Supporting Information for

Coordination of Diatomic Ligands to Heme: Simply CO

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Experimental Section

General Information. All reactions were carried out under anaerobic conditions using standard Schlenk techniques under an argon atmosphere. Free base [H_2OEP] (Mid-Century Chemicals) and ethanethiol (Acros) were used as received. Carbon monoxide gas (Mittler Specialty Gases) was passed through a trap containing 4 Å molecular sieves to remove residual water. Benzene (Fisher) was purified by distillation in a nitrogen atmosphere over sodium/benzophenone ketyl. Methylene chloride (Fisher) was purified by distillation in a nitrogen atmosphere over calcium hydride. All solvents were freeze/pump/thaw degassed (3×) prior to use. [Fe(OEP)(Cl)] was prepared according to the metalation procedure of Adler et al.[1] [Fe(OEP)]$_2$O was prepared by washing a solution of [Fe(OEP)Cl] in methylene chloride with 2 M aqueous sodium hydroxide solution (3×), drying the collected organic layers over magnesium sulfate followed by recrystallization from methylene chloride/hexanes.[2] [Fe(OEP)] was prepared by stirring a solution of [Fe(OEP)]$_2$O and excess ethanethiol in benzene for 2 d.[3] After reduction, solvent and excess ethanethiol were removed under vacuum.

Infrared spectra were recorded on a Nicolet Nexus 870 FT-IR spectrometer. Solid state infrared samples were prepared by gently mulling a suitable crystal between two NaCl plates with a small amount of Nujol to allow dispersion. Samples were prepared for Mössbauer spectroscopy by weighing approximately 2 mg of selected crystals, grinding them in a small volume of Apiezon M grease to form a mull and placing them into a Mössbauer cup. Measurements were performed on a constant acceleration spectrometer from 4.2 K to 300 K.

Synthesis of [Fe(OEP)(CO)] and [Fe(OEP)(CO)$_2$]. A solution of 30 mg (0.49 mmol) [Fe(OEP)] in 7 mL benzene was purged with CO for 10 min while stirring, then heated slightly to dissolve all material. The solution was then cannula transferred into 8 mm glass tubes, carefully

layered with hexanes and the tubes were flame sealed. The tubes were stored at 4 °C for 30 d, after which X-ray quality crystals were isolated. Each crystallization tube yielded a single crystalline species, i.e. mixtures of crystal species were *not* found. The "plate-like" crystals of [Fe(OEP)(CO)] could be differentiated from the "block-like" crystals of [Fe(OEP)$(CO)_2$] by visual inspection and by IR spectroscopy of crushed single crystals. IR ν_{CO} in Nujol mull: Fe(OEP)(CO)], 1944 cm^{-1}; [Fe(OEP)$(CO)_2$], 2021 cm^{-1}.

Synthesis of [Fe(OEP)(CO)]·C_6H_6. A solution of 30 mg (0.49 mmol) [Fe(OEP)] in 10 mL benzene was purged with CO for 10 min while stirring, then heated slightly to dissolve all material. The solution was then cannula transferred into 8 mm glass tubes, carefully layered with hexanes and the tubes were flame sealed. The tubes were stored at 4 °C for 30 d, after which X-ray quality crystals were isolated. IR ν_{CO} in Nujol mull: [Fe(OEP)(CO)]·C_6H_6, 1948 cm^{-1}.

X-Ray Crystallographic Studies. The crystals were placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Crystal data were collected and integrated using a Bruker Apex system, with graphite monochromated Mo-Kα (λ= 0.71073 Å) radiation at 100 K (700 Series Oxford Cryostream) for all complexes. Data was collected to a $2\theta_{max} \geq 62°$. The program SADABS[4] was applied for absorption correction.

All structures were solved by direct methods in SHELXS-97[5] and refined using SHELXL-97.[6] All atoms were found after successive full-matrix least-squares refinement cycles on F^2 and refined with anisotropic thermal parameters. Hydrogen atom positions were idealized with a riding model and fixed thermal parameters [U_{ij} = 1.2Uij(eq) or 1.5Uij(eq)] for the atom to which they are bonded. Complete crystallographic details are given below.

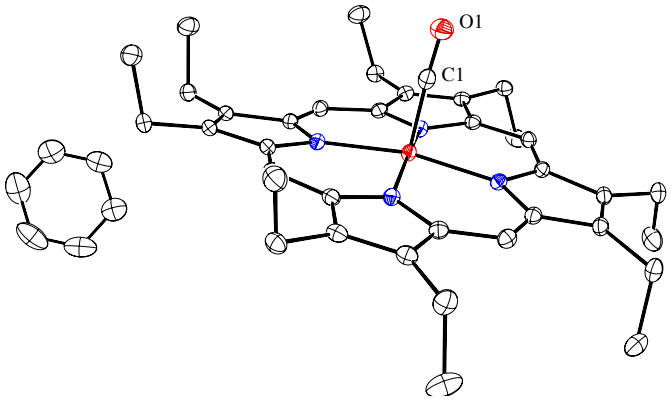

Figure S1. Thermal ellipsoid plot of [Fe(OEP)(CO)]·C_6H_6.

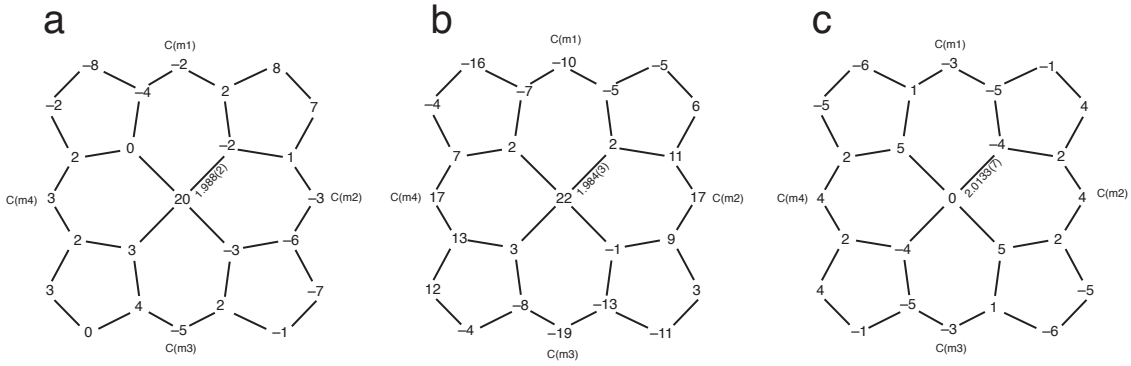

Figure S2. Formal diagrams of the porphyrinato core of [Fe(OEP)(CO)] (a), [Fe(OEP)(CO)]·C_6H_6 (b), and [Fe(OEP)$(CO)_2$] (c) displaying the perpendicular displacements (in units of 0.01 Å) of the core atoms from the 24-atom mean plane. Positive displacements are toward the CO-coordinated face.

Table S1. Mössbauer data for [Fe(OEP)(CO)] and related complexes.

Complex[a]	Temp, K	ΔE_Q[b]	δ[b]	ref
[Fe(OEP)(CO)]	298	1.81	0.14	tw
	250	1.83	0.20	tw
	225	1.84	0.20	tw
	100	1.84	0.23	tw
	25	1.84	0.23	tw
	4.2	1.84	0.27	tw
[Fe(OEP)$(CO)_2$]	298	0.18	0.18	tw
	200	0.11	0.27	tw
	100	0.10	0.28	tw
	15	0.097	0.28	tw
	4.2	0	0.31	tw
[Fe(OEP)(CS)]	293	1.95	−0.03	10
	4.2	1.93	0.08	10
[Fe(OEP)(NO)]	100	1.26	0.35	13
[Fe(TPP)(NO)]	4.2	1.24	0.35	12
[Fe(OEP)(CO)(1-MeIm)]-	293	0.40	0.18	7
$\cdot C_6H_6$	200	0.37	0.25	7
	100	0.37	0.23	7
	15	0.34	0.24	7
[Fe(TPP)(CO)(1,2-Me_2Im)]-	293	0.71	0.17	7
$\cdot C_7H_8$	200	0.65	0.23	7
	100	0.66	0.29	7
	15	0.64	0.25	7
[Fe(TPP)(CO)(1-MeIm)]	293	0.35	0.16	7
$\cdot C_6H_6$	200	0.32	0.24	7
	100	0.32	0.25	7
	15	0.30	0.26	7
[Fe(TPP)(NO)(1-MeIm)]	293	0.80	0.24	9
	4.2	0.73	0.35	9
[Fe(OEP)(CS)(1-MeIm)]	293	0.47	0.03	10
	4.2	0.42	0.14	10

[a]Abbreviations given in the References. [b] Value in mm/sec.

References and Notes

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Table S2. Complete Crystallographic Details for [Fe(OEP)(CO)]

formula	$C_{37}H_{44}FeN_4O$
FW, amu	616.61
a, Å	10.440(2)
b, Å	10.540(2)
c, Å	15.470(3)
α, deg	109.85(3)
β, deg	100.43(3)
γ, deg	98.65(3)
V, Å^3	1532.8(5)
space group	$P\bar{1}$
Z	2
D_c, g/cm^3	1.336
F(000)	656
μ, mm^{-1}	0.529
crystal dimensions, mm	0.25 × 0.24 × 0.11
radiation	MoKα, $\bar{\lambda}$ = 0.71073 Å
temperature, K	100(2)
diffractometer	Bruker Apex CCD
θ range for collected data, deg	1.45–31.55
index range	$-15 \leq h \leq 15$
	$-15 \leq k \leq 13$
	$-22 \leq l \leq 22$
total data collected	36545
absorption correction	Semi-empirical from equiv
relative transmission coefficients (I)	0.9431 and 0.8791
unique data	10168 (R_{int} = 0.015)
unique observed data [I > 2σ(I)]	9496
refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	10168/0/397
goodness-of-fit (pased on F^2)	1.038
final R indices [I > 2σ(I)]	R_1 = 0.0285, wR_2 = 0.0795
final R indices (all data)	R_1 = 0.0308, wR_2 = 0.0815

Table S3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for [Fe(OEP)(CO)][a]

atom	x	y	z	U(eq)
Fe(1)	0.43597(1)	0.22769(1)	0.25283(1)	0.0108(1)
N(1)	0.29522(7)	0.18971(7)	0.31725(5)	0.0120(1)
N(2)	0.42308(7)	0.02540(7)	0.19303(5)	0.0122(1)
N(3)	0.60277(7)	0.26352(7)	0.21148(5)	0.0125(1)
N(4)	0.47254(7)	0.42812(7)	0.33355(5)	0.0125(1)
C(m1)	0.23150(8)	−0.06333(9)	0.24273(6)	0.0134(1)
C(m2)	0.60401(9)	0.02675(9)	0.11245(6)	0.0140(2)
C(m3)	0.66299(9)	0.51668(9)	0.28240(6)	0.0143(2)
C(m4)	0.29223(9)	0.42660(9)	0.41445(6)	0.0142(2)
C(a1)	0.24297(8)	0.28480(9)	0.37850(6)	0.0129(1)
C(a2)	0.21825(8)	0.06256(9)	0.30287(6)	0.0124(1)
C(a3)	0.32507(8)	−0.08092(9)	0.18984(6)	0.0124(1)
C(a4)	0.49467(8)	−0.03976(9)	0.13148(6)	0.0126(1)
C(a5)	0.65554(8)	0.16801(9)	0.15062(6)	0.0129(1)
C(a6)	0.68012(8)	0.39056(9)	0.22564(6)	0.0132(1)
C(a7)	0.56787(9)	0.53465(9)	0.33418(6)	0.0133(1)
C(a8)	0.40044(9)	0.49358(9)	0.39469(6)	0.0132(1)
C(b1)	0.13317(9)	0.21643(9)	0.40350(6)	0.0138(1)
C(b2)	0.11883(9)	0.07773(9)	0.35716(6)	0.0133(1)
C(b3)	0.33481(8)	−0.21339(9)	0.12532(6)	0.0129(1)
C(b4)	0.44114(8)	−0.18771(9)	0.08916(6)	0.0130(1)
C(b5)	0.76899(8)	0.23551(9)	0.12827(6)	0.0138(1)
C(b6)	0.78324(8)	0.37433(9)	0.17425(6)	0.0137(1)
C(b7)	0.55680(9)	0.66772(9)	0.39753(6)	0.0138(1)
C(b8)	0.45324(9)	0.64191(9)	0.43592(6)	0.0139(1)
C(10)	0.05103(10)	0.28737(10)	0.46633(7)	0.0182(2)
C(11)	−0.06697(12)	0.32169(13)	0.41109(9)	0.0282(2)
C(20)	0.02232(9)	−0.03943(9)	0.36102(7)	0.0168(2)
C(21)	−0.09603(10)	−0.10757(11)	0.27361(8)	0.0216(2)
C(30)	0.24474(9)	−0.35021(9)	0.10492(6)	0.0155(2)
C(31)	0.29494(11)	−0.42216(10)	0.17090(8)	0.0221(2)
C(40)	0.49676(9)	−0.28863(9)	0.02041(6)	0.0151(2)
C(41)	0.62321(10)	−0.32034(10)	0.06798(7)	0.0202(2)
C(50)	0.85416(9)	0.16196(10)	0.06909(7)	0.0164(2)

Table S3. Continued

atom	x	y	z	U(eq)
C(51)	0.95309(12)	0.10642(14)	0.12399(9)	0.0289(2)
C(60)	0.88367(9)	0.49110(9)	0.17341(7)	0.0162(2)
C(61)	0.99863(10)	0.55624(11)	0.26295(7)	0.0210(2)
C(70)	0.64223(9)	0.80550(9)	0.41388(6)	0.0161(2)
C(71)	0.58834(10)	0.86569(10)	0.34128(7)	0.0205(2)
C(80)	0.40053(9)	0.74440(9)	0.50632(6)	0.0162(2)
C(81)	0.28397(10)	0.78986(10)	0.45879(7)	0.0205(2)
C(1)	0.32679(9)	0.22802(9)	0.15579(6)	0.0148(2)
O(1)	0.25272(8)	0.22244(8)	0.08940(5)	0.0227(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. The estimated standard deviations of the least significant digits are given in parentheses.

Table S4. Bond Lengths for [Fe(OEP)(CO)][a]

bond	length (Å)	bond	length (Å)
Fe(1)–C(1)	1.7140(11)	C(11)–H(11a)	0.9800
Fe(1)–N(1)	1.9843(9)	C(11)–H(11b)	0.9800
Fe(1)–N(2)	1.9872(10)	C(11)–H(11C)	0.9800
Fe(1)–N(3)	1.9884(9)	C(20)–C(21)	1.5296(16)
Fe(1)–N(4)	1.9902(11)	C(20)–H(20a)	0.9900
N(1)–C(a2)	1.3784(12)	C(20)–H(20b)	0.9900
N(1)–C(a1)	1.3808(12)	C(21)–H(21a)	0.9800
N(2)–C(a3)	1.3800(12)	C(21)–H(21b)	0.9800
N(2)–C(a4)	1.3802(11)	C(21)–H(21C)	0.9800
N(3)–C(a6)	1.3801(12)	C(30)–C(31)	1.5307(14)
N(3)–C(a5)	1.3836(12)	C(30)–H(30a)	0.9900
N(4)–C(a7)	1.3799(12)	C(30)–H(30b)	0.9900
N(4)–C(a8)	1.3814(12)	C(31)–H(31a)	0.9800
C(m1)–C(a3)	1.3780(12)	C(31)–H(31b)	0.9800
C(m1)–C(a2)	1.3816(13)	C(31)–H(31C)	0.9800
C(m1)–H(ma)	0.9500	C(40)–C(41)	1.5310(14)
C(m2)–C(a5)	1.3791(13)	C(40)–H(40a)	0.9900
C(m2)–C(a4)	1.3792(12)	C(40)–H(40b)	0.9900
C(m2)–H(mb)	0.9500	C(41)–H(41a)	0.9800
C(m3)–C(a7)	1.3804(13)	C(41)–H(41b)	0.9800
C(m3)–C(a6)	1.3804(13)	C(41)–H(41C)	0.9800
C(m3)–H(mC)	0.9500	C(50)–C(51)	1.5273(15)
C(m4)–C(a8)	1.3783(13)	C(50)–H(50a)	0.9900
C(m4)–C(a1)	1.3815(13)	C(50)–H(50b)	0.9900
C(m4)–H(md)	0.9500	C(51)–H(51a)	0.9800
C(a1)–C(b1)	1.4437(12)	C(51)–H(51b)	0.9800
C(a2)–C(b2)	1.4431(12)	C(51)–H(51C)	0.9800
C(a3)–C(b3)	1.4454(13)	C(60)–C(61)	1.5280(15)
C(a4)–C(b4)	1.4439(13)	C(60)–H(60a)	0.9900
C(a5)–C(b5)	1.4459(12)	C(60)–H(60b)	0.9900
C(a6)–C(b6)	1.4467(12)	C(61)–H(61a)	0.9800
C(a7)–C(b7)	1.4482(13)	C(61)–H(61b)	0.9800
C(a8)–C(b8)	1.4461(13)	C(61)–H(61C)	0.9800
C(b1)–C(b2)	1.3628(13)	C(70)–C(71)	1.5306(14)

Table S4. Continued

bond	length (Å)	bond	length (Å)
C(b1)–C(10)	1.4967(13)	C(70)–H(70a)	0.9900
C(b2)–C(20)	1.4971(13)	C(70)–H(70b)	0.9900
C(b3)–C(b4)	1.3623(12)	C(71)–H(71a)	0.9800
C(b3)–C(30)	1.4963(13)	C(71)–H(71b)	0.9800
C(b4)–C(40)	1.4969(13)	C(71)–H(71C)	0.9800
C(b5)–C(b6)	1.3632(13)	C(80)–C(81)	1.5303(14)
C(b5)–C(50)	1.5000(13)	C(80)–H(80a)	0.9900
C(b6)–C(60)	1.4973(13)	C(80)–H(80b)	0.9900
C(b7)–C(b8)	1.3599(13)	C(81)–H(81a)	0.9800
C(b7)–C(70)	1.4992(13)	C(81)–H(81b)	0.9800
C(b8)–C(80)	1.5009(13)	C(81)–H(81C)	0.9800
C(10)–C(11)	1.5302(16)	C(1)–O(1)	1.1463(12)
C(10)–H(10a)	0.9900		
C(10)–H(10b)	0.9900		

[a]The estimated standard deviations of the least significant digits are given in parentheses.

Table S5. Bond Angles for [Fe(OEP)(CO)][a]

angle	degree	angle	degree
C(1)–Fe(1)–N(1)	94.88(4)	H(11a)–C(11)–H(11b)	109.5
C(1)–Fe(1)–N(2)	92.42(5)	C(10)–C(11)–H(11C)	109.5
N(1)–Fe(1)–N(2)	89.65(4)	H(11a)–C(11)–H(11C)	109.5
C(1)–Fe(1)–N(3)	97.16(4)	H(11b)–C(11)–H(11C)	109.5
N(1)–Fe(1)–N(3)	167.94(3)	C(b2)–C(20)–C(21)	113.88(8)
N(2)–Fe(1)–N(3)	89.28(4)	C(b2)–C(20)–H(20a)	108.8
C(1)–Fe(1)–N(4)	98.49(5)	C(21)–C(20)–H(20a)	108.8
N(1)–Fe(1)–N(4)	89.34(4)	C(b2)–C(20)–H(20b)	108.8
N(2)–Fe(1)–N(4)	169.09(3)	C(21)–C(20)–H(20b)	108.8
N(3)–Fe(1)–N(4)	89.44(4)	H(20a)–C(20)–H(20b)	107.7
C(a2)–N(1)–C(a1)	104.66(7)	C(20)–C(21)–H(21a)	109.5
C(a2)–N(1)–Fe(1)	127.37(6)	C(20)–C(21)–H(21b)	109.5
C(a1)–N(1)–Fe(1)	127.64(6)	H(21a)–C(21)–H(21b)	109.5
C(a3)–N(2)–C(a4)	104.33(7)	C(20)–C(21)–H(21C)	109.5
C(a3)–N(2)–Fe(1)	127.29(6)	H(21a)–C(21)–H(21C)	109.5
C(a4)–N(2)–Fe(1)	127.44(6)	H(21b)–C(21)–H(21C)	109.5
C(a6)–N(3)–C(a5)	104.53(7)	C(b3)–C(30)–C(31)	113.34(8)
C(a6)–N(3)–Fe(1)	127.29(6)	C(b3)–C(30)–H(30a)	108.9
C(a5)–N(3)–Fe(1)	127.54(6)	C(31)–C(30)–H(30a)	108.9
C(a7)–N(4)–C(a8)	104.38(7)	C(b3)–C(30)–H(30b)	108.9
C(a7)–N(4)–Fe(1)	127.58(6)	C(31)–C(30)–H(30b)	108.9
C(a8)–N(4)–Fe(1)	127.79(6)	H(30a)–C(30)–H(30b)	107.7
C(a3)–C(m1)–C(a2)	125.26(8)	C(30)–C(31)–H(31a)	109.5
C(a3)–C(m1)–H(ma)	117.4	C(30)–C(31)–H(31b)	109.5
C(a2)–C(m1)–H(ma)	117.4	H(31a)–C(31)–H(31b)	109.5
C(a5)–C(m2)–C(a4)	124.84(8)	C(30)–C(31)–H(31C)	109.5
C(a5)–C(m2)–H(mb)	117.6	H(31a)–C(31)–H(31C)	109.5
C(a4)–C(m2)–H(mb)	117.6	H(31b)–C(31)–H(31C)	109.5
C(a7)–C(m3)–C(a6)	125.34(8)	C(b4)–C(40)–C(41)	113.17(8)
C(a7)–C(m3)–H(mC)	117.3	C(b4)–C(40)–H(40a)	108.9
C(a6)–C(m3)–H(mC)	117.3	C(41)–C(40)–H(40a)	108.9
C(a8)–C(m4)–C(a1)	125.08(8)	C(b4)–C(40)–H(40b)	108.9
C(a8)–C(m4)–H(md)	117.5	C(41)–C(40)–H(40b)	108.9
C(a1)–C(m4)–H(md)	117.5	H(40a)–C(40)–H(40b)	107.8

Table S5. Continued

angle	degree	angle	degree
N(1)–C(a1)–C(m4)	124.70(8)	C(40)–C(41)–H(41a)	109.5
N(1)–C(a1)–C(b1)	111.12(8)	C(40)–C(41)–H(41b)	109.5
C(m4)–C(a1)–C(b1)	124.13(8)	H(41a)–C(41)–H(41b)	109.5
N(1)–C(a2)–C(m1)	124.85(8)	C(40)–C(41)–H(41C)	109.5
N(1)–C(a2)–C(b2)	111.14(8)	H(41a)–C(41)–H(41C)	109.5
C(m1)–C(a2)–C(b2)	123.99(8)	H(41b)–C(41)–H(41C)	109.5
C(m1)–C(a3)–N(2)	124.34(8)	C(b5)–C(50)–C(51)	112.31(8)
C(m1)–C(a3)–C(b3)	124.34(8)	C(b5)–C(50)–H(50a)	109.1
N(2)–C(a3)–C(b3)	111.31(8)	C(51)–C(50)–H(50a)	109.1
C(m2)–C(a4)–N(2)	124.78(8)	C(b5)–C(50)–H(50b)	109.1
C(m2)–C(a4)–C(b4)	123.75(8)	C(51)–C(50)–H(50b)	109.1
N(2)–C(a4)–C(b4)	111.47(8)	H(50a)–C(50)–H(50b)	107.9
C(m2)–C(a5)–N(3)	124.83(8)	C(50)–C(51)–H(51a)	109.5
C(m2)–C(a5)–C(b5)	123.78(8)	C(50)–C(51)–H(51b)	109.5
N(3)–C(a5)–C(b5)	111.34(8)	H(51a)–C(51)–H(51b)	109.5
N(3)–C(a6)–C(m3)	124.64(8)	C(50)–C(51)–H(51C)	109.5
N(3)–C(a6)–C(b6)	111.07(8)	H(51a)–C(51)–H(51C)	109.5
C(m3)–C(a6)–C(b6)	124.28(8)	H(51b)–C(51)–H(51C)	109.5
N(4)–C(a7)–C(m3)	124.43(8)	C(b6)–C(60)–C(61)	113.69(8)
N(4)–C(a7)–C(b7)	111.25(8)	C(b6)–C(60)–H(60a)	108.8
C(m3)–C(a7)–C(b7)	124.31(8)	C(61)–C(60)–H(60a)	108.8
C(m4)–C(a8)–N(4)	124.56(8)	C(b6)–C(60)–H(60b)	108.8
C(m4)–C(a8)–C(b8)	124.07(8)	C(61)–C(60)–H(60b)	108.8
N(4)–C(a8)–C(b8)	111.37(8)	H(60a)–C(60)–H(60b)	107.7
C(b2)–C(b1)–C(a1)	106.47(8)	C(60)–C(61)–H(61a)	109.5
C(b2)–C(b1)–C(10)	127.93(8)	C(60)–C(61)–H(61b)	109.5
C(a1)–C(b1)–C(10)	125.59(8)	H(61a)–C(61)–H(61b)	109.5
C(b1)–C(b2)–C(a2)	106.58(8)	C(60)–C(61)–H(61C)	109.5
C(b1)–C(b2)–C(20)	128.27(8)	H(61a)–C(61)–H(61C)	109.5
C(a2)–C(b2)–C(20)	125.13(8)	H(61b)–C(61)–H(61C)	109.5
C(b4)–C(b3)–C(a3)	106.51(8)	C(b7)–C(70)–C(71)	112.54(8)
C(b4)–C(b3)–C(30)	128.01(8)	C(b7)–C(70)–H(70a)	109.1
C(a3)–C(b3)–C(30)	125.47(8)	C(71)–C(70)–H(70a)	109.1
C(b3)–C(b4)–C(a4)	106.37(8)	C(b7)–C(70)–H(70b)	109.1

Table S5. Continued

angle	degree	angle	degree
C(b3)–C(b4)–C(40)	128.66(8)	C(71)–C(70)–H(70b)	109.1
C(a4)–C(b4)–C(40)	124.97(8)	H(70a)–C(70)–H(70b)	107.8
C(b6)–C(b5)–C(a5)	106.24(8)	C(70)–C(71)–H(71a)	109.5
C(b6)–C(b5)–C(50)	128.73(8)	C(70)–C(71)–H(71b)	109.5
C(a5)–C(b5)–C(50)	124.98(8)	H(71a)–C(71)–H(71b)	109.5
C(b5)–C(b6)–C(a6)	106.79(8)	C(70)–C(71)–H(71C)	109.5
C(b5)–C(b6)–C(60)	128.25(8)	H(71a)–C(71)–H(71C)	109.5
C(a6)–C(b6)–C(60)	124.95(8)	H(71b)–C(71)–H(71C)	109.5
C(b8)–C(b7)–C(a7)	106.54(8)	C(b8)–C(80)–C(81)	112.61(8)
C(b8)–C(b7)–C(70)	127.90(8)	C(b8)–C(80)–H(80a)	109.1
C(a7)–C(b7)–C(70)	125.54(8)	C(81)–C(80)–H(80a)	109.1
C(b7)–C(b8)–C(a8)	106.44(8)	C(b8)–C(80)–H(80b)	109.1
C(b7)–C(b8)–C(80)	127.99(8)	C(81)–C(80)–H(80b)	109.1
C(a8)–C(b8)–C(80)	125.58(8)	H(80a)–C(80)–H(80b)	107.8
C(b1)–C(10)–C(11)	112.14(8)	C(80)–C(81)–H(81a)	109.5
C(b1)–C(10)–H(10a)	109.2	C(80)–C(81)–H(81b)	109.5
C(11)–C(10)–H(10a)	109.2	H(81a)–C(81)–H(81b)	109.5
C(b1)–C(10)–H(10b)	109.2	C(80)–C(81)–H(81C)	109.5
C(11)–C(10)–H(10b)	109.2	H(81a)–C(81)–H(81C)	109.5
H(10a)–C(10)–H(10b)	107.9	H(81b)–C(81)–H(81C)	109.5
C(10)–C(11)–H(11a)	109.5	O(1)–C(1)–Fe(1)	177.20(8)
C(10)–C(11)–H(11b)	109.5		

[a]The estimated standard deviations of the least significant digits are given in parentheses.

Table S6. Anisotropic Displacement Parameters (Å^2) for [Fe(OEP)(CO)][a]

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(1)	0.0107(1)	0.0084(1)	0.0129(1)	0.0032(1)	0.0038(1)	0.0023(1)
N(1)	0.0127(3)	0.0097(3)	0.0134(3)	0.0037(2)	0.0043(2)	0.0027(2)
N(2)	0.0124(3)	0.0097(3)	0.0146(3)	0.0041(2)	0.0049(2)	0.0026(2)
N(3)	0.0119(3)	0.0095(3)	0.0154(3)	0.0034(2)	0.0044(2)	0.0021(2)
N(4)	0.0126(3)	0.0097(3)	0.0143(3)	0.0032(2)	0.0036(2)	0.0023(2)
C(M1)	0.0132(3)	0.0111(3)	0.0161(4)	0.0049(3)	0.0050(3)	0.0022(3)
C(M2)	0.0141(3)	0.0114(3)	0.0170(4)	0.0043(3)	0.0064(3)	0.0038(3)
C(M3)	0.0134(3)	0.0108(3)	0.0173(4)	0.0043(3)	0.0038(3)	0.0012(3)
C(M4)	0.0151(3)	0.0120(3)	0.0150(3)	0.0032(3)	0.0053(3)	0.0040(3)
C(A1)	0.0133(3)	0.0122(3)	0.0134(3)	0.0042(3)	0.0047(3)	0.0035(3)
C(A2)	0.0123(3)	0.0116(3)	0.0139(3)	0.0049(3)	0.0042(3)	0.0028(3)
C(A3)	0.0124(3)	0.0100(3)	0.0147(3)	0.0042(3)	0.0038(3)	0.0026(3)
C(A4)	0.0130(3)	0.0100(3)	0.0149(3)	0.0040(3)	0.0045(3)	0.0032(3)
C(A5)	0.0120(3)	0.0117(3)	0.0157(3)	0.0049(3)	0.0051(3)	0.0029(3)
C(A6)	0.0120(3)	0.0113(3)	0.0156(3)	0.0046(3)	0.0036(3)	0.0019(3)
C(A7)	0.0133(3)	0.0100(3)	0.0151(3)	0.0036(3)	0.0024(3)	0.0022(3)
C(A8)	0.0140(3)	0.0105(3)	0.0136(3)	0.0029(3)	0.0029(3)	0.0034(3)
C(B1)	0.0142(3)	0.0144(4)	0.0141(3)	0.0055(3)	0.0059(3)	0.0041(3)
C(B2)	0.0135(3)	0.0135(3)	0.0142(3)	0.0057(3)	0.0053(3)	0.0033(3)
C(B3)	0.0136(3)	0.0096(3)	0.0144(3)	0.0035(3)	0.0033(3)	0.0026(3)
C(B4)	0.0138(3)	0.0100(3)	0.0142(3)	0.0032(3)	0.0036(3)	0.0031(3)
C(B5)	0.0124(3)	0.0138(4)	0.0158(3)	0.0058(3)	0.0049(3)	0.0027(3)
C(B6)	0.0119(3)	0.0129(3)	0.0159(3)	0.0052(3)	0.0039(3)	0.0014(3)
C(B7)	0.0145(3)	0.0099(3)	0.0149(3)	0.0032(3)	0.0015(3)	0.0025(3)
C(B8)	0.0150(3)	0.0102(3)	0.0142(3)	0.0024(3)	0.0019(3)	0.0037(3)
C(10)	0.0215(4)	0.0166(4)	0.0201(4)	0.0067(3)	0.0125(3)	0.0063(3)
C(11)	0.0278(5)	0.0313(5)	0.0366(6)	0.0170(5)	0.0178(5)	0.0177(4)
C(20)	0.0182(4)	0.0152(4)	0.0194(4)	0.0080(3)	0.0085(3)	0.0029(3)
C(21)	0.0166(4)	0.0197(4)	0.0274(5)	0.0094(4)	0.0057(3)	−0.0001(3)
C(30)	0.0156(4)	0.0105(3)	0.0182(4)	0.0034(3)	0.0045(3)	0.0011(3)
C(31)	0.0240(4)	0.0161(4)	0.0272(5)	0.0109(4)	0.0057(4)	0.0022(3)
C(40)	0.0168(4)	0.0112(3)	0.0158(4)	0.0024(3)	0.0055(3)	0.0040(3)
C(41)	0.0215(4)	0.0174(4)	0.0225(4)	0.0057(3)	0.0066(3)	0.0097(3)
C(50)	0.0161(4)	0.0166(4)	0.0194(4)	0.0074(3)	0.0090(3)	0.0052(3)

Table S6. Continued

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(51)	0.0255(5)	0.0418(6)	0.0322(5)	0.0203(5)	0.0148(4)	0.0207(5)
C(60)	0.0148(4)	0.0148(4)	0.0182(4)	0.0063(3)	0.0051(3)	−0.0003(3)
C(61)	0.0166(4)	0.0215(4)	0.0209(4)	0.0069(4)	0.0032(3)	−0.0025(3)
C(70)	0.0167(4)	0.0102(3)	0.0176(4)	0.0030(3)	0.0012(3)	0.0007(3)
C(71)	0.0223(4)	0.0158(4)	0.0225(4)	0.0086(3)	0.0025(3)	0.0021(3)
C(80)	0.0174(4)	0.0123(3)	0.0152(4)	0.0010(3)	0.0028(3)	0.0045(3)
C(81)	0.0206(4)	0.0187(4)	0.0216(4)	0.0051(3)	0.0043(3)	0.0091(3)
C(1)	0.0152(4)	0.0116(3)	0.0181(4)	0.0051(3)	0.0070(3)	0.0027(3)
O(1)	0.0211(3)	0.0251(4)	0.0217(3)	0.0106(3)	0.0022(3)	0.0040(3)

[a]The estimated standard deviations of the least significant digits are given in parentheses. The anisotropic displacement factor exponent takes the form: $-2\ \pi\ [h^2\ U_{11}\ +...+\ 2\ h\ k\ a^*\ b^*\ U_{12}]$.

Table S7. Hydrogen Atom Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$) for [Fe(OEP)(CO)][a]

atom	x	y	z	U(eq)
H(MA	0.1712	−0.1443	0.2374	0.016
H(MB	0.6470	−0.0289	0.0699	0.017
H(MC	0.7215	0.5977	0.2861	0.017
H(MD	0.2481	0.4823	0.4560	0.017
H(10A)	0.1085	0.3740	0.5163	0.022
H(10B)	0.0167	0.2268	0.4979	0.022
H(11A)	−0.1183	0.3673	0.4547	0.042
H(11B)	−0.1248	0.2360	0.3621	0.042
H(11C)	−0.0334	0.3837	0.3812	0.042
H(20A)	−0.0124	−0.0044	0.4180	0.020
H(20B)	0.0708	−0.1106	0.3680	0.020
H(21A)	−0.1539	−0.1841	0.2804	0.032
H(21B)	−0.0628	−0.1433	0.2167	0.032
H(21C)	−0.1472	−0.0389	0.2677	0.032
H(30A)	0.2360	−0.4116	0.0385	0.019
H(30B)	0.1547	−0.3360	0.1111	0.019
H(31A)	0.2308	−0.5096	0.1552	0.033
H(31B)	0.3042	−0.3619	0.2369	0.033
H(31C)	0.3820	−0.4411	0.1628	0.033
H(40A)	0.5177	−0.2507	−0.0271	0.018
H(40B)	0.4277	−0.3761	−0.0137	0.018
H(41A)	0.6564	−0.3846	0.0195	0.030
H(41B)	0.6022	−0.3626	0.1127	0.030
H(41C)	0.6920	−0.2342	0.1022	0.030
H(50A)	0.9043	0.2267	0.0466	0.020
H(50B)	0.7957	0.0839	0.0126	0.020
H(51A)	1.0081	0.0616	0.0833	0.043
H(51B)	0.9038	0.0388	0.1437	0.043
H(51C)	1.0108	0.1832	0.1802	0.043
H(60A)	0.8375	0.5636	0.1659	0.019
H(60B)	0.9211	0.4563	0.1177	0.019
H(61A)	1.0598	0.6323	0.2581	0.031
H(61B)	1.0471	0.4860	0.2697	0.031
H(61C)	0.9627	0.5922	0.3185	0.031

Table S7. Continued

atom	x	y	z	U(eq)
H(70A)	0.7341	0.7950	0.4106	0.019
H(70B)	0.6472	0.8712	0.4784	0.019
H(71A)	0.6501	0.9528	0.3526	0.031
H(71B)	0.5003	0.8833	0.3476	0.031
H(71C)	0.5802	0.7996	0.2771	0.031
H(80A)	0.4738	0.8270	0.5449	0.019
H(80B)	0.3704	0.7024	0.5497	0.019
H(81A)	0.2515	0.8544	0.5076	0.031
H(81B)	0.2114	0.7085	0.4201	0.031
H(81C)	0.3144	0.8359	0.4183	0.031

[a] U(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor the estimated standard deviations of the least significant digits are given in parentheses.

Table S8. Complete Crystallographic Details for [Fe(OEP)(CO)]·C_6H_6

formula	$C_{43}H_{50}FeN_4O$
FW, amu	694.72
a, Å	10.6217(3)
b, Å	11.9368(3)
c, Å	14.8297(4)
α, deg	77.0770(10)
β, deg	86.616(2)
γ, deg	80.194(2)
V, Å^3	1805.42(8)
space group	$P\bar{1}$
Z	2
D_c, g/cm^3	1.278
F(000)	740
μ, mm^{-1}	0.457
crystal dimensions, mm	0.49 × 0.20 × 0.16
radiation	MoKα, $\bar{\lambda}$ = 0.71073 Å
temperature, K	100(2)
diffractometer	Bruker Apex CCD
θ range for collected data, deg	1.41–31.00
index range	$-15 \leq h \leq 15$
	$-16 \leq k \leq 17$
	$-21 \leq l \leq 21$
total data collected	62663
absorption correction	Multiscan
relative transmission coefficients (I)	0.9321 and 0.8070
unique data	11512 (R_{int} = 0.036)
unique observed data [I > 2σ(I)]	9475
refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	11512/0/450
goodness-of-fit (pased on F^2)	1.045
final R indices [I > 2σ(I)]	R_1 = 0.0348, wR_2 = 0.0843
final R indices (all data)	R_1 = 0.0486, wR_2 = 0.0919

Table S9. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for [Fe(OEP)(CO)]·C_6H_6[a]

atom	x	y	z	U(eq)
Fe(1)	0.37734(2)	0.35000(1)	0.45554(1)	0.0118(1)
N(1)	0.44414(9)	0.25436(9)	0.36431(7)	0.0124(2)
N(2)	0.26846(9)	0.45975(8)	0.35922(7)	0.0124(2)
N(3)	0.33908(9)	0.46522(8)	0.53569(7)	0.0126(2)
N(4)	0.51211(9)	0.25894(9)	0.54168(7)	0.0128(2)
C(m1)	0.31494(11)	0.35947(10)	0.23160(8)	0.0141(2)
C(m2)	0.16761(11)	0.60134(10)	0.44862(8)	0.0140(2)
C(m3)	0.48818(11)	0.37450(10)	0.66007(8)	0.0142(2)
C(m4)	0.59338(11)	0.10295(10)	0.46114(8)	0.0135(2)
C(a1)	0.53071(11)	0.15239(10)	0.37936(8)	0.0125(2)
C(a2)	0.40580(11)	0.26963(10)	0.27474(8)	0.0128(2)
C(a3)	0.25066(11)	0.44830(10)	0.27066(8)	0.0132(2)
C(a4)	0.18141(11)	0.55592(10)	0.37012(8)	0.0127(2)
C(a5)	0.24321(11)	0.56060(10)	0.52513(8)	0.0132(2)
C(a6)	0.39181(11)	0.46029(10)	0.61927(8)	0.0134(2)
C(a7)	0.54156(11)	0.27918(10)	0.62505(8)	0.0134(2)
C(a8)	0.58619(11)	0.15350(10)	0.53678(8)	0.0131(2)
C(b1)	0.54994(11)	0.10488(10)	0.29703(8)	0.0136(2)
C(b2)	0.47394(11)	0.17957(10)	0.23125(8)	0.0139(2)
C(b3)	0.15401(11)	0.53989(10)	0.22491(8)	0.0145(2)
C(b4)	0.11003(11)	0.60644(10)	0.28702(8)	0.0138(2)
C(b5)	0.23544(11)	0.61527(10)	0.60354(8)	0.0141(2)
C(b6)	0.32926(11)	0.55353(10)	0.66172(8)	0.0139(2)
C(b7)	0.63515(11)	0.18589(10)	0.67284(8)	0.0141(2)
C(b8)	0.66104(11)	0.10607(10)	0.61890(8)	0.0135(2)
C(11)	0.64141(11)	−0.00261(11)	0.28789(9)	0.0163(2)
C(12)	0.77913(13)	0.01917(12)	0.26990(11)	0.0258(3)
C(21)	0.46465(13)	0.17777(11)	0.13144(8)	0.0188(2)
C(22)	0.52649(16)	0.27340(13)	0.06697(10)	0.0282(3)
C(31)	0.11401(12)	0.55857(12)	0.12695(8)	0.0192(2)
C(32)	0.19947(16)	0.62794(16)	0.05853(10)	0.0334(3)
C(41)	0.00477(11)	0.70902(10)	0.27463(8)	0.0155(2)
C(42)	−0.12585(12)	0.67093(11)	0.29681(9)	0.0200(2)
C(51)	0.13683(12)	0.71548(10)	0.61793(9)	0.0170(2)

Table S9. Continued

atom	x	y	z	U(eq)
C(52)	0.01644(13)	0.67419(12)	0.66574(10)	0.0249(3)
C(61)	0.36280(12)	0.57186(11)	0.75340(8)	0.0173(2)
C(62)	0.30452(14)	0.49457(13)	0.83620(9)	0.0241(3)
C(71)	0.68766(12)	0.18096(11)	0.76535(8)	0.0170(2)
C(72)	0.59808(14)	0.14053(14)	0.84566(9)	0.0256(3)
C(81)	0.75305(11)	−0.00600(10)	0.63676(8)	0.0155(2)
C(82)	0.88487(13)	0.00863(12)	0.59375(11)	0.0262(3)
C(1)	0.26187(12)	0.26712(11)	0.49735(8)	0.0159(2)
O(1)	0.18732(9)	0.20987(9)	0.52230(7)	0.0225(2)
C(90)	0.84363(16)	0.73398(16)	0.98868(12)	0.0359(4)
C(91)	0.90715(16)	0.77079(18)	0.90674(13)	0.0399(4)
C(92)	0.92837(18)	0.88518(19)	0.88154(14)	0.0469(5)
C(93)	0.8863(2)	0.96126(19)	0.93885(16)	0.0560(6)
C(94)	0.8223(2)	0.9229(2)	1.02077(15)	0.0569(6)
C(95)	0.80212(19)	0.80932(18)	1.04512(12)	0.0437(4)

[a] U(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. The estimated standard deviations of the least significant digits are given in parentheses.

Table S10. Bond Lengths for [Fe(OEP)(CO)]·C_6H_6[a]

bond	length (Å)	bond	length (Å)
Fe(1)–C(1)	1.7077(13)	C(22)–H(22a)	0.9800
Fe(1)–N(4)	1.9818(10)	C(22)–H(22b)	0.9800
Fe(1)–N(2)	1.9839(10)	C(22)–H(22C)	0.9800
Fe(1)–N(1)	1.9846(10)	C(31)–C(32)	1.520(2)
Fe(1)–N(3)	1.9883(10)	C(31)–H(31a)	0.9900
N(1)–C(a2)	1.3761(15)	C(31)–H(31b)	0.9900
N(1)–C(a1)	1.3778(14)	C(32)–H(32a)	0.9800
N(2)–C(a3)	1.3776(15)	C(32)–H(32b)	0.9800
N(2)–C(a4)	1.3794(14)	C(32)–H(32C)	0.9800
N(3)–C(a6)	1.3753(15)	C(41)–C(42)	1.5277(17)
N(3)–C(a5)	1.3791(14)	C(41)–H(41a)	0.9900
N(4)–C(a7)	1.3748(15)	C(41)–H(41b)	0.9900
N(4)–C(a8)	1.3803(14)	C(42)–H(42a)	0.9800
C(m1)–C(a2)	1.3799(16)	C(42)–H(42b)	0.9800
C(m1)–C(a3)	1.3811(16)	C(42)–H(42C)	0.9800
C(m1)–H(ma)	0.9500	C(51)–C(52)	1.5271(18)
C(m2)–C(a5)	1.3771(16)	C(51)–H(51a)	0.9900
C(m2)–C(a4)	1.3805(16)	C(51)–H(51b)	0.9900
C(m2)–H(mb)	0.9500	C(52)–H(52a)	0.9800
C(m3)–C(a7)	1.3767(16)	C(52)–H(52b)	0.9800
C(m3)–C(a6)	1.3789(16)	C(52)–H(52C)	0.9800
C(m3)–H(mC)	0.9500	C(61)–C(62)	1.5297(18)
C(m4)–C(a1)	1.3797(16)	C(61)–H(61a)	0.9900
C(m4)–C(a8)	1.3802(16)	C(61)–H(61b)	0.9900
C(m4)–H(md)	0.9500	C(62)–H(62a)	0.9800
C(a1)–C(b1)	1.4472(16)	C(62)–H(62b)	0.9800
C(a2)–C(b2)	1.4441(16)	C(62)–H(62C)	0.9800
C(a3)–C(b3)	1.4413(16)	C(71)–C(72)	1.5238(18)
C(a4)–C(b4)	1.4420(16)	C(71)–H(71a)	0.9900
C(a5)–C(b5)	1.4472(16)	C(71)–H(71b)	0.9900
C(a6)–C(b6)	1.4451(16)	C(72)–H(72a)	0.9800
C(a7)–C(b7)	1.4436(16)	C(72)–H(72b)	0.9800
C(a8)–C(b8)	1.4452(16)	C(72)–H(72C)	0.9800
C(b1)–C(b2)	1.3627(16)	C(81)–C(82)	1.5250(17)

Table S10. Continued

bond	length (Å)	bond	length (Å)
C(b1)–C(11)	1.4988(16)	C(81)–H(81a)	0.9900
C(b2)–C(21)	1.4943(16)	C(81)–H(81b)	0.9900
C(b3)–C(b4)	1.3593(17)	C(82)–H(82a)	0.9800
C(b3)–C(31)	1.4955(17)	C(82)–H(82b)	0.9800
C(b4)–C(41)	1.4968(16)	C(82)–H(82C)	0.9800
C(b5)–C(b6)	1.3592(17)	C(1)–O(1)	1.1259(16)
C(b5)–C(51)	1.4948(16)	C(90)–C(95)	1.364(3)
C(b6)–C(61)	1.4968(17)	C(90)–C(91)	1.375(2)
C(b7)–C(b8)	1.3597(16)	C(90)–H(90a)	0.9500
C(b7)–C(71)	1.4965(16)	C(91)–C(92)	1.386(3)
C(b8)–C(81)	1.4973(16)	C(91)–H(91a)	0.9500
C(11)–C(12)	1.5268(18)	C(92)–C(93)	1.382(3)
C(11)–H(11a)	0.9900	C(92)–H(92a)	0.9500
C(11)–H(11b)	0.9900	C(93)–C(94)	1.381(3)
C(12)–H(12a)	0.9800	C(93)–H(93a)	0.9500
C(12)–H(12b)	0.9800	C(94)–C(95)	1.373(3)
C(12)–H(12C)	0.9800	C(94)–H(94a)	0.9500
C(21)–C(22)	1.5304(19)	C(95)–H(95a)	0.9500
C(21)–H(21a)	0.9900		
C(21)–H(21b)	0.9900		

[a]The estimated standard deviations of the least significant digits are given in parentheses.

Table S11. Bond Angles for [Fe(OEP)(CO)]·C_6H_6[a]

angle	degree	angle	degree
C(1)–Fe(1)–N(4)	96.38(5)	H(21a)–C(21)–H(21b)	107.8
C(1)–Fe(1)–N(2)	94.80(5)	C(21)–C(22)–H(22a)	109.5
N(4)–Fe(1)–N(2)	168.82(4)	C(21)–C(22)–H(22b)	109.5
C(1)–Fe(1)–N(1)	93.31(5)	H(22a)–C(22)–H(22b)	109.5
N(4)–Fe(1)–N(1)	89.12(4)	C(21)–C(22)–H(22C)	109.5
N(2)–Fe(1)–N(1)	89.99(4)	H(22a)–C(22)–H(22C)	109.5
C(1)–Fe(1)–N(3)	98.76(5)	H(22b)–C(22)–H(22C)	109.5
N(4)–Fe(1)–N(3)	89.62(4)	C(b3)–C(31)–C(32)	112.65(11)
N(2)–Fe(1)–N(3)	88.92(4)	C(b3)–C(31)–H(31a)	109.1
N(1)–Fe(1)–N(3)	167.92(4)	C(32)–C(31)–H(31a)	109.1
C(a2)–N(1)–C(a1)	104.87(9)	C(b3)–C(31)–H(31b)	109.1
C(a2)–N(1)–Fe(1)	127.49(8)	C(32)–C(31)–H(31b)	109.1
C(a1)–N(1)–Fe(1)	127.42(8)	H(31a)–C(31)–H(31b)	107.8
C(a3)–N(2)–C(a4)	104.70(9)	C(31)–C(32)–H(32a)	109.5
C(a3)–N(2)–Fe(1)	127.53(8)	C(31)–C(32)–H(32b)	109.5
C(a4)–N(2)–Fe(1)	127.27(8)	H(32a)–C(32)–H(32b)	109.5
C(a6)–N(3)–C(a5)	104.49(9)	C(31)–C(32)–H(32C)	109.5
C(a6)–N(3)–Fe(1)	127.78(8)	H(32a)–C(32)–H(32C)	109.5
C(a5)–N(3)–Fe(1)	127.34(8)	H(32b)–C(32)–H(32C)	109.5
C(a7)–N(4)–C(a8)	104.60(9)	C(b4)–C(41)–C(42)	111.37(10)
C(a7)–N(4)–Fe(1)	127.59(8)	C(b4)–C(41)–H(41a)	109.4
C(a8)–N(4)–Fe(1)	127.37(8)	C(42)–C(41)–H(41a)	109.4
C(a2)–C(m1)–C(a3)	125.50(11)	C(b4)–C(41)–H(41b)	109.4
C(a2)–C(m1)–H(ma)	117.3	C(42)–C(41)–H(41b)	109.4
C(a3)–C(m1)–H(ma)	117.3	H(41a)–C(41)–H(41b)	108.0
C(a5)–C(m2)–C(a4)	124.70(11)	C(41)–C(42)–H(42a)	109.5
C(a5)–C(m2)–H(mb)	117.7	C(41)–C(42)–H(42b)	109.5
C(a4)–C(m2)–H(mb)	117.7	H(42a)–C(42)–H(42b)	109.5
C(a7)–C(m3)–C(a6)	124.97(11)	C(41)–C(42)–H(42C)	109.5
C(a7)–C(m3)–H(mC)	117.5	H(42a)–C(42)–H(42C)	109.5
C(a6)–C(m3)–H(mC)	117.5	H(42b)–C(42)–H(42C)	109.5
C(a1)–C(m4)–C(a8)	124.69(11)	C(b5)–C(51)–C(52)	111.45(10)
C(a1)–C(m4)–H(md)	117.7	C(b5)–C(51)–H(51a)	109.3
C(a8)–C(m4)–H(md)	117.7	C(52)–C(51)–H(51a)	109.3

Table S11. Continued

angle	degree	angle	degree
N(1)–C(a1)–C(m4)	124.82(10)	C(b5)–C(51)–H(51b)	109.3
N(1)–C(a1)–C(b1)	111.01(10)	C(52)–C(51)–H(51b)	109.3
C(m4)–C(a1)–C(b1)	124.15(11)	H(51a)–C(51)–H(51b)	108.0
N(1)–C(a2)–C(m1)	124.67(10)	C(51)–C(52)–H(52a)	109.5
N(1)–C(a2)–C(b2)	111.08(10)	C(51)–C(52)–H(52b)	109.5
C(m1)–C(a2)–C(b2)	124.24(11)	H(52a)–C(52)–H(52b)	109.5
N(2)–C(a3)–C(m1)	124.49(11)	C(51)–C(52)–H(52C)	109.5
N(2)–C(a3)–C(b3)	110.98(10)	H(52a)–C(52)–H(52C)	109.5
C(m1)–C(a3)–C(b3)	124.51(11)	H(52b)–C(52)–H(52C)	109.5
N(2)–C(a4)–C(m2)	124.76(11)	C(b6)–C(61)–C(62)	113.80(10)
N(2)–C(a4)–C(b4)	111.11(10)	C(b6)–C(61)–H(61a)	108.8
C(m2)–C(a4)–C(b4)	124.08(11)	C(62)–C(61)–H(61a)	108.8
C(m2)–C(a5)–N(3)	124.61(10)	C(b6)–C(61)–H(61b)	108.8
C(m2)–C(a5)–C(b5)	124.21(11)	C(62)–C(61)–H(61b)	108.8
N(3)–C(a5)–C(b5)	111.14(10)	H(61a)–C(61)–H(61b)	107.7
N(3)–C(a6)–C(m3)	124.66(11)	C(61)–C(62)–H(62a)	109.5
N(3)–C(a6)–C(b6)	111.48(10)	C(61)–C(62)–H(62b)	109.5
C(m3)–C(a6)–C(b6)	123.79(11)	H(62a)–C(62)–H(62b)	109.5
N(4)–C(a7)–C(m3)	125.08(11)	C(61)–C(62)–H(62C)	109.5
N(4)–C(a7)–C(b7)	111.14(10)	H(62a)–C(62)–H(62C)	109.5
C(m3)–C(a7)–C(b7)	123.77(11)	H(62b)–C(62)–H(62C)	109.5
C(m4)–C(a8)–N(4)	124.42(11)	C(b7)–C(71)–C(72)	113.07(10)
C(m4)–C(a8)–C(b8)	124.24(11)	C(b7)–C(71)–H(71a)	109.0
N(4)–C(a8)–C(b8)	111.25(10)	C(72)–C(71)–H(71a)	109.0
C(b2)–C(b1)–C(a1)	106.38(10)	C(b7)–C(71)–H(71b)	109.0
C(b2)–C(b1)–C(11)	128.40(11)	C(72)–C(71)–H(71b)	109.0
C(a1)–C(b1)–C(11)	125.16(11)	H(71a)–C(71)–H(71b)	107.8
C(b1)–C(b2)–C(a2)	106.56(10)	C(71)–C(72)–H(72a)	109.5
C(b1)–C(b2)–C(21)	128.88(11)	C(71)–C(72)–H(72b)	109.5
C(a2)–C(b2)–C(21)	124.46(11)	H(72a)–C(72)–H(72b)	109.5
C(b4)–C(b3)–C(a3)	106.76(10)	C(71)–C(72)–H(72C)	109.5
C(b4)–C(b3)–C(31)	127.33(11)	H(72a)–C(72)–H(72C)	109.5
C(a3)–C(b3)–C(31)	125.88(11)	H(72b)–C(72)–H(72C)	109.5
C(b3)–C(b4)–C(a4)	106.42(10)	C(b8)–C(81)–C(82)	112.19(10)

Table S11. Continued

angle	degree	angle	degree
C(b3)–C(b4)–C(41)	127.59(11)	C(b8)–C(81)–H(81a)	109.2
C(a4)–C(b4)–C(41)	125.94(11)	C(82)–C(81)–H(81a)	109.2
C(b6)–C(b5)–C(a5)	106.53(10)	C(b8)–C(81)–H(81b)	109.2
C(b6)–C(b5)–C(51)	128.04(11)	C(82)–C(81)–H(81b)	109.2
C(a5)–C(b5)–C(51)	125.34(11)	H(81a)–C(81)–H(81b)	107.9
C(b5)–C(b6)–C(a6)	106.34(10)	C(81)–C(82)–H(82a)	109.5
C(b5)–C(b6)–C(61)	128.82(11)	C(81)–C(82)–H(82b)	109.5
C(a6)–C(b6)–C(61)	124.81(11)	H(82a)–C(82)–H(82b)	109.5
C(b8)–C(b7)–C(a7)	106.78(10)	C(81)–C(82)–H(82C)	109.5
C(b8)–C(b7)–C(71)	128.51(11)	H(82a)–C(82)–H(82C)	109.5
C(a7)–C(b7)–C(71)	124.68(11)	H(82b)–C(82)–H(82C)	109.5
C(b7)–C(b8)–C(a8)	106.19(10)	O(1)–C(1)–Fe(1)	177.20(11)
C(b7)–C(b8)–C(81)	127.93(11)	C(95)–C(90)–C(91)	120.28(18)
C(a8)–C(b8)–C(81)	125.82(11)	C(95)–C(90)–H(90a)	119.9
C(b1)–C(11)–C(12)	112.86(10)	C(91)–C(90)–H(90a)	119.9
C(b1)–C(11)–H(11a)	109.0	C(90)–C(91)–C(92)	119.60(19)
C(12)–C(11)–H(11a)	109.0	C(90)–C(91)–H(91a)	120.2
C(b1)–C(11)–H(11b)	109.0	C(92)–C(91)–H(91a)	120.2
C(12)–C(11)–H(11b)	109.0	C(93)–C(92)–C(91)	119.98(19)
H(11a)–C(11)–H(11b)	107.8	C(93)–C(92)–H(92a)	120.0
C(11)–C(12)–H(12a)	109.5	C(91)–C(92)–H(92a)	120.0
C(11)–C(12)–H(12b)	109.5	C(94)–C(93)–C(92)	119.64(19)
H(12a)–C(12)–H(12b)	109.5	C(94)–C(93)–H(93a)	120.2
C(11)–C(12)–H(12C)	109.5	C(92)–C(93)–H(93a)	120.2
H(12a)–C(12)–H(12C)	109.5	C(95)–C(94)–C(93)	119.9(2)
H(12b)–C(12)–H(12C)	109.5	C(95)–C(94)–H(94a)	120.1
C(b2)–C(21)–C(22)	112.60(11)	C(93)–C(94)–H(94a)	120.1
C(b2)–C(21)–H(21a)	109.1	C(90)–C(95)–C(94)	120.63(19)
C(22)–C(21)–H(21a)	109.1	C(90)–C(95)–H(95a)	119.7
C(b2)–C(21)–H(21b)	109.1	C(94)–C(95)–H(95a)	119.7
C(22)–C(21)–H(21b)	109.1		

[a]The estimated standard deviations of the least significant digits are given in parentheses.

Table S12. Anisotropic Displacement Parameters (Å^2) for [Fe(OEP)(CO)]·C_6H_6[a]

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(1)	0.0120(1)	0.0118(1)	0.0115(1)	−0.0035(1)	0.0000(1)	−0.0001(1)
N(1)	0.0116(4)	0.0132(4)	0.0122(4)	−0.0030(3)	0.0004(3)	−0.0014(3)
N(2)	0.0124(4)	0.0119(4)	0.0127(4)	−0.0028(3)	0.0006(3)	−0.0013(3)
N(3)	0.0129(4)	0.0123(4)	0.0124(4)	−0.0032(3)	0.0005(3)	−0.0014(3)
N(4)	0.0122(4)	0.0137(4)	0.0127(4)	−0.0045(3)	0.0004(3)	−0.0010(3)
C(M1)	0.0137(5)	0.0162(5)	0.0129(5)	−0.0036(4)	−0.0012(4)	−0.0028(4)
C(M2)	0.0138(5)	0.0116(5)	0.0159(5)	−0.0025(4)	0.0019(4)	−0.0014(4)
C(M3)	0.0144(5)	0.0153(5)	0.0139(5)	−0.0046(4)	0.0004(4)	−0.0035(4)
C(M4)	0.0132(5)	0.0113(5)	0.0154(5)	−0.0029(4)	0.0008(4)	−0.0006(4)
C(A1)	0.0119(5)	0.0124(5)	0.0137(5)	−0.0039(4)	0.0012(4)	−0.0020(4)
C(A2)	0.0120(5)	0.0141(5)	0.0131(5)	−0.0041(4)	0.0007(4)	−0.0032(4)
C(A3)	0.0115(5)	0.0143(5)	0.0137(5)	−0.0024(4)	−0.0001(4)	−0.0025(4)
C(A4)	0.0116(5)	0.0108(5)	0.0148(5)	−0.0013(4)	0.0006(4)	−0.0019(4)
C(A5)	0.0146(5)	0.0104(5)	0.0146(5)	−0.0029(4)	0.0022(4)	−0.0028(4)
C(A6)	0.0144(5)	0.0132(5)	0.0135(5)	−0.0044(4)	0.0020(4)	−0.0040(4)
C(A7)	0.0120(5)	0.0152(5)	0.0129(5)	−0.0028(4)	0.0001(4)	−0.0023(4)
C(A8)	0.0111(5)	0.0135(5)	0.0139(5)	−0.0021(4)	0.0010(4)	−0.0018(4)
C(B1)	0.0129(5)	0.0131(5)	0.0161(5)	−0.0059(4)	0.0009(4)	−0.0025(4)
C(B2)	0.0142(5)	0.0143(5)	0.0145(5)	−0.0056(4)	0.0004(4)	−0.0034(4)
C(B3)	0.0132(5)	0.0139(5)	0.0154(5)	−0.0011(4)	−0.0014(4)	−0.0025(4)
C(B4)	0.0127(5)	0.0121(5)	0.0156(5)	−0.0002(4)	−0.0009(4)	−0.0026(4)
C(B5)	0.0171(5)	0.0111(5)	0.0151(5)	−0.0041(4)	0.0033(4)	−0.0044(4)
C(B6)	0.0164(5)	0.0124(5)	0.0144(5)	−0.0046(4)	0.0034(4)	−0.0053(4)
C(B7)	0.0122(5)	0.0166(5)	0.0133(5)	−0.0025(4)	−0.0008(4)	−0.0022(4)
C(B8)	0.0115(5)	0.0143(5)	0.0138(5)	−0.0013(4)	−0.0002(4)	−0.0019(4)
C(11)	0.0164(5)	0.0149(5)	0.0188(6)	−0.0077(4)	−0.0004(4)	−0.0004(4)
C(12)	0.0174(6)	0.0204(6)	0.0406(8)	−0.0120(6)	0.0046(5)	−0.0002(5)
C(21)	0.0216(6)	0.0201(6)	0.0159(5)	−0.0081(4)	−0.0022(4)	−0.0009(5)
C(22)	0.0401(8)	0.0282(7)	0.0163(6)	−0.0065(5)	0.0059(6)	−0.0054(6)
C(31)	0.0199(6)	0.0209(6)	0.0154(5)	−0.0032(4)	−0.0040(4)	0.0009(5)
C(32)	0.0356(8)	0.0452(9)	0.0164(6)	0.0006(6)	0.0019(6)	−0.0087(7)
C(41)	0.0150(5)	0.0122(5)	0.0177(5)	−0.0010(4)	−0.0019(4)	−0.0007(4)
C(42)	0.0156(5)	0.0179(6)	0.0261(6)	−0.0054(5)	0.0013(5)	−0.0017(4)
C(51)	0.0206(6)	0.0115(5)	0.0190(6)	−0.0051(4)	0.0031(4)	−0.0016(4)

Table S12. Continued

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(52)	0.0217(6)	0.0179(6)	0.0308(7)	−0.0017(5)	0.0083(5)	0.0008(5)
C(61)	0.0217(6)	0.0167(6)	0.0162(5)	−0.0070(4)	0.0017(4)	−0.0064(4)
C(62)	0.0305(7)	0.0288(7)	0.0157(6)	−0.0060(5)	0.0016(5)	−0.0113(6)
C(71)	0.0163(5)	0.0188(6)	0.0161(5)	−0.0034(4)	−0.0028(4)	−0.0028(4)
C(72)	0.0287(7)	0.0339(8)	0.0156(6)	−0.0043(5)	0.0004(5)	−0.0103(6)
C(81)	0.0147(5)	0.0144(5)	0.0159(5)	−0.0008(4)	−0.0011(4)	−0.0009(4)
C(82)	0.0159(6)	0.0178(6)	0.0399(8)	0.0000(5)	0.0051(5)	0.0014(5)
C(1)	0.0174(5)	0.0157(5)	0.0141(5)	−0.0045(4)	−0.0011(4)	0.0007(4)
O(1)	0.0230(5)	0.0236(5)	0.0222(5)	−0.0052(4)	0.0018(4)	−0.0079(4)
C(90)	0.0318(8)	0.0388(9)	0.0344(8)	0.0032(7)	−0.0126(7)	−0.0086(7)
C(91)	0.0283(8)	0.0496(11)	0.0401(9)	−0.0057(8)	−0.0053(7)	−0.0052(7)
C(92)	0.0316(9)	0.0629(13)	0.0403(10)	0.0121(9)	−0.0116(7)	−0.0185(9)
C(93)	0.0691(14)	0.0386(11)	0.0576(13)	0.0107(9)	−0.0372(11)	−0.0175(10)
C(94)	0.0782(16)	0.0481(12)	0.0430(11)	−0.0123(9)	−0.0265(11)	0.0053(11)
C(95)	0.0459(10)	0.0529(11)	0.0276(8)	0.0006(7)	−0.0127(7)	−0.0034(9)

[a]The estimated standard deviations of the least significant digits are given in parentheses. The anisotropic displacement factor exponent takes the form: $-2\,\pi\,[h^2\,U_{11}\,+...+\,2\,h\,k\,a^*\,b^*\,U_{12}]$.

Table S13. Hydrogen Atom Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$) for [Fe(OEP)(CO)]·C_6H_6[a]

atom	x	y	z	U(eq)
H(MA	0.2949	0.3603	0.1698	0.017
H(MB	0.1012	0.6653	0.4500	0.017
H(MC	0.5202	0.3817	0.7166	0.017
H(MD	0.6452	0.0288	0.4657	0.016
H(11A)	0.6147	−0.0329	0.2364	0.020
H(11B)	0.6373	−0.0630	0.3454	0.020
H(12A)	0.8336	−0.0521	0.2599	0.039
H(12B)	0.8091	0.0419	0.3234	0.039
H(12C)	0.7831	0.0818	0.2148	0.039
H(21A)	0.3735	0.1876	0.1159	0.023
H(21B)	0.5068	0.1010	0.1210	0.023
H(22A)	0.5139	0.2713	0.0025	0.042
H(22B)	0.6182	0.2607	0.0788	0.042
H(22C)	0.4870	0.3495	0.0783	0.042
H(31A)	0.0250	0.6003	0.1211	0.023
H(31B)	0.1158	0.4820	0.1112	0.023
H(32A)	0.1693	0.6378	−0.0044	0.050
H(32B)	0.2875	0.5862	0.0630	0.050
H(32C)	0.1967	0.7046	0.0729	0.050
H(41A)	0.0067	0.7540	0.2099	0.019
H(41B)	0.0185	0.7605	0.3158	0.019
H(42A)	−0.1925	0.7399	0.2893	0.030
H(42B)	−0.1279	0.6262	0.3608	0.030
H(42C)	−0.1409	0.6223	0.2546	0.030
H(51A)	0.1143	0.7680	0.5573	0.020
H(51B)	0.1726	0.7602	0.6561	0.020
H(52A)	−0.0465	0.7418	0.6736	0.037
H(52B)	0.0381	0.6239	0.7265	0.037
H(52C)	−0.0196	0.6304	0.6278	0.037
H(61A)	0.3334	0.6544	0.7558	0.021
H(61B)	0.4569	0.5564	0.7587	0.021
H(62A)	0.3333	0.5085	0.8937	0.036
H(62B)	0.3318	0.4126	0.8339	0.036
H(62C)	0.2111	0.5131	0.8340	0.036

Table S13. Continued

atom	x	y	z	U(eq)
H(71A)	0.7045	0.2593	0.7677	0.020
H(71B)	0.7702	0.1272	0.7727	0.020
H(72A)	0.6355	0.1423	0.9040	0.038
H(72B)	0.5856	0.0609	0.8463	0.038
H(72C)	0.5155	0.1924	0.8382	0.038
H(81A)	0.7189	−0.0642	0.6111	0.019
H(81B)	0.7611	−0.0360	0.7044	0.019
H(82A)	0.9429	−0.0657	0.6094	0.039
H(82B)	0.9181	0.0676	0.6178	0.039
H(82C)	0.8783	0.0334	0.5263	0.039
H(90A)	0.8286	0.6557	1.0061	0.043
H(91A)	0.9363	0.7182	0.8676	0.048
H(92A)	0.9719	0.9113	0.8249	0.056
H(93A)	0.9013	1.0395	0.9220	0.067
H(94A)	0.7924	0.9749	1.0602	0.068
H(95A)	0.7588	0.7829	1.1018	0.052

[a] U(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor the estimated standard deviations of the least significant digits are given in parentheses.

Table S14. Complete Crystallographic Details for [Fe(OEP)(CO)$_2$]

formula	$C_{38}H_{44}FeN_4O_2$
FW, amu	644.62
a, Å	8.6165(2)
b, Å	10.1648(2)
c, Å	10.4369(2)
α, deg	81.2450(10)
β, deg	67.2870(10)
γ, deg	69.4660(10)
V, Å^3	789.50(3)
space group	$P\bar{1}$
Z	1
D_c, g/cm^3	1.356
F(000)	342
μ, mm^{-1}	0.519
crystal dimensions, mm	0.15 × 0.09 × 0.08
radiation	MoKα, $\bar{\lambda}$ = 0.71073 Å
temperature, K	100(2)
diffractometer	Bruker Apex CCD
θ range for collected data, deg	2.12–34.95
index range	$-13 \leq h \leq 13$
	$-16 \leq k \leq 16$
	$-16 \leq l \leq 16$
total data collected	32619
absorption correction	Semi-empirical fromequiv
relative transmission coefficients (I)	0.9597 and 0.9262
unique data	6727 (R_{int} = 0.0297)
unique observed data [I > 2σ(I)]	5944
refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	6727/0/209
goodness-of-fit (pased on F^2)	1.061
final R indices [I > 2σ(I)]	R_1 = 0.0329, wR_2 = 0.0826
final R indices (all data)	R_1 = 0.0395, wR_2 = 0.0863

Table S15. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for [Fe(OEP)(CO)$_2$][a]

atom	x	y	z	U(eq)
Fe(1)	0.5000	0.5000	0.5000	0.0088(1)
N(1)	0.56919(10)	0.29160(8)	0.53950(8)	0.0104(1)
N(2)	0.39155(10)	0.53624(8)	0.70538(8)	0.0105(1)
C(m1)	0.70407(12)	0.20635(9)	0.30187(9)	0.0119(1)
C(m2)	0.45048(12)	0.29399(9)	0.79390(9)	0.0122(1)
C(a1)	0.65303(11)	0.18543(9)	0.44469(9)	0.0107(1)
C(a2)	0.53363(11)	0.22598(9)	0.66770(9)	0.0110(1)
C(a3)	0.38776(11)	0.43807(9)	0.81170(9)	0.0111(1)
C(a4)	0.31886(11)	0.66471(9)	0.76766(9)	0.0108(1)
C(b1)	0.67248(11)	0.04901(9)	0.51488(9)	0.0114(1)
C(b2)	0.59642(12)	0.07481(9)	0.65371(9)	0.0114(1)
C(b3)	0.31163(11)	0.50607(9)	0.94506(9)	0.0111(1)
C(b4)	0.27025(11)	0.64699(9)	0.91684(9)	0.0113(1)
C(11)	0.76016(12)	−0.09150(9)	0.44663(10)	0.0137(2)
C(12)	0.95845(14)	−0.15239(11)	0.42214(12)	0.0213(2)
C(21)	0.57875(13)	−0.02948(10)	0.77189(10)	0.0151(2)
C(22)	0.71750(15)	−0.05488(11)	0.83804(11)	0.0189(2)
C(31)	0.28627(12)	0.43414(10)	1.08481(9)	0.0137(2)
C(32)	0.09782(14)	0.42709(12)	1.16169(11)	0.0215(2)
C(41)	0.19253(13)	0.76396(10)	1.01757(9)	0.0148(2)
C(42)	−0.00884(14)	0.83026(11)	1.05916(11)	0.0206(2)
C(1)	0.70700(13)	0.51143(10)	0.50671(10)	0.0154(2)
O(1)	0.82292(12)	0.52755(11)	0.51872(11)	0.0324(2)

[a] U(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. The estimated standard deviations of the least significant digits are given in parentheses.

Table S16. Bond Lengths for $[Fe(OEP)(CO)_2]$[a]

bond	length (Å)	bond	length (Å)
Fe(1)–C(1)#1)	1.8558(10)	C(11)–C(12)	1.5286(14)
Fe(1)–C(1)	1.8558(10)	C(11)–H(11a)	0.9900
Fe(1)–N(1)#1)	2.0126(7)	C(11)–H(11b)	0.9900
Fe(1)–N(1)	2.0127(7)	C(12)–H(12a)	0.9800
Fe(1)–N(2)#1)	2.0138(7)	C(12)–H(12b)	0.9800
Fe(1)–N(2)	2.0138(7)	C(12)–H(12C)	0.9800
N(1)–C(a2)	1.3726(11)	C(21)–C(22)	1.5295(14)
N(1)–C(a1)	1.3754(11)	C(21)–H(21a)	0.9900
N(2)–C(a3)	1.3733(11)	C(21)–H(21b)	0.9900
N(2)–C(a4)	1.3749(10)	C(22)–H(22a)	0.9800
C(m1)–C(a4#1)	1.3867(12)	C(22)–H(22b)	0.9800
C(m1)–C(a1)	1.3869(12)	C(22)–H(22C)	0.9800
C(m1)–H(m1)	0.9500	C(31)–C(32)	1.5309(14)
C(m2)–C(a3)	1.3862(12)	C(31)–H(31a)	0.9900
C(m2)–C(a2)	1.3881(12)	C(31)–H(31b)	0.9900
C(m2)–H(m2)	0.9500	C(32)–H(32a)	0.9800
C(a1)–C(b1)	1.4526(12)	C(32)–H(32b)	0.9800
C(a2)–C(b2)	1.4489(12)	C(32)–H(32C)	0.9800
C(a3)–C(b3)	1.4544(12)	C(41)–C(42)	1.5298(14)
C(a4)–C(m1#1)	1.3867(12)	C(41)–H(41a)	0.9900
C(a4)–C(b4)	1.4478(12)	C(41)–H(41b)	0.9900
C(b1)–C(b2)	1.3637(12)	C(42)–H(42a)	0.9800
C(b1)–C(11)	1.5017(12)	C(42)–H(42b)	0.9800
C(b2)–C(21)	1.4961(13)	C(42)–H(42C)	0.9800
C(b3)–C(b4)	1.3639(12)	C(1)–O(1)	1.1216(13)
C(b3)–C(31)	1.5003(12)		
C(b4)–C(41)	1.4985(12)		

[a]The estimated standard deviations of the least significant digits are given in parentheses.

Table S17. Bond Angles for $[Fe(OEP)(CO)_2]^a$

angle	degree	angle	degree
C(1)#1–Fe(1)–C(1)	179.999(3)	C(b1)–C(11)–C(12)	113.49(8)
C(1)#1–Fe(1)–N(1)#1	92.61(4)	C(b1)–C(11)–H(11a)	108.9
C(1)–Fe(1)–N(1)#1	87.39(4)	C(12)–C(11)–H(11a)	108.9
C(1)#1–Fe(1)–N(1)	87.39(4)	C(b1)–C(11)–H(11b)	108.9
C(1)–Fe(1)–N(1)	92.61(4)	C(12)–C(11)–H(11b)	108.9
N(1)#1–Fe(1)–N(1)	180.000(2)	H(11a)–C(11)–H(11b)	107.7
C(1)#1–Fe(1)–N(2)#1	86.76(4)	C(11)–C(12)–H(12a)	109.5
C(1)–Fe(1)–N(2)#1	93.24(4)	C(11)–C(12)–H(12b)	109.5
N(1)#1–Fe(1)–N(2)#1	90.08(3)	H(12a)–C(12)–H(12b)	109.5
N(1)–Fe(1)–N(2)#1	89.92(3)	C(11)–C(12)–H(12C)	109.5
C(1)#1–Fe(1)–N(2)	93.24(4)	H(12a)–C(12)–H(12C)	109.5
C(1)–Fe(1)–N(2)	86.76(4)	H(12b)–C(12)–H(12C)	109.5
N(1)#1–Fe(1)–N(2)	89.92(3)	C(b2)–C(21)–C(22)	112.65(8)
N(1)–Fe(1)–N(2)	90.08(3)	C(b2)–C(21)–H(21a)	109.1
N(2)#1–Fe(1)–N(2)	179.999(2)	C(22)–C(21)–H(21a)	109.1
C(a2)–N(1)–C(a1)	105.60(7)	C(b2)–C(21)–H(21b)	109.1
C(a2)–N(1)–Fe(1)	126.83(6)	C(22)–C(21)–H(21b)	109.1
C(a1)–N(1)–Fe(1)	127.49(6)	H(21a)–C(21)–H(21b)	107.8
C(a3)–N(2)–C(a4)	105.73(7)	C(21)–C(22)–H(22a)	109.5
C(a3)–N(2)–Fe(1)	127.24(6)	C(21)–C(22)–H(22b)	109.5
C(a4)–N(2)–Fe(1)	126.84(6)	H(22a)–C(22)–H(22b)	109.5
C(a4#1–C(m1)–C(a1)	126.00(8)	C(21)–C(22)–H(22C)	109.5
C(a4#1–C(m1)–H(m1)	117.0	H(22a)–C(22)–H(22C)	109.5
C(a1)–C(m1)–H(m1)	117.0	H(22b)–C(22)–H(22C)	109.5
C(a3)–C(m2)–C(a2)	126.04(8)	C(b3)–C(31)–C(32)	113.40(8)
C(a3)–C(m2)–H(m2)	117.0	C(b3)–C(31)–H(31a)	108.9
C(a2)–C(m2)–H(m2)	117.0	C(32)–C(31)–H(31a)	108.9
N(1)–C(a1)–C(m1)	124.47(8)	C(b3)–C(31)–H(31b)	108.9
N(1)–C(a1)–C(b1)	110.72(7)	C(32)–C(31)–H(31b)	108.9
C(m1)–C(a1)–C(b1)	124.74(8)	H(31a)–C(31)–H(31b)	107.7
N(1)–C(a2)–C(m2)	125.08(8)	C(31)–C(32)–H(32a)	109.5
N(1)–C(a2)–C(b2)	110.64(7)	C(31)–C(32)–H(32b)	109.5
C(m2)–C(a2)–C(b2)	124.28(8)	H(32a)–C(32)–H(32b)	109.5
N(2)–C(a3)–C(m2)	124.56(8)	C(31)–C(32)–H(32C)	109.5

Table S17. Continued

angle	degree	angle	degree
N(2)–C(a3)–C(b3)	110.66(7)	H(32a)–C(32)–H(32C)	109.5
C(m2)–C(a3)–C(b3)	124.77(8)	H(32b)–C(32)–H(32C)	109.5
N(2)–C(a4)–C(m1#1	125.11(8)	C(b4)–C(41)–C(42)	113.32(8)
N(2)–C(a4)–C(b4)	110.50(7)	C(b4)–C(41)–H(41a)	108.9
C(m1#1–C(a4)–C(b4)	124.39(8)	C(42)–C(41)–H(41a)	108.9
C(b2)–C(b1)–C(a1)	106.24(7)	C(b4)–C(41)–H(41b)	108.9
C(b2)–C(b1)–C(11)	127.42(8)	C(42)–C(41)–H(41b)	108.9
C(a1)–C(b1)–C(11)	126.34(8)	H(41a)–C(41)–H(41b)	107.7
C(b1)–C(b2)–C(a2)	106.80(8)	C(41)–C(42)–H(42a)	109.5
C(b1)–C(b2)–C(21)	128.03(8)	C(41)–C(42)–H(42b)	109.5
C(a2)–C(b2)–C(21)	125.17(8)	H(42a)–C(42)–H(42b)	109.5
C(b4)–C(b3)–C(a3)	106.20(7)	C(41)–C(42)–H(42C)	109.5
C(b4)–C(b3)–C(31)	127.39(8)	H(42a)–C(42)–H(42C)	109.5
C(a3)–C(b3)–C(31)	126.41(8)	H(42b)–C(42)–H(42C)	109.5
C(b3)–C(b4)–C(a4)	106.91(7)	O(1)–C(1)–Fe(1)	173.95(9)
C(b3)–C(b4)–C(41)	127.86(8)		
C(a4)–C(b4)–C(41)	125.22(8)		

[a]The estimated standard deviations of the least significant digits are given in parentheses.

Table S18. Anisotropic Displacement Parameters (Å^2) for [Fe(OEP)(CO)$_2$][a]

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(1)	0.0102(1)	0.0073(1)	0.0072(1)	−0.0009(1)	−0.0018(1)	−0.0018(1)
N(1)	0.0124(3)	0.0085(3)	0.0087(3)	−0.0008(2)	−0.0026(2)	−0.0024(2)
N(2)	0.0124(3)	0.0085(3)	0.0085(3)	−0.0009(2)	−0.0022(2)	−0.0023(2)
C(M1)	0.0142(3)	0.0092(3)	0.0101(3)	−0.0020(3)	−0.0028(3)	−0.0022(3)
C(M2)	0.0153(3)	0.0100(3)	0.0092(3)	0.0005(3)	−0.0027(3)	−0.0037(3)
C(A1)	0.0119(3)	0.0087(3)	0.0103(3)	−0.0013(3)	−0.0030(3)	−0.0023(3)
C(A2)	0.0134(3)	0.0090(3)	0.0095(3)	−0.0002(3)	−0.0030(3)	−0.0034(3)
C(A3)	0.0124(3)	0.0102(3)	0.0088(3)	−0.0006(3)	−0.0025(3)	−0.0029(3)
C(A4)	0.0120(3)	0.0096(3)	0.0091(3)	−0.0019(3)	−0.0025(3)	−0.0024(3)
C(B1)	0.0129(3)	0.0083(3)	0.0118(4)	−0.0007(3)	−0.0037(3)	−0.0025(3)
C(B2)	0.0140(3)	0.0084(3)	0.0108(3)	0.0001(3)	−0.0036(3)	−0.0035(3)
C(B3)	0.0118(3)	0.0113(3)	0.0086(3)	−0.0008(3)	−0.0024(3)	−0.0030(3)
C(B4)	0.0125(3)	0.0114(3)	0.0083(3)	−0.0018(3)	−0.0025(3)	−0.0028(3)
C(11)	0.0161(4)	0.0088(3)	0.0138(4)	−0.0020(3)	−0.0035(3)	−0.0027(3)
C(12)	0.0173(4)	0.0178(4)	0.0241(5)	−0.0062(4)	−0.0060(4)	0.0007(3)
C(21)	0.0212(4)	0.0107(3)	0.0127(4)	0.0018(3)	−0.0048(3)	−0.0068(3)
C(22)	0.0282(5)	0.0158(4)	0.0151(4)	0.0041(3)	−0.0107(4)	−0.0082(4)
C(31)	0.0171(4)	0.0138(4)	0.0089(3)	0.0007(3)	−0.0038(3)	−0.0046(3)
C(32)	0.0187(4)	0.0211(5)	0.0182(4)	0.0047(4)	−0.0017(4)	−0.0065(4)
C(41)	0.0195(4)	0.0130(4)	0.0101(4)	−0.0032(3)	−0.0043(3)	−0.0030(3)
C(42)	0.0197(4)	0.0164(4)	0.0172(4)	−0.0046(3)	−0.0012(3)	0.0001(3)
C(1)	0.0154(4)	0.0129(4)	0.0145(4)	−0.0012(3)	−0.0034(3)	−0.0026(3)
O(1)	0.0206(4)	0.0365(5)	0.0440(5)	−0.0038(4)	−0.0141(4)	−0.0096(4)

[a]The estimated standard deviations of the least significant digits are given in parentheses. The anisotropic displacement factor exponent takes the form: $-2\,\pi\,[h^2\,U_{11} + ... + 2\,h\,k\,a^*\,b^*\,U_{12}]$.

Table S19. Hydrogen Atom Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$) for $[Fe(OEP)(CO)_2]^a$

atom	x	y	z	U(eq)
H(M1	0.7599	0.1248	0.2466	0.014
H(M2	0.4351	0.2365	0.8756	0.015
H(11A)	0.7442	−0.0819	0.3563	0.016
H(11B)	0.7002	−0.1583	0.5056	0.016
H(12A)	1.0080	−0.2428	0.3760	0.032
H(12B)	0.9753	−0.1661	0.5115	0.032
H(12C)	1.0192	−0.0873	0.3633	0.032
H(21A)	0.5910	−0.1197	0.7379	0.018
H(21B)	0.4587	0.0049	0.8435	0.018
H(22A)	0.6971	−0.1205	0.9171	0.028
H(22B)	0.7078	0.0344	0.8701	0.028
H(22C)	0.8365	−0.0948	0.7692	0.028
H(31A)	0.3142	0.4848	1.1426	0.016
H(31B)	0.3712	0.3374	1.0727	0.016
H(32A)	0.0907	0.3767	1.2506	0.032
H(32B)	0.0688	0.3774	1.1051	0.032
H(32C)	0.0133	0.5226	1.1786	0.032
H(41A)	0.2490	0.8376	0.9755	0.018
H(41B)	0.2208	0.7272	1.1022	0.018
H(42A)	−0.0510	0.9081	1.1219	0.031
H(42B)	−0.0664	0.7594	1.1064	0.031
H(42C)	−0.0382	0.8657	0.9758	0.031

[a] U(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor the estimated standard deviations of the least significant digits are given in parentheses.

Supporting Information

Table S18. Anisotropic Isotropic Displacement Parameters for [Fe(OEP)$(CO)_2$].

Table S19. Hydrogen Coordinates and Isotropic Displacement Parameters for [Fe(OEP)$(CO)_2$].