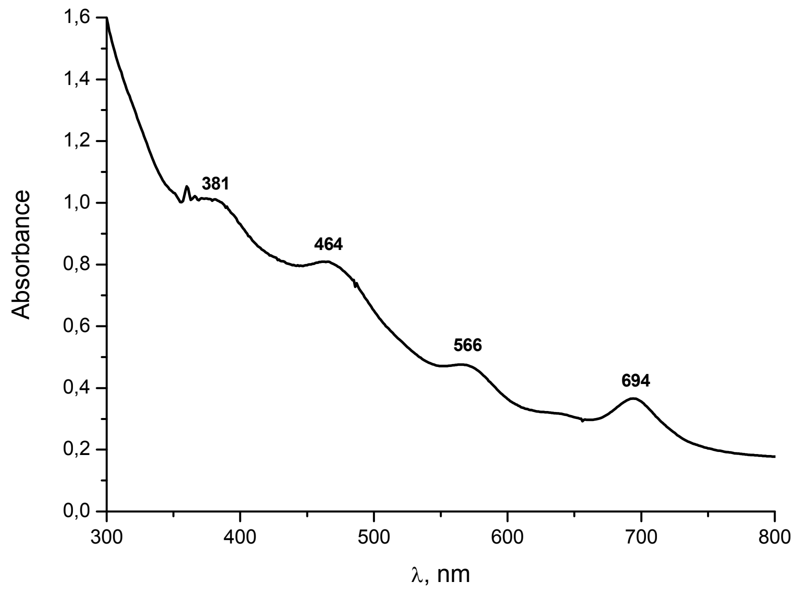

Figure S5. UV-Vis spectrum of iron octapropylporphyrazine (**5**) in air-saturated CH_2Cl_2.

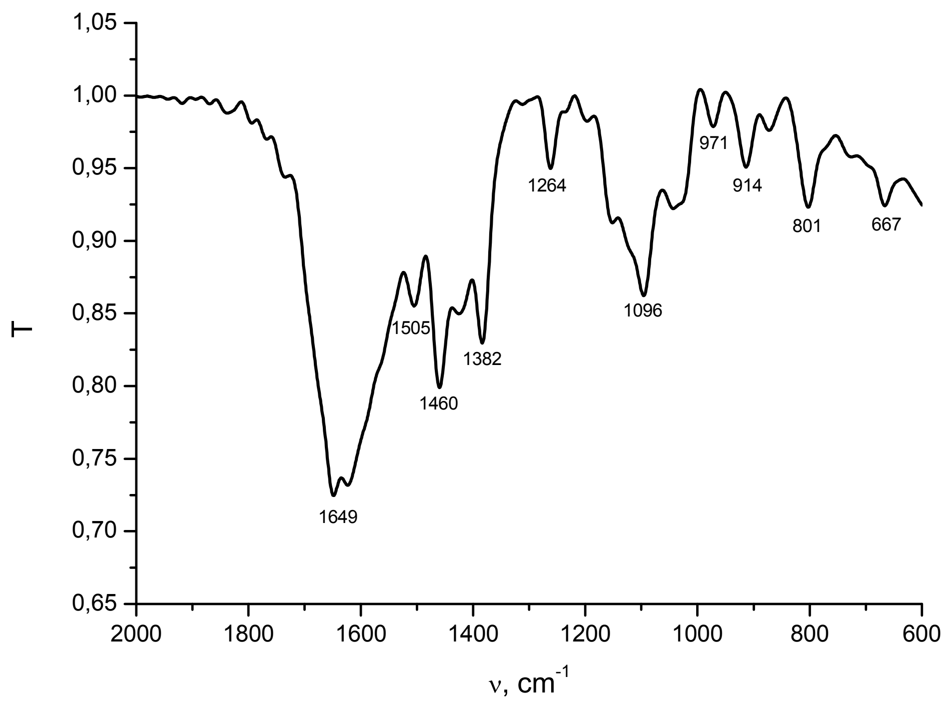

Figure S6. IR spectrum of μ-nitrido diiron octapropylporphyrazine (**7**), KBr.

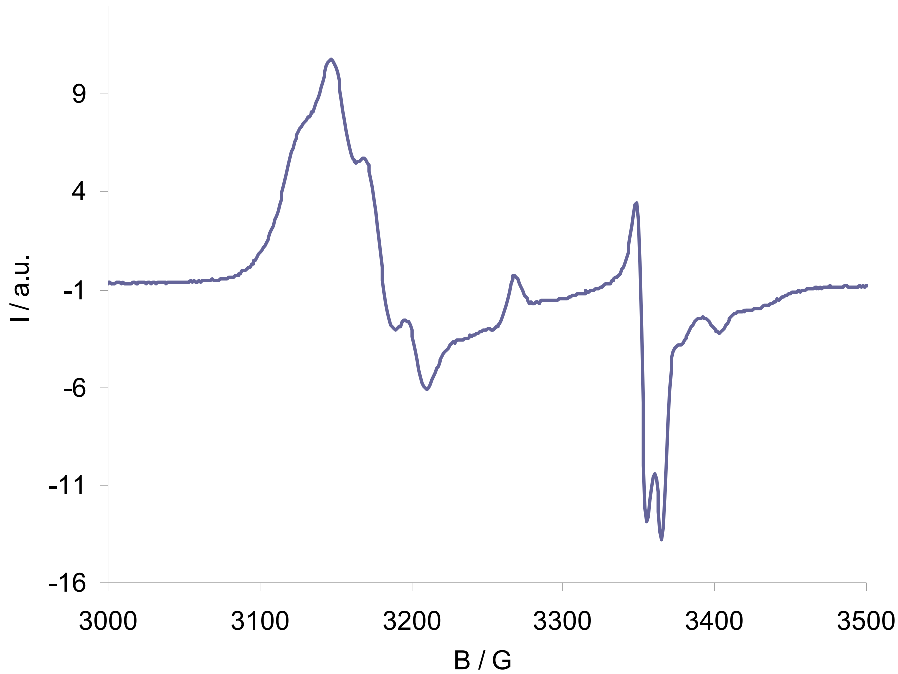

Figure S7. EPR spectrum of [(TAP)Fe^{III}(μ-N)Fe^{IV}(TAP)] (**7**) in toluene under argon (120 K). Unchanged spectrum was observed after exposure to air.

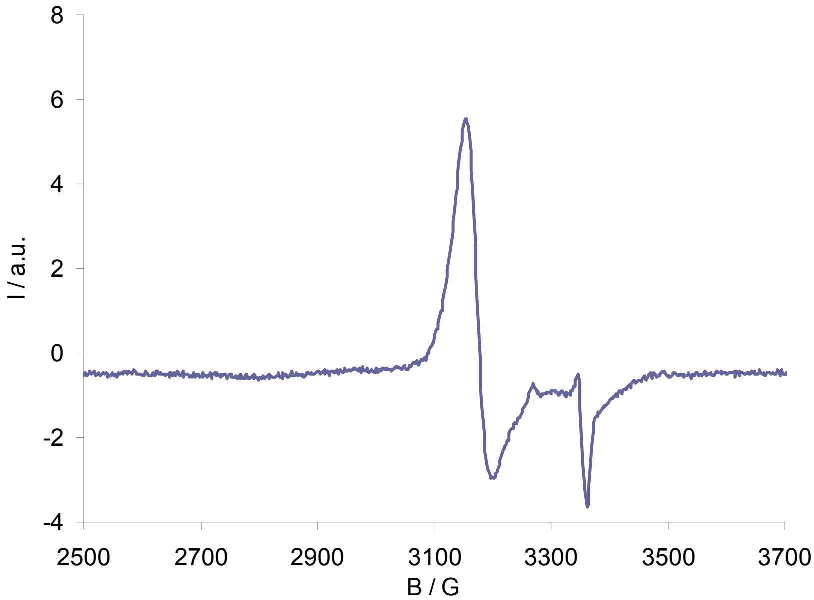

Figure S8. EPR spectrum of [(TAP)Fe^{III}(μ-N)Fe^{IV}(TAP)] (**7**) in CH_2Cl_2 under argon (120K). Unchanged spectrum was observed after exposure to air.

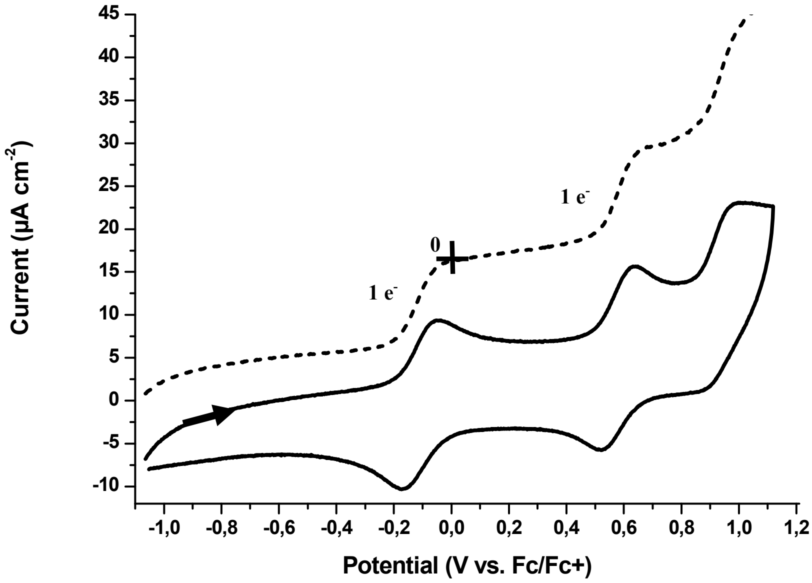

Figure S9. Cyclic voltammograms of [(TAP)Fe^{III}(μ-N)Fe^{IV}(TAP)] (**7**). Insert: RDE voltammogram of **7**) (0.2 mM; 100 mV s^{-1}, CH_2Cl_2, 0.1 M TBAP, glassy carbon WE ∅ = 6 mm, E vs. Fc/Fc^{+}.

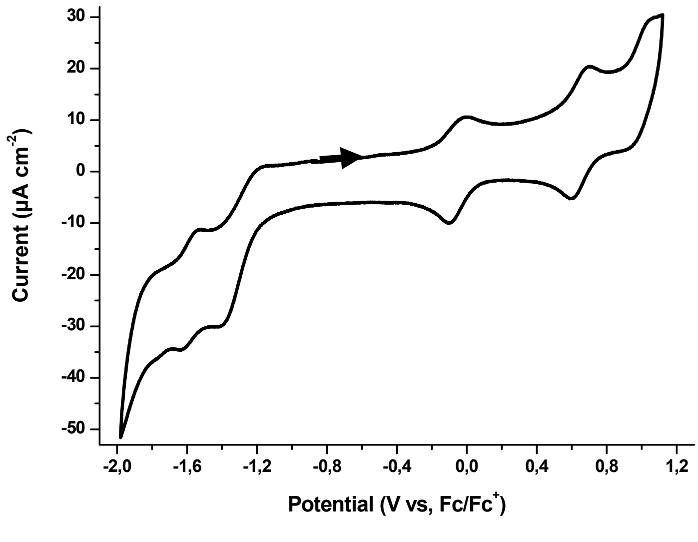

Figure S10. Cyclic voltammograms of [(TAP)Fe^{III}(μ-N)Fe^{IV}(TAP)] (**7**), 0.2 mM; 100 mV s^{-1}, CH_2Cl_2, 0.1 M TBAP, glassy carbon WE ∅ = 6 mm, E vs. Fc/Fc^{+}).

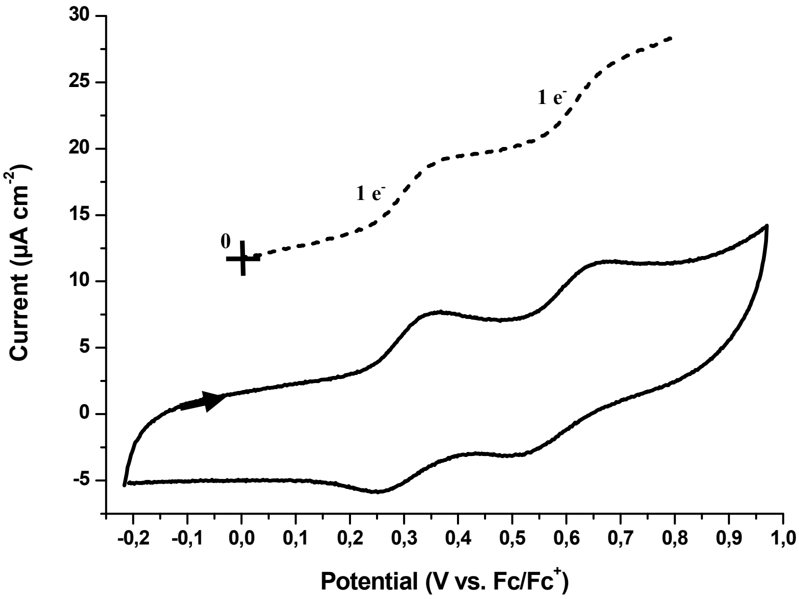

Figure S11. Cyclic voltammograms of [(TAP)Fe^{IV}(μ-C)Fe^{IV}(TAP)] (**8**). Insert: RDE voltammogram of **8**) (0.1 mM; 100 mV s^{-1}, CH_2Cl_2, 0.1 M TBAP, glassy carbon WE ∅ = 6 mm, E vs. Fc/Fc^{+}).

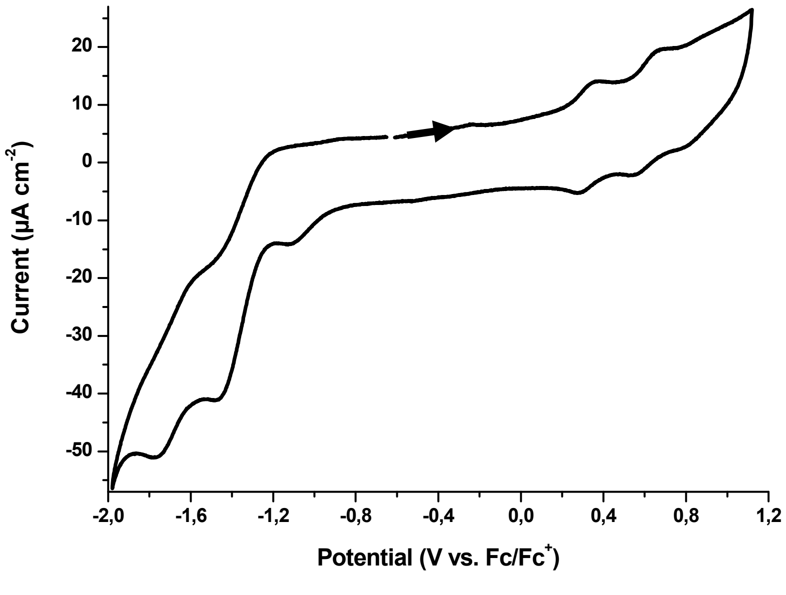

Figure S12. Cyclic voltammograms of [(TAP)Fe^{IV}(μ-C)Fe^{IV}(TAP)] (**8**), 0.1 mM; 100 mV s^{-1}, CH_2Cl_2, 0.1 M TBAP, glassy carbon WE ∅ = 6mm, E vs. Fc/Fc^{+}).

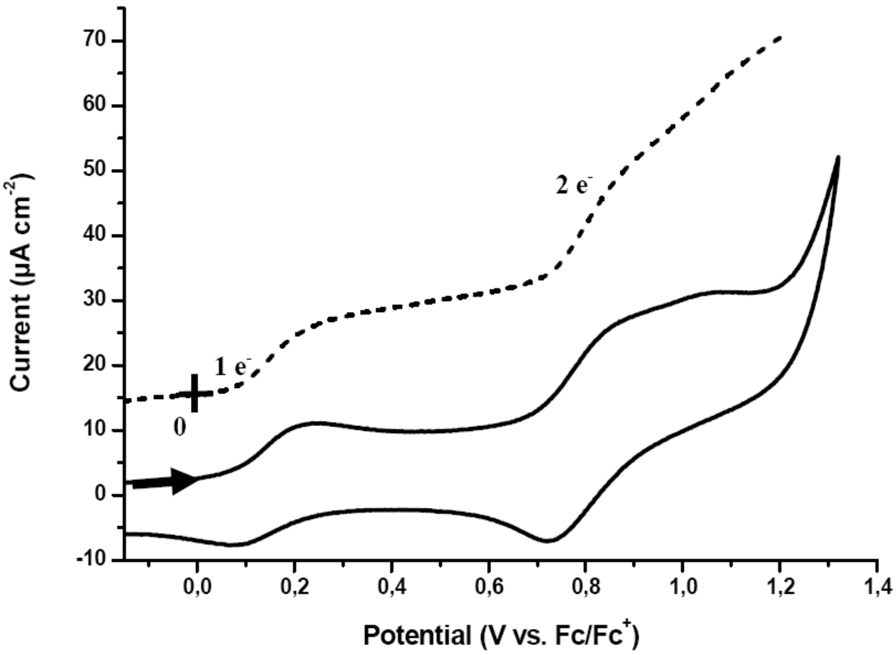

Figure S13. Cyclic voltammograms of [(TAP)Fe^{III}(μ-O)Fe^{III}(TAP)] (**6**). Insert: RDE voltammogram of **6**) (0.3 mM; 100 mV s^{-1}, CH_2Cl_2, 0.1 M TBAP, glassy carbon WE ∅ = 6 mm, E vs. Fc/Fc^{+}).

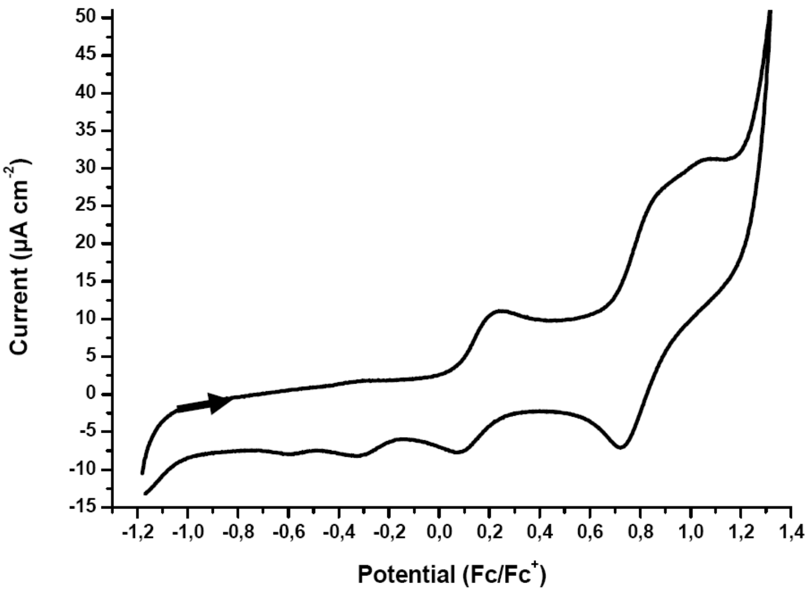

Figure S14. Cyclic voltammograms of [(TAP)Fe^{III}(μ-O)Fe^{III}(TAP)] (**6**), 0.1 mM; 100 mV s^{-1}, CH_2Cl_2, 0.1 M TBAP, glassy carbon WE ∅ = 6 mm, E vs. Fc/Fc^{+}).

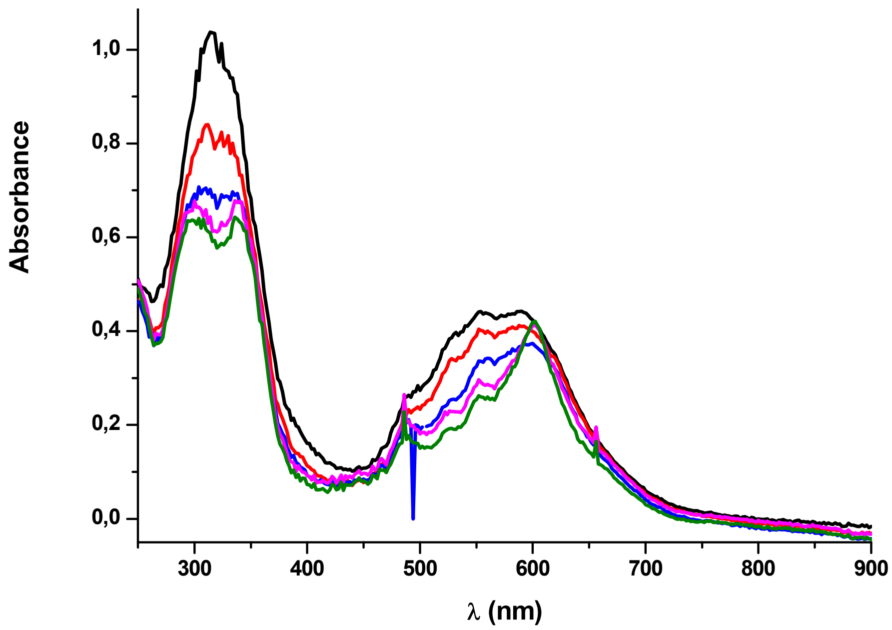

Figure S15. Changes of UV-vis spectrum of [(TAP)Fe^{III}(μ-N)Fe^{IV}(TAP)] (**7**) during electrolysis at 805 mV at -60°C: initial complex (black line 1), after 1 hour (red line 2), after 2 hours (blue line 3), after 4 hours (purple line 4) and after 5 hours (green line 5). Experimental conditions: 40 mL of 0.023 mM solution of **7** in CH_2Cl_2 of in the presence of 0.1 M TBAP, -60°C, argon atmosphere, glassy carbon WE ∅ = 6 mm, E vs. Fc/Fc^+).

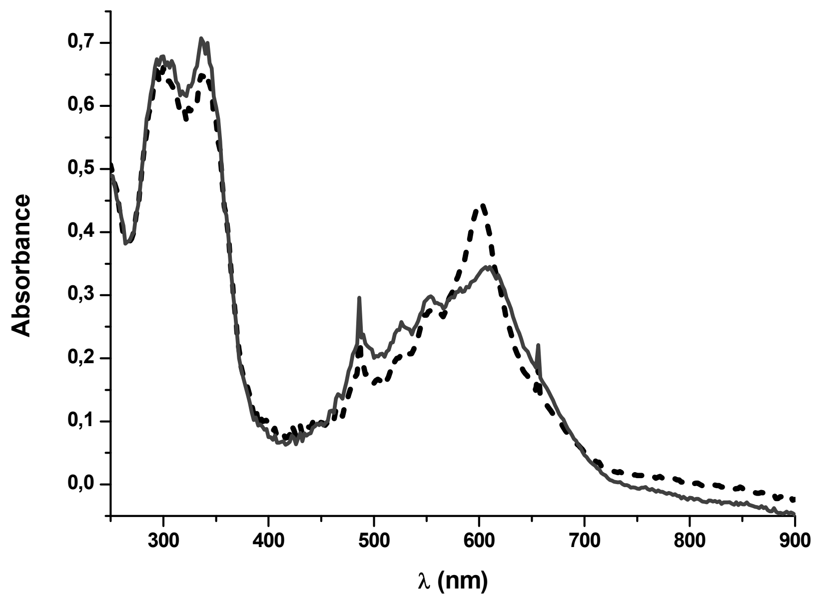

Figure S16. Changes of UV-vis spectrum of oxidized **7** during electrolysis at -495 mV at -60°C: initial complex (dash black line 1), after 1 hour (grey solid line 2). Experimental conditions: 40 mL of 0.023 mM solution of **7** in CH_2Cl_2 of in the presence of 0.1 M TBAP, -60°C, argon atmosphere, glassy carbon WE ∅ = 6 mm, E vs. Fc/Fc^+).

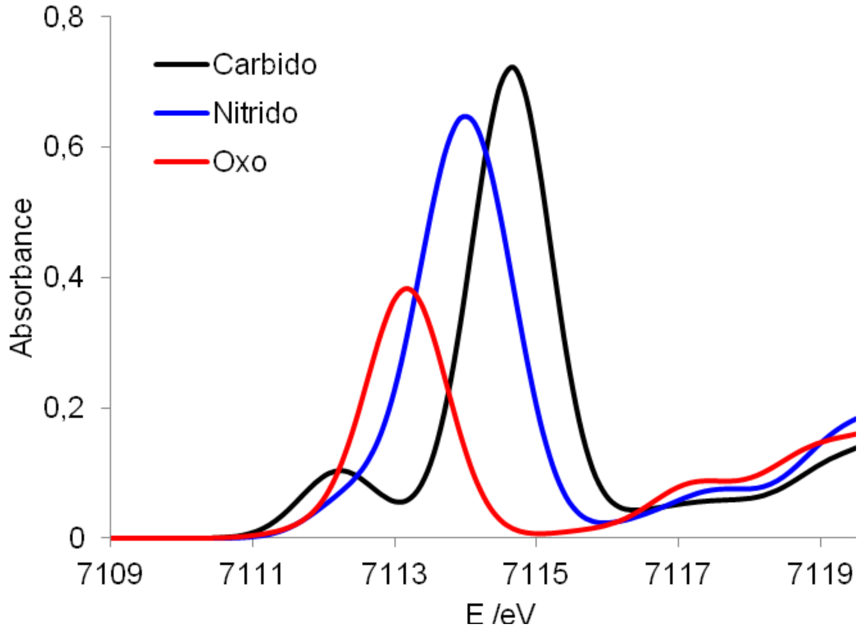

Figure S17. DFT simulated pre-edges for the Fe K XAS spectra of **6** (red), **7** (blue) and **8** black).

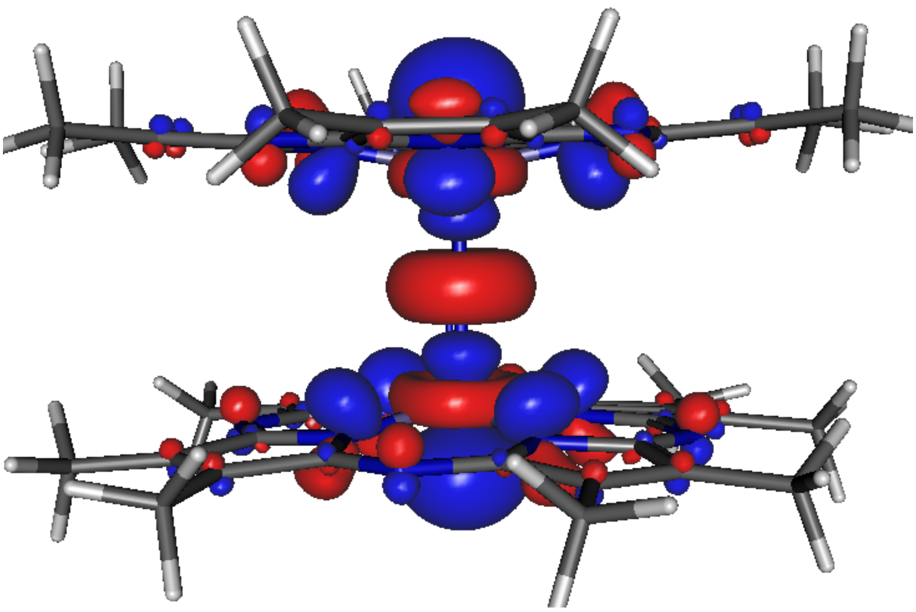

Figure S18. Canonical HOMO orbital of μ-nitrido dimer **7** (isosurface at 0.0025).

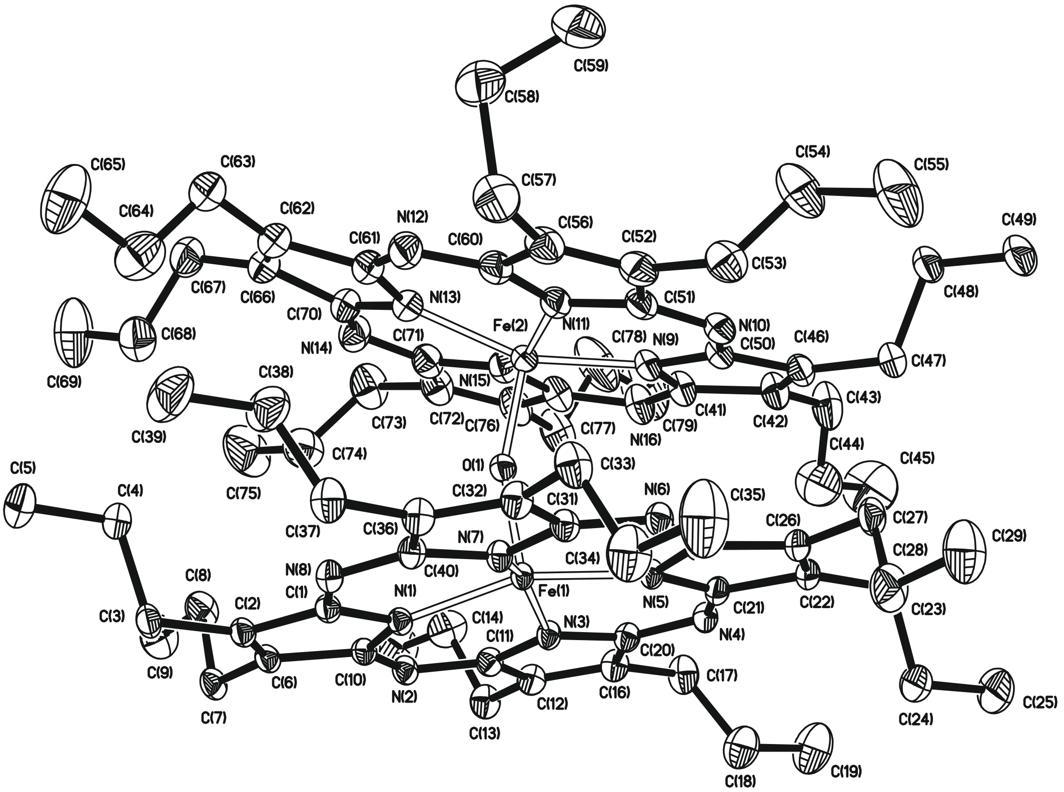

Figure S19. Molecular structure of complex **6**. Displacement ellipsoids are drawn at 30 % probability level. Hydrogen atoms are omitted for clarity.

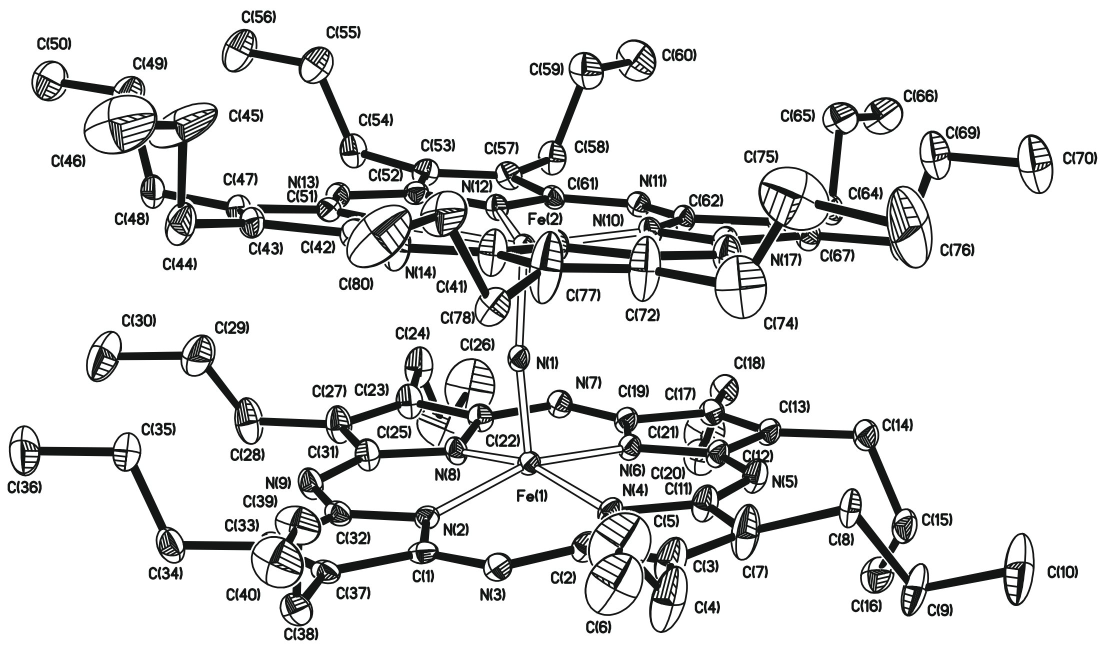

Figure S20. Molecular structure of complex **7**. Displacement ellipsoids are drawn at 30 % probability level. Solvat benzene molecular and hydrogen atoms are omitted for clarity.

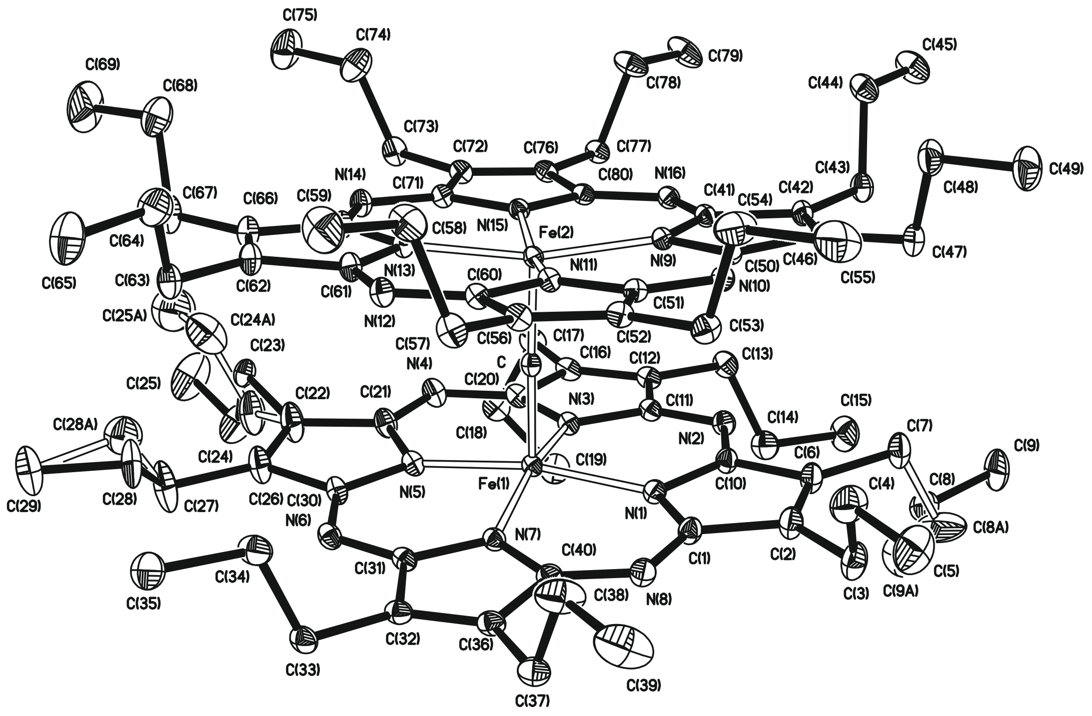

Figure S21. Molecular structure of complex **8**. Displacement ellipsoids are drawn at 30 % probability level. Solvat benzene molecular and hydrogen atoms are omitted for clarity.

Table S1. Crystal Data and Structure Refinement for Compounds

	6	**7 x C_6H_6**	**8 x C_6H_6**
empirical formula	$C_{80}H_{112}Fe_2N_{16}O$	$C_{83}H_{115}Fe_2N_{17}$	$C_{84}H_{115}Fe_2N_{16}$
f.w.	1425.56	1462.62	1460.62
colour	violet-blue	violet	violet
temp (K)	150(2)	150(2)	150(2)
crystal system	triclinic	triclinic	triclinic
space group	P-1	P-1	P-1
unit cell dimensions	a = 15.5842(13)	a = 15.790(6)	a = 15.6968(7)
(Å,deg)	b = 16.0628(13)	b = 16.216(6)	b = 16.2539(7)
	c = 17.9023(14)	c = 18.585(7)	c = 18.4666(8)
	α = 72.5610(10)	α = 88.406(5)	α = 88.8450(10)
	β = 84.5580(10)	β = 76.726(5)	β = 76.6470(10)
	γ = 68.5410(10)	γ = 62.152(4)	γ = 62.2450(10)
V($Å^3$)	3978.5(6)	4078(2)	4035.7(3)
Z	2	2	2
d(calculated) (Mg/m^3)	1.190	1.191	1.202
abs coeff (mm^{-1})	0.418	0.409	0.413
F(000)	1528	1568	1566
cryst size (mm)	0.14 x 0.12 x 0.10	0.20 x 0.18 x 0.14	0.26 x 0.24 x 0.20
θ range for data collection (deg).	1.86 to 29.00	1.73 to 28.00	2.28 to 30.00
index ranges	-21<=h<=21, -21<=k<=21, -24<=l<=24	-20<=h<=20, -21<=k<=21, -24<=l<=24	-22<=h<=22, -22<=k<=22, -25<=l<=25
reflns collected	44144	39887	47755
independent reflns	20972 [R(int) = 0.0214]	19404 [R(int) = 0.0736]	23302 [R(int) = 0.0200]
data / restraints / params	20972 / 0 / 926	19404 / 2 / 976	23302 / 5 / 972
goodness-of-fit on F^2	1.014	1.105	1.020
[a]final R indices [I>2sigma(I)]	R1 = 0.0468, wR2 = 0.12260	R1 = 0.0807, wR2 = 0.1980	R1 = 0.0436, wR2 = 0.1105
[a]R indices (all data)	R1 = 0.0699, wR2 = 0.1392	R1 = 0.1679, wR2 = 0.2480	R1 = 0.0583, wR2 = 0.1209
[b]largest diff. peak and hole(e.A^{-3})	0.729 and -0.388	1.631 and -0.923	0.777 and -0.464

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$

[b] In all structures the largest diff. peak is observed in the vicinity of heavy atom

Table S2. Crystal data and structure refinement for $(FeTAP)_2O$ (**6**).

Identification code	Fe2o	
Empirical formula	C80 H112 Fe2 N16 O	
Formula weight	1425.56	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 15.5842(13) Å	α= 72.5610(10)°.
	b = 16.0628(13) Å	β= 84.5580(10)°.
	c = 17.9023(14)Å	γ = 68.5410(10)°.
Volume	3978.5(6)$Å^3$	
Z	2	
Density (calculated)	1.190 Mg/m^3	
Absorption coefficient	0.418 mm^{-1}	
F(000)	1528	
Crystal size	0.14 x 0.12 x 0.10 mm^3	
Theta range for data collection	1.86 to 29.00°.	
Index ranges	-21<=h<=21, -21<=k<=21, -24<=l<=24	
Reflections collected	44144	
Independent reflections	20972 [R(int) = 0.0214]	
Completeness to theta = 29.00°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9594 and 0.9438	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	20972 / 0 / 926	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0468, wR2 = 0.1226	
R indices (all data)	R1 = 0.0699, wR2 = 0.1392	
Largest diff. peak and hole	0.729 and -0.388 e.$Å^{-3}$	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) For μ-oxo complex **6**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	9907(1)	1233(1)	3609(1)	24(1)
Fe(2)	10139(1)	1640(1)	1610(1)	32(1)
O(1)	10102(1)	1213(1)	2629(1)	31(1)
N(1)	10084(1)	-74(1)	4074(1)	26(1)
N(2)	11737(1)	-732(1)	4285(1)	32(1)
N(3)	11157(1)	956(1)	3927(1)	29(1)
N(4)	11207(1)	2508(1)	3635(1)	32(1)
N(5)	9659(1)	2529(1)	3530(1)	28(1)
N(6)	8003(1)	3185(1)	3337(1)	32(1)
N(7)	8590(1)	1499(1)	3664(1)	28(1)
N(8)	8542(1)	-55(1)	3967(1)	31(1)
N(9)	10436(1)	2739(1)	1508(1)	36(1)
N(10)	8910(1)	3903(1)	1467(1)	38(1)
N(11)	8864(1)	2448(1)	1372(1)	39(1)
N(12)	8192(1)	1384(1)	1188(1)	54(1)
N(13)	9854(1)	720(1)	1280(1)	44(1)
N(14)	11381(2)	-401(1)	1235(1)	52(1)
N(15)	11428(1)	1006(1)	1424(1)	40(1)
N(16)	12100(1)	2103(1)	1525(1)	51(1)
C(1)	9445(1)	-481(1)	4107(1)	28(1)
C(2)	9883(1)	-1495(1)	4319(1)	31(1)
C(3)	9372(1)	-2132(1)	4361(1)	37(1)
C(4)	9176(2)	-2166(2)	3556(1)	50(1)
C(5)	8600(2)	-2763(2)	3592(2)	67(1)
C(6)	10795(1)	-1687(1)	4412(1)	31(1)
C(7)	11587(1)	-2596(1)	4585(1)	37(1)
C(8)	12082(2)	-2783(2)	3848(1)	50(1)
C(9)	12953(2)	-3651(2)	4020(2)	67(1)
C(10)	10917(1)	-791(1)	4257(1)	29(1)
C(11)	11836(1)	88(1)	4128(1)	31(1)
C(12)	12736(1)	167(1)	4142(1)	36(1)
C(13)	13615(1)	-660(1)	4283(1)	43(1)
C(14)	13898(2)	-996(2)	3570(2)	60(1)

C(15)	14750(2)	-1873(2)	3692(2)	74(1)
C(16)	12585(1)	1096(1)	3958(1)	37(1)
C(17)	13259(1)	1579(2)	3898(2)	49(1)
C(18)	13174(2)	2027(2)	4552(2)	66(1)
C(19)	13776(2)	2606(3)	4431(2)	91(1)
C(20)	11595(1)	1582(1)	3824(1)	32(1)
C(21)	10301(1)	2930(1)	3525(1)	29(1)
C(22)	9853(1)	3939(1)	3382(1)	33(1)
C(23)	10363(2)	4573(1)	3354(1)	40(1)
C(24)	10671(2)	4522(2)	4136(2)	63(1)
C(25)	11220(3)	5158(2)	4065(2)	86(1)
C(26)	8936(1)	4130(1)	3293(1)	33(1)
C(27)	8144(1)	5046(1)	3133(1)	41(1)
C(28)	7526(2)	5172(2)	3815(2)	60(1)
C(29)	6687(2)	6065(2)	3616(2)	81(1)
C(30)	8825(1)	3247(1)	3386(1)	30(1)
C(31)	7910(1)	2363(1)	3473(1)	31(1)
C(32)	7012(1)	2278(1)	3459(1)	36(1)
C(33)	6129(1)	3102(1)	3304(1)	47(1)
C(34)	5829(2)	3485(2)	4003(2)	63(1)
C(35)	5000(2)	4386(2)	3834(3)	96(1)
C(36)	7167(1)	1350(1)	3636(1)	36(1)
C(37)	6515(1)	851(2)	3679(1)	44(1)
C(38)	6575(2)	473(2)	2982(2)	65(1)
C(39)	5956(2)	-73(3)	3056(2)	83(1)
C(40)	8157(1)	871(1)	3766(1)	30(1)
C(41)	11298(1)	2786(1)	1511(1)	43(1)
C(42)	11225(2)	3729(2)	1473(1)	48(1)
C(43)	12047(2)	4031(2)	1394(2)	71(1)
C(44)	12700(3)	3600(3)	2022(2)	95(1)
C(45)	13529(3)	3940(4)	1867(3)	123(2)
C(46)	10309(2)	4243(1)	1461(1)	40(1)
C(47)	9819(2)	5253(1)	1406(1)	45(1)
C(48)	9534(2)	5885(2)	576(1)	57(1)
C(49)	8935(2)	6871(2)	581(2)	71(1)
C(50)	9825(1)	3616(1)	1484(1)	36(1)
C(51)	8470(1)	3349(1)	1414(1)	39(1)
C(52)	7473(2)	3669(2)	1358(1)	46(1)

C(53)	6855(2)	4614(2)	1388(2)	53(1)
C(54)	6948(2)	5393(2)	715(2)	82(1)
C(55)	6396(3)	6346(2)	822(3)	112(1)
C(56)	7268(2)	2942(2)	1276(1)	50(1)
C(57)	6351(2)	2893(2)	1157(2)	69(1)
C(58)	6192(5)	3027(5)	257(5)	79(2)
C(59)	6135(5)	4004(4)	-274(4)	88(2)
C(58A)	5865(8)	3502(8)	424(7)	92(3)
C(59A)	6387(13)	3325(15)	-223(8)	152(8)
C(60)	8142(2)	2189(2)	1283(1)	45(1)
C(61)	9003(2)	720(2)	1165(1)	51(1)
C(62)	9086(2)	-139(2)	977(2)	62(1)
C(63)	8264(2)	-349(2)	798(2)	78(1)
C(64)	7955(2)	-954(3)	1490(2)	82(1)
C(65)	7143(2)	-1169(3)	1259(3)	108(1)
C(66)	9992(2)	-638(2)	995(1)	59(1)
C(67)	10506(3)	-1578(2)	848(2)	75(1)
C(68)	10781(2)	-2345(2)	1595(2)	72(1)
C(69)	11443(3)	-3264(3)	1445(3)	119(2)
C(70)	10473(2)	-100(2)	1184(1)	50(1)
C(71)	11815(2)	125(2)	1345(1)	47(1)
C(72)	12816(2)	-176(2)	1366(2)	56(1)
C(73)	13451(2)	-1119(2)	1295(2)	75(1)
C(74)	13415(2)	-1946(2)	1984(2)	78(1)
C(75)	14148(3)	-2848(2)	1924(3)	123(2)
C(76)	13025(2)	535(2)	1458(2)	56(1)
C(77)	13932(2)	637(2)	1497(2)	72(1)
C(78)	14216(2)	1150(3)	704(3)	109(1)
C(79)	15038(3)	1374(3)	759(3)	131(2)
C(80)	12148(2)	1274(1)	1483(1)	46(1)

Table S4. Bond lengths Å] and angles [°] for μ-oxo complex **6**.

Fe(1)-O(1)	1.7601(12)
Fe(1)-N(3)	1.9345(14)
Fe(1)-N(1)	1.9358(14)
Fe(1)-N(5)	1.9362(14)
Fe(1)-N(7)	1.9365(14)
Fe(2)-O(1)	1.7501(12)
Fe(2)-N(9)	1.9365(16)
Fe(2)-N(11)	1.9377(17)
Fe(2)-N(15)	1.9401(17)
Fe(2)-N(13)	1.9456(17)
N(1)-C(1)	1.365(2)
N(1)-C(10)	1.371(2)
N(2)-C(10)	1.323(2)
N(2)-C(11)	1.325(2)
N(3)-C(20)	1.370(2)
N(3)-C(11)	1.372(2)
N(4)-C(21)	1.328(2)
N(4)-C(20)	1.332(2)
N(5)-C(30)	1.369(2)
N(5)-C(21)	1.372(2)
N(6)-C(31)	1.327(2)
N(6)-C(30)	1.333(2)
N(7)-C(40)	1.368(2)
N(7)-C(31)	1.369(2)
N(8)-C(40)	1.329(2)
N(8)-C(1)	1.331(2)
N(9)-C(50)	1.373(2)
N(9)-C(41)	1.374(3)
N(10)-C(50)	1.328(3)
N(10)-C(51)	1.334(3)
N(11)-C(60)	1.372(3)
N(11)-C(51)	1.373(3)
N(12)-C(60)	1.326(3)
N(12)-C(61)	1.328(3)
N(13)-C(61)	1.362(3)
N(13)-C(70)	1.367(3)

N(14)-C(70)	1.321(3)
N(14)-C(71)	1.323(3)
N(15)-C(80)	1.365(3)
N(15)-C(71)	1.366(3)
N(16)-C(41)	1.324(3)
N(16)-C(80)	1.331(3)
C(1)-C(2)	1.460(2)
C(2)-C(6)	1.355(3)
C(2)-C(3)	1.492(2)
C(3)-C(4)	1.521(3)
C(4)-C(5)	1.520(3)
C(6)-C(10)	1.461(2)
C(6)-C(7)	1.495(2)
C(7)-C(8)	1.517(3)
C(8)-C(9)	1.523(3)
C(11)-C(12)	1.458(3)
C(12)-C(16)	1.360(3)
C(12)-C(13)	1.496(3)
C(13)-C(14)	1.498(3)
C(14)-C(15)	1.517(3)
C(16)-C(20)	1.458(2)
C(16)-C(17)	1.497(3)
C(17)-C(18)	1.521(4)
C(18)-C(19)	1.507(4)
C(21)-C(22)	1.462(2)
C(22)-C(26)	1.362(3)
C(22)-C(23)	1.492(2)
C(23)-C(24)	1.493(3)
C(24)-C(25)	1.528(3)
C(26)-C(30)	1.449(2)
C(26)-C(27)	1.502(2)
C(27)-C(28)	1.498(3)
C(28)-C(29)	1.517(3)
C(31)-C(32)	1.457(2)
C(32)-C(36)	1.361(3)
C(32)-C(33)	1.498(3)
C(33)-C(34)	1.517(3)
C(34)-C(35)	1.516(3)

C(36)-C(40)	1.456(2)
C(36)-C(37)	1.491(3)
C(37)-C(38)	1.525(3)
C(38)-C(39)	1.497(4)
C(41)-C(42)	1.457(3)
C(42)-C(46)	1.360(3)
C(42)-C(43)	1.508(3)
C(43)-C(44)	1.419(4)
C(44)-C(45)	1.548(5)
C(46)-C(50)	1.452(3)
C(46)-C(47)	1.497(3)
C(47)-C(48)	1.525(3)
C(48)-C(49)	1.519(3)
C(51)-C(52)	1.450(3)
C(52)-C(56)	1.367(3)
C(52)-C(53)	1.485(3)
C(53)-C(54)	1.493(4)
C(54)-C(55)	1.518(5)
C(56)-C(60)	1.451(3)
C(56)-C(57)	1.500(3)
C(57)-C(58A)	1.458(10)
C(57)-C(58)	1.591(9)
C(58)-C(59)	1.548(10)
C(58A)-C(59A)	1.39(2)
C(61)-C(62)	1.474(3)
C(62)-C(66)	1.343(4)
C(62)-C(63)	1.521(4)
C(63)-C(64)	1.489(4)
C(64)-C(65)	1.548(4)
C(66)-C(70)	1.456(3)
C(66)-C(67)	1.517(4)
C(67)-C(68)	1.492(4)
C(68)-C(69)	1.545(4)
C(71)-C(72)	1.455(3)
C(72)-C(76)	1.353(4)
C(72)-C(73)	1.511(3)
C(73)-C(74)	1.532(4)
C(74)-C(75)	1.509(4)

C(76)-C(80)	1.452(3)
C(76)-C(77)	1.491(4)
C(77)-C(78)	1.528(5)
C(78)-C(79)	1.470(5)
O(1)-Fe(1)-N(3)	99.19(6)
O(1)-Fe(1)-N(1)	97.94(6)
N(3)-Fe(1)-N(1)	88.36(6)
O(1)-Fe(1)-N(5)	102.47(6)
N(3)-Fe(1)-N(5)	88.27(6)
N(1)-Fe(1)-N(5)	159.60(6)
O(1)-Fe(1)-N(7)	100.48(6)
N(3)-Fe(1)-N(7)	160.32(6)
N(1)-Fe(1)-N(7)	88.11(6)
N(5)-Fe(1)-N(7)	88.32(6)
O(1)-Fe(2)-N(9)	100.95(6)
O(1)-Fe(2)-N(11)	100.68(6)
N(9)-Fe(2)-N(11)	88.41(7)
O(1)-Fe(2)-N(15)	100.97(6)
N(9)-Fe(2)-N(15)	87.77(7)
N(11)-Fe(2)-N(15)	158.35(7)
O(1)-Fe(2)-N(13)	101.05(6)
N(9)-Fe(2)-N(13)	158.00(7)
N(11)-Fe(2)-N(13)	87.43(7)
N(15)-Fe(2)-N(13)	88.17(8)
Fe(2)-O(1)-Fe(1)	158.52(7)
C(1)-N(1)-C(10)	106.06(14)
C(1)-N(1)-Fe(1)	126.38(11)
C(10)-N(1)-Fe(1)	125.85(12)
C(10)-N(2)-C(11)	121.19(15)
C(20)-N(3)-C(11)	105.87(14)
C(20)-N(3)-Fe(1)	126.57(11)
C(11)-N(3)-Fe(1)	125.99(12)
C(21)-N(4)-C(20)	120.97(15)
C(30)-N(5)-C(21)	105.99(14)
C(30)-N(5)-Fe(1)	127.17(12)
C(21)-N(5)-Fe(1)	126.52(11)
C(31)-N(6)-C(30)	121.30(15)
C(40)-N(7)-C(31)	106.04(14)

C(40)-N(7)-Fe(1)	126.51(11)
C(31)-N(7)-Fe(1)	126.56(12)
C(40)-N(8)-C(1)	121.09(15)
C(50)-N(9)-C(41)	105.70(16)
C(50)-N(9)-Fe(2)	126.81(13)
C(41)-N(9)-Fe(2)	127.27(13)
C(50)-N(10)-C(51)	121.64(17)
C(60)-N(11)-C(51)	105.52(17)
C(60)-N(11)-Fe(2)	126.98(14)
C(51)-N(11)-Fe(2)	126.33(13)
C(60)-N(12)-C(61)	121.0(2)
C(61)-N(13)-C(70)	106.23(18)
C(61)-N(13)-Fe(2)	127.22(16)
C(70)-N(13)-Fe(2)	126.33(15)
C(70)-N(14)-C(71)	121.5(2)
C(80)-N(15)-C(71)	105.71(18)
C(80)-N(15)-Fe(2)	126.88(14)
C(71)-N(15)-Fe(2)	126.49(15)
C(41)-N(16)-C(80)	121.56(19)
N(8)-C(1)-N(1)	127.40(15)
N(8)-C(1)-C(2)	121.89(15)
N(1)-C(1)-C(2)	110.71(15)
C(6)-C(2)-C(1)	106.32(15)
C(6)-C(2)-C(3)	130.28(16)
C(1)-C(2)-C(3)	123.30(16)
C(2)-C(3)-C(4)	112.49(15)
C(5)-C(4)-C(3)	112.67(19)
C(2)-C(6)-C(10)	106.72(15)
C(2)-C(6)-C(7)	130.52(16)
C(10)-C(6)-C(7)	122.65(16)
C(6)-C(7)-C(8)	112.12(16)
C(7)-C(8)-C(9)	112.75(19)
N(2)-C(10)-N(1)	127.74(15)
N(2)-C(10)-C(6)	122.05(15)
N(1)-C(10)-C(6)	110.20(15)
N(2)-C(11)-N(3)	127.44(16)
N(2)-C(11)-C(12)	121.94(16)
N(3)-C(11)-C(12)	110.62(15)

C(16)-C(12)-C(11)	106.35(16)
C(16)-C(12)-C(13)	130.83(18)
C(11)-C(12)-C(13)	122.68(17)
C(12)-C(13)-C(14)	111.65(18)
C(13)-C(14)-C(15)	114.2(2)
C(12)-C(16)-C(20)	106.65(16)
C(12)-C(16)-C(17)	129.49(18)
C(20)-C(16)-C(17)	123.87(17)
C(16)-C(17)-C(18)	113.26(19)
C(19)-C(18)-C(17)	112.6(2)
N(4)-C(20)-N(3)	127.09(16)
N(4)-C(20)-C(16)	122.40(16)
N(3)-C(20)-C(16)	110.51(15)
N(4)-C(21)-N(5)	127.78(15)
N(4)-C(21)-C(22)	121.89(16)
N(5)-C(21)-C(22)	110.34(15)
C(26)-C(22)-C(21)	106.18(15)
C(26)-C(22)-C(23)	130.46(16)
C(21)-C(22)-C(23)	123.36(16)
C(22)-C(23)-C(24)	114.26(17)
C(23)-C(24)-C(25)	111.6(2)
C(22)-C(26)-C(30)	106.83(15)
C(22)-C(26)-C(27)	129.84(17)
C(30)-C(26)-C(27)	123.33(17)
C(28)-C(27)-C(26)	114.49(17)
C(27)-C(28)-C(29)	113.2(2)
N(6)-C(30)-N(5)	127.02(15)
N(6)-C(30)-C(26)	122.31(15)
N(5)-C(30)-C(26)	110.66(15)
N(6)-C(31)-N(7)	127.51(16)
N(6)-C(31)-C(32)	122.09(16)
N(7)-C(31)-C(32)	110.38(15)
C(36)-C(32)-C(31)	106.58(16)
C(36)-C(32)-C(33)	130.47(18)
C(31)-C(32)-C(33)	122.90(17)
C(32)-C(33)-C(34)	112.45(19)
C(35)-C(34)-C(33)	113.7(3)
C(32)-C(36)-C(40)	106.33(16)

C(32)-C(36)-C(37)	130.57(17)
C(40)-C(36)-C(37)	123.08(17)
C(36)-C(37)-C(38)	113.27(18)
C(39)-C(38)-C(37)	112.6(2)
N(8)-C(40)-N(7)	127.34(16)
N(8)-C(40)-C(36)	121.99(16)
N(7)-C(40)-C(36)	110.67(15)
N(16)-C(41)-N(9)	126.94(19)
N(16)-C(41)-C(42)	122.74(19)
N(9)-C(41)-C(42)	110.30(18)
C(46)-C(42)-C(41)	106.77(19)
C(46)-C(42)-C(43)	129.8(2)
C(41)-C(42)-C(43)	123.3(2)
C(44)-C(43)-C(42)	117.4(3)
C(43)-C(44)-C(45)	112.9(3)
C(42)-C(46)-C(50)	106.36(17)
C(42)-C(46)-C(47)	130.9(2)
C(50)-C(46)-C(47)	122.69(19)
C(46)-C(47)-C(48)	114.42(18)
C(49)-C(48)-C(47)	111.1(2)
N(10)-C(50)-N(9)	127.16(18)
N(10)-C(50)-C(46)	121.97(17)
N(9)-C(50)-C(46)	110.86(17)
N(10)-C(51)-N(11)	126.85(18)
N(10)-C(51)-C(52)	122.09(19)
N(11)-C(51)-C(52)	111.02(18)
C(56)-C(52)-C(51)	106.15(19)
C(56)-C(52)-C(53)	130.3(2)
C(51)-C(52)-C(53)	123.5(2)
C(52)-C(53)-C(54)	114.4(2)
C(53)-C(54)-C(55)	112.5(3)
C(52)-C(56)-C(60)	106.59(19)
C(52)-C(56)-C(57)	129.5(2)
C(60)-C(56)-C(57)	123.8(2)
C(58A)-C(57)-C(56)	115.9(5)
C(58A)-C(57)-C(58)	32.8(5)
C(56)-C(57)-C(58)	110.2(3)
C(59)-C(58)-C(57)	112.9(6)

C(59A)-C(58A)-C(57)	111.7(13)
N(12)-C(60)-N(11)	127.0(2)
N(12)-C(60)-C(56)	122.2(2)
N(11)-C(60)-C(56)	110.72(19)
N(12)-C(61)-N(13)	127.6(2)
N(12)-C(61)-C(62)	122.3(2)
N(13)-C(61)-C(62)	110.1(2)
C(66)-C(62)-C(61)	106.2(2)
C(66)-C(62)-C(63)	130.2(3)
C(61)-C(62)-C(63)	123.6(3)
C(64)-C(63)-C(62)	113.3(2)
C(63)-C(64)-C(65)	110.5(3)
C(62)-C(66)-C(70)	107.1(2)
C(62)-C(66)-C(67)	130.9(3)
C(70)-C(66)-C(67)	121.9(3)
C(68)-C(67)-C(66)	111.7(2)
C(67)-C(68)-C(69)	111.2(3)
N(14)-C(70)-N(13)	127.8(2)
N(14)-C(70)-C(66)	121.9(2)
N(13)-C(70)-C(66)	110.3(2)
N(14)-C(71)-N(15)	127.3(2)
N(14)-C(71)-C(72)	122.3(2)
N(15)-C(71)-C(72)	110.3(2)
C(76)-C(72)-C(71)	106.8(2)
C(76)-C(72)-C(73)	129.6(2)
C(71)-C(72)-C(73)	123.6(2)
C(72)-C(73)-C(74)	114.4(2)
C(75)-C(74)-C(73)	111.4(3)
C(72)-C(76)-C(80)	106.1(2)
C(72)-C(76)-C(77)	131.0(2)
C(80)-C(76)-C(77)	122.9(2)
C(76)-C(77)-C(78)	112.6(3)
C(79)-C(78)-C(77)	112.8(4)
N(16)-C(80)-N(15)	126.91(19)
N(16)-C(80)-C(76)	122.0(2)
N(15)-C(80)-C(76)	111.03(19)

Symmetry transformations used to generate equivalent atoms:

Table S5. Crystal data and structure refinement for μ-nitrido complex **7**.

Identification code	fe2n	
Empirical formula	C83 H115 Fe2 N17	
Formula weight	1462.62	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 15.790(6) Å	α= 88.406(5)°.
	b = 16.216(6)Å	β= 76.726(5)°.
	c = 18.585(7) Å	γ = 62.152(4)°.
Volume	4078(2) E3	
Z	2	
Density (calculated)	1.191 Mg/m3	
Absorption coefficient	0.409 mm-1	
F(000)	1568	
Crystal size	0.20 x 0.18 x 0.14 mm3	
Theta range for data collection	1.73 to 28.00°.	
Index ranges	-20<=h<=20, -21<=k<=21, -24<=l<=24	
Reflections collected	39887	
Independent reflections	19404 [R(int) = 0.0736]	
Completeness to theta = 28.00°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9450 and 0.9227	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	19404 / 2 / 976	
Goodness-of-fit on F2	1.105	
Final R indices [I>2sigma(I)]	R1 = 0.0807, wR2 = 0.1980	
R indices (all data)	R1 = 0.1679, wR2 = 0.2480	
Largest diff. peak and hole	1.631 and -0.923 e.Å-3	

Table S6. Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for μ-nitrido complex **7**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x
Fe(1)	5199(1)
Fe(2)	5305(1)
N(1)	5235(3)
N(2)	4753(3)
N(3)	6313(3)
N(4)	6531(3)
N(5)	7401(3)
N(6)	5631(3)
N(7)	4080(3)
N(8)	3860(3)
N(9)	2981(3)
N(10)	6253(3)
N(11)	5166(3)
N(12)	4275(3)
N(13)	2855(3)
N(14)	4390(3)
N(15)	5477(3)
N(16)	6377(3)
N(17)	7786(3)
C(1)	5315(4)
C(2)	6857(4)
C(3)	7931(4)
C(4)	8501(5)
C(5)	8425(7)
C(6)	8992(6)
C(7)	8237(5)
C(8)	9291(10)
C(9)	9773(11)
C(10)	10784(16)
C(8A)	9253(13)
C(9A)	9837(15)
C(10A)	10860(17)
C(11)	7368(4)
C(12)	6587(4)
C(13)	6608(4)

C(14)	7545(4)
C(15)	8020(4)
C(16)	7382(5)
C(17)	5653(4)
C(18)	5199(5)
C(19)	5044(4)
C(20)	4658(5)
C(21)	4108(6)
C(22)	3524(4)
C(23)	2460(4)
C(24)	1897(5)
C(25)	1787(8)
C(26)	1421(8)
C(27)	2134(4)
C(28)	1123(4)
C(29)	923(5)
C(30)	-102(6)
C(31)	3025(4)
C(32)	3793(4)
C(33)	3759(4)
C(34)	2827(4)
C(35)	2471(6)
C(36)	1436(7)
C(37)	4714(4)
C(38)	5151(4)
C(39)	5536(6)
C(40)	6088(6)
C(41)	6300(4)
C(42)	4597(4)
C(43)	3685(4)
C(44)	3686(5)
C(45)	4061(9)
C(46)	4205(10)
C(47)	2939(4)
C(48)	1858(4)
C(49)	1532(5)
C(50)	412(5)
C(51)	3389(4)

C(52)	3285(4)
C(53)	2726(4)
C(54)	1643(4)
C(55)	1371(5)
C(56)	266(5)
C(57)	3387(4)
C(58)	3250(4)
C(59)	3513(5)
C(60)	3492(7)
C(61)	4343(4)
C(62)	6051(4)
C(63)	6961(4)
C(64)	6979(4)
C(65)	6861(5)
C(66)	6792(6)
C(67)	7712(4)
C(68)	8795(4)
C(69)	9282(5)
C(70)	10413(5)
C(71)	7254(4)
C(72)	7362(4)
C(73)	7939(5)
C(74)	9055(6)
C(75)	9504(8)
C(76)	10706(6)
C(77)	7273(5)
C(78)	7412(9)
C(79)	7292(14)
C(80)	7390(40)
C(78A)	7477(12)
C(79A)	7257(17)
C(80A)	7430(30)
C(81)	5953(7)
C(82)	5744(6)
C(83)	4761(6)

Table S7. Bond lengths [Å] and angles [°] for μ-nitrido complex **7**.

Fe(1)-N(1)	1.656(4)
Fe(1)-N(8)	1.914(4)
Fe(1)-N(6)	1.922(4)
Fe(1)-N(4)	1.929(4)
Fe(1)-N(2)	1.929(4)
Fe(2)-N(1)	1.662(4)
Fe(2)-N(12)	1.915(4)
Fe(2)-N(10)	1.926(4)
Fe(2)-N(16)	1.933(4)
Fe(2)-N(14)	1.933(4)
N(2)-C(1)	1.353(6)
N(2)-C(32)	1.374(6)
N(3)-C(2)	1.327(6)
N(3)-C(1)	1.352(7)
N(4)-C(2)	1.371(6)
N(4)-C(11)	1.372(6)
N(5)-C(12)	1.324(7)
N(5)-C(11)	1.331(6)
N(6)-C(19)	1.369(6)
N(6)-C(12)	1.374(6)
N(7)-C(19)	1.313(6)
N(7)-C(22)	1.345(6)
N(8)-C(31)	1.370(6)
N(8)-C(22)	1.369(6)
N(9)-C(32)	1.325(6)
N(9)-C(31)	1.334(6)
N(10)-C(71)	1.361(6)
N(10)-C(62)	1.373(6)
N(11)-C(61)	1.330(6)
N(11)-C(62)	1.331(6)
N(12)-C(61)	1.371(6)
N(12)-C(52)	1.380(6)
N(13)-C(52)	1.326(6)
N(13)-C(51)	1.326(6)
N(14)-C(51)	1.365(6)
N(14)-C(42)	1.367(6)

N(15)-C(42)	1.321(7)
N(15)-C(41)	1.329(7)
N(16)-C(41)	1.363(6)
N(16)-C(72)	1.365(7)
N(17)-C(71)	1.324(7)
N(17)-C(72)	1.328(7)
C(1)-C(37)	1.447(6)
C(2)-C(3)	1.454(8)
C(3)-C(7)	1.370(8)
C(3)-C(4)	1.486(8)
C(4)-C(5)	1.353(11)
C(5)-C(6)	1.504(9)
C(7)-C(11)	1.433(8)
C(7)-C(8)	1.550(16)
C(7)-C(8A)	1.571(19)
C(8)-C(9)	1.53(2)
C(9)-C(10)	1.49(2)
C(8A)-C(9A)	1.44(3)
C(9A)-C(10A)	1.56(3)
C(12)-C(13)	1.456(6)
C(13)-C(17)	1.359(7)
C(13)-C(14)	1.502(7)
C(14)-C(15)	1.524(8)
C(15)-C(16)	1.506(9)
C(17)-C(19)	1.464(6)
C(17)-C(18)	1.505(7)
C(18)-C(20)	1.508(9)
C(20)-C(21)	1.523(9)
C(22)-C(23)	1.447(7)
C(23)-C(27)	1.359(7)
C(23)-C(24)	1.503(8)
C(24)-C(25)	1.482(11)
C(25)-C(26)	1.541(12)
C(27)-C(31)	1.463(8)
C(27)-C(28)	1.488(8)
C(28)-C(29)	1.463(10)
C(29)-C(30)	1.540(10)
C(32)-C(33)	1.456(7)

C(33)-C(37)	1.360(7)
C(33)-C(34)	1.487(7)
C(34)-C(35)	1.491(9)
C(35)-C(36)	1.539(10)
C(37)-C(38)	1.494(7)
C(38)-C(39)	1.522(8)
C(39)-C(40)	1.523(9)
C(41)-C(77)	1.449(8)
C(42)-C(43)	1.463(7)
C(43)-C(47)	1.344(8)
C(43)-C(44)	1.498(7)
C(44)-C(45)	1.562(11)
C(45)-C(46)	1.453(11)
C(47)-C(51)	1.465(6)
C(47)-C(48)	1.494(7)
C(48)-C(49)	1.499(8)
C(49)-C(50)	1.524(9)
C(52)-C(53)	1.463(7)
C(53)-C(57)	1.355(7)
C(53)-C(54)	1.494(7)
C(54)-C(55)	1.511(8)
C(55)-C(56)	1.515(9)
C(57)-C(61)	1.449(7)
C(57)-C(58)	1.497(7)
C(58)-C(59)	1.532(9)
C(59)-C(60)	1.526(8)
C(62)-C(63)	1.454(7)
C(63)-C(67)	1.358(7)
C(63)-C(64)	1.508(7)
C(64)-C(65)	1.496(8)
C(65)-C(66)	1.533(8)
C(67)-C(71)	1.455(6)
C(67)-C(68)	1.481(7)
C(68)-C(69)	1.500(10)
C(69)-C(70)	1.534(9)
C(72)-C(73)	1.452(8)
C(73)-C(77)	1.361(9)
C(73)-C(74)	1.517(10)

C(74)-C(75)	1.358(13)
C(75)-C(76)	1.659(14)
C(77)-C(78)	1.523(13)
C(77)-C(78A)	1.71(2)
C(78)-C(79)	1.513(19)
C(79)-C(80)	1.51(4)
C(78A)-C(79A)	1.33(3)
C(79A)-C(80A)	1.57(4)
C(81)-C(83)#1	1.288(11)
C(81)-C(82)	1.4193(11)
C(82)-C(83)	1.4193(11)
C(83)-C(81)#1	1.288(11)

N(1)-Fe(1)-N(8)	97.54(19)
N(1)-Fe(1)-N(6)	99.05(17)
N(8)-Fe(1)-N(6)	89.22(17)
N(1)-Fe(1)-N(4)	98.73(19)
N(8)-Fe(1)-N(4)	163.72(18)
N(6)-Fe(1)-N(4)	88.39(16)
N(1)-Fe(1)-N(2)	98.47(17)
N(8)-Fe(1)-N(2)	88.58(16)
N(6)-Fe(1)-N(2)	162.48(17)
N(4)-Fe(1)-N(2)	88.87(16)
N(1)-Fe(2)-N(12)	99.83(19)
N(1)-Fe(2)-N(10)	97.76(17)
N(12)-Fe(2)-N(10)	88.98(16)
N(1)-Fe(2)-N(16)	98.4(2)
N(12)-Fe(2)-N(16)	161.76(18)
N(10)-Fe(2)-N(16)	88.39(17)
N(1)-Fe(2)-N(14)	99.04(17)
N(12)-Fe(2)-N(14)	88.62(16)
N(10)-Fe(2)-N(14)	163.19(17)
N(16)-Fe(2)-N(14)	88.69(17)
Fe(1)-N(1)-Fe(2)	168.6(2)
C(1)-N(2)-C(32)	105.5(4)
C(1)-N(2)-Fe(1)	127.1(3)
C(32)-N(2)-Fe(1)	126.1(3)
C(2)-N(3)-C(1)	121.2(4)

C(2)-N(4)-C(11)	105.5(4)
C(2)-N(4)-Fe(1)	126.1(3)
C(11)-N(4)-Fe(1)	127.1(3)
C(12)-N(5)-C(11)	121.8(4)
C(19)-N(6)-C(12)	106.3(4)
C(19)-N(6)-Fe(1)	126.1(3)
C(12)-N(6)-Fe(1)	127.3(3)
C(19)-N(7)-C(22)	121.2(4)
C(31)-N(8)-C(22)	104.7(4)
C(31)-N(8)-Fe(1)	127.1(3)
C(22)-N(8)-Fe(1)	126.6(3)
C(32)-N(9)-C(31)	121.1(4)
C(71)-N(10)-C(62)	105.8(4)
C(71)-N(10)-Fe(2)	127.2(3)
C(62)-N(10)-Fe(2)	126.6(3)
C(61)-N(11)-C(62)	122.0(4)
C(61)-N(12)-C(52)	105.1(4)
C(61)-N(12)-Fe(2)	127.6(3)
C(52)-N(12)-Fe(2)	127.1(3)
C(52)-N(13)-C(51)	120.8(4)
C(51)-N(14)-C(42)	106.3(4)
C(51)-N(14)-Fe(2)	126.7(3)
C(42)-N(14)-Fe(2)	126.4(3)
C(42)-N(15)-C(41)	121.7(4)
C(41)-N(16)-C(72)	106.3(4)
C(41)-N(16)-Fe(2)	126.5(4)
C(72)-N(16)-Fe(2)	126.4(3)
C(71)-N(17)-C(72)	121.3(5)
N(3)-C(1)-N(2)	126.8(4)
N(3)-C(1)-C(37)	121.8(4)
N(2)-C(1)-C(37)	111.4(5)
N(3)-C(2)-N(4)	127.5(5)
N(3)-C(2)-C(3)	121.7(5)
N(4)-C(2)-C(3)	110.8(4)
C(7)-C(3)-C(2)	105.6(5)
C(7)-C(3)-C(4)	131.1(6)
C(2)-C(3)-C(4)	123.4(5)
C(5)-C(4)-C(3)	119.9(7)

C(4)-C(5)-C(6)	121.1(8)
C(3)-C(7)-C(11)	107.2(5)
C(3)-C(7)-C(8)	126.0(8)
C(11)-C(7)-C(8)	124.7(7)
C(3)-C(7)-C(8A)	128.0(9)
C(11)-C(7)-C(8A)	120.6(8)
C(8)-C(7)-C(8A)	31.3(7)
C(9)-C(8)-C(7)	107.7(14)
C(10)-C(9)-C(8)	109.4(16)
C(9A)-C(8A)-C(7)	103.5(17)
C(8A)-C(9A)-C(10A)	115(2)
N(5)-C(11)-N(4)	126.3(5)
N(5)-C(11)-C(7)	122.9(5)
N(4)-C(11)-C(7)	110.9(5)
N(5)-C(12)-N(6)	127.0(4)
N(5)-C(12)-C(13)	122.5(4)
N(6)-C(12)-C(13)	110.5(4)
C(17)-C(13)-C(12)	106.3(4)
C(17)-C(13)-C(14)	130.6(5)
C(12)-C(13)-C(14)	123.1(5)
C(13)-C(14)-C(15)	114.5(5)
C(16)-C(15)-C(14)	113.2(5)
C(13)-C(17)-C(19)	106.9(4)
C(13)-C(17)-C(18)	131.4(5)
C(19)-C(17)-C(18)	121.6(5)
C(17)-C(18)-C(20)	112.9(5)
N(7)-C(19)-N(6)	128.1(4)
N(7)-C(19)-C(17)	122.0(4)
N(6)-C(19)-C(17)	109.9(4)
C(18)-C(20)-C(21)	113.3(6)
N(7)-C(22)-N(8)	126.3(5)
N(7)-C(22)-C(23)	122.2(4)
N(8)-C(22)-C(23)	111.5(4)
C(27)-C(23)-C(22)	106.9(5)
C(27)-C(23)-C(24)	130.4(5)
C(22)-C(23)-C(24)	122.7(5)
C(25)-C(24)-C(23)	112.3(6)
C(24)-C(25)-C(26)	109.4(8)

C(23)-C(27)-C(31)	105.4(5)
C(23)-C(27)-C(28)	131.4(6)
C(31)-C(27)-C(28)	123.2(5)
C(29)-C(28)-C(27)	114.3(6)
C(28)-C(29)-C(30)	113.8(7)
N(9)-C(31)-N(8)	126.7(5)
N(9)-C(31)-C(27)	121.7(5)
N(8)-C(31)-C(27)	111.5(4)
N(9)-C(32)-N(2)	127.6(4)
N(9)-C(32)-C(33)	121.8(5)
N(2)-C(32)-C(33)	110.6(4)
C(37)-C(33)-C(32)	106.0(4)
C(37)-C(33)-C(34)	130.7(5)
C(32)-C(33)-C(34)	123.3(5)
C(33)-C(34)-C(35)	113.7(5)
C(34)-C(35)-C(36)	112.1(7)
C(33)-C(37)-C(1)	106.5(4)
C(33)-C(37)-C(38)	131.0(5)
C(1)-C(37)-C(38)	122.4(5)
C(37)-C(38)-C(39)	110.9(4)
C(40)-C(39)-C(38)	113.0(5)
N(15)-C(41)-N(16)	127.3(5)
N(15)-C(41)-C(77)	122.6(5)
N(16)-C(41)-C(77)	110.1(5)
N(15)-C(42)-N(14)	127.4(5)
N(15)-C(42)-C(43)	122.7(5)
N(14)-C(42)-C(43)	109.9(5)
C(47)-C(43)-C(42)	107.1(4)
C(47)-C(43)-C(44)	130.7(5)
C(42)-C(43)-C(44)	122.1(5)
C(43)-C(44)-C(45)	111.8(5)
C(46)-C(45)-C(44)	114.2(8)
C(43)-C(47)-C(51)	106.4(4)
C(43)-C(47)-C(48)	130.1(5)
C(51)-C(47)-C(48)	123.5(5)
C(47)-C(48)-C(49)	114.3(5)
C(48)-C(49)-C(50)	112.5(6)
N(13)-C(51)-N(14)	127.7(4)

N(13)-C(51)-C(47)	121.9(5)
N(14)-C(51)-C(47)	110.3(4)
N(13)-C(52)-N(12)	127.5(4)
N(13)-C(52)-C(53)	122.0(4)
N(12)-C(52)-C(53)	110.5(4)
C(57)-C(53)-C(52)	106.5(4)
C(57)-C(53)-C(54)	131.0(5)
C(52)-C(53)-C(54)	122.5(5)
C(53)-C(54)-C(55)	114.3(5)
C(54)-C(55)-C(56)	113.0(6)
C(53)-C(57)-C(61)	106.6(4)
C(53)-C(57)-C(58)	130.5(5)
C(61)-C(57)-C(58)	122.8(5)
C(57)-C(58)-C(59)	112.6(5)
C(60)-C(59)-C(58)	111.5(6)
N(11)-C(61)-N(12)	126.3(4)
N(11)-C(61)-C(57)	122.3(4)
N(12)-C(61)-C(57)	111.4(4)
N(11)-C(62)-N(10)	126.9(4)
N(11)-C(62)-C(63)	122.7(4)
N(10)-C(62)-C(63)	110.4(4)
C(67)-C(63)-C(62)	106.5(4)
C(67)-C(63)-C(64)	130.6(5)
C(62)-C(63)-C(64)	122.8(5)
C(65)-C(64)-C(63)	114.6(5)
C(64)-C(65)-C(66)	110.5(5)
C(63)-C(67)-C(71)	106.3(4)
C(63)-C(67)-C(68)	130.4(5)
C(71)-C(67)-C(68)	123.4(5)
C(67)-C(68)-C(69)	112.5(5)
C(68)-C(69)-C(70)	113.0(7)
N(17)-C(71)-N(10)	127.2(4)
N(17)-C(71)-C(67)	121.8(5)
N(10)-C(71)-C(67)	111.0(4)
N(17)-C(72)-N(16)	127.5(5)
N(17)-C(72)-C(73)	121.8(5)
N(16)-C(72)-C(73)	110.6(5)
C(77)-C(73)-C(72)	105.9(6)

C(77)-C(73)-C(74)	131.4(6)
C(72)-C(73)-C(74)	122.6(6)
C(75)-C(74)-C(73)	111.3(9)
C(74)-C(75)-C(76)	107.9(10)
C(73)-C(77)-C(41)	107.0(5)
C(73)-C(77)-C(78)	129.0(7)
C(41)-C(77)-C(78)	121.6(7)
C(73)-C(77)-C(78A)	124.4(9)
C(41)-C(77)-C(78A)	119.3(8)
C(78)-C(77)-C(78A)	41.0(7)
C(79)-C(78)-C(77)	108.3(13)
C(80)-C(79)-C(78)	116(2)
C(79A)-C(78A)-C(77)	100(2)
C(78A)-C(79A)-C(80A)	111(3)
C(83)#1-C(81)-C(82)	118.9(8)
C(83)-C(82)-C(81)	119.7(8)
C(81)#1-C(83)-C(82)	121.3(8)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

Table S8. Crystal data and structure refinement for μ-carbido complex **8**.

Identification code	fe2c
Empirical formula	C84 H115 Fe2 N16
Formula weight	1460.62
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 15.6968(7) Å α= 88.8450(10)°.
	b = 16.2539(7) Å β= 76.6470(10)°.
	c = 18.4666(8) Å γ = 62.2450(10)°.
Volume	4035.7(3) Å3
Z	2
Density (calculated)	1.202 Mg/m3
Absorption coefficient	0.413 mm-1
F(000)	1566
Crystal size	0.26 x 0.24 x 0.20 mm3
Theta range for data collection	2.28 to 30.00°.
Index ranges	-22<=h<=22, -22<=k<=22, -25<=l<=25
Reflections collected	47755
Independent reflections	23302 [R(int) = 0.0200]
Completeness to theta = 30.00°	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9220 and 0.9002
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	23302 / 5 / 972
Goodness-of-fit on F2	1.020
Final R indices [I>2sigma(I)]	R1 = 0.0436, wR2 = 0.1105
R indices (all data)	R1 = 0.0583, wR2 = 0.1209
Largest diff. peak and hole	0.777 and -0.464 eÅ-3

Table S9. Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for μ-carbido complex **8**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x
Fe(1)	4803(1)
Fe(2)	4709(1)
C	4771(1)
N(1)	6155(1)
N(2)	5943(1)
N(3)	4373(1)
N(4)	2584(1)
N(5)	3460(1)
N(6)	3677(1)
N(7)	5243(1)
N(8)	7026(1)
N(9)	5752(1)
N(10)	7174(1)
N(11)	5631(1)
N(12)	4542(1)
N(13)	3639(1)
N(14)	2217(1)
N(15)	3766(1)
N(16)	4852(1)
C(1)	6988(1)
C(2)	7879(1)
C(3)	8901(1)
C(4)	9084(2)
C(5)	10103(2)
C(6)	7566(1)
C(7)	8133(1)
C(8)	8186(3)
C(9)	8565(2)
C(8A)	8558(9)
C(9A)	7978(9)
C(10)	6489(1)
C(11)	4961(1)
C(12)	4360(1)

C(13)	4818(1)
C(14)	5347(2)
C(15)	5916(2)
C(16)	3395(1)
C(17)	2457(1)
C(18)	1970(1)
C(19)	2608(2)
C(20)	3411(1)
C(21)	2618(1)
C(22)	1728(1)
C(23)	692(2)
C(24)	226(2)
C(25)	-832(3)
C(23A)	723(4)
C(24A)	94(6)
C(25A)	-915(7)
C(26)	2042(1)
C(27)	1452(2)
C(28)	1711(3)
C(28A)	1403(8)
C(29)	1007(2)
C(30)	3125(1)
C(31)	4661(1)
C(32)	5269(1)
C(33)	4833(1)
C(34)	4453(2)
C(35)	3900(2)
C(36)	6232(1)
C(37)	7176(1)
C(38)	7562(2)
C(39)	8600(2)
C(40)	6206(1)
C(41)	5673(1)
C(42)	6641(1)
C(43)	6775(1)
C(44)	6458(1)
C(45)	6469(2)
C(46)	7308(1)

C(47)	8397(1)
C(48)	8656(1)
C(49)	9774(1)
C(50)	6741(1)
C(51)	6639(1)
C(52)	7088(1)
C(53)	8172(1)
C(54)	8432(1)
C(55)	9553(2)
C(56)	6328(1)
C(57)	6314(1)
C(58)	5917(2)
C(59)	5770(2)
C(60)	5426(1)
C(61)	3715(1)
C(62)	2734(1)
C(63)	2574(1)
C(64)	2799(2)
C(65)	2671(2)
C(66)	2066(1)
C(67)	957(1)
C(68)	454(2)
C(69)	-682(2)
C(70)	2641(1)
C(71)	2751(1)
C(72)	2296(1)
C(73)	1197(1)
C(74)	702(1)
C(75)	-427(2)
C(76)	3053(1)
C(77)	3039(1)
C(78)	3134(2)
C(79)	3197(2)
C(80)	3967(1)
C(81)	4013(3)
C(82)	4293(3)
C(83)	5266(3)
C(81A)	4028(3)

C(82A)	4789(4)
C(83A)	5762(4)

Table S10. Bond lengths [Å] and angles [°] for μ-carbido complex **8**.

Fe(1)-C	1.6692(14)
Fe(1)-N(7)	1.9102(12)
Fe(1)-N(3)	1.9109(12)
Fe(1)-N(1)	1.9125(12)
Fe(1)-N(5)	1.9161(12)
Fe(2)-C	1.6714(14)
Fe(2)-N(15)	1.9115(12)
Fe(2)-N(11)	1.9131(12)
Fe(2)-N(9)	1.9149(12)
Fe(2)-N(13)	1.9154(12)
N(1)-C(1)	1.3705(19)
N(1)-C(10)	1.3752(18)
N(2)-C(10)	1.3271(19)
N(2)-C(11)	1.3289(19)
N(3)-C(11)	1.3708(18)
N(3)-C(20)	1.3746(18)
N(4)-C(21)	1.327(2)
N(4)-C(20)	1.331(2)
N(5)-C(30)	1.3738(18)
N(5)-C(21)	1.379(2)
N(6)-C(31)	1.325(2)
N(6)-C(30)	1.328(2)
N(7)-C(31)	1.3704(18)
N(7)-C(40)	1.3741(19)
N(8)-C(40)	1.324(2)
N(8)-C(1)	1.3283(19)
N(9)-C(50)	1.3690(18)
N(9)-C(41)	1.3718(17)
N(10)-C(50)	1.3273(18)
N(10)-C(51)	1.3311(18)
N(11)-C(51)	1.3707(18)
N(11)-C(60)	1.3716(17)
N(12)-C(61)	1.3261(19)
N(12)-C(60)	1.3276(19)
N(13)-C(70)	1.3725(18)
N(13)-C(61)	1.3755(18)

N(14)-C(71)	1.3253(19)
N(14)-C(70)	1.3274(19)
N(15)-C(71)	1.3728(18)
N(15)-C(80)	1.3731(17)
N(16)-C(41)	1.3270(18)
N(16)-C(80)	1.3274(18)
C(1)-C(2)	1.460(2)
C(2)-C(6)	1.361(2)
C(2)-C(3)	1.500(2)
C(3)-C(4)	1.510(3)
C(4)-C(5)	1.529(3)
C(6)-C(10)	1.457(2)
C(6)-C(7)	1.499(2)
C(7)-C(8A)	1.5011(10)
C(7)-C(8)	1.532(5)
C(8)-C(9)	1.490(4)
C(8A)-C(9A)	1.275(16)
C(11)-C(12)	1.456(2)
C(12)-C(16)	1.361(2)
C(12)-C(13)	1.498(2)
C(13)-C(14)	1.538(2)
C(14)-C(15)	1.522(2)
C(16)-C(20)	1.462(2)
C(16)-C(17)	1.496(2)
C(17)-C(18)	1.537(2)
C(18)-C(19)	1.520(3)
C(21)-C(22)	1.457(2)
C(22)-C(26)	1.364(3)
C(22)-C(23)	1.506(4)
C(22)-C(23A)	1.570(6)
C(23)-C(24)	1.518(5)
C(24)-C(25)	1.525(5)
C(23A)-C(24A)	1.467(10)
C(24A)-C(25A)	1.561(11)
C(26)-C(30)	1.457(2)
C(26)-C(27)	1.502(2)
C(27)-C(28A)	1.409(4)
C(27)-C(28)	1.477(4)

C(28)-C(29)	1.484(4)
C(28A)-C(29)	1.533(12)
C(31)-C(32)	1.456(2)
C(32)-C(36)	1.361(2)
C(32)-C(33)	1.493(2)
C(33)-C(34)	1.528(2)
C(34)-C(35)	1.520(2)
C(36)-C(40)	1.456(2)
C(36)-C(37)	1.493(2)
C(37)-C(38)	1.515(3)
C(38)-C(39)	1.524(3)
C(41)-C(42)	1.457(2)
C(42)-C(46)	1.360(2)
C(42)-C(43)	1.495(2)
C(43)-C(44)	1.532(2)
C(44)-C(45)	1.525(2)
C(46)-C(50)	1.4646(19)
C(46)-C(47)	1.492(2)
C(47)-C(48)	1.529(2)
C(48)-C(49)	1.523(2)
C(51)-C(52)	1.4601(19)
C(52)-C(56)	1.360(2)
C(52)-C(53)	1.496(2)
C(53)-C(54)	1.521(2)
C(54)-C(55)	1.526(3)
C(56)-C(60)	1.4527(19)
C(56)-C(57)	1.496(2)
C(57)-C(58)	1.545(2)
C(58)-C(59)	1.517(3)
C(61)-C(62)	1.457(2)
C(62)-C(66)	1.362(2)
C(62)-C(63)	1.502(2)
C(63)-C(64)	1.509(3)
C(64)-C(65)	1.536(3)
C(66)-C(70)	1.459(2)
C(66)-C(67)	1.494(2)
C(67)-C(68)	1.498(3)
C(68)-C(69)	1.545(3)

C(71)-C(72)	1.4570(19)
C(72)-C(76)	1.359(2)
C(72)-C(73)	1.493(2)
C(73)-C(74)	1.526(3)
C(74)-C(75)	1.523(3)
C(76)-C(80)	1.4563(19)
C(76)-C(77)	1.496(2)
C(77)-C(78)	1.521(2)
C(78)-C(79)	1.526(2)
C(81)-C(82)	1.381(5)
C(81)-C(83)#1	1.395(5)
C(82)-C(83)	1.382(5)
C(83)-C(81)#1	1.396(5)
C(81A)-C(83A)#1	1.345(7)
C(81A)-C(82A)	1.3986(10)
C(82A)-C(83A)	1.3996(10)
C(83A)-C(81A)#1	1.345(7)

C-Fe(1)-N(7)	98.41(6)
C-Fe(1)-N(3)	95.57(6)
N(7)-Fe(1)-N(3)	166.02(5)
C-Fe(1)-N(1)	94.89(6)
N(7)-Fe(1)-N(1)	89.01(5)
N(3)-Fe(1)-N(1)	89.60(5)
C-Fe(1)-N(5)	96.91(6)
N(7)-Fe(1)-N(5)	89.40(5)
N(3)-Fe(1)-N(5)	89.12(5)
N(1)-Fe(1)-N(5)	168.20(5)
C-Fe(2)-N(15)	94.00(6)
C-Fe(2)-N(11)	98.50(6)
N(15)-Fe(2)-N(11)	167.50(5)
C-Fe(2)-N(9)	97.32(6)
N(15)-Fe(2)-N(9)	89.20(5)
N(11)-Fe(2)-N(9)	89.17(5)
C-Fe(2)-N(13)	96.49(6)
N(15)-Fe(2)-N(13)	89.33(5)
N(11)-Fe(2)-N(13)	89.30(5)
N(9)-Fe(2)-N(13)	166.19(5)

Fe(1)-C-Fe(2)	175.10(9)
C(1)-N(1)-C(10)	105.60(12)
C(1)-N(1)-Fe(1)	126.92(10)
C(10)-N(1)-Fe(1)	126.28(10)
C(10)-N(2)-C(11)	121.38(13)
C(11)-N(3)-C(20)	105.81(12)
C(11)-N(3)-Fe(1)	126.66(10)
C(20)-N(3)-Fe(1)	127.30(10)
C(21)-N(4)-C(20)	121.40(14)
C(30)-N(5)-C(21)	105.70(12)
C(30)-N(5)-Fe(1)	126.75(10)
C(21)-N(5)-Fe(1)	126.83(10)
C(31)-N(6)-C(30)	121.51(13)
C(31)-N(7)-C(40)	105.46(12)
C(31)-N(7)-Fe(1)	126.96(10)
C(40)-N(7)-Fe(1)	127.06(10)
C(40)-N(8)-C(1)	121.21(13)
C(50)-N(9)-C(41)	105.79(11)
C(50)-N(9)-Fe(2)	127.17(9)
C(41)-N(9)-Fe(2)	126.90(10)
C(50)-N(10)-C(51)	120.86(12)
C(51)-N(11)-C(60)	105.65(11)
C(51)-N(11)-Fe(2)	127.28(9)
C(60)-N(11)-Fe(2)	126.96(10)
C(61)-N(12)-C(60)	121.41(13)
C(70)-N(13)-C(61)	105.79(12)
C(70)-N(13)-Fe(2)	126.85(10)
C(61)-N(13)-Fe(2)	126.88(10)
C(71)-N(14)-C(70)	121.53(13)
C(71)-N(15)-C(80)	105.57(11)
C(71)-N(15)-Fe(2)	126.99(10)
C(80)-N(15)-Fe(2)	126.97(10)
C(41)-N(16)-C(80)	121.08(12)
N(8)-C(1)-N(1)	127.02(14)
N(8)-C(1)-C(2)	122.27(14)
N(1)-C(1)-C(2)	110.70(13)
C(6)-C(2)-C(1)	106.53(14)
C(6)-C(2)-C(3)	130.86(15)

C(1)-C(2)-C(3)	122.60(15)
C(2)-C(3)-C(4)	113.40(16)
C(3)-C(4)-C(5)	112.89(18)
C(2)-C(6)-C(10)	106.35(14)
C(2)-C(6)-C(7)	131.26(15)
C(10)-C(6)-C(7)	122.38(14)
C(6)-C(7)-C(8A)	110.35(19)
C(6)-C(7)-C(8)	113.4(2)
C(8A)-C(7)-C(8)	24.2(6)
C(9)-C(8)-C(7)	113.9(3)
C(9A)-C(8A)-C(7)	119.6(11)
N(2)-C(10)-N(1)	126.87(14)
N(2)-C(10)-C(6)	122.30(14)
N(1)-C(10)-C(6)	110.80(13)
N(2)-C(11)-N(3)	127.36(13)
N(2)-C(11)-C(12)	122.01(13)
N(3)-C(11)-C(12)	110.63(13)
C(16)-C(12)-C(11)	106.68(13)
C(16)-C(12)-C(13)	131.30(14)
C(11)-C(12)-C(13)	121.96(14)
C(12)-C(13)-C(14)	111.65(13)
C(15)-C(14)-C(13)	113.35(16)
C(12)-C(16)-C(20)	106.33(13)
C(12)-C(16)-C(17)	130.62(14)
C(20)-C(16)-C(17)	123.05(14)
C(16)-C(17)-C(18)	113.99(13)
C(19)-C(18)-C(17)	113.81(15)
N(4)-C(20)-N(3)	127.05(13)
N(4)-C(20)-C(16)	122.52(14)
N(3)-C(20)-C(16)	110.44(13)
N(4)-C(21)-N(5)	126.72(14)
N(4)-C(21)-C(22)	122.80(15)
N(5)-C(21)-C(22)	110.43(14)
C(26)-C(22)-C(21)	106.69(15)
C(26)-C(22)-C(23)	128.3(2)
C(21)-C(22)-C(23)	124.32(19)
C(26)-C(22)-C(23A)	129.0(3)
C(21)-C(22)-C(23A)	118.8(3)

C(23)-C(22)-C(23A)	28.2(3)
C(22)-C(23)-C(24)	110.8(3)
C(23)-C(24)-C(25)	111.2(3)
C(24A)-C(23A)-C(22)	102.6(6)
C(23A)-C(24A)-C(25A)	111.2(6)
C(22)-C(26)-C(30)	106.39(14)
C(22)-C(26)-C(27)	130.08(17)
C(30)-C(26)-C(27)	123.52(16)
C(28A)-C(27)-C(28)	21.8(4)
C(28A)-C(27)-C(26)	117.1(5)
C(28)-C(27)-C(26)	117.4(2)
C(27)-C(28)-C(29)	116.2(3)
C(27)-C(28A)-C(29)	117.4(6)
C(28)-C(29)-C(28A)	20.9(4)
N(6)-C(30)-N(5)	126.93(14)
N(6)-C(30)-C(26)	122.32(14)
N(5)-C(30)-C(26)	110.76(13)
N(6)-C(31)-N(7)	127.30(13)
N(6)-C(31)-C(32)	121.75(13)
N(7)-C(31)-C(32)	110.93(13)
C(36)-C(32)-C(31)	106.40(13)
C(36)-C(32)-C(33)	130.77(14)
C(31)-C(32)-C(33)	122.64(14)
C(32)-C(33)-C(34)	110.84(13)
C(35)-C(34)-C(33)	113.07(15)
C(32)-C(36)-C(40)	106.44(13)
C(32)-C(36)-C(37)	130.73(14)
C(40)-C(36)-C(37)	122.77(14)
C(36)-C(37)-C(38)	113.18(14)
C(37)-C(38)-C(39)	112.28(18)
N(8)-C(40)-N(7)	127.18(13)
N(8)-C(40)-C(36)	122.05(14)
N(7)-C(40)-C(36)	110.76(13)
N(16)-C(41)-N(9)	127.42(13)
N(16)-C(41)-C(42)	121.87(13)
N(9)-C(41)-C(42)	110.70(12)
C(46)-C(42)-C(41)	106.62(13)
C(46)-C(42)-C(43)	130.72(14)

C(41)-C(42)-C(43)	122.60(13)
C(42)-C(43)-C(44)	112.74(13)
C(45)-C(44)-C(43)	112.43(15)
C(42)-C(46)-C(50)	106.21(13)
C(42)-C(46)-C(47)	130.67(14)
C(50)-C(46)-C(47)	123.10(13)
C(46)-C(47)-C(48)	113.17(13)
C(49)-C(48)-C(47)	112.16(15)
N(10)-C(50)-N(9)	127.58(13)
N(10)-C(50)-C(46)	121.75(13)
N(9)-C(50)-C(46)	110.67(12)
N(10)-C(51)-N(11)	127.27(13)
N(10)-C(51)-C(52)	121.99(13)
N(11)-C(51)-C(52)	110.69(12)
C(56)-C(52)-C(51)	106.22(12)
C(56)-C(52)-C(53)	130.14(13)
C(51)-C(52)-C(53)	123.58(13)
C(52)-C(53)-C(54)	113.29(13)
C(53)-C(54)-C(55)	111.87(16)
C(52)-C(56)-C(60)	106.68(12)
C(52)-C(56)-C(57)	130.83(13)
C(60)-C(56)-C(57)	122.29(13)
C(56)-C(57)-C(58)	110.92(13)
C(59)-C(58)-C(57)	113.43(16)
N(12)-C(60)-N(11)	127.30(13)
N(12)-C(60)-C(56)	121.91(13)
N(11)-C(60)-C(56)	110.75(12)
N(12)-C(61)-N(13)	126.99(13)
N(12)-C(61)-C(62)	122.33(13)
N(13)-C(61)-C(62)	110.66(13)
C(66)-C(62)-C(61)	106.39(13)
C(66)-C(62)-C(63)	130.39(15)
C(61)-C(62)-C(63)	123.20(14)
C(62)-C(63)-C(64)	114.47(15)
C(63)-C(64)-C(65)	111.23(18)
C(62)-C(66)-C(70)	106.66(13)
C(62)-C(66)-C(67)	130.51(15)
C(70)-C(66)-C(67)	122.83(14)

C(66)-C(67)-C(68)	113.75(17)
C(67)-C(68)-C(69)	110.6(2)
N(14)-C(70)-N(13)	127.11(13)
N(14)-C(70)-C(66)	122.39(14)
N(13)-C(70)-C(66)	110.49(13)
N(14)-C(71)-N(15)	127.07(13)
N(14)-C(71)-C(72)	122.29(13)
N(15)-C(71)-C(72)	110.63(12)
C(76)-C(72)-C(71)	106.60(13)
C(76)-C(72)-C(73)	130.46(13)
C(71)-C(72)-C(73)	122.90(13)
C(72)-C(73)-C(74)	112.33(14)
C(75)-C(74)-C(73)	112.43(18)
C(72)-C(76)-C(80)	106.40(12)
C(72)-C(76)-C(77)	130.79(14)
C(80)-C(76)-C(77)	122.80(13)
C(76)-C(77)-C(78)	113.62(13)
C(77)-C(78)-C(79)	111.54(14)
N(16)-C(80)-N(15)	127.15(13)
N(16)-C(80)-C(76)	122.03(13)
N(15)-C(80)-C(76)	110.79(12)
C(82)-C(81)-C(83)#1	119.0(3)
C(81)-C(82)-C(83)	121.9(3)
C(82)-C(83)-C(81)#1	119.0(3)
C(83A)#1-C(81A)-C(82A)	119.3(4)
C(81A)-C(82A)-C(83A)	120.5(4)
C(81A)#1-C(83A)-C(82A)	120.1(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

Table S11. Molecular geometry parameters of the compounds **6-8,** obtained from DFT optimization and by EXAFS fitting.

Geometry parameter	**8** (carbido)	**7** (nitrido)	**6** (oxo)
d(Fe-X) DFT[a]	1.675	1.657	1.777
d(Fe-X) EXAFS	1.68(1)	1.65(1)	1.79(1)
d(Fe-N)planar DFT	1.933	1.949	1.955
d(Fe-N)planar EXAFS	1.92(1)	1.93(1)	1.93(1)
α(Fe-X-Fe) DFT[b]	179.5	179.5	178.2
α(X-Fe-N) DFT[b]	98.4	100.8	99.9

[a] distances in Å; [b]the corresponding values of angles cannot be calculated from EXAFS.