Supporting Information

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Structural Insights into Ligand Dynamics: Correlated Oxygen and Picket Motion in Oxycobalt Picket Fence Porphyrins

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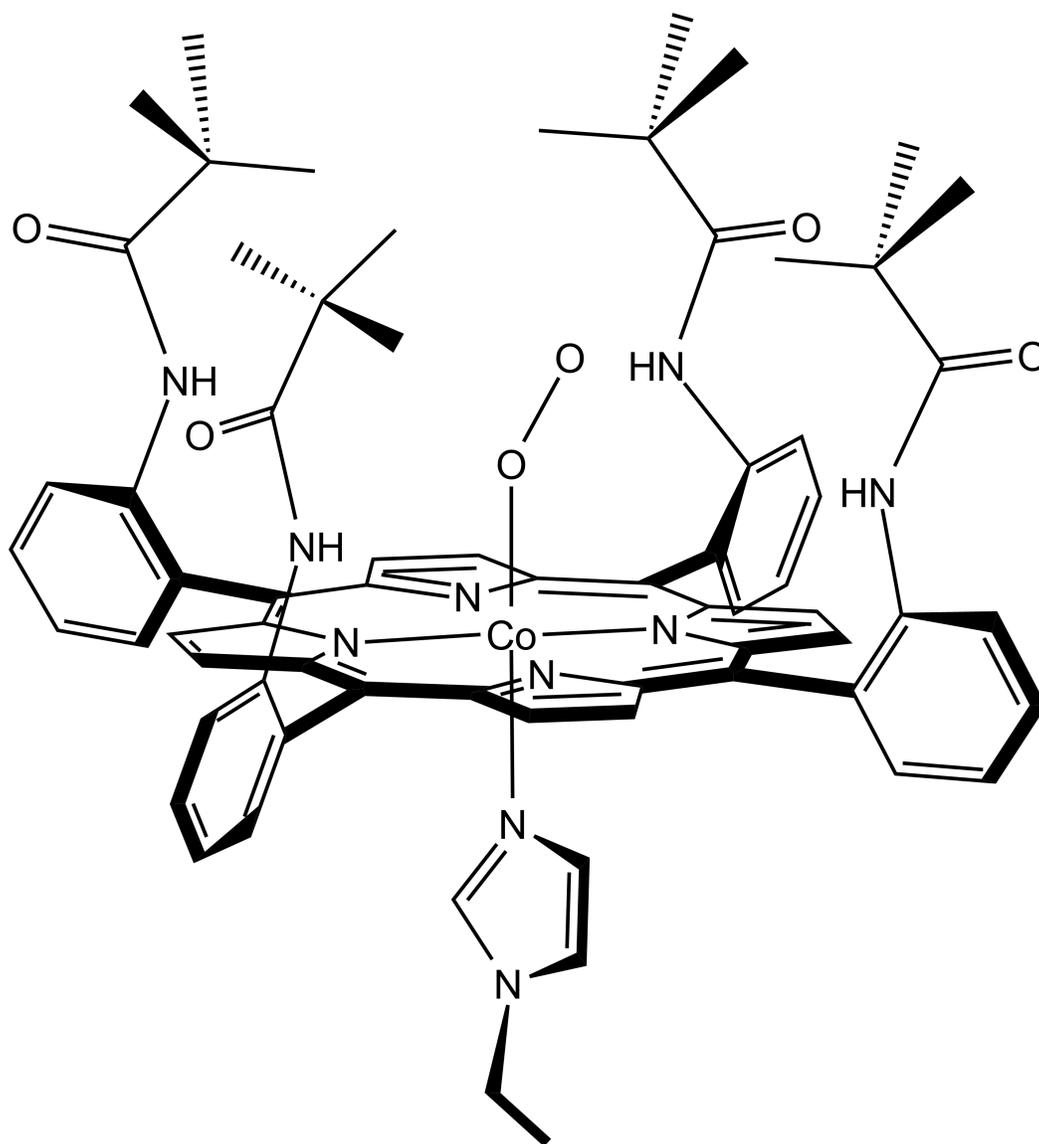
**Figure S1.** A line drawing depiction of [Co(TpivPP)(1-EtIm)(O$_2$)].
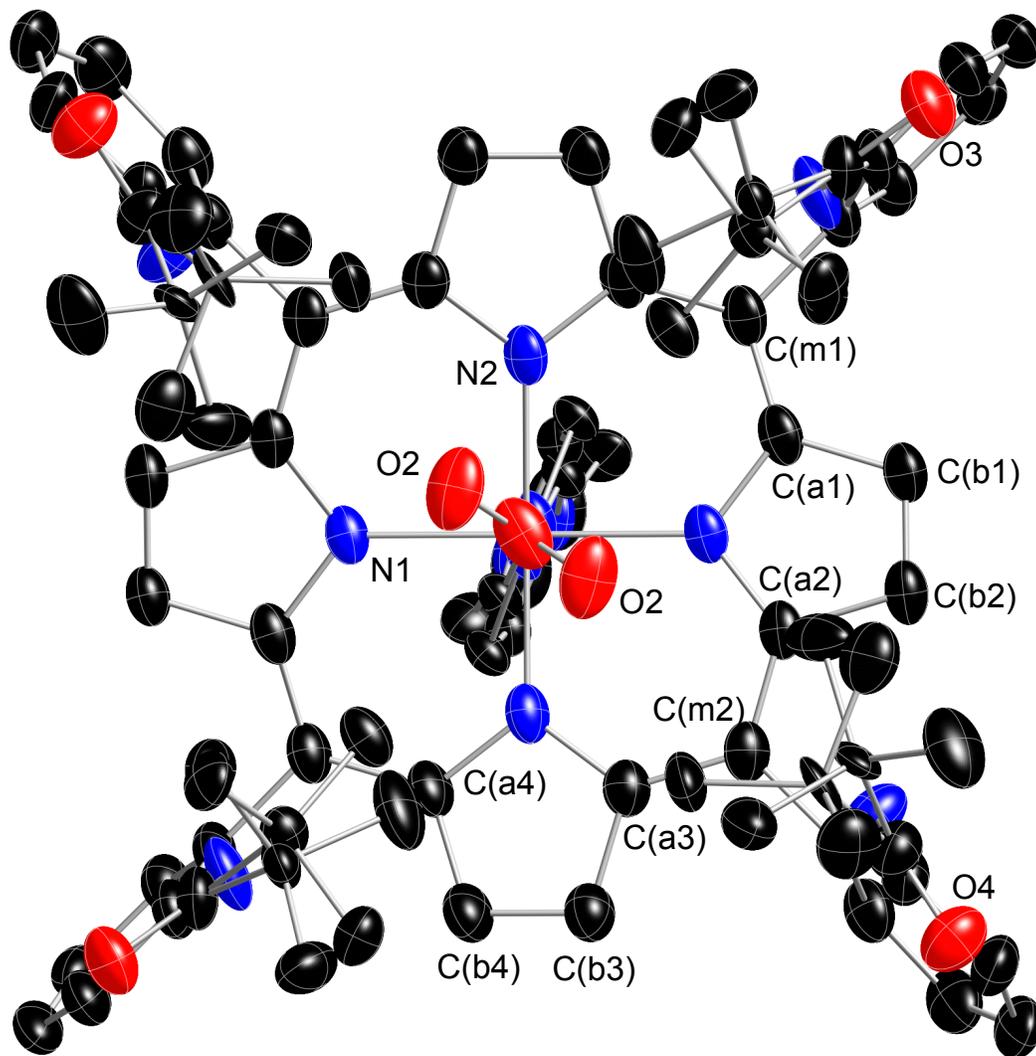
Figure S2. Top down view of the thermal ellipsoid plot for [Co(TpivPP)(1-EtIm)(O$_2$)] ($C2/c$ form, 100 K) displaying the atom labelingscheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. The crystallographically required twofold axis is perpendicular to the plane of the paper. Hydrogen atoms have been omitted for clarity. Nonbonded contacts to the alternate picket closest contacts: O2···C27 = 3.26 Å, O2···C27b = 4.02 Å, O2···C25 = 4.441 Å, O2···C25b = 3.33 Å.
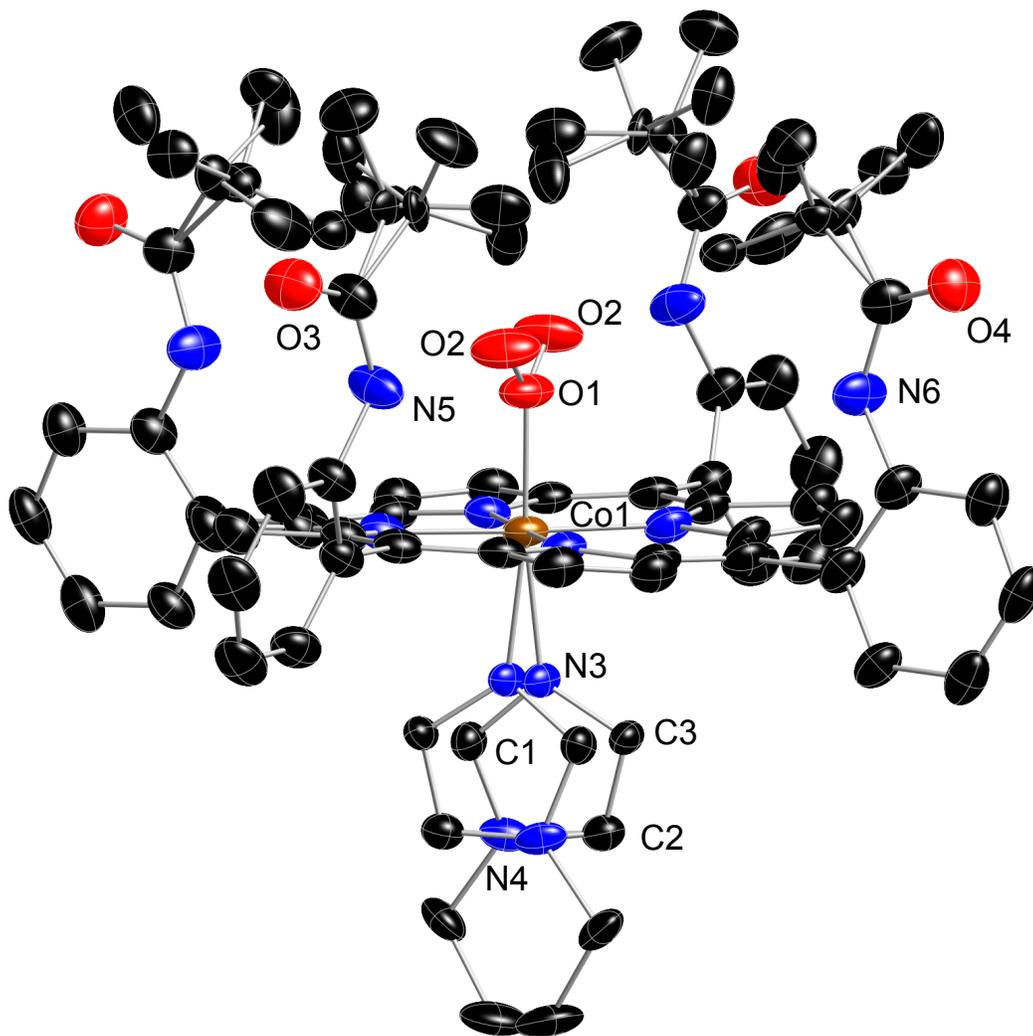
Figure S3. Edge-on thermal ellipsoid plot of [Co(TpivPP)(1-EtIm)(O₂)] (*C2/c* form, 100 K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.
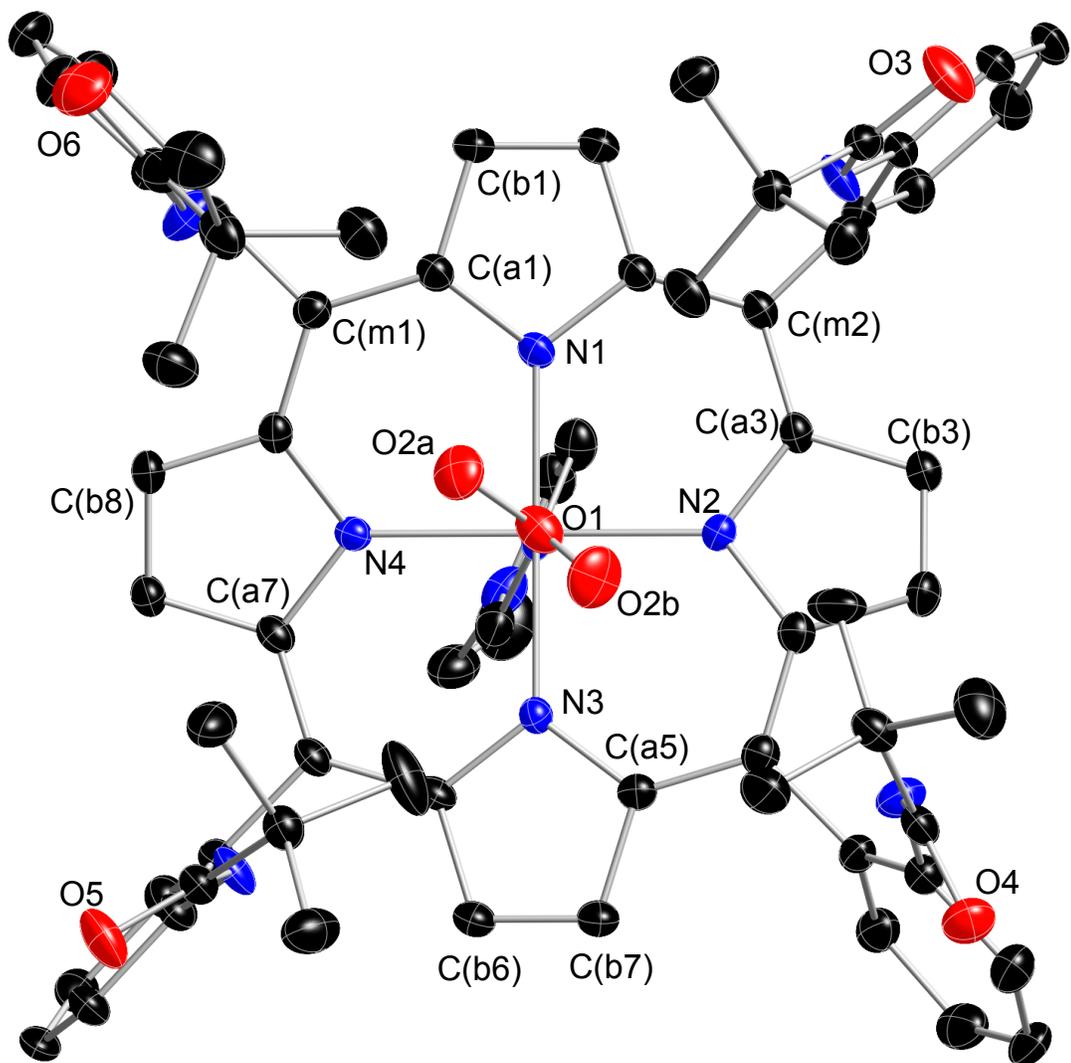
Figure S4. Top down view of the thermal ellipsoid plot of [Co(TpivPP)(1-EtIm)(O$_2$)] ($P\bar{1}$ form, 100 K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity. Nonbonded contacts to the closest picket contacts: O2a···C38 = 3.34 Å, O2a···C39 = 4.03 Å, O2b···C49 = 3.21 Å, O2b···C47 = 4.33 Å.
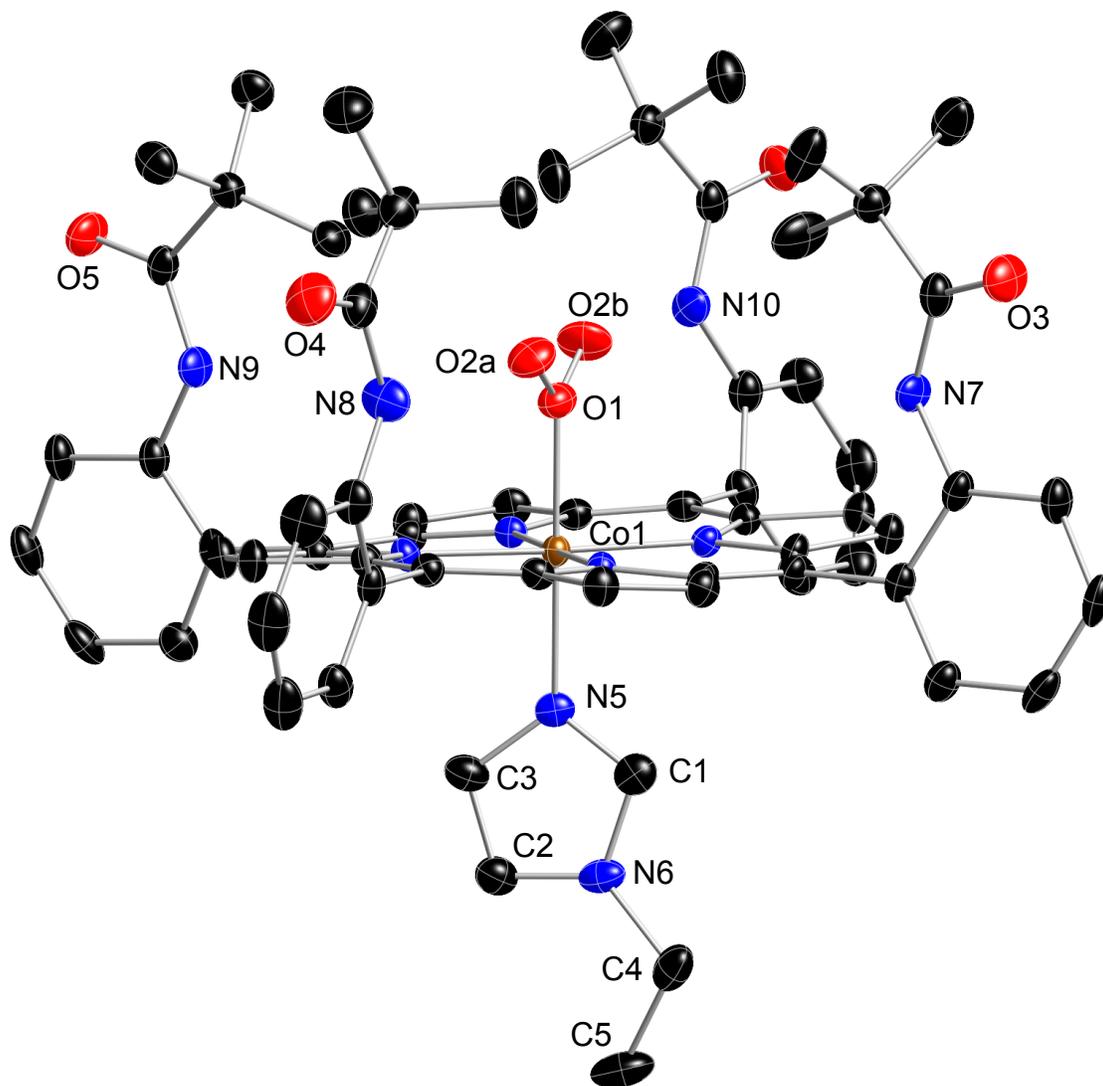
Figure S5. Edge-on thermal ellipsoid plot of [Co(TpivPP)(1-EtIm)(O$_2$)] (P$\bar{1}$ form, 100 K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity. O Distances to possible H-donors: O2a···HN8 = 3.19 Å, O2a···N8 = 4.05 Å, O1···HN8 = 4.26 Å.
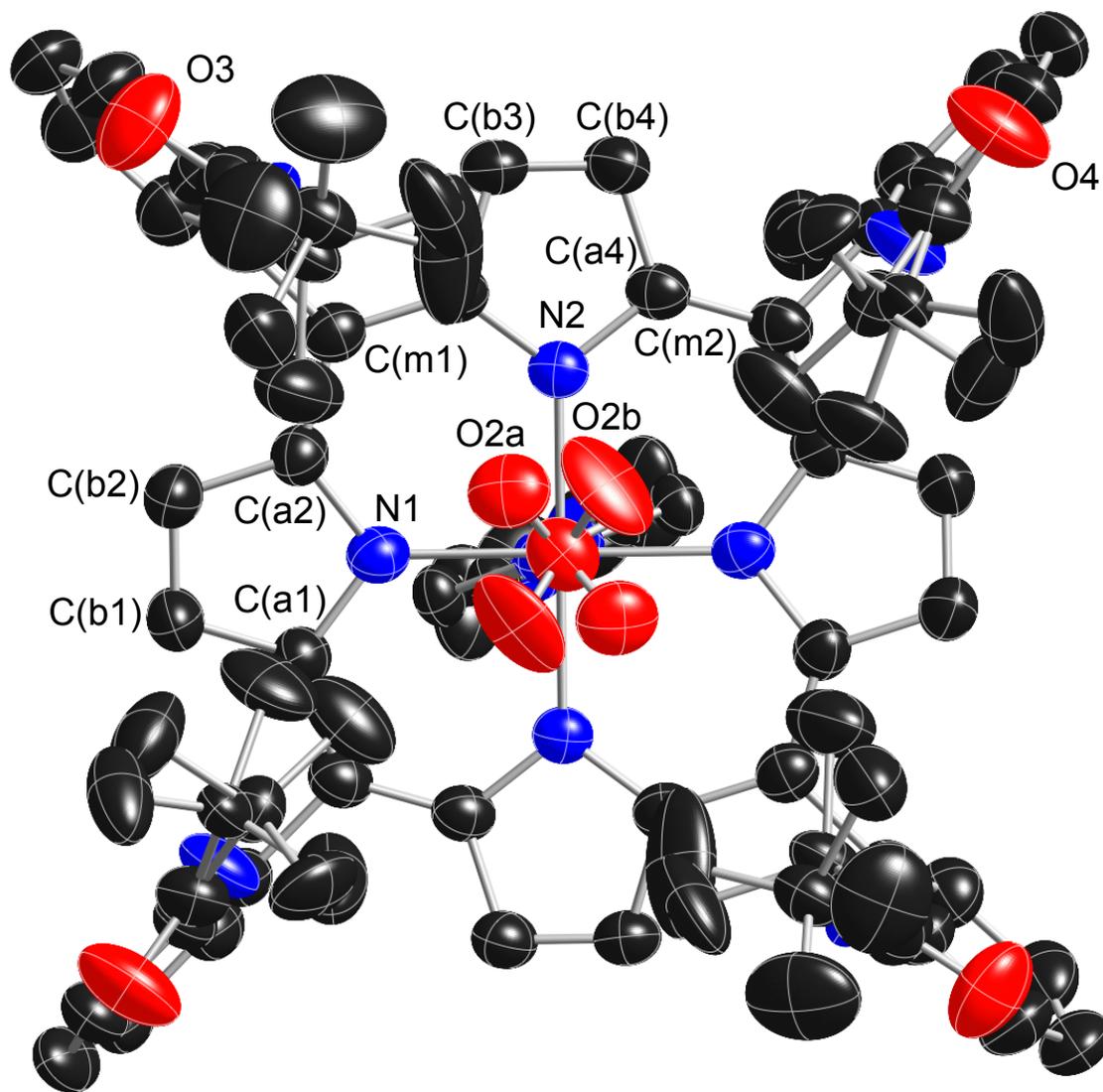
Figure S6. Top down view of the thermal ellipsoid plot of [Co(TpivPP)(1-EtIm)(O$_2$)] ($C2/c$ form, 200 K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Populations: O2a = 0.412 (11), O2b = 0.088 (11). Hydrogen atoms have been omitted for clarity. Nonbonded contacts to the alternate picket closest contacts: O2a···C26a = 3.31 Å, O2a···C26b = 4.31 Å, O2a···C25a = 3.86 Å, O2a···C25b = 3.25 Å, two < o conformations; O2b···C23a = 2.50 Å, O2b···C23b = 3.14 Å, O2b···C22b = 4.26 Å, one < o conformations and one > conformation.
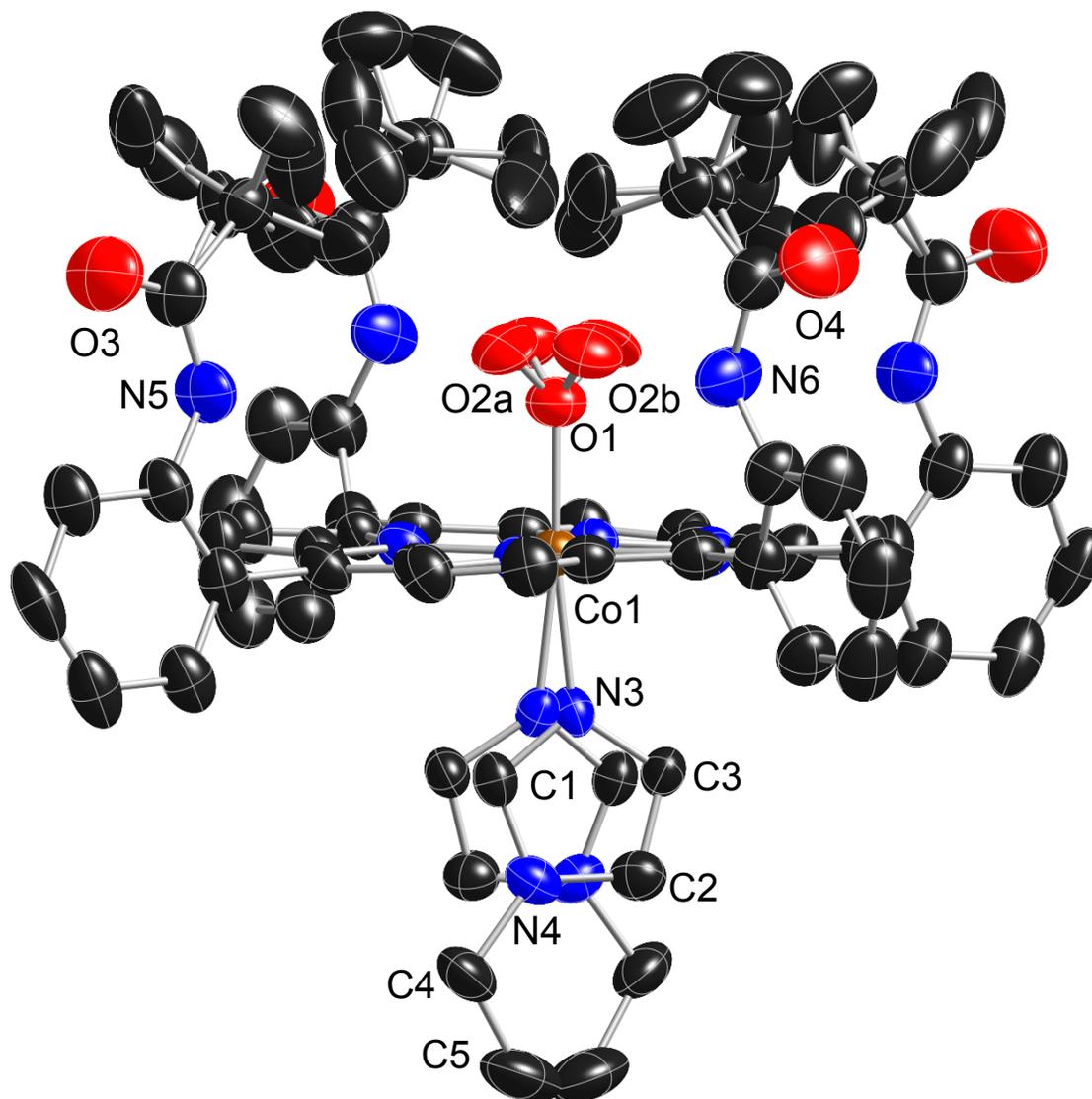
Figure S7. Edge-on thermal ellipsoid plot of [Co(TpivPP)(1-EtIm)(O$_2$)] (*C*2/*c* form, 200 K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.
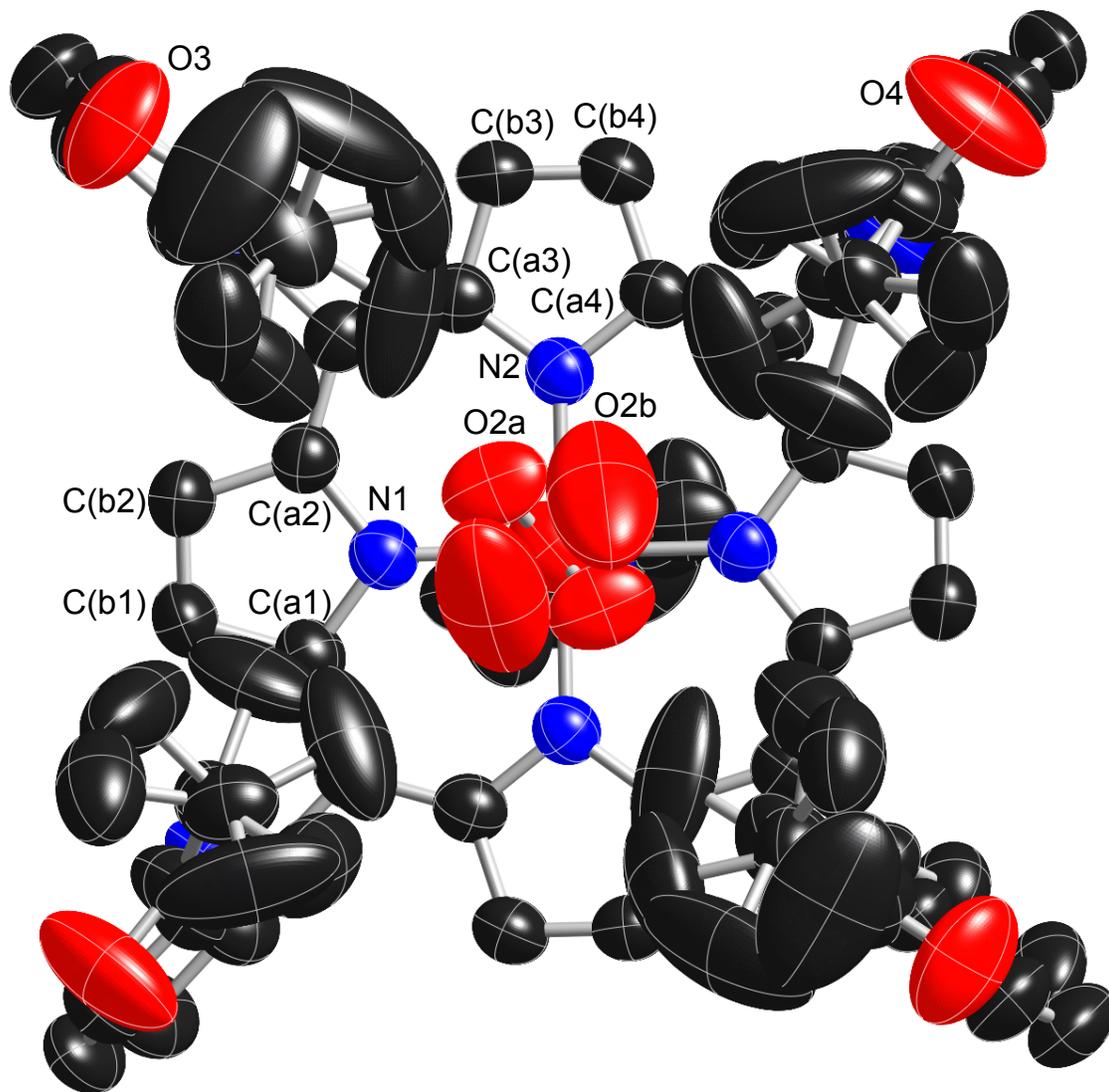
Figure S8. Top view thermal ellipsoid plot of $[Co(TpivPP)(1\text{-EtIm})(O_2)]$ ($C2/c$ form, 300 K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Populations: O2a = 0.271 (15), O2b = 0.229 (15). Hydrogen atoms have been omitted for clarity. Nonbonded contacts to the alternate picket closest contacts: O2a$\cdots$C22 = 2.70 Å, O2a$\cdots$C23b = 3.58 Å, O2a$\cdots$C22b = 3.78 Å, O2a$\cdots$C23 = 4.62 Å, O2b$\cdots$C27b = 2.59 Å, O2b$\cdots$C27 = 2.98 Å, O2b$\cdots$C26 = 4.29 Å, O2b$\cdots$C26b = 5.02 Å.
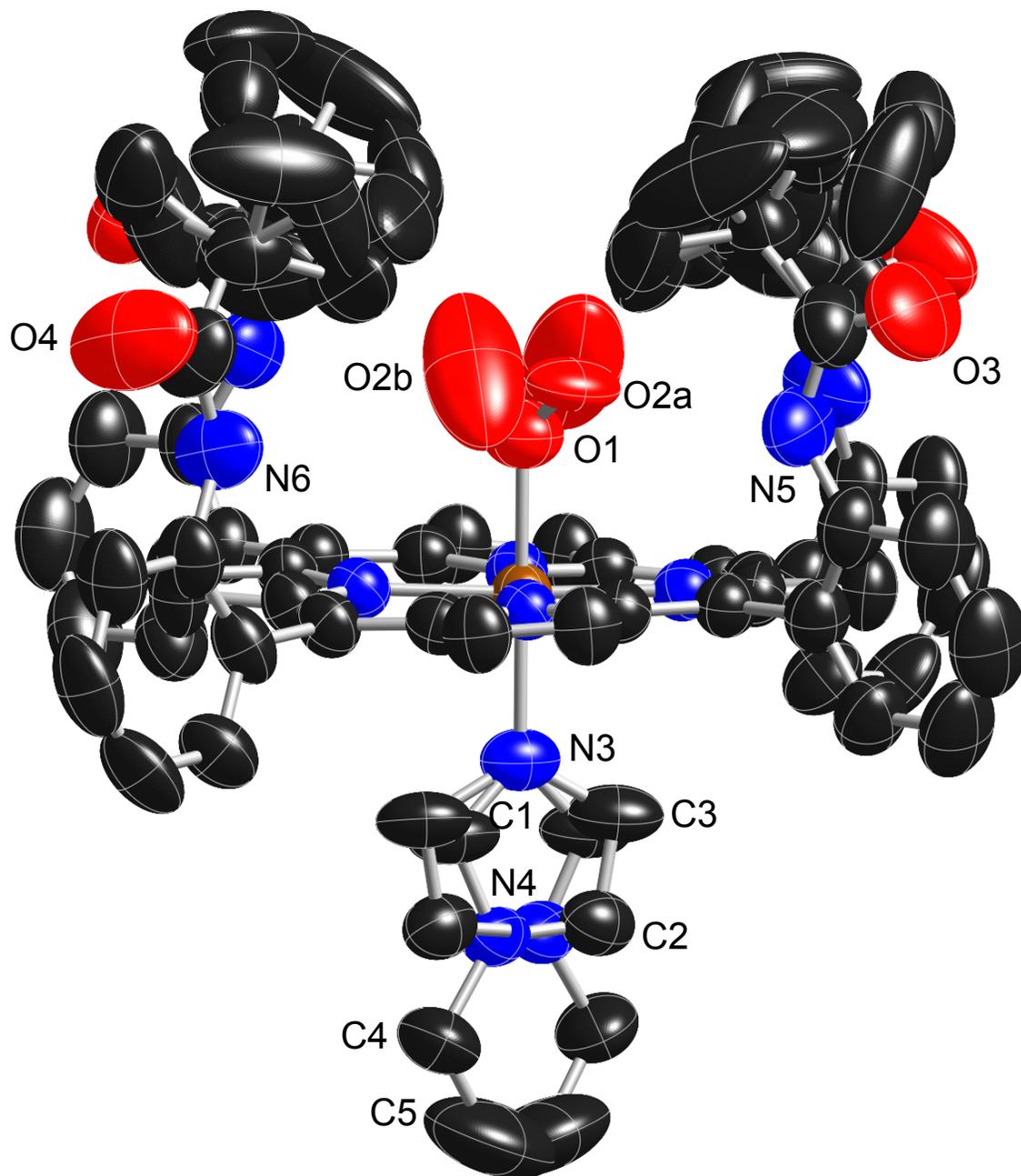
Figure S9. Edge-on thermal ellipsoid plot of [Co(TpivPP)(1-EtIm)(O$_2$)] (*C*2/*c* form, 300 K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

[CoTpivPP(1-EtIm)(O$_2$)]

flash cool
to 100 K

100 K	a 18.464(2)	α 90.00
Monoclinic	b 19.165(2)	β 90.082(4)
C2/c	c 18.3257(18)	γ 90.00
	V 6484.8(13)	
	R factor 0.1028	

warm to 200 K, stand 30 mins,
cool to 100 K(120K/hr)

100 K	a 13.2631(15)	α 90.150(7)
Triclinic	b 13.3117(14)	β 90.412(7)
P-1	c 18.2358(19)	γ 92.053(7)
	V 3217.4(6)	
	R factor 0.1271	

warm to 188 K, stand 1 hr,
cool to 100 K (120K/hr)

warm to 188 K, stand 1 hr,
cool to 100 K(120K/hr)

warm to RT, stand overnight,
cool to 80 K (120K/hr)

80 K	a 13.155(2)	α 89.416(11)
Triclinic	b 13.517(2)	β 88.707(11)
P-1	c 18.249(3)	γ 88.007(11)
	V 3242.1(10)	
	R factor 0.0869	
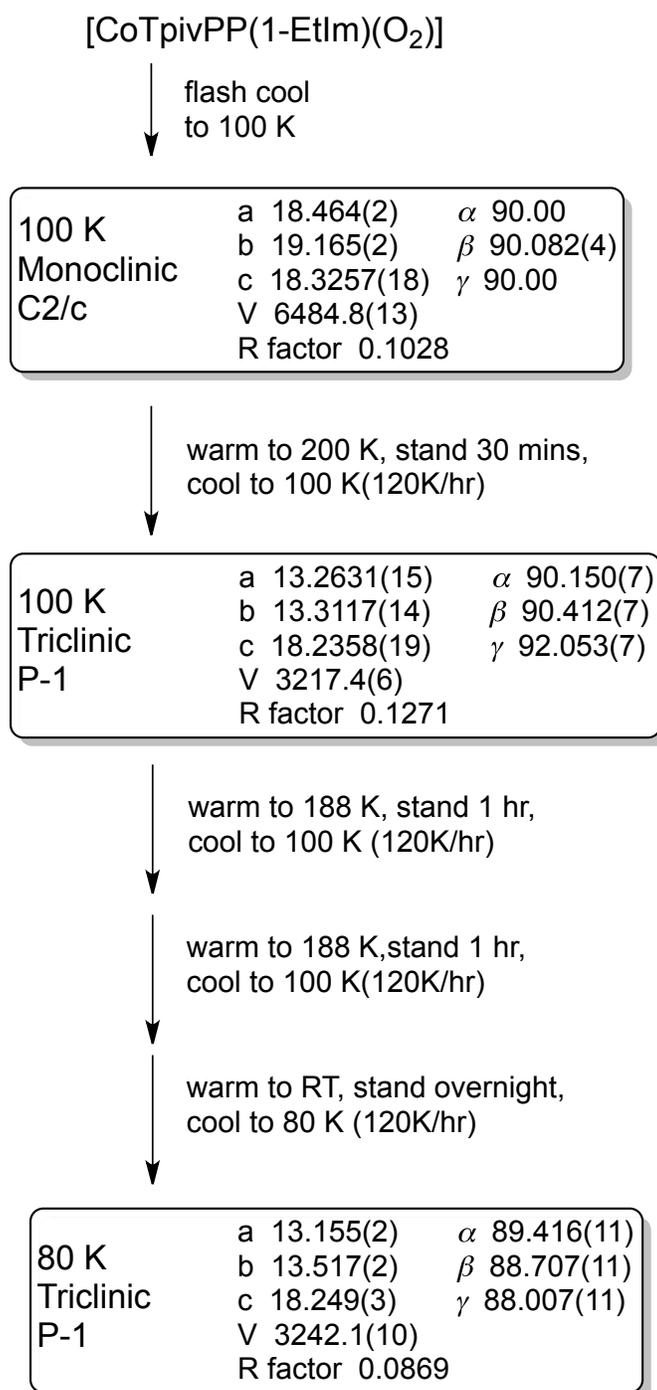
Figure S10. Scheme showing the temperature-dependent behavior of a second [Co(TpivPP)(1-EtIm)(O$_2$)] crystal. The annealing experiments are described. The temperature, corresponding space group, unit cell parameters, and observed R factor are given in the highlighted boxes.
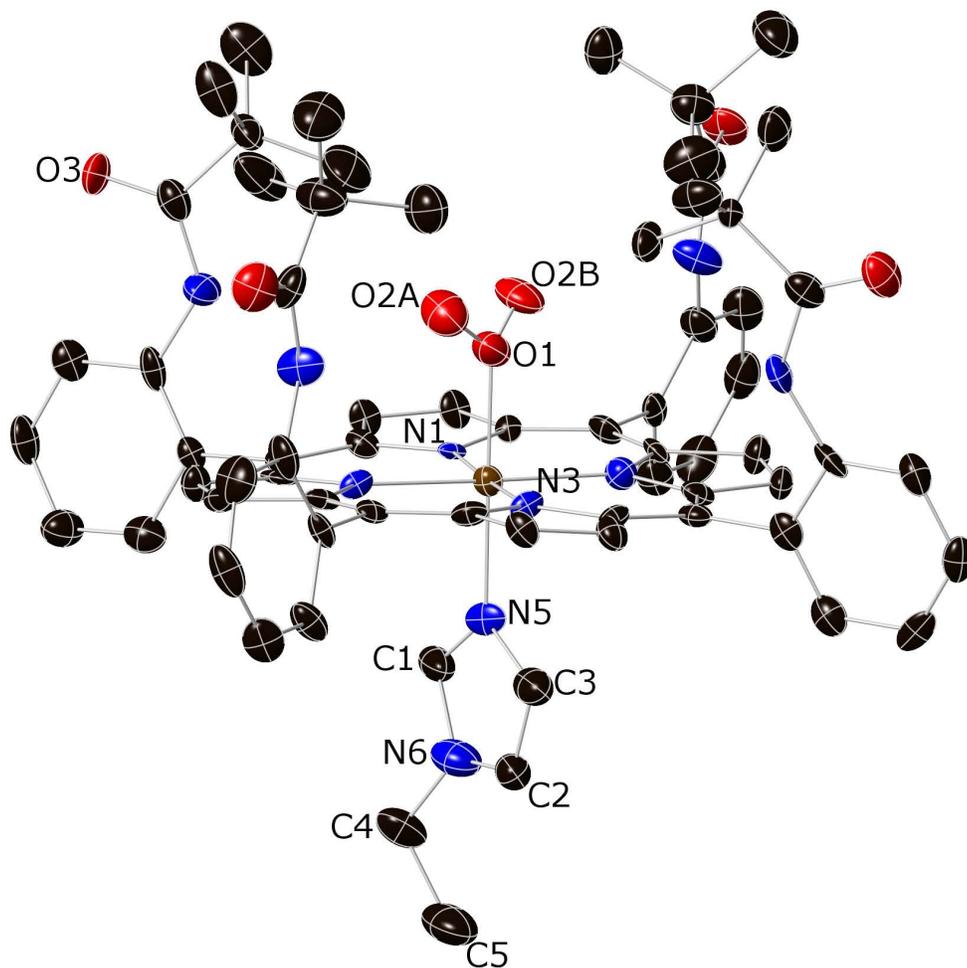
Figure S11. Edge-on view of the second [Co(TpivPP)(1-EtIm)(O$_2$)] ($P\bar{1}$ form) crystal structure at 80 K displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Populations: O2A = 0.77 (2), O2B = 0.23 (2).Hydrogen atoms have been omitted for clarity.
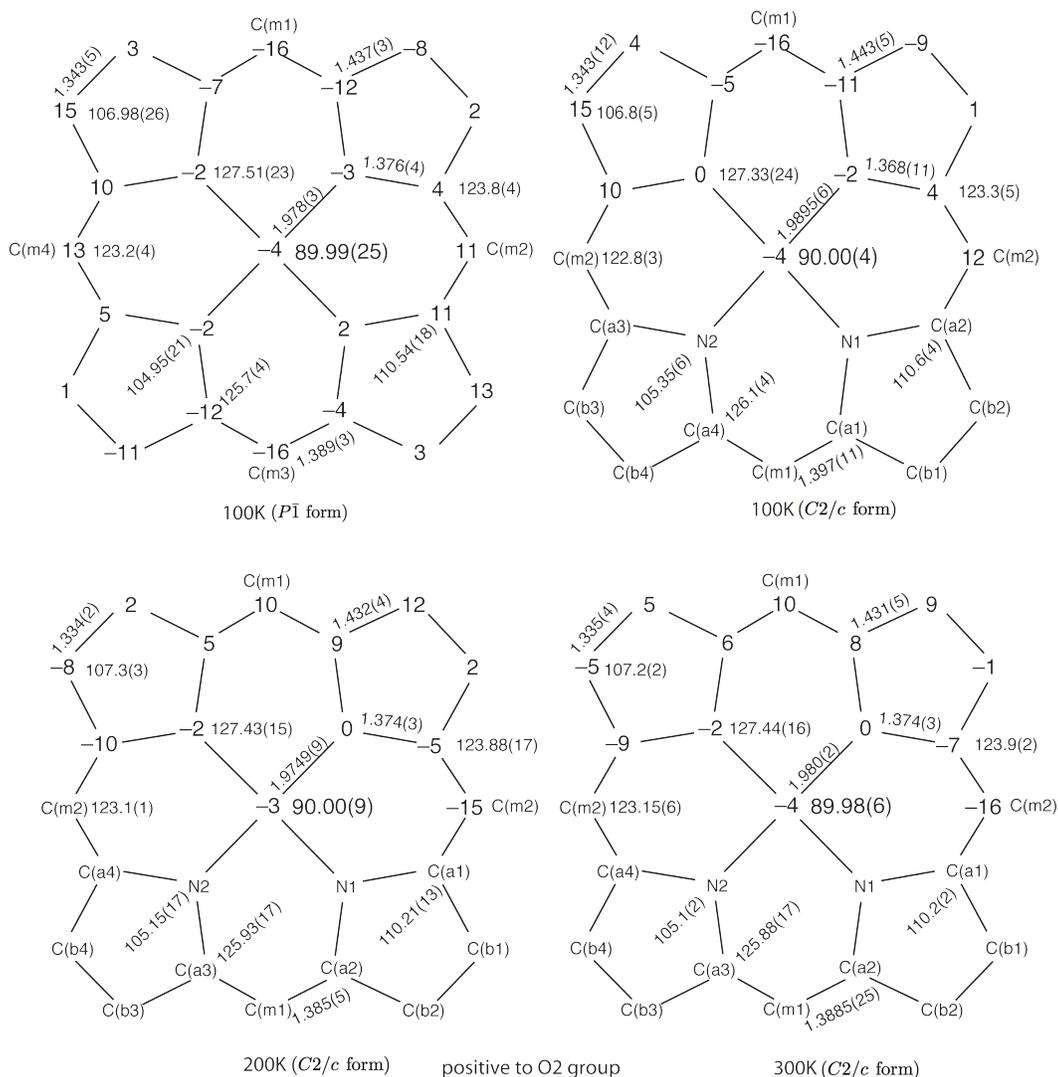
Figure S12. Formal diagrams of the porphyrin cores for [Co(TpivPP)(1-EtIm)(O₂)] at 100, 200 and 300 K. Averaged values of the chemically unique bond distances (in Å) and angles (in degrees) are shown. The numbers in parentheses are the esd's calculated on the assumption that the averaged values were all drawn from the same population. The perpendicular displacements (in units of 0.01 Å) of the porphyrin core atoms from the 24-atom mean plane are also displayed (positive values to pocket porphyrin side). For the three $C2/c$ form structures, the molecule has twofold symmetry; the twofold axis-related atoms have the same value of the displacement.
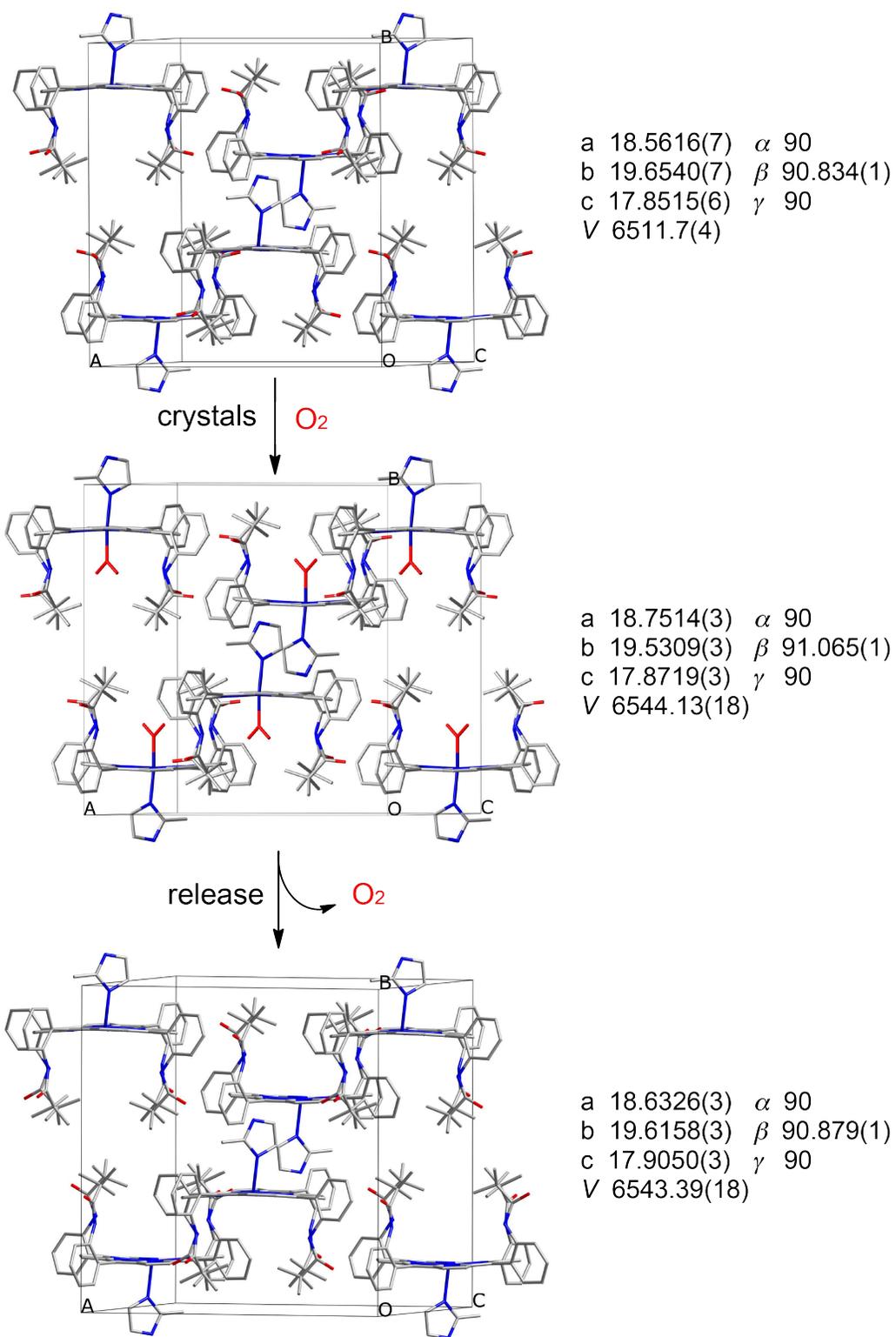
a 18.5616(7) α 90
b 19.6540(7) β 90.834(1)
c 17.8515(6) γ 90
V 6511.7(4)

crystals | O$_2$

a 18.7514(3) α 90
b 19.5309(3) β 91.065(1)
c 17.8719(3) γ 90
V 6544.13(18)

release | O$_2$

a 18.6326(3) α 90
b 19.6158(3) β 90.879(1)
c 17.9050(3) γ 90
V 6543.39(18)

Figure S13.   Packing diagrams of [Co(TpivPP)(2-MeHIm)] and the oxygen adduct [Co(TpivPP)(2-MeHIm)(O$_2$)], showing the unit cell.   Only one orientation of the pickets is shown in the oxygen complexes and hydrogens omitted for clarity.
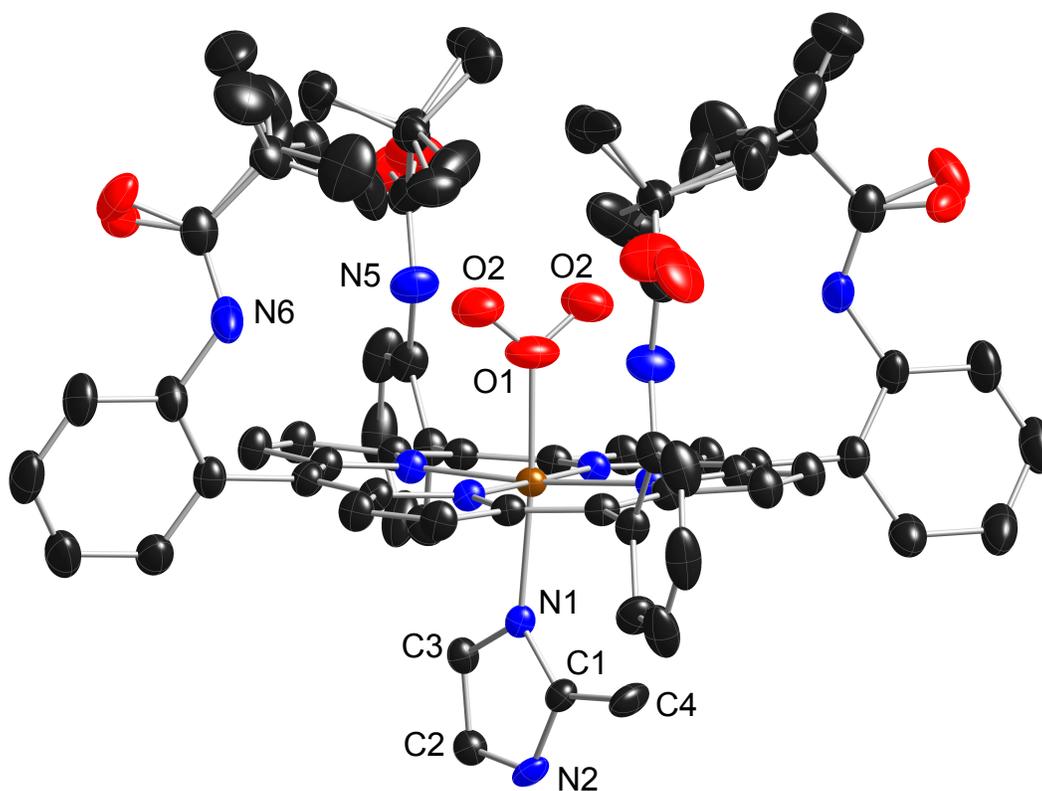
Figure S14. An edge-on thermal ellipsoid diagram of [Co(TpivPP)(2-MeHIm)(O₂)] (100 K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.
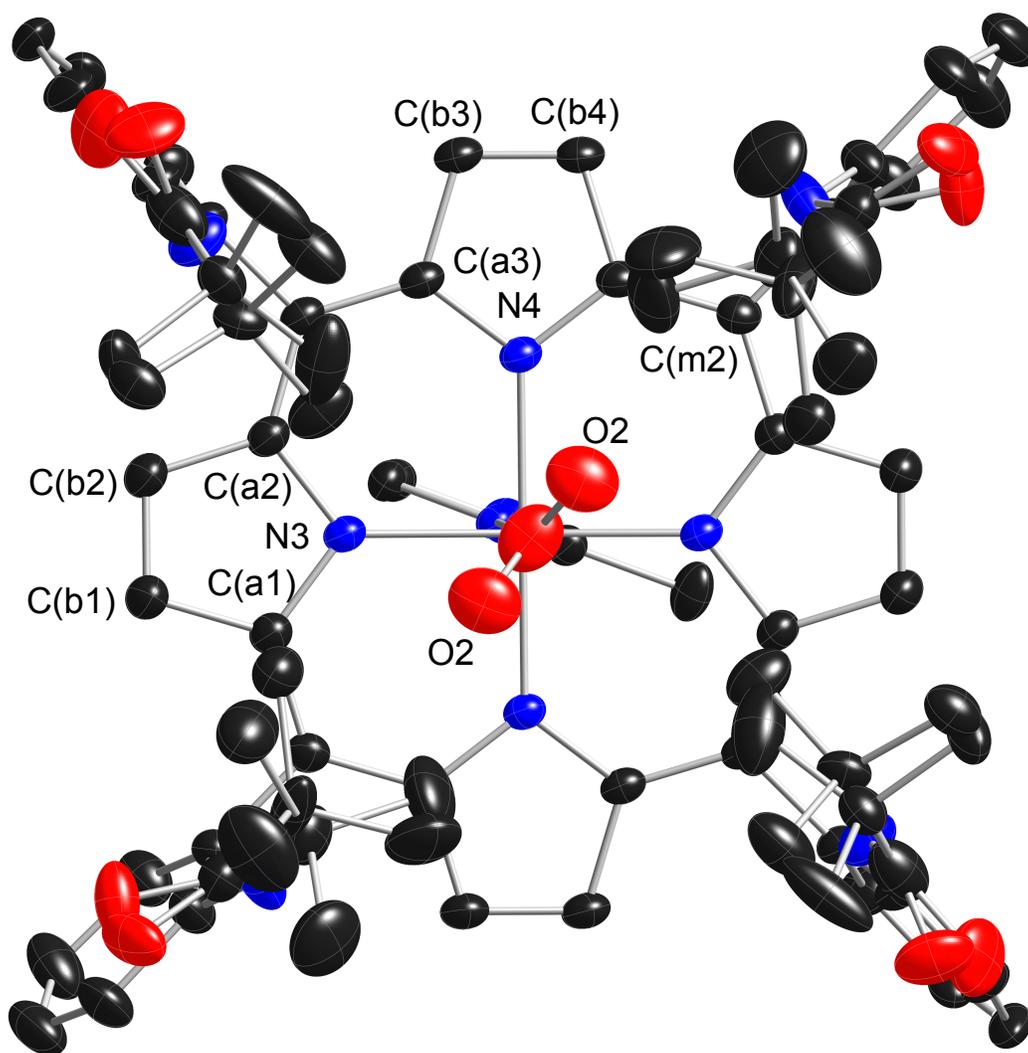
Figure S15. Top down view of the thermal ellipsoid diagram of [Co(TpivPP)(2-MeHIm)(O₂)] (100 K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.
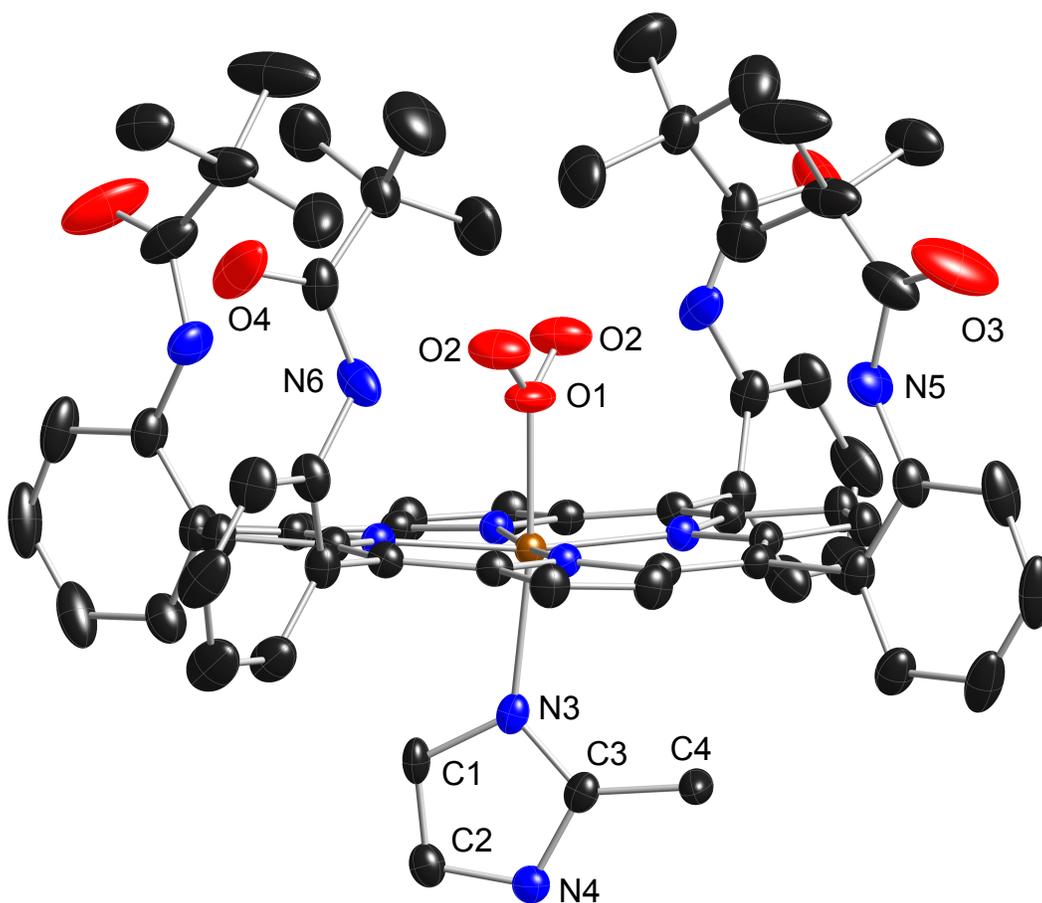
Figure S16. An edge-on thermal ellipsoid diagram of [Co(TpivPP)(2-MeHIm)0.4(O₂)] (100 K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.
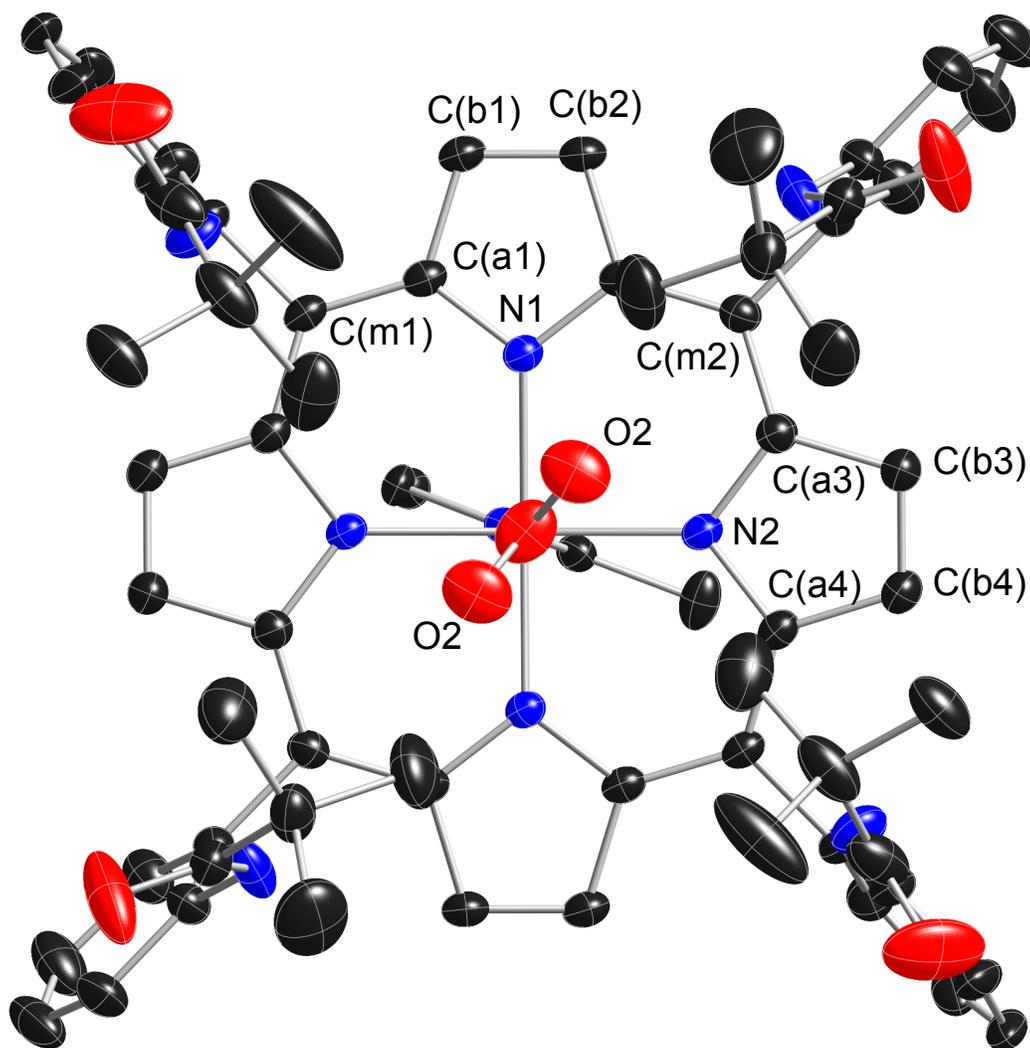
Figure S17. A top down view of the thermal ellipsoid diagram of [Co(TpivPP)(2-MeHIm)0.4(O$_2$)] (100 K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.
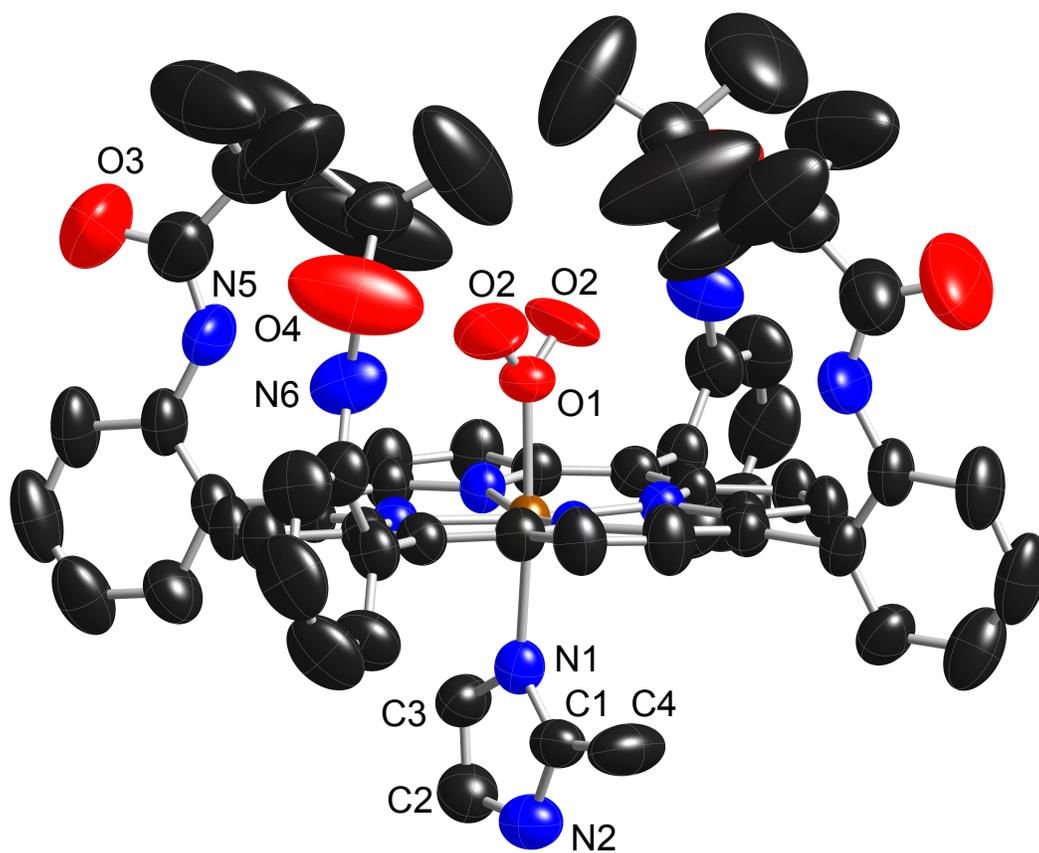
Figure S18. An edge-on view of the thermal ellipsoid diagram of [Co(TpivPP)(2-MeHIm)0.3(O$_2$)] (300 K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.
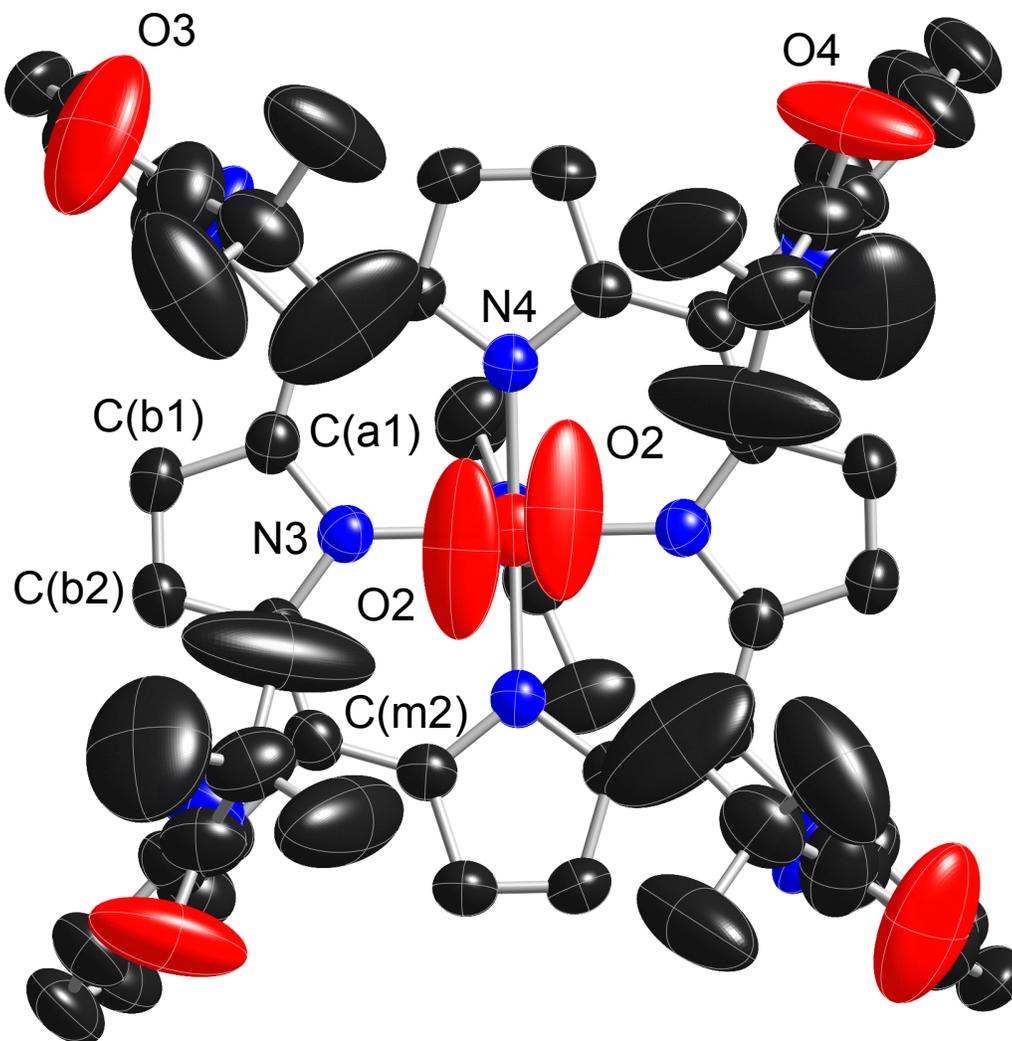
Figure S19. A top down view of the thermal ellipsoid diagram of [Co(TpivPP)(2-MeHIm)0.3(O₂)] (300 K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.
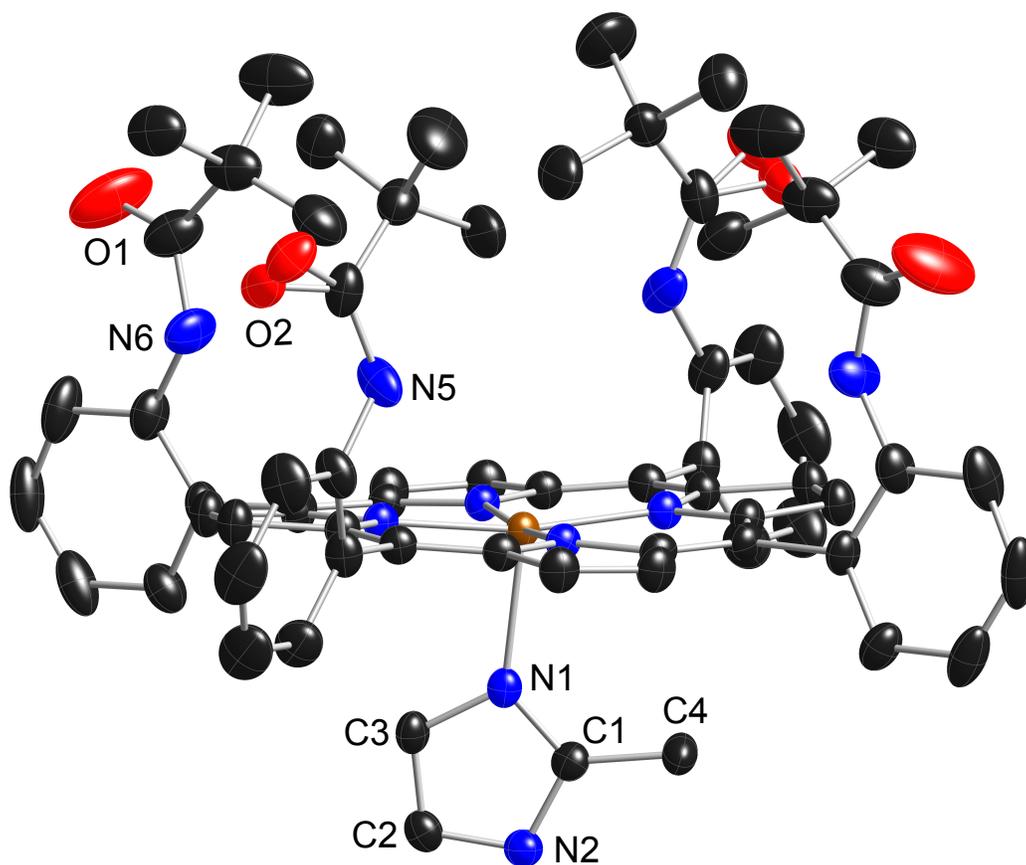
Figure S20. An edge-on thermal ellipsoid diagram of [Co(TpivPP)(2-MeHIm)] (100 K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.
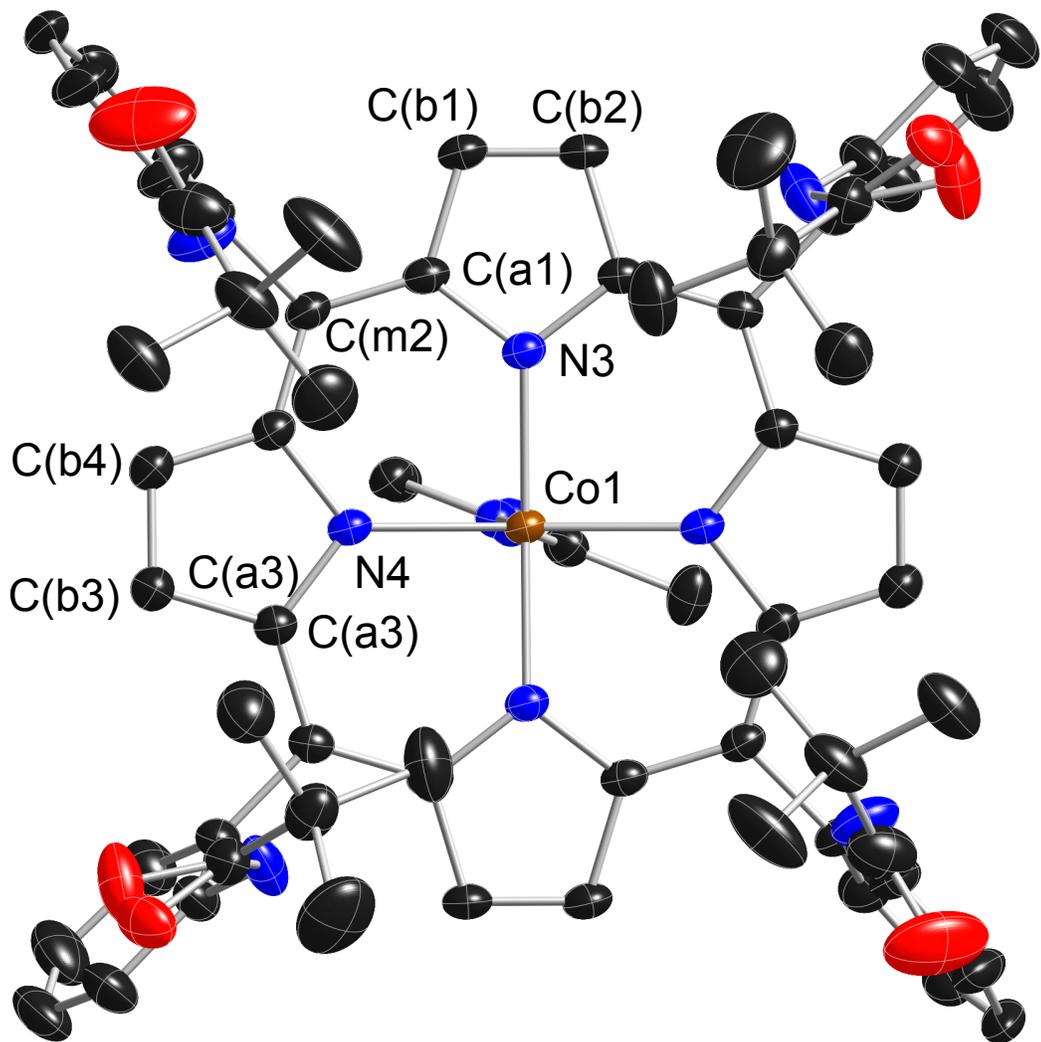
Figure S21. A top down view of the thermal ellipsoid diagram of [Co(TpivPP)(2-MeHIm)] (100 K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure S22. Formal diagram of the porphyrin cores of [Co(TpivPP)(2-MeHIm)] and oxygen adducts structure. Averaged values of the chemically unique bond distances (in Å) and angles (in degrees) are shown. The numbers in parentheses are the esd's calculated on the assumption that the averaged values were all drawn from the same population. The perpendicular displacements (in units of 0.01 Å) of the porphyrin core atoms from the 24-atom mean plane are also displayed (positive values to picket porphyrin side). All molecules have twofold symmetry; the twofold axis-related atoms have the same value of the displacement.

PF Synthesis modifications

Separation of the $\alpha,\alpha,\alpha,\alpha$-H$_2T_{NH_2}$PP

Modifications has been made on the separation of H$_2$T$_{NH_2}$PP isomers to improve the yield of the $\alpha,\alpha,\alpha,\alpha$-H$_2T_{NH_2}$PP, which is the most polar of the four atropisomers of H$_2$T$_{NH_2}$PP.

Adsorption and equilibrium. In a three-neck 2 L round bottom flask, 3 g of H$_2$T$_{NH_2}$PP was dissolved in ~1 L of CHCl$_3$, then ~250 g of silica gel (mesh 60-200) was added to this solution. The resultant red-green mixture was refluxed for two days with a stir bar to prevent "bumping" and under argon to avoid oxidation. After filtration, the silica gel was washed several times with CHCl$_3$ until the filtrate became almost colorless. This filtrate, called Fraction **I**, contains the "other" three isomers. Then the silica gel was washed with acetone-ethyl ether (1:1). This filtrate, called Fraction **II**, contains mainly the $\alpha,\alpha,\alpha,\alpha$-H$_2T_{NH_2}$PP isomer. CHCl$_3$ from Fraction **I** is removed to give solid H$_2$T$_{NH_2}$PP. Fraction **II** is evaporated to dryness and kept in freezer to prevent isomerization. Care must be exercised to prevent excessive heating which leads to isomerization of the $\alpha,\alpha,\alpha,\alpha$ isomer (the temperature of the water bath should below 30°C).

Chromatography. The chromatography can be followed by TLC (CHCl$_3$-EtO$_2$ 1:1 or C$_6$H$_6$-EtO$_2$ 1:1). The eluant used for the column chromatography is cooled to help prevent isomerization.

First column. Solid Fraction **II** is dissolved in about 300 mL of CHCl$_3$ then loaded onto a silica gel column (mesh 60-200, 6~7 in. × 2 in.). The column is eluted with CHCl$_3$ until the eluant is light red in color, then eluted with CHCl$_3$-EtO$_2$ (1:1) until the eluant is very pale in color. These fractions are combined with Fraction **I** (see above). Acetone-ethyl ether (1:1) is then used to remove the remaining $\alpha,\alpha,\alpha,\alpha$ isomer. The solution containing this isomer is

brought to dryness on a rotary evaporator.

Second column. The crude $\alpha, \alpha, \alpha, \alpha$ isomer from the first column (in $\sim$200 mL CHCl$_3$) is loaded onto a silica gel column (mesh 60-200, 5$\sim$6 in. $\times$ 2 in.), then eluted with benzene-ethyl ether (1:1) until the eluant is very pale. The pure $\alpha, \alpha, \alpha, \alpha$ isomer is then removed by elution with acetone-ethyl ether (1:1). This deeply red solution is brought to dryness on a rotary evaporator. The TLC showed some pink-blue impurities. To get rid of these, the solid was dissolved in $\sim$300 mL of CH$_2$Cl$_2$ and $\sim$100 g of "carbon, decolorizing NORIT A" was added. This mixture was stirred for $\sim$30 min at room temperature. After filtration and evaporation of the solvent, the compound can be either recrystallized (CH$_2$Cl$_2$-EtOH) or used as is to synthesize picket fence porphyrin.

The combined Fraction **I**, which contains four isomers mixture, is evaporated to yield solid H$_2$T$_{NH_2}$PP. This H$_2$T$_{NH_2}$PP will be used in the next preparation of the $\alpha, \alpha, \alpha, \alpha$ isomer.

Modifications on the Synthesis of [Co(TpivPP)]

50 mL freshly distilled PhCl is transferred to a Schlenk where 0.8 g anhydrous CoCl$_2$ has been loaded. The mixture is refluxed for 2 hours and then the solvent is distilled under argon. The residue is evaporated to dryness under vacuum to give homogeneous fine powder. Then the [H$_2$(TpivPP)], 2,6-lutidine and THF is transferred to the Schlenk to conduct the metalation reaction following the reported reaction and separation procedures (Collman, J. P. *et al.* *J. Am. Chem. Soc.* **1978**, *100*, 2761.).

Table S1. Complete Crystallographic Details for $[\text{Co(TpivPP)(1-EtIm)(O}_2)]\cdot\text{C}_6\text{H}_6$ (100 K, $P\bar{1}$ form)

formula	$\text{C}_{75}\text{H}_{78}\text{CoN}_{10}\text{O}_6$
FW, amu	1274.40
a, Å	13.0971(9)
b, Å	13.5557(9)
c, Å	18.2431(12)
α, deg	89.216(4)
β, deg	88.444(3)
γ, deg	88.190(3)
V, Å^3	3235.8(4)
space group	$P\bar{1}$
Z	2
D_c, g/cm^3	1.308
F(000)	1346
μ, mm^{-1}	0.328
crystal dimensions, mm	$0.39 \times 0.26 \times 0.19$
radiation	MoKα, $\bar{\lambda} = 0.71073$ Å
temperature, K	100(2)
diffractometer	Bruker Apex CCD
θ range for collected data, deg	1.12–27.50
index range	$-16 \leq \text{h} \leq 17$
	$-17 \leq \text{k} \leq 17$
	$0 \leq \text{l} \leq 23$
total data collected	14752
absorption correction	Semi-empirical from equiv
relative transmission coefficients (I)	0.9402 and 0.8826
unique data	14752 ($R_\text{int} = 0.000$)
unique observed data $[\text{I} > 2\sigma(\text{I})]$	11334
refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	14752/0/840
goodness-of-fit (pased on F^2)	1.084
final R indices $[\text{I} > 2\sigma(\text{I})]$	$R_1 = 0.0496$, $wR_2 = 0.1276$
final R indices (all data)	$R_1 = 0.0744$, $wR_2 = 0.1466$

Table S2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters
(Å^2) for $[\text{Co}(\text{TpivPP})(1\text{-EtIm})(\text{O}_2)]\cdot\text{C}_6\text{H}_6$ (100 K, $P\bar{1}$ form)^a

atom	x	y	z	$U(\text{eq})$
Co(1)	0.86574(2)	0.86177(3)	0.74498(2)	0.0142(1)
O(1)	0.75770(16)	0.77108(15)	0.74678(11)	0.0249(4)
O(2a)	0.7684(2)	0.68960(19)	0.77771(14)	0.0306(8)
O(2b)	0.6817(9)	0.7784(10)	0.7305(7)	0.037(4)
O(3)	0.53787(18)	0.79972(18)	1.08660(11)	0.0356(5)
O(4)	0.98034(19)	0.32767(17)	0.88924(14)	0.0412(6)
O(5)	0.79572(18)	0.53612(18)	0.41818(11)	0.0348(5)
O(6)	0.32231(15)	0.97895(17)	0.61707(12)	0.0312(5)
N(1)	0.76791(16)	0.95892(16)	0.78998(11)	0.0153(4)
N(2)	0.90821(16)	0.81843(16)	0.84371(11)	0.0153(4)
N(3)	0.95930(16)	0.76127(17)	0.70000(11)	0.0167(4)
N(4)	0.82165(16)	0.90433(16)	0.64613(11)	0.0154(4)
N(5)	0.97810(16)	0.96019(17)	0.74048(12)	0.0193(4)
N(6)	1.07772(17)	1.08020(18)	0.76685(14)	0.0250(5)
N(7)	0.63301(18)	0.86855(19)	0.99561(12)	0.0244(5)
N(8)	0.9725(2)	0.49006(19)	0.86017(15)	0.0313(6)
N(9)	0.85828(18)	0.64212(19)	0.49880(12)	0.0241(5)
N(10)	0.49547(18)	0.97243(18)	0.61948(13)	0.0256(5)
C(a1)	0.69636(19)	1.0184(2)	0.75472(14)	0.0171(5)
C(a2)	0.7528(2)	0.9791(2)	0.86299(14)	0.0184(5)
C(a3)	0.87794(19)	0.8581(2)	0.91016(13)	0.0170(5)
C(a4)	0.97577(19)	0.7424(2)	0.86078(13)	0.0168(5)
C(a5)	1.01948(19)	0.6915(2)	0.73558(14)	0.0177(5)
C(a6)	0.98019(19)	0.7466(2)	0.62653(13)	0.0174(5)
C(a7)	0.86185(19)	0.8739(2)	0.57976(13)	0.0169(5)
C(a8)	0.7460(2)	0.9730(2)	0.62948(14)	0.0180(5)
C(b1)	0.6354(2)	1.0743(2)	0.80711(14)	0.0215(6)
C(b2)	0.6712(2)	1.0507(2)	0.87354(15)	0.0214(6)
C(b3)	0.9267(2)	0.8054(2)	0.96928(14)	0.0198(5)
C(b4)	0.9867(2)	0.7344(2)	0.93907(14)	0.0211(6)
C(b5)	1.0766(2)	0.6316(2)	0.68359(14)	0.0218(6)
C(b6)	1.0528(2)	0.6662(2)	0.61624(15)	0.0222(6)
C(b7)	0.8107(2)	0.9244(2)	0.52046(14)	0.0200(6)
C(b8)	0.7389(2)	0.9845(2)	0.55129(14)	0.0215(6)

Table S2. Continued

atom	x	y	z	U(eq)
C(m1)	0.8065(2)	0.9348(2)	0.92004(14)	0.0182(5)
C(m2)	1.0282(2)	0.6820(2)	0.81104(14)	0.0176(5)
C(m3)	0.93812(19)	0.8013(2)	0.56926(13)	0.0171(5)
C(m4)	0.6852(2)	1.0265(2)	0.67913(14)	0.0180(5)
C(1)	0.9887(2)	1.0356(2)	0.78350(16)	0.0249(6)
C(2)	1.1259(2)	1.0309(2)	0.71219(15)	0.0263(6)
C(3)	1.0644(2)	0.9569(2)	0.69524(16)	0.0255(6)
C(4)	1.1156(2)	1.1621(2)	0.81007(17)	0.0311(7)
C(5)	1.2018(3)	1.2144(3)	0.7688(2)	0.0436(9)
C(6)	0.7808(2)	0.9687(2)	0.99653(14)	0.0188(5)
C(7)	0.6934(2)	0.9333(2)	1.03375(14)	0.0213(6)
C(8)	0.6680(2)	0.9662(2)	1.10426(15)	0.0250(6)
C(9)	0.7301(2)	1.0327(2)	1.13725(15)	0.0271(7)
C(10)	0.8162(2)	1.0677(2)	1.10177(16)	0.0265(6)
C(11)	0.8411(2)	1.0351(2)	1.03122(15)	0.0236(6)
C(12)	1.1042(2)	0.6073(2)	0.83994(13)	0.0188(5)
C(13)	1.0759(2)	0.5139(2)	0.86567(15)	0.0245(6)
C(14)	1.1492(3)	0.4487(3)	0.89389(17)	0.0341(7)
C(15)	1.2501(2)	0.4744(3)	0.89424(17)	0.0368(8)
C(16)	1.2794(2)	0.5642(3)	0.86740(17)	0.0340(8)
C(17)	1.2067(2)	0.6309(2)	0.84145(15)	0.0260(6)
C(18)	0.9704(2)	0.7770(2)	0.49196(14)	0.0194(6)
C(19)	0.9282(2)	0.6983(2)	0.45656(14)	0.0194(6)
C(20)	0.9549(2)	0.6776(2)	0.38387(14)	0.0235(6)
C(21)	1.0235(2)	0.7379(2)	0.34684(15)	0.0267(7)
C(22)	1.0659(2)	0.8161(2)	0.38040(15)	0.0273(7)
C(23)	1.0394(2)	0.8354(2)	0.45357(15)	0.0234(6)
C(24)	0.6082(2)	1.1010(2)	0.65135(14)	0.0203(6)
C(25)	0.5150(2)	1.0735(2)	0.62297(15)	0.0228(6)
C(26)	0.4453(2)	1.1459(2)	0.59872(16)	0.0289(7)
C(27)	0.4668(2)	1.2445(2)	0.60530(16)	0.0305(7)
C(28)	0.5571(2)	1.2725(2)	0.63468(17)	0.0303(7)
C(29)	0.6277(2)	1.2004(2)	0.65647(15)	0.0248(6)
C(30)	0.5612(2)	0.8069(2)	1.02161(14)	0.0234(6)

Table S2. Continued

atom	x	y	z	U(eq)
C(31)	0.5086(2)	0.7457(2)	0.96425(15)	0.0232(6)
C(32)	0.3932(2)	0.7625(3)	0.97739(19)	0.0365(8)
C(33)	0.5369(3)	0.6370(2)	0.97927(18)	0.0363(8)
C(34)	0.5361(3)	0.7730(3)	0.88485(16)	0.0446(9)
C(35)	0.9317(2)	0.3999(2)	0.86842(15)	0.0269(6)
C(36)	0.8185(2)	0.3958(2)	0.85183(16)	0.0290(7)
C(37)	0.7887(3)	0.2871(3)	0.8524(2)	0.0417(8)
C(38)	0.7985(3)	0.4397(3)	0.77569(17)	0.0344(7)
C(39)	0.7579(2)	0.4510(3)	0.91179(17)	0.0361(8)
C(40)	0.7984(2)	0.5680(2)	0.48016(14)	0.0200(6)
C(41)	0.7354(2)	0.5232(2)	0.54399(14)	0.0198(5)
C(42)	0.6259(2)	0.5137(2)	0.51839(16)	0.0277(6)
C(43)	0.7836(2)	0.4213(2)	0.55941(17)	0.0280(6)
C(44)	0.7335(2)	0.5848(2)	0.61379(15)	0.0255(6)
C(45)	0.4022(2)	0.9308(2)	0.61884(14)	0.0222(6)
C(46)	0.4017(2)	0.8178(2)	0.62260(15)	0.0250(6)
C(47)	0.3550(2)	0.7912(3)	0.69790(17)	0.0339(7)
C(48)	0.3301(3)	0.7838(3)	0.56279(18)	0.0398(8)
C(49)	0.5066(3)	0.7680(2)	0.61110(18)	0.0348(7)
C(1S)	0.3990(3)	0.5090(3)	0.70056(18)	0.0385(8)
C(2S)	0.3685(3)	0.4163(3)	0.72187(19)	0.0388(8)
C(3S)	0.4205(3)	0.3641(3)	0.77608(19)	0.0373(8)
C(4S)	0.5027(2)	0.4051(3)	0.80864(17)	0.0343(7)
C(5S)	0.5332(3)	0.4986(3)	0.78780(19)	0.0365(8)
C(6S)	0.4815(3)	0.5501(3)	0.73332(19)	0.0394(8)

[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 S3. Bond Lengths for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (100 K, $P\bar{1}$ form)[a]

bond	length (Å)	bond	length (Å)
Co(1)–O(1)	1.9029(19)	C(14)–C(15)	1.377(5)
Co(1)–N(3)	1.975(2)	C(14)–H(14a)	0.9500
Co(1)–N(2)	1.976(2)	C(15)–C(16)	1.368(5)
Co(1)–N(1)	1.979(2)	C(15)–H(15a)	0.9500
Co(1)–N(4)	1.981(2)	C(16)–C(17)	1.381(4)
Co(1)–N(5)	2.017(2)	C(16)–H(16a)	0.9500
O(1)–O(2b)	1.048(12)	C(17)–H(17a)	0.9500
O(1)–O(2a)	1.239(3)	C(18)–C(23)	1.389(4)
O(3)–C(30)	1.220(3)	C(18)–C(19)	1.391(4)
O(4)–C(35)	1.213(4)	C(19)–C(20)	1.392(4)
O(5)–C(40)	1.218(3)	C(20)–C(21)	1.389(4)
O(6)–C(45)	1.217(3)	C(20)–H(20a)	0.9500
N(1)–C(a2)	1.371(3)	C(21)–C(22)	1.372(5)
N(1)–C(a1)	1.383(3)	C(21)–H(21a)	0.9500
N(2)–C(a4)	1.375(3)	C(22)–C(23)	1.397(4)
N(2)–C(a3)	1.376(3)	C(22)–H(22a)	0.9500
N(3)–C(a6)	1.377(3)	C(23)–H(23a)	0.9500
N(3)–C(a5)	1.379(3)	C(24)–C(29)	1.385(4)
N(4)–C(a7)	1.371(3)	C(24)–C(25)	1.402(4)
N(4)–C(a8)	1.375(3)	C(25)–C(26)	1.395(4)
N(5)–C(1)	1.310(4)	C(26)–C(27)	1.383(5)
N(5)–C(3)	1.381(4)	C(26)–H(26a)	0.9500
N(6)–C(2)	1.340(4)	C(27)–C(28)	1.379(5)
N(6)–C(1)	1.356(4)	C(27)–H(27a)	0.9500
N(6)–C(4)	1.476(4)	C(28)–C(29)	1.385(4)
N(7)–C(30)	1.350(4)	C(28)–H(28a)	0.9500
N(7)–C(7)	1.404(4)	C(29)–H(29a)	0.9500
N(7)–H(7a)	0.8800	C(30)–C(31)	1.535(4)
N(8)–C(35)	1.354(4)	C(31)–C(34)	1.527(4)
N(8)–C(13)	1.410(4)	C(31)–C(33)	1.531(4)
N(8)–H(8a)	0.8800	C(31)–C(32)	1.534(4)
N(9)–C(40)	1.347(4)	C(32)–H(32a)	0.9800
N(9)–C(19)	1.415(4)	C(32)–H(32b)	0.9800
N(9)–H(9a)	0.8800	C(32)–H(32C)	0.9800

Table S3. Continued

bond	length (Å)	bond	length (Å)
N(10)–C(45)	1.362(4)	C(33)–H(33a)	0.9800
N(10)–C(25)	1.404(4)	C(33)–H(33b)	0.9800
N(10)–H(10a)	0.8800	C(33)–H(33C)	0.9800
C(a1)–C(m4)	1.393(4)	C(34)–H(34a)	0.9800
C(a1)–C(b1)	1.437(4)	C(34)–H(34b)	0.9800
C(a2)–C(m1)	1.391(4)	C(34)–H(34C)	0.9800
C(a2)–C(b2)	1.432(4)	C(35)–C(36)	1.524(5)
C(a3)–C(m1)	1.386(4)	C(36)–C(39)	1.525(4)
C(a3)–C(b3)	1.439(4)	C(36)–C(38)	1.529(4)
C(a4)–C(m2)	1.384(4)	C(36)–C(37)	1.536(5)
C(a4)–C(b4)	1.442(3)	C(37)–H(37a)	0.9800
C(a5)–C(m2)	1.388(4)	C(37)–H(37b)	0.9800
C(a5)–C(b5)	1.436(4)	C(37)–H(37C)	0.9800
C(a6)–C(m3)	1.389(4)	C(38)–H(38a)	0.9800
C(a6)–C(b6)	1.434(4)	C(38)–H(38b)	0.9800
C(a7)–C(m3)	1.391(4)	C(38)–H(38C)	0.9800
C(a7)–C(b7)	1.441(3)	C(39)–H(39a)	0.9800
C(a8)–C(m4)	1.387(4)	C(39)–H(39b)	0.9800
C(a8)–C(b8)	1.438(4)	C(39)–H(39C)	0.9800
C(b1)–C(b2)	1.342(4)	C(40)–C(41)	1.538(4)
C(b1)–H(ba)	0.9500	C(41)–C(43)	1.527(4)
C(b2)–H(bb)	0.9500	C(41)–C(42)	1.531(4)
C(b3)–C(b4)	1.338(4)	C(41)–C(44)	1.531(4)
C(b3)–H(bC)	0.9500	C(42)–H(42a)	0.9800
C(b4)–H(bd)	0.9500	C(42)–H(42b)	0.9800
C(b5)–C(b6)	1.350(4)	C(42)–H(42C)	0.9800
C(b5)–H(be)	0.9500	C(43)–H(43a)	0.9800
C(b6)–H(bF)	0.9500	C(43)–H(43b)	0.9800
C(b7)–C(b8)	1.342(4)	C(43)–H(43C)	0.9800
C(b7)–H(bg)	0.9500	C(44)–H(44a)	0.9800
C(b8)–H(bH)	0.9500	C(44)–H(44b)	0.9800
C(m1)–C(6)	1.501(3)	C(44)–H(44C)	0.9800
C(m2)–C(12)	1.498(3)	C(45)–C(46)	1.532(4)
C(m3)–C(18)	1.499(3)	C(46)–C(49)	1.522(4)

Table S3. Continued

bond	length (Å)	bond	length (Å)
C(m4)–C(24)	1.498(3)	C(46)–C(47)	1.532(4)
C(1)–H(1a)	0.9500	C(46)–C(48)	1.542(4)
C(2)–C(3)	1.350(4)	C(47)–H(47a)	0.9800
C(2)–H(2a)	0.9500	C(47)–H(47b)	0.9800
C(3)–H(3a)	0.9500	C(47)–H(47C)	0.9800
C(4)–C(5)	1.527(5)	C(48)–H(48a)	0.9800
C(4)–H(4a)	0.9900	C(48)–H(48b)	0.9800
C(4)–H(4b)	0.9900	C(48)–H(48C)	0.9800
C(5)–H(5a)	0.9800	C(49)–H(49a)	0.9800
C(5)–H(5b)	0.9800	C(49)–H(49b)	0.9800
C(5)–H(5C)	0.9800	C(49)–H(49C)	0.9800
C(6)–C(11)	1.388(4)	C(1S)–C(2S)	1.378(5)
C(6)–C(7)	1.408(4)	C(1S)–C(6S)	1.385(5)
C(7)–C(8)	1.396(4)	C(1S)–H(1Sa)	0.9500
C(8)–C(9)	1.386(4)	C(2S)–C(3S)	1.389(5)
C(8)–H(8b)	0.9500	C(2S)–H(2Sa)	0.9500
C(9)–C(10)	1.379(5)	C(3S)–C(4S)	1.379(5)
C(9)–H(9b)	0.9500	C(3S)–H(3Sa)	0.9500
C(10)–C(11)	1.394(4)	C(4S)–C(5S)	1.385(5)
C(10)–H(10b)	0.9500	C(4S)–H(4Sa)	0.9500
C(11)–H(11a)	0.9500	C(5S)–C(6S)	1.386(5)
C(12)–C(17)	1.391(4)	C(5S)–H(5Sa)	0.9500
C(12)–C(13)	1.401(4)	C(6S)–H(6Sa)	0.9500
C(13)–C(14)	1.389(4)		

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

Table S4. Bond Angles for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (100 K, $P\bar{1}$ form)^a

angle	degree	angle	degree
O(1)–Co(1)–N(3)	90.41(9)	C(12)–C(17)–H(17a)	119.4
O(1)–Co(1)–N(2)	91.53(9)	C(23)–C(18)–C(19)	119.1(2)
N(3)–Co(1)–N(2)	90.32(9)	C(23)–C(18)–C(m3)	120.4(3)
O(1)–Co(1)–N(1)	87.48(9)	C(19)–C(18)–C(m3)	120.5(2)
N(3)–Co(1)–N(1)	177.89(8)	C(18)–C(19)–C(20)	120.8(3)
N(2)–Co(1)–N(1)	89.79(8)	C(18)–C(19)–N(9)	116.1(2)
O(1)–Co(1)–N(4)	87.80(9)	C(20)–C(19)–N(9)	123.2(3)
N(3)–Co(1)–N(4)	89.80(9)	C(21)–C(20)–C(19)	118.8(3)
N(2)–Co(1)–N(4)	179.32(8)	C(21)–C(20)–H(20a)	120.6
N(1)–Co(1)–N(4)	90.06(8)	C(19)–C(20)–H(20a)	120.6
O(1)–Co(1)–N(5)	178.20(10)	C(22)–C(21)–C(20)	121.6(3)
N(3)–Co(1)–N(5)	90.11(10)	C(22)–C(21)–H(21a)	119.2
N(2)–Co(1)–N(5)	90.18(9)	C(20)–C(21)–H(21a)	119.2
N(1)–Co(1)–N(5)	92.00(9)	C(21)–C(22)–C(23)	119.1(3)
N(4)–Co(1)–N(5)	90.48(9)	C(21)–C(22)–H(22a)	120.5
O(2b)–O(1)–O(2a)	107.6(8)	C(23)–C(22)–H(22a)	120.5
O(2b)–O(1)–Co(1)	131.7(8)	C(18)–C(23)–C(22)	120.7(3)
O(2a)–O(1)–Co(1)	120.3(2)	C(18)–C(23)–H(23a)	119.6
C(a2)–N(1)–C(a1)	104.7(2)	C(22)–C(23)–H(23a)	119.6
C(a2)–N(1)–Co(1)	127.83(17)	C(29)–C(24)–C(25)	118.8(2)
C(a1)–N(1)–Co(1)	127.40(16)	C(29)–C(24)–C(m4)	119.1(3)
C(a4)–N(2)–C(a3)	105.0(2)	C(25)–C(24)–C(m4)	122.1(3)
C(a4)–N(2)–Co(1)	127.24(16)	C(26)–C(25)–C(24)	119.8(3)
C(a3)–N(2)–Co(1)	127.78(17)	C(26)–C(25)–N(10)	122.0(3)
C(a6)–N(3)–C(a5)	104.9(2)	C(24)–C(25)–N(10)	118.1(2)
C(a6)–N(3)–Co(1)	127.71(17)	C(27)–C(26)–C(25)	119.8(3)
C(a5)–N(3)–Co(1)	127.40(17)	C(27)–C(26)–H(26a)	120.1
C(a7)–N(4)–C(a8)	105.2(2)	C(25)–C(26)–H(26a)	120.1
C(a7)–N(4)–Co(1)	127.48(16)	C(28)–C(27)–C(26)	120.8(3)
C(a8)–N(4)–Co(1)	127.27(17)	C(28)–C(27)–H(27a)	119.6
C(1)–N(5)–C(3)	105.8(2)	C(26)–C(27)–H(27a)	119.6
C(1)–N(5)–Co(1)	127.27(19)	C(27)–C(28)–C(29)	119.2(3)
C(3)–N(5)–Co(1)	126.7(2)	C(27)–C(28)–H(28a)	120.4
C(2)–N(6)–C(1)	108.6(3)	C(29)–C(28)–H(28a)	120.4

angle	degree	angle	degree
C(2)–N(6)–C(4)	128.3(3)	C(24)–C(29)–C(28)	121.5(3)
C(1)–N(6)–C(4)	122.8(3)	C(24)–C(29)–H(29a)	119.3
C(30)–N(7)–C(7)	129.5(2)	C(28)–C(29)–H(29a)	119.3
C(30)–N(7)–H(7a)	115.3	O(3)–C(30)–N(7)	122.9(3)
C(7)–N(7)–H(7a)	115.3	O(3)–C(30)–C(31)	121.0(3)
C(35)–N(8)–C(13)	127.4(3)	N(7)–C(30)–C(31)	116.1(2)
C(35)–N(8)–H(8a)	116.3	C(34)–C(31)–C(33)	110.1(3)
C(13)–N(8)–H(8a)	116.3	C(34)–C(31)–C(32)	109.0(3)
C(40)–N(9)–C(19)	131.1(2)	C(33)–C(31)–C(32)	109.1(3)
C(40)–N(9)–H(9a)	114.4	C(34)–C(31)–C(30)	114.5(3)
C(19)–N(9)–H(9a)	114.4	C(33)–C(31)–C(30)	107.5(2)
C(45)–N(10)–C(25)	126.8(2)	C(32)–C(31)–C(30)	106.5(2)
C(45)–N(10)–H(10a)	116.6	C(31)–C(32)–H(32a)	109.5
C(25)–N(10)–H(10a)	116.6	C(31)–C(32)–H(32b)	109.5
N(1)–C(a1)–C(m4)	125.8(2)	H(32a)–C(32)–H(32b)	109.5
N(1)–C(a1)–C(b1)	110.5(2)	C(31)–C(32)–H(32C)	109.5
C(m4)–C(a1)–C(b1)	123.7(2)	H(32a)–C(32)–H(32C)	109.5
N(1)–C(a2)–C(m1)	125.4(2)	H(32b)–C(32)–H(32C)	109.5
N(1)–C(a2)–C(b2)	110.8(2)	C(31)–C(33)–H(33a)	109.5
C(m1)–C(a2)–C(b2)	123.8(2)	C(31)–C(33)–H(33b)	109.5
N(2)–C(a3)–C(m1)	125.4(2)	H(33a)–C(33)–H(33b)	109.5
N(2)–C(a3)–C(b3)	110.5(2)	C(31)–C(33)–H(33C)	109.5
C(m1)–C(a3)–C(b3)	124.0(2)	H(33a)–C(33)–H(33C)	109.5
N(2)–C(a4)–C(m2)	125.9(2)	H(33b)–C(33)–H(33C)	109.5
N(2)–C(a4)–C(b4)	110.4(2)	C(31)–C(34)–H(34a)	109.5
C(m2)–C(a4)–C(b4)	123.7(2)	C(31)–C(34)–H(34b)	109.5
N(3)–C(a5)–C(m2)	125.5(2)	H(34a)–C(34)–H(34b)	109.5
N(3)–C(a5)–C(b5)	110.6(2)	C(31)–C(34)–H(34C)	109.5
C(m2)–C(a5)–C(b5)	123.8(2)	H(34a)–C(34)–H(34C)	109.5
N(3)–C(a6)–C(m3)	125.6(2)	H(34b)–C(34)–H(34C)	109.5
N(3)–C(a6)–C(b6)	110.7(2)	O(4)–C(35)–N(8)	123.0(3)
C(m3)–C(a6)–C(b6)	123.7(2)	O(4)–C(35)–C(36)	121.9(3)
N(4)–C(a7)–C(m3)	125.8(2)	N(8)–C(35)–C(36)	115.1(3)
N(4)–C(a7)–C(b7)	110.6(2)	C(35)–C(36)–C(39)	108.3(3)

Table S4. Continued

angle	degree	angle	degree
C(m3)–C(a7)–C(b7)	123.5(2)	C(35)–C(36)–C(38)	110.2(2)
N(4)–C(a8)–C(m4)	126.5(2)	C(39)–C(36)–C(38)	112.0(3)
N(4)–C(a8)–C(b8)	110.2(2)	C(35)–C(36)–C(37)	108.3(3)
C(m4)–C(a8)–C(b8)	123.3(2)	C(39)–C(36)–C(37)	109.7(3)
C(b2)–C(b1)–C(a1)	106.7(2)	C(38)–C(36)–C(37)	108.4(3)
C(b2)–C(b1)–H(ba)	126.6	C(36)–C(37)–H(37a)	109.5
C(a1)–C(b1)–H(ba)	126.6	C(36)–C(37)–H(37b)	109.5
C(b1)–C(b2)–C(a2)	107.3(2)	H(37a)–C(37)–H(37b)	109.5
C(b1)–C(b2)–H(bb)	126.4	C(36)–C(37)–H(37C)	109.5
C(a2)–C(b2)–H(bb)	126.4	H(37a)–C(37)–H(37C)	109.5
C(b4)–C(b3)–C(a3)	107.0(2)	H(37b)–C(37)–H(37C)	109.5
C(b4)–C(b3)–H(bC)	126.5	C(36)–C(38)–H(38a)	109.5
C(a3)–C(b3)–H(bC)	126.5	C(36)–C(38)–H(38b)	109.5
C(b3)–C(b4)–C(a4)	107.1(2)	H(38a)–C(38)–H(38b)	109.5
C(b3)–C(b4)–H(bd)	126.5	C(36)–C(38)–H(38C)	109.5
C(a4)–C(b4)–H(bd)	126.5	H(38a)–C(38)–H(38C)	109.5
C(b6)–C(b5)–C(a5)	106.8(2)	H(38b)–C(38)–H(38C)	109.5
C(b6)–C(b5)–H(be)	126.6	C(36)–C(39)–H(39a)	109.5
C(a5)–C(b5)–H(be)	126.6	C(36)–C(39)–H(39b)	109.5
C(b5)–C(b6)–C(a6)	107.0(2)	H(39a)–C(39)–H(39b)	109.5
C(b5)–C(b6)–H(bF)	126.5	C(36)–C(39)–H(39C)	109.5
C(a6)–C(b6)–H(bF)	126.5	H(39a)–C(39)–H(39C)	109.5
C(b8)–C(b7)–C(a7)	106.6(2)	H(39b)–C(39)–H(39C)	109.5
C(b8)–C(b7)–H(bg)	126.7	O(5)–C(40)–N(9)	123.3(3)
C(a7)–C(b7)–H(bg)	126.7	O(5)–C(40)–C(41)	121.8(3)
C(b7)–C(b8)–C(a8)	107.3(2)	N(9)–C(40)–C(41)	114.9(2)
C(b7)–C(b8)–H(bH)	126.3	C(43)–C(41)–C(42)	110.3(2)
C(a8)–C(b8)–H(bH)	126.3	C(43)–C(41)–C(44)	109.8(2)
C(a3)–C(m1)–C(a2)	123.5(2)	C(42)–C(41)–C(44)	108.9(2)
C(a3)–C(m1)–C(6)	118.8(2)	C(43)–C(41)–C(40)	106.3(2)
C(a2)–C(m1)–C(6)	117.6(2)	C(42)–C(41)–C(40)	107.7(2)
C(a4)–C(m2)–C(a5)	123.6(2)	C(44)–C(41)–C(40)	113.8(2)
C(a4)–C(m2)–C(12)	118.1(2)	C(41)–C(42)–H(42a)	109.5
C(a5)–C(m2)–C(12)	118.1(2)	C(41)–C(42)–H(42b)	109.5

Table S4. Continued

angle	degree	angle	degree
C(a6)–C(m3)–C(a7)	123.0(2)	H(42a)–C(42)–H(42b)	109.5
C(a6)–C(m3)–C(18)	119.0(2)	C(41)–C(42)–H(42C)	109.5
C(a7)–C(m3)–C(18)	117.8(2)	H(42a)–C(42)–H(42C)	109.5
C(a8)–C(m4)–C(a1)	122.8(2)	H(42b)–C(42)–H(42C)	109.5
C(a8)–C(m4)–C(24)	119.5(2)	C(41)–C(43)–H(43a)	109.5
C(a1)–C(m4)–C(24)	117.7(2)	C(41)–C(43)–H(43b)	109.5
N(5)–C(1)–N(6)	110.0(3)	H(43a)–C(43)–H(43b)	109.5
N(5)–C(1)–H(1a)	125.0	C(41)–C(43)–H(43C)	109.5
N(6)–C(1)–H(1a)	125.0	H(43a)–C(43)–H(43C)	109.5
N(6)–C(2)–C(3)	106.1(3)	H(43b)–C(43)–H(43C)	109.5
N(6)–C(2)–H(2a)	127.0	C(41)–C(44)–H(44a)	109.5
C(3)–C(2)–H(2a)	127.0	C(41)–C(44)–H(44b)	109.5
C(2)–C(3)–N(5)	109.6(3)	H(44a)–C(44)–H(44b)	109.5
C(2)–C(3)–H(3a)	125.2	C(41)–C(44)–H(44C)	109.5
N(5)–C(3)–H(3a)	125.2	H(44a)–C(44)–H(44C)	109.5
N(6)–C(4)–C(5)	111.2(3)	H(44b)–C(44)–H(44C)	109.5
N(6)–C(4)–H(4a)	109.4	O(6)–C(45)–N(10)	123.1(3)
C(5)–C(4)–H(4a)	109.4	O(6)–C(45)–C(46)	120.5(3)
N(6)–C(4)–H(4b)	109.4	N(10)–C(45)–C(46)	116.4(2)
C(5)–C(4)–H(4b)	109.4	C(49)–C(46)–C(47)	111.2(3)
H(4a)–C(4)–H(4b)	108.0	C(49)–C(46)–C(45)	114.0(3)
C(4)–C(5)–H(5a)	109.5	C(47)–C(46)–C(45)	106.1(2)
C(4)–C(5)–H(5b)	109.5	C(49)–C(46)–C(48)	109.2(3)
H(5a)–C(5)–H(5b)	109.5	C(47)–C(46)–C(48)	108.8(3)
C(4)–C(5)–H(5C)	109.5	C(45)–C(46)–C(48)	107.3(2)
H(5a)–C(5)–H(5C)	109.5	C(46)–C(47)–H(47a)	109.5
H(5b)–C(5)–H(5C)	109.5	C(46)–C(47)–H(47b)	109.5
C(11)–C(6)–C(7)	119.2(2)	H(47a)–C(47)–H(47b)	109.5
C(11)–C(6)–C(m1)	121.1(2)	C(46)–C(47)–H(47C)	109.5
C(7)–C(6)–C(m1)	119.7(2)	H(47a)–C(47)–H(47C)	109.5
C(8)–C(7)–N(7)	123.0(3)	H(47b)–C(47)–H(47C)	109.5
C(8)–C(7)–C(6)	119.9(3)	C(46)–C(48)–H(48a)	109.5
N(7)–C(7)–C(6)	117.1(2)	C(46)–C(48)–H(48b)	109.5
C(9)–C(8)–C(7)	119.4(3)	H(48a)–C(48)–H(48b)	109.5

Table S4. Continued

angle	degree	angle	degree
C(9)–C(8)–H(8b)	120.3	C(46)–C(48)–H(48C)	109.5
C(7)–C(8)–H(8b)	120.3	H(48a)–C(48)–H(48C)	109.5
C(10)–C(9)–C(8)	121.5(3)	H(48b)–C(48)–H(48C)	109.5
C(10)–C(9)–H(9b)	119.2	C(46)–C(49)–H(49a)	109.5
C(8)–C(9)–H(9b)	119.2	C(46)–C(49)–H(49b)	109.5
C(9)–C(10)–C(11)	119.0(3)	H(49a)–C(49)–H(49b)	109.5
C(9)–C(10)–H(10b)	120.5	C(46)–C(49)–H(49C)	109.5
C(11)–C(10)–H(10b)	120.5	H(49a)–C(49)–H(49C)	109.5
C(6)–C(11)–C(10)	121.0(3)	H(49b)–C(49)–H(49C)	109.5
C(6)–C(11)–H(11a)	119.5	C(2S)–C(1S)–C(6S)	119.9(3)
C(10)–C(11)–H(11a)	119.5	C(2S)–C(1S)–H(1Sa)	120.0
C(17)–C(12)–C(13)	118.4(2)	C(6S)–C(1S)–H(1Sa)	120.0
C(17)–C(12)–C(m2)	119.2(3)	C(1S)–C(2S)–C(3S)	120.1(4)
C(13)–C(12)–C(m2)	122.4(2)	C(1S)–C(2S)–H(2Sa)	120.0
C(14)–C(13)–C(12)	119.9(3)	C(3S)–C(2S)–H(2Sa)	120.0
C(14)–C(13)–N(8)	122.8(3)	C(4S)–C(3S)–C(2S)	120.0(4)
C(12)–C(13)–N(8)	117.3(2)	C(4S)–C(3S)–H(3Sa)	120.0
C(15)–C(14)–C(13)	120.0(3)	C(2S)–C(3S)–H(3Sa)	120.0
C(15)–C(14)–H(14a)	120.0	C(3S)–C(4S)–C(5S)	120.2(3)
C(13)–C(14)–H(14a)	120.0	C(3S)–C(4S)–H(4Sa)	119.9
C(16)–C(15)–C(14)	120.8(3)	C(5S)–C(4S)–H(4Sa)	119.9
C(16)–C(15)–H(15a)	119.6	C(4S)–C(5S)–C(6S)	119.7(4)
C(14)–C(15)–H(15a)	119.6	C(4S)–C(5S)–H(5Sa)	120.2
C(15)–C(16)–C(17)	119.7(3)	C(6S)–C(5S)–H(5Sa)	120.2
C(15)–C(16)–H(16a)	120.2	C(1S)–C(6S)–C(5S)	120.2(4)
C(17)–C(16)–H(16a)	120.2	C(1S)–C(6S)–H(6Sa)	119.9
C(16)–C(17)–C(12)	121.1(3)	C(5S)–C(6S)–H(6Sa)	119.9
C(16)–C(17)–H(17a)	119.4		

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

Table S5. Anisotropic Displacement Parameters (Å^2) for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (100 K, $P\bar{1}$ form)^a

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co(1)	0.0156(2)	0.0147(2)	0.0122(2)	−0.0005(1)	0.0001(1)	0.0003(1)
O(1)	0.0288(12)	0.0239(11)	0.0223(10)	−0.0028(9)	0.0028(9)	−0.0075(8)
O(2A)	0.0398(16)	0.0196(15)	0.0327(15)	0.0045(11)	−0.0024(12)	−0.0072(11)
O(2B)	0.022(7)	0.047(9)	0.043(8)	0.000(6)	−0.014(5)	−0.005(5)
O(3)	0.0481(14)	0.0429(14)	0.0161(10)	−0.0026(10)	0.0049(9)	−0.0101(11)
O(4)	0.0481(14)	0.0259(12)	0.0489(14)	0.0061(11)	−0.0006(11)	0.0071(11)
O(5)	0.0407(13)	0.0446(14)	0.0198(10)	−0.0118(10)	0.0022(9)	−0.0110(11)
O(6)	0.0225(10)	0.0347(13)	0.0358(12)	−0.0007(10)	0.0002(9)	0.0057(9)
N(1)	0.0168(10)	0.0160(11)	0.0132(10)	−0.0009(8)	−0.0020(8)	−0.0002(8)
N(2)	0.0165(10)	0.0143(11)	0.0149(10)	−0.0010(8)	0.0012(8)	−0.0005(8)
N(3)	0.0173(10)	0.0186(12)	0.0141(10)	−0.0001(9)	0.0026(8)	0.0009(9)
N(4)	0.0153(10)	0.0154(11)	0.0155(10)	0.0012(9)	−0.0017(8)	0.0003(8)
N(5)	0.0205(11)	0.0200(12)	0.0177(10)	0.0045(9)	−0.0054(9)	−0.0014(8)
N(6)	0.0239(12)	0.0184(12)	0.0333(14)	0.0038(10)	−0.0079(10)	−0.0034(9)
N(7)	0.0281(12)	0.0336(14)	0.0119(10)	−0.0076(10)	0.0011(9)	−0.0066(11)
N(8)	0.0299(13)	0.0230(13)	0.0407(15)	0.0096(12)	−0.0036(11)	0.0034(11)
N(9)	0.0314(13)	0.0309(14)	0.0099(10)	−0.0032(10)	0.0042(9)	−0.0050(11)
N(10)	0.0201(11)	0.0235(13)	0.0334(13)	−0.0040(11)	−0.0050(10)	0.0050(10)
C(A1)	0.0164(12)	0.0166(13)	0.0183(12)	−0.0009(10)	0.0004(10)	0.0000(10)
C(A2)	0.0210(13)	0.0184(14)	0.0158(12)	−0.0064(10)	0.0007(10)	0.0009(10)
C(A3)	0.0191(12)	0.0178(13)	0.0145(12)	−0.0037(10)	−0.0004(10)	−0.0034(10)
C(A4)	0.0165(12)	0.0197(14)	0.0145(12)	0.0014(10)	−0.0016(10)	−0.0019(10)
C(A5)	0.0177(12)	0.0198(14)	0.0153(12)	−0.0005(10)	0.0010(10)	0.0005(10)
C(A6)	0.0185(12)	0.0194(14)	0.0143(12)	−0.0011(10)	0.0016(10)	−0.0006(10)
C(A7)	0.0179(12)	0.0200(14)	0.0129(12)	0.0002(10)	−0.0018(10)	−0.0018(10)
C(A8)	0.0175(12)	0.0189(14)	0.0176(12)	0.0007(10)	−0.0022(10)	−0.0021(10)
C(B1)	0.0255(14)	0.0185(14)	0.0200(13)	−0.0026(11)	0.0005(11)	0.0043(11)
C(B2)	0.0236(13)	0.0215(14)	0.0189(13)	−0.0051(11)	0.0003(11)	0.0039(11)
C(B3)	0.0236(13)	0.0217(14)	0.0140(12)	0.0000(11)	−0.0015(10)	0.0000(11)
C(B4)	0.0252(14)	0.0238(15)	0.0141(12)	0.0023(11)	−0.0019(10)	0.0019(11)
C(B5)	0.0251(14)	0.0210(15)	0.0188(13)	−0.0018(11)	0.0017(11)	0.0069(11)
C(B6)	0.0242(14)	0.0236(15)	0.0180(13)	−0.0010(11)	0.0040(11)	0.0057(11)
C(B7)	0.0228(13)	0.0226(14)	0.0146(12)	−0.0003(11)	−0.0015(10)	0.0006(11)
C(B8)	0.0225(13)	0.0245(15)	0.0175(13)	0.0013(11)	−0.0062(11)	0.0019(11)

Table S5. Continued

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(M1)	0.0206(13)	0.0207(14)	0.0135(12)	−0.0052(10)	−0.0010(10)	−0.0013(11)
C(M2)	0.0177(12)	0.0169(13)	0.0182(12)	0.0008(10)	−0.0006(10)	0.0004(10)
C(M3)	0.0182(12)	0.0196(14)	0.0135(12)	−0.0006(10)	0.0010(10)	−0.0022(10)
C(M4)	0.0178(12)	0.0175(13)	0.0189(13)	0.0003(10)	−0.0028(10)	−0.0018(10)
C(1)	0.0280(15)	0.0238(15)	0.0230(14)	0.0049(12)	−0.0056(11)	−0.0012(12)
C(2)	0.0251(14)	0.0312(16)	0.0227(14)	0.0013(12)	−0.0018(11)	−0.0041(12)
C(3)	0.0246(14)	0.0282(16)	0.0238(14)	0.0051(12)	−0.0024(11)	−0.0057(12)
C(4)	0.0335(16)	0.0257(16)	0.0349(16)	−0.0101(13)	−0.0071(13)	−0.0018(12)
C(5)	0.048(2)	0.0306(19)	0.053(2)	0.0026(17)	−0.0171(17)	−0.0167(15)
C(6)	0.0225(13)	0.0184(14)	0.0155(12)	−0.0027(10)	−0.0027(10)	0.0046(11)
C(7)	0.0243(13)	0.0232(15)	0.0164(12)	−0.0061(11)	−0.0034(10)	0.0033(11)
C(8)	0.0280(14)	0.0309(16)	0.0158(13)	−0.0052(12)	0.0006(11)	0.0053(12)
C(9)	0.0373(16)	0.0266(16)	0.0169(13)	−0.0095(12)	−0.0039(12)	0.0129(13)
C(10)	0.0334(16)	0.0219(15)	0.0245(14)	−0.0098(12)	−0.0108(12)	0.0052(12)
C(11)	0.0272(14)	0.0233(15)	0.0204(13)	−0.0038(12)	−0.0048(11)	0.0022(12)
C(12)	0.0224(13)	0.0224(14)	0.0114(11)	−0.0034(10)	−0.0013(10)	0.0054(11)
C(13)	0.0266(14)	0.0247(15)	0.0218(14)	0.0016(12)	−0.0042(11)	0.0069(12)
C(14)	0.0412(18)	0.0298(17)	0.0308(16)	0.0057(14)	−0.0086(14)	0.0094(15)
C(15)	0.0318(16)	0.048(2)	0.0300(16)	−0.0041(15)	−0.0120(13)	0.0193(15)
C(16)	0.0250(15)	0.049(2)	0.0278(16)	−0.0093(15)	−0.0084(12)	0.0080(14)
C(17)	0.0237(14)	0.0342(17)	0.0200(13)	−0.0055(12)	−0.0018(11)	0.0031(12)
C(18)	0.0190(12)	0.0243(15)	0.0144(12)	0.0026(11)	0.0020(10)	0.0063(11)
C(19)	0.0227(13)	0.0219(14)	0.0132(12)	0.0003(11)	0.0012(10)	0.0049(11)
C(20)	0.0265(14)	0.0284(16)	0.0150(13)	−0.0020(11)	0.0023(11)	0.0074(12)
C(21)	0.0286(15)	0.0370(18)	0.0132(12)	0.0028(12)	0.0065(11)	0.0097(13)
C(22)	0.0246(14)	0.0362(18)	0.0200(14)	0.0092(12)	0.0074(11)	0.0069(13)
C(23)	0.0237(14)	0.0259(15)	0.0206(13)	0.0024(12)	0.0002(11)	−0.0001(12)
C(24)	0.0203(13)	0.0230(14)	0.0171(12)	0.0022(11)	0.0008(10)	0.0055(11)
C(25)	0.0247(14)	0.0249(15)	0.0186(13)	−0.0016(11)	−0.0012(11)	0.0046(12)
C(26)	0.0274(15)	0.0308(17)	0.0284(15)	0.0030(13)	−0.0051(12)	0.0050(13)
C(27)	0.0355(16)	0.0268(16)	0.0280(15)	0.0084(13)	−0.0001(13)	0.0138(13)
C(28)	0.0363(17)	0.0218(15)	0.0321(16)	0.0052(13)	0.0060(13)	0.0037(13)
C(29)	0.0245(14)	0.0258(15)	0.0236(14)	0.0037(12)	0.0022(11)	0.0019(12)
C(30)	0.0278(14)	0.0254(15)	0.0167(13)	−0.0017(11)	0.0001(11)	0.0050(12)

Table S5. Continued

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(31)	0.0256(14)	0.0250(15)	0.0190(13)	−0.0014(11)	−0.0013(11)	−0.0014(12)
C(32)	0.0316(16)	0.0353(19)	0.0430(19)	−0.0140(15)	−0.0109(14)	0.0083(14)
C(33)	0.0449(19)	0.0312(18)	0.0328(17)	−0.0107(14)	−0.0134(14)	0.0128(15)
C(34)	0.064(2)	0.054(2)	0.0173(15)	−0.0043(15)	−0.0052(15)	−0.0235(19)
C(35)	0.0375(16)	0.0229(15)	0.0197(14)	0.0011(12)	0.0074(12)	0.0004(13)
C(36)	0.0414(17)	0.0245(16)	0.0211(14)	0.0012(12)	0.0041(12)	−0.0052(13)
C(37)	0.047(2)	0.0318(19)	0.046(2)	0.0005(16)	0.0053(16)	−0.0056(15)
C(38)	0.0383(17)	0.0389(19)	0.0255(15)	−0.0002(14)	0.0039(13)	0.0002(14)
C(39)	0.0336(17)	0.044(2)	0.0307(16)	−0.0094(15)	0.0047(13)	0.0012(15)
C(40)	0.0197(13)	0.0219(14)	0.0182(13)	−0.0034(11)	−0.0029(10)	0.0050(11)
C(41)	0.0203(13)	0.0208(14)	0.0182(12)	0.0007(11)	−0.0006(10)	−0.0001(11)
C(42)	0.0228(14)	0.0336(17)	0.0268(15)	0.0003(13)	−0.0043(11)	0.0009(12)
C(43)	0.0264(14)	0.0246(15)	0.0324(16)	0.0050(13)	0.0004(12)	0.0030(12)
C(44)	0.0291(14)	0.0279(16)	0.0198(13)	−0.0011(12)	0.0050(11)	−0.0075(12)
C(45)	0.0250(14)	0.0278(15)	0.0137(12)	−0.0030(11)	0.0007(10)	0.0023(12)
C(46)	0.0268(14)	0.0284(16)	0.0197(13)	−0.0052(12)	0.0018(11)	−0.0017(12)
C(47)	0.0383(17)	0.0361(18)	0.0264(15)	0.0007(13)	0.0063(13)	0.0068(14)
C(48)	0.054(2)	0.0348(19)	0.0313(17)	−0.0065(14)	−0.0096(15)	−0.0050(16)
C(49)	0.0409(18)	0.0259(17)	0.0363(17)	−0.0036(14)	0.0136(14)	0.0083(13)
C(1S)	0.0440(19)	0.043(2)	0.0275(16)	0.0017(15)	−0.0029(14)	0.0110(16)
C(2S)	0.0378(18)	0.044(2)	0.0349(18)	−0.0097(16)	−0.0025(15)	0.0042(16)
C(3S)	0.0393(18)	0.0333(19)	0.0388(18)	−0.0006(15)	0.0052(15)	0.0024(15)
C(4S)	0.0318(16)	0.040(2)	0.0302(16)	0.0027(14)	0.0012(13)	0.0067(14)
C(5S)	0.0311(16)	0.040(2)	0.0380(18)	−0.0028(16)	0.0037(14)	0.0024(14)
C(6S)	0.045(2)	0.037(2)	0.0351(18)	0.0037(15)	0.0053(15)	0.0018(16)

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

Table S6. Hydrogen Atom Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $[Co(TpivPP)(1\text{-EtIm})(O_2)]\cdot C_6H_6$ (100K, $P\bar{1}$ form)^a

atom	x	y	z	$U(\text{eq})$
H(7A)	0.6435	0.8681	0.9478	0.029
H(8A)	0.9295	0.5393	0.8503	0.038
H(9A)	0.8530	0.6585	0.5453	0.029
H(10A)	0.5491	0.9317	0.6175	0.031
H(BA	0.5804	1.1193	0.7967	0.026
H(BB	0.6469	1.0767	0.9191	0.026
H(BC	0.9179	0.8185	1.0201	0.024
H(BD	1.0287	0.6876	0.9644	0.025
H(BE	1.1223	0.5779	0.6945	0.026
H(BF	1.0792	0.6420	0.5707	0.027
H(BG	0.8250	0.9166	0.4695	0.024
H(BH	0.6920	1.0269	0.5261	0.026
H(1A)	0.9409	1.0560	0.8209	0.030
H(2A)	1.1902	1.0451	0.6899	0.032
H(3A)	1.0783	0.9098	0.6579	0.031
H(4A)	1.1409	1.1359	0.8574	0.037
H(4B)	1.0588	1.2100	0.8207	0.037
H(5A)	1.2257	1.2680	0.7987	0.065
H(5B)	1.1765	1.2415	0.7224	0.065
H(5C)	1.2584	1.1671	0.7587	0.065
H(8B)	0.6087	0.9433	1.1294	0.030
H(9B)	0.7129	1.0546	1.1854	0.033
H(10B)	0.8578	1.1133	1.1251	0.032
H(11A)	0.9004	1.0589	1.0065	0.028
H(14A)	1.1298	0.3863	0.9129	0.041
H(15A)	1.2999	0.4293	0.9134	0.044
H(16A)	1.3494	0.5806	0.8666	0.041
H(17A)	1.2270	0.6940	0.8243	0.031
H(20A)	0.9267	0.6233	0.3600	0.028
H(21A)	1.0414	0.7246	0.2971	0.032
H(22A)	1.1128	0.8565	0.3542	0.033
H(23A)	1.0688	0.8891	0.4774	0.028
H(26A)	0.3832	1.1274	0.5777	0.035
H(27A)	0.4187	1.2936	0.5894	0.037

Table S6. Continued

atom	x	y	z	$U(\text{eq})$
H(28A)	0.5709	1.3404	0.6399	0.036
H(29A)	0.6909	1.2197	0.6753	0.030
H(32A)	0.3749	0.7445	1.0281	0.055
H(32B)	0.3562	0.7216	0.9438	0.055
H(32C)	0.3749	0.8323	0.9686	0.055
H(33A)	0.5193	0.6203	1.0304	0.054
H(33B)	0.6104	0.6257	0.9704	0.054
H(33C)	0.4991	0.5955	0.9466	0.054
H(34A)	0.6098	0.7625	0.8761	0.067
H(34B)	0.5174	0.8426	0.8757	0.067
H(34C)	0.4989	0.7315	0.8518	0.067
H(37A)	0.8008	0.2579	0.9009	0.063
H(37B)	0.8302	0.2511	0.8154	0.063
H(37C)	0.7163	0.2830	0.8412	0.063
H(38A)	0.8176	0.5090	0.7742	0.052
H(38B)	0.7258	0.4353	0.7652	0.052
H(38C)	0.8393	0.4027	0.7388	0.052
H(39A)	0.7772	0.5203	0.9114	0.054
H(39B)	0.7729	0.4209	0.9596	0.054
H(39C)	0.6847	0.4473	0.9029	0.054
H(42A)	0.6264	0.4740	0.4739	0.042
H(42B)	0.5962	0.5795	0.5079	0.042
H(42C)	0.5849	0.4815	0.5570	0.042
H(43A)	0.7843	0.3821	0.5146	0.042
H(43B)	0.7437	0.3880	0.5980	0.042
H(43C)	0.8538	0.4283	0.5754	0.042
H(44A)	0.8034	0.5909	0.6307	0.038
H(44B)	0.6921	0.5522	0.6520	0.038
H(44C)	0.7038	0.6506	0.6033	0.038
H(47A)	0.3999	0.8125	0.7364	0.051
H(47B)	0.3474	0.7196	0.7016	0.051
H(47C)	0.2879	0.8245	0.7039	0.051
H(48A)	0.3277	0.7116	0.5638	0.060
H(48B)	0.3559	0.8060	0.5146	0.060

Table S6. Continued

atom	x	y	z	$U(\text{eq})$
H(48C)	0.2613	0.8122	0.5719	0.060
H(49A)	0.5522	0.7888	0.6493	0.052
H(49B)	0.5349	0.7869	0.5628	0.052
H(49C)	0.5003	0.6962	0.6137	0.052
H(1SA)	0.3634	0.5446	0.6634	0.046
H(2SA)	0.3119	0.3881	0.6995	0.047
H(3SA)	0.3995	0.3002	0.7907	0.045
H(4SA)	0.5385	0.3692	0.8455	0.041
H(5SA)	0.5892	0.5272	0.8107	0.044
H(6SA)	0.5028	0.6138	0.7184	0.047

[a] $U(\text{eq})$ 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 S7. Complete Crystallographic Details for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (100 K, $C2/c$ form)

formula	C$_{75}$H$_{78}$CoN$_{10}$O$_6$
FW, amu	1274.40
a, Å	18.586(4)
b, Å	19.170(4)
c, Å	18.316(4)
β, deg	90.25(3)
V, Å^3	6526(2)
space group	$C2/c$
Z	4
D$_c$, g/cm^3	1.297
F(000)	2692
μ, mm^{-1}	0.326
crystal dimensions, mm	0.39 × 0.26 × 0.19
radiation	MoKα, $\bar{\lambda} = 0.71073$ Å
temperature, K	100(2)
diffractometer	Bruker Apex CCD
θ range for collected data, deg	1.89–27.68
index range	$-24 \leq \text{h} \leq 19$
	$-16 \leq \text{k} \leq 25$
	$-23 \leq \text{l} \leq 22$
total data collected	13615
absorption correction	Semi-empirical from equiv
relative transmission coefficients (I)	0.9407 and 0.8835
unique data	4875 ($R_{\text{int}} = 0.0283$)
unique observed data [I > 2σ(I)]	3157
refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	4875/12/484
goodness-of-fit (pased on F^2)	0.945
final R indices [I > 2σ(I)]	$R_1 = 0.0477$, $wR_2 = 0.1139$
final R indices (all data)	$R_1 = 0.0783$, $wR_2 = 0.1226$

Table S8. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (100 K, $C2/c$ form)^a

atom	x	y	z	U(eq)
Co(1)	0.5000	0.86334(2)	0.7500	0.0268(2)
O(1)	0.5000	0.76431(12)	0.7500	0.0446(7)
O(2)	0.5405(2)	0.72887(18)	0.7247(2)	0.0534(10)
O(3)	0.63055(12)	0.66644(11)	1.08331(10)	0.0500(5)
O(4)	0.82864(11)	0.65239(11)	0.61533(13)	0.0533(5)
N(1)	0.59747(12)	0.86157(10)	0.79525(11)	0.0320(5)
N(2)	0.54424(11)	0.86269(9)	0.65126(11)	0.0292(5)
N(5)	0.61142(14)	0.74995(12)	0.99830(11)	0.0450(6)
N(6)	0.74012(12)	0.73249(11)	0.62806(14)	0.0447(6)
C(a1)	0.61427(15)	0.86424(12)	0.86755(14)	0.0337(6)
C(a2)	0.66273(14)	0.85608(11)	0.75970(14)	0.0321(5)
C(a3)	0.61532(14)	0.85918(11)	0.63473(13)	0.0290(5)
C(a4)	0.50922(15)	0.86732(11)	0.58541(13)	0.0318(6)
C(b1)	0.69079(16)	0.85942(14)	0.87851(15)	0.0410(6)
C(b2)	0.72092(15)	0.85373(14)	0.81169(15)	0.0386(6)
C(b3)	0.62589(16)	0.86101(12)	0.55637(14)	0.0362(6)
C(b4)	0.56055(14)	0.86636(12)	0.52656(14)	0.0339(6)
C(m1)	0.56457(14)	0.86994(12)	0.92512(13)	0.0336(6)
C(m2)	0.67274(14)	0.85534(11)	0.68444(14)	0.0317(5)
C(6)	0.59367(14)	0.87306(13)	1.00195(13)	0.0356(6)
C(7)	0.61622(14)	0.81257(13)	1.03813(13)	0.0366(6)
C(8)	0.64254(15)	0.81640(16)	1.10890(14)	0.0416(6)
C(9)	0.64573(14)	0.88046(17)	1.14390(15)	0.0435(7)
C(10)	0.62414(14)	0.94084(16)	1.10932(15)	0.0424(7)
C(11)	0.59851(14)	0.93718(15)	1.03823(14)	0.0381(6)
C(12)	0.61817(15)	0.68297(13)	1.02023(13)	0.0376(6)
C(13)	0.74824(14)	0.85517(12)	0.65635(13)	0.0323(5)
C(14)	0.78071(13)	0.79492(14)	0.62833(13)	0.0365(6)
C(15)	0.85111(14)	0.79761(16)	0.60193(15)	0.0455(7)
C(16)	0.88947(16)	0.85862(15)	0.60597(15)	0.0474(7)
C(17)	0.85869(16)	0.91868(16)	0.63529(15)	0.0488(7)
C(18)	0.78848(15)	0.91605(14)	0.65887(14)	0.0402(6)
C(19)	0.76536(14)	0.66651(14)	0.62484(15)	0.0404(6)
C(20)	0.6050(3)	0.6292(3)	0.9552(2)	0.0315(17)

Table S8. Continued

atom	x	y	z	$U(\text{eq})$
C(21)	0.6797(2)	0.6026(3)	0.9401(4)	0.0408(18)
C(22)	0.5729(5)	0.6585(2)	0.8860(2)	0.0365(17)
C(23)	0.5587(3)	0.5702(6)	0.9824(7)	0.039(2)
C(20b)	0.6206(4)	0.6255(4)	0.9643(3)	0.032(2)
C(21b)	0.6842(3)	0.5781(5)	0.9765(5)	0.049(2)
C(22b)	0.6208(7)	0.6515(4)	0.8867(3)	0.056(3)
C(23b)	0.5521(3)	0.5856(9)	0.9782(8)	0.051(3)
C(24)	0.70842(17)	0.60818(16)	0.62210(18)	0.0296(13)
C(25)	0.7162(2)	0.5761(3)	0.69686(17)	0.0471(15)
C(26)	0.7265(3)	0.5546(2)	0.5649(2)	0.0598(18)
C(27)	0.6321(2)	0.6327(3)	0.6112(3)	0.0525(18)
C(24b)	0.71257(17)	0.60771(14)	0.64826(18)	0.0309(18)
C(25b)	0.67725(17)	0.61681(16)	0.72155(19)	0.0435(17)
C(26b)	0.75228(19)	0.53919(13)	0.6467(2)	0.0529(19)
C(27b)	0.6559(2)	0.60827(17)	0.5891(2)	0.052(2)
C(1S)	0.97516(11)	1.01660(9)	0.77921(13)	0.0688(10)
C(2S)	0.94799(9)	0.95447(10)	0.80334(10)	0.0468(7)
C(3S)	0.97413(8)	0.89328(9)	0.77688(13)	0.0498(7)
N(3)	0.4913(3)	0.96866(10)	0.7409(4)	0.0241(13)
C(1)	0.5249(2)	1.01349(17)	0.7829(2)	0.0267(11)
N(4)	0.5035(3)	1.07930(12)	0.76649(18)	0.0291(14)
C(2)	0.4556(3)	1.07626(14)	0.71169(19)	0.0290(10)
C(3)	0.4474(2)	1.00792(18)	0.6958(3)	0.0247(11)
C(4)	0.5278(3)	1.1417(2)	0.8069(3)	0.0379(12)
C(5)	0.5119(5)	1.2089(2)	0.7673(3)	0.053(3)

[a] $U(\text{eq})$ 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 S9. Bond Lengths for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (100 K, $C2/c$ form)^a

bond	length (Å)	bond	length (Å)
Co(1)–O(1)	1.899(2)	C(21)–H(21b)	0.9800
Co(1)–N(1)#1)	1.989(2)	C(21)–H(21C)	0.9800
Co(1)–N(1)	1.989(2)	C(22)–H(22a)	0.9800
Co(1)–N(2)#1)	1.9900(19)	C(22)–H(22b)	0.9800
Co(1)–N(2)	1.9900(19)	C(22)–H(22C)	0.9800
Co(1)–N(3)#1)	2.032(2)	C(23)–H(23a)	0.9800
Co(1)–N(3)	2.0322(19)	C(23)–H(23b)	0.9800
O(1)–O(2)#1	1.116(4)	C(23)–H(23C)	0.9800
O(1)–O(2)	1.116(4)	C(20b)–C(21b)	1.5067
O(2)–O(2)#1	1.771(8)	C(20b)–C(23b)	1.5070
O(3)–C(12)	1.219(3)	C(20b)–C(22b)	1.5070
O(4)–C(19)	1.220(3)	C(21b)–H(21d)	0.9800
N(1)–C(a1)	1.360(3)	C(21b)–H(21e)	0.9800
N(1)–C(a2)	1.383(3)	C(21b)–H(21F)	0.9800
N(2)–C(a3)	1.358(3)	C(22b)–H(22d)	0.9800
N(2)–C(a4)	1.371(4)	C(22b)–H(22e)	0.9800
N(5)–C(12)	1.351(3)	C(22b)–H(22F)	0.9800
N(5)–C(7)	1.407(3)	C(23b)–H(23d)	0.9800
N(5)–H(5a)	0.8800	C(23b)–H(23e)	0.9800
N(6)–C(19)	1.350(3)	C(23b)–H(23F)	0.9800
N(6)–C(14)	1.415(3)	C(24)–C(27)	1.5070
N(6)–H(6a)	0.8800	C(24)–C(25)	1.5070
C(a1)–C(m1)	1.409(3)	C(24)–C(26)	1.5070
C(a1)–C(b1)	1.438(4)	C(25)–H(25a)	0.9800
C(a2)–C(m2)	1.392(3)	C(25)–H(25b)	0.9800
C(a2)–C(b2)	1.439(4)	C(25)–H(25C)	0.9800
C(a3)–C(m2)	1.402(4)	C(26)–H(26a)	0.9800
C(a3)–C(b3)	1.450(3)	C(26)–H(26b)	0.9800
C(a4)–C(m1#1)	1.385(4)	C(26)–H(26C)	0.9800
C(a4)–C(b4)	1.443(3)	C(27)–H(27a)	0.9800
C(b1)–C(b2)	1.353(4)	C(27)–H(27b)	0.9800
C(b1)–H(ba)	0.9500	C(27)–H(27C)	0.9800
C(b2)–H(bb)	0.9500	C(24b)–C(27b)	1.5068
C(b3)–C(b4)	1.333(4)	C(24b)–C(26b)	1.5069

Table S9. Continued

bond	length (Å)	bond	length (Å)
C(b3)–H(bC)	0.9500	C(24b)–C(25b)	1.5070
C(b4)–H(bd)	0.9500	C(25b)–H(25d)	0.9800
C(m1)–C(a4#1)	1.385(4)	C(25b)–H(25e)	0.9800
C(m1)–C(6)	1.506(4)	C(25b)–H(25F)	0.9800
C(m2)–C(13)	1.497(3)	C(26b)–H(26d)	0.9800
C(6)–C(7)	1.399(4)	C(26b)–H(26e)	0.9800
C(6)–C(11)	1.400(3)	C(26b)–H(26F)	0.9800
C(7)–C(8)	1.385(4)	C(27b)–H(27d)	0.9800
C(8)–C(9)	1.387(4)	C(27b)–H(27e)	0.9800
C(8)–H(8a)	0.9500	C(27b)–H(27F)	0.9800
C(9)–C(10)	1.378(4)	C(1S)–C(2S)	1.3679
C(9)–H(9a)	0.9500	C(1S)–C(1S)#2	1.416(5)
C(10)–C(11)	1.386(4)	C(1S)–H(1Sa)	0.9500
C(10)–H(10a)	0.9500	C(2S)–C(3S)	1.3598
C(11)–H(11a)	0.9500	C(2S)–H(2Sa)	0.9500
C(12)–C(20b)	1.505(7)	C(3S)–C(3S)#2	1.379(4)
C(12)–C(20)	1.593(7)	C(3S)–H(3Sa)	0.9500
C(13)–C(18)	1.387(3)	N(3)–C(1)	1.3102
C(13)–C(14)	1.402(3)	N(3)–C(3)	1.3810
C(14)–C(15)	1.398(3)	C(1)–N(4)	1.3562
C(15)–C(16)	1.372(4)	C(1)–H(1a)	0.9500
C(15)–H(15a)	0.9500	N(4)–C(2)	1.3404
C(16)–C(17)	1.394(4)	N(4)–C(4)	1.477(5)
C(16)–H(16a)	0.9500	C(2)–C(3)	1.3503
C(17)–C(18)	1.377(4)	C(2)–H(2a)	0.9500
C(17)–H(17a)	0.9500	C(3)–H(3a)	0.9500
C(18)–H(18a)	0.9500	C(4)–C(5)	1.507(7)
C(19)–C(24)	1.540(4)	C(4)–H(4a)	0.9900
C(19)–C(24b)	1.556(4)	C(4)–H(4b)	0.9900
C(20)–C(22)	1.5069	C(5)–H(5b)	0.9800
C(20)–C(21)	1.5069	C(5)–H(5C)	0.9800
C(20)–C(23)	1.5070	C(5)–H(5d)	0.9800
C(21)–H(21a)	0.9800		

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

Table S10. Bond Angles for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (100 K, $C2/c$ form)^a

angle	degree	angle	degree
O(1)–Co(1)–N(1)#1	89.02(5)	C(20)–C(21)–H(21C)	109.5
O(1)–Co(1)–N(1)	89.02(5)	H(21a)–C(21)–H(21C)	109.5
N(1)#1–Co(1)–N(1)	178.05(11)	H(21b)–C(21)–H(21C)	109.5
O(1)–Co(1)–N(2)#1	89.64(5)	C(20)–C(22)–H(22a)	109.5
N(1)#1–Co(1)–N(2)#1	89.96(9)	C(20)–C(22)–H(22b)	109.5
N(1)–Co(1)–N(2)#1	90.03(9)	H(22a)–C(22)–H(22b)	109.5
O(1)–Co(1)–N(2)	89.64(5)	C(20)–C(22)–H(22C)	109.5
N(1)#1–Co(1)–N(2)	90.03(9)	H(22a)–C(22)–H(22C)	109.5
N(1)–Co(1)–N(2)	89.96(9)	H(22b)–C(22)–H(22C)	109.5
N(2)#1–Co(1)–N(2)	179.28(10)	C(20)–C(23)–H(23a)	109.5
O(1)–Co(1)–N(3)#1	173.44(11)	C(20)–C(23)–H(23b)	109.5
N(1)#1–Co(1)–N(3)#1	97.07(13)	H(23a)–C(23)–H(23b)	109.5
N(1)–Co(1)–N(3)#1	84.88(13)	C(20)–C(23)–H(23C)	109.5
N(2)#1–Co(1)–N(3)#1	88.0(2)	H(23a)–C(23)–H(23C)	109.5
N(2)–Co(1)–N(3)#1	92.8(2)	H(23b)–C(23)–H(23C)	109.5
O(1)–Co(1)–N(3)	173.44(11)	C(12)–C(20b)–C(21b)	111.4(5)
N(1)#1–Co(1)–N(3)	84.88(13)	C(12)–C(20b)–C(23b)	103.2(8)
N(1)–Co(1)–N(3)	97.07(13)	C(21b)–C(20b)–C(23b)	109.5
N(2)#1–Co(1)–N(3)	92.8(2)	C(12)–C(20b)–C(22b)	113.5(5)
N(2)–Co(1)–N(3)	88.0(2)	C(21b)–C(20b)–C(22b)	109.5
N(3)#1–Co(1)–N(3)	13.1(2)	C(23b)–C(20b)–C(22b)	109.5
O(2)#1–O(1)–O(2)	105.0(4)	C(20b)–C(21b)–H(21d)	109.5
O(2)#1–O(1)–Co(1)	127.5(2)	C(20b)–C(21b)–H(21e)	109.5
O(2)–O(1)–Co(1)	127.5(2)	H(21d)–C(21b)–H(21e)	109.5
O(1)–O(2)–O(2)#1	37.5(2)	C(20b)–C(21b)–H(21F)	109.5
C(a1)–N(1)–C(a2)	105.3(2)	H(21d)–C(21b)–H(21f)	109.5
C(a1)–N(1)–Co(1)	127.57(18)	H(21e)–C(21b)–H(21f)	109.5
C(a2)–N(1)–Co(1)	127.16(18)	C(20b)–C(22b)–H(22d)	109.5
C(a3)–N(2)–C(a4)	105.4(2)	C(20b)–C(22b)–H(22e)	109.5
C(a3)–N(2)–Co(1)	127.52(18)	H(22d)–C(22b)–H(22e)	109.5
C(a4)–N(2)–Co(1)	127.06(17)	C(20b)–C(22b)–H(22F)	109.5
C(12)–N(5)–C(7)	130.6(2)	H(22d)–C(22b)–H(22f)	109.5
C(12)–N(5)–H(5a)	114.7	H(22e)–C(22b)–H(22f)	109.5
C(7)–N(5)–H(5a)	114.7	C(20b)–C(23b)–H(23d)	109.5

angle	degree	angle	degree
C(19)–N(6)–C(14)	127.4(2)	C(20b)–C(23b)–H(23e)	109.5
C(19)–N(6)–H(6a)	116.3	H(23d)–C(23b)–H(23e)	109.5
C(14)–N(6)–H(6a)	116.3	C(20b)–C(23b)–H(23F)	109.5
N(1)–C(a1)–C(m1)	125.7(3)	H(23d)–C(23b)–H(23f)	109.5
N(1)–C(a1)–C(b1)	110.9(2)	H(23e)–C(23b)–H(23f)	109.5
C(m1)–C(a1)–C(b1)	123.5(3)	C(27)–C(24)–C(25)	109.5
N(1)–C(a2)–C(m2)	126.0(3)	C(27)–C(24)–C(26)	109.5
N(1)–C(a2)–C(b2)	110.4(2)	C(25)–C(24)–C(26)	109.5
C(m2)–C(a2)–C(b2)	123.5(3)	C(27)–C(24)–C(19)	115.1(3)
N(2)–C(a3)–C(m2)	126.6(2)	C(25)–C(24)–C(19)	101.7(3)
N(2)–C(a3)–C(b3)	110.8(2)	C(26)–C(24)–C(19)	111.3(3)
C(m2)–C(a3)–C(b3)	122.6(2)	C(24)–C(25)–H(25a)	109.5
N(2)–C(a4)–C(m1#1	126.2(2)	C(24)–C(25)–H(25b)	109.5
N(2)–C(a4)–C(b4)	110.1(2)	H(25a)–C(25)–H(25b)	109.5
C(m1#1–C(a4)–C(b4)	123.6(2)	C(24)–C(25)–H(25C)	109.5
C(b2)–C(b1)–C(a1)	107.0(3)	H(25a)–C(25)–H(25C)	109.5
C(b2)–C(b1)–H(ba)	126.5	H(25b)–C(25)–H(25C)	109.5
C(a1)–C(b1)–H(ba)	126.5	C(24)–C(26)–H(26a)	109.5
C(b1)–C(b2)–C(a2)	106.5(3)	C(24)–C(26)–H(26b)	109.5
C(b1)–C(b2)–H(bb)	126.8	H(26a)–C(26)–H(26b)	109.5
C(a2)–C(b2)–H(bb)	126.8	C(24)–C(26)–H(26C)	109.5
C(b4)–C(b3)–C(a3)	106.3(2)	H(26a)–C(26)–H(26C)	109.5
C(b4)–C(b3)–H(bC)	126.9	H(26b)–C(26)–H(26C)	109.5
C(a3)–C(b3)–H(bC)	126.9	C(24)–C(27)–H(27a)	109.5
C(b3)–C(b4)–C(a4)	107.4(2)	C(24)–C(27)–H(27b)	109.5
C(b3)–C(b4)–H(bd)	126.3	H(27a)–C(27)–H(27b)	109.5
C(a4)–C(b4)–H(bd)	126.3	C(24)–C(27)–H(27C)	109.5
C(a4#1–C(m1)–C(a1)	123.0(2)	H(27a)–C(27)–H(27C)	109.5
C(a4#1–C(m1)–C(6)	118.9(2)	H(27b)–C(27)–H(27C)	109.5
C(a1)–C(m1)–C(6)	117.9(2)	C(27b)–C(24b)–C(26b)	109.5
C(a2)–C(m2)–C(a3)	122.5(2)	C(27b)–C(24b)–C(25b)	109.5
C(a2)–C(m2)–C(13)	118.0(2)	C(26b)–C(24b)–C(25b)	109.5
C(a3)–C(m2)–C(13)	119.3(2)	C(27b)–C(24b)–C(19)	103.65(15)
C(7)–C(6)–C(11)	119.0(2)	C(26b)–C(24b)–C(19)	108.47(17)

Table S10. Continued

angle	degree	angle	degree
C(7)–C(6)–C(m1)	121.0(2)	C(25b)–C(24b)–C(19)	116.06(13)
C(11)–C(6)–C(m1)	120.0(2)	C(24b)–C(25b)–H(25d)	109.5
C(8)–C(7)–C(6)	120.2(2)	C(24b)–C(25b)–H(25e)	109.5
C(8)–C(7)–N(5)	123.5(3)	H(25d)–C(25b)–H(25e)	109.5
C(6)–C(7)–N(5)	116.3(2)	C(24b)–C(25b)–H(25F)	109.5
C(7)–C(8)–C(9)	119.6(3)	H(25d)–C(25b)–H(25f)	109.5
C(7)–C(8)–H(8a)	120.2	H(25e)–C(25b)–H(25f)	109.5
C(9)–C(8)–H(8a)	120.2	C(24b)–C(26b)–H(26d)	109.5
C(10)–C(9)–C(8)	121.3(3)	C(24b)–C(26b)–H(26e)	109.5
C(10)–C(9)–H(9a)	119.4	H(26d)–C(26b)–H(26e)	109.5
C(8)–C(9)–H(9a)	119.4	C(24b)–C(26b)–H(26F)	109.5
C(9)–C(10)–C(11)	119.2(3)	H(26d)–C(26b)–H(26f)	109.5
C(9)–C(10)–H(10a)	120.4	H(26e)–C(26b)–H(26f)	109.5
C(11)–C(10)–H(10a)	120.4	C(24b)–C(27b)–H(27d)	109.5
C(10)–C(11)–C(6)	120.8(3)	C(24b)–C(27b)–H(27e)	109.5
C(10)–C(11)–H(11a)	119.6	H(27d)–C(27b)–H(27e)	109.5
C(6)–C(11)–H(11a)	119.6	C(24b)–C(27b)–H(27F)	109.5
O(3)–C(12)–N(5)	123.1(2)	H(27d)–C(27b)–H(27f)	109.5
O(3)–C(12)–C(20b)	116.6(3)	H(27e)–C(27b)–H(27f)	109.5
N(5)–C(12)–C(20b)	119.8(3)	C(2S)–C(1S)–C(1S)#2	119.1
O(3)–C(12)–C(20)	124.6(3)	C(2S)–C(1S)–H(1Sa)	120.4
N(5)–C(12)–C(20)	112.3(3)	C(1S)#2–C(1S)–H(1Sa)	120.4
C(20b)–C(12)–C(20)	12.3(3)	C(3S)–C(2S)–C(1S)	120.2
C(18)–C(13)–C(14)	118.2(2)	C(3S)–C(2S)–H(2Sa)	119.9
C(18)–C(13)–C(m2)	119.5(2)	C(1S)–C(2S)–H(2Sa)	119.9
C(14)–C(13)–C(m2)	122.2(2)	C(2S)–C(3S)–C(3S)#2	120.4
C(15)–C(14)–C(13)	120.1(2)	C(2S)–C(3S)–H(3Sa)	119.8
C(15)–C(14)–N(6)	122.0(2)	C(3S)#2–C(3S)–H(3Sa)	119.8
C(13)–C(14)–N(6)	117.9(2)	C(1)–N(3)–C(3)	105.8
C(16)–C(15)–C(14)	120.0(3)	C(1)–N(3)–Co(1)	124.5(3)
C(16)–C(15)–H(15a)	120.0	C(3)–N(3)–Co(1)	129.6(2)
C(14)–C(15)–H(15a)	120.0	N(3)–C(1)–N(4)	110.0
C(15)–C(16)–C(17)	120.7(3)	N(3)–C(1)–H(1a)	125.0
C(15)–C(16)–H(16a)	119.6	N(4)–C(1)–H(1a)	125.0

Table S10. Continued

angle	degree	angle	degree
C(17)–C(16)–H(16a)	119.6	C(2)–N(4)–C(1)	108.6
C(18)–C(17)–C(16)	118.8(3)	C(2)–N(4)–C(4)	127.7(3)
C(18)–C(17)–H(17a)	120.6	C(1)–N(4)–C(4)	123.7(3)
C(16)–C(17)–H(17a)	120.6	N(4)–C(2)–C(3)	106.1
C(17)–C(18)–C(13)	122.1(3)	N(4)–C(2)–H(2a)	127.0
C(17)–C(18)–H(18a)	118.9	C(3)–C(2)–H(2a)	127.0
C(13)–C(18)–H(18a)	118.9	C(2)–C(3)–N(3)	109.5
O(4)–C(19)–N(6)	123.3(3)	C(2)–C(3)–H(3a)	125.2
O(4)–C(19)–C(24)	119.8(3)	N(3)–C(3)–H(3a)	125.2
N(6)–C(19)–C(24)	116.3(2)	N(4)–C(4)–C(5)	113.1(4)
O(4)–C(19)–C(24b)	119.2(3)	N(4)–C(4)–H(4a)	109.0
N(6)–C(19)–C(24b)	116.5(2)	C(5)–C(4)–H(4a)	109.0
C(24)–C(19)–C(24b)	18.01(17)	N(4)–C(4)–H(4b)	109.0
C(22)–C(20)–C(21)	109.5	C(5)–C(4)–H(4b)	109.0
C(22)–C(20)–C(23)	109.5	H(4a)–C(4)–H(4b)	107.8
C(21)–C(20)–C(23)	109.5	C(4)–C(5)–H(5b)	109.5
C(22)–C(20)–C(12)	116.5(4)	C(4)–C(5)–H(5C)	109.5
C(21)–C(20)–C(12)	102.6(4)	H(5b)–C(5)–H(5C)	109.5
C(23)–C(20)–C(12)	109.0(6)	C(4)–C(5)–H(5d)	109.5
C(20)–C(21)–H(21a)	109.5	H(5b)–C(5)–H(5d)	109.5
C(20)–C(21)–H(21b)	109.5	H(5C)–C(5)–H(5d)	109.5
H(21a)–C(21)–H(21b)	109.5		

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

Table S11. Anisotropic Displacement Parameters (Å^2) for $[\text{Co}(\text{TpivPP})(1\text{-EtIm})(\text{O}_2)]\cdot\text{C}_6\text{H}_6$ (100 K, $C2/c$ form)[a]

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co(1)	0.0406(3)	0.0174(2)	0.0223(2)	0.000	0.0060(2)	0.000
O(1)	0.0761(19)	0.0218(12)	0.0359(14)	0.000	−0.0034(14)	0.000
O(2)	0.073(3)	0.0272(19)	0.060(3)	−0.0031(17)	0.026(2)	0.0055(18)
O(3)	0.0662(13)	0.0523(12)	0.0315(10)	0.0060(9)	−0.0002(9)	0.0012(10)
O(4)	0.0431(11)	0.0490(12)	0.0679(14)	−0.0049(10)	0.0107(10)	0.0046(9)
N(1)	0.0441(12)	0.0270(10)	0.0251(11)	−0.0070(8)	0.0058(9)	−0.0042(8)
N(2)	0.0448(12)	0.0196(9)	0.0234(10)	0.0015(7)	0.0041(9)	0.0029(8)
N(5)	0.0799(17)	0.0367(12)	0.0185(9)	−0.0037(9)	0.0000(10)	0.0026(12)
N(6)	0.0336(11)	0.0345(12)	0.0662(15)	−0.0119(11)	0.0112(10)	−0.0040(9)
C(A1)	0.0439(14)	0.0340(13)	0.0233(12)	−0.0094(10)	0.0003(10)	−0.0071(11)
C(A2)	0.0396(13)	0.0267(12)	0.0301(13)	−0.0048(10)	0.0044(10)	−0.0042(10)
C(A3)	0.0425(13)	0.0185(10)	0.0262(12)	0.0000(9)	0.0068(10)	−0.0030(9)
C(A4)	0.0498(15)	0.0218(11)	0.0237(12)	0.0034(9)	0.0032(11)	0.0003(10)
C(B1)	0.0451(15)	0.0491(16)	0.0289(14)	−0.0096(11)	0.0007(12)	−0.0053(12)
C(B2)	0.0411(14)	0.0420(15)	0.0328(14)	−0.0060(11)	0.0036(11)	−0.0043(11)
C(B3)	0.0512(16)	0.0313(13)	0.0263(13)	−0.0002(10)	0.0092(12)	0.0018(11)
C(B4)	0.0456(14)	0.0314(12)	0.0246(12)	0.0034(10)	0.0050(11)	0.0012(11)
C(M1)	0.0470(15)	0.0287(12)	0.0251(12)	−0.0067(9)	0.0048(11)	−0.0041(10)
C(M2)	0.0440(13)	0.0215(11)	0.0296(13)	−0.0053(9)	0.0077(11)	−0.0020(10)
C(6)	0.0400(14)	0.0429(15)	0.0239(12)	−0.0101(11)	0.0045(10)	−0.0042(11)
C(7)	0.0456(14)	0.0406(14)	0.0237(12)	−0.0086(11)	0.0038(10)	−0.0043(11)
C(8)	0.0433(14)	0.0546(17)	0.0269(13)	−0.0077(12)	−0.0015(11)	−0.0020(12)
C(9)	0.0375(14)	0.0647(19)	0.0283(13)	−0.0144(13)	−0.0012(11)	−0.0075(13)
C(10)	0.0349(13)	0.0552(17)	0.0371(14)	−0.0190(13)	0.0049(11)	−0.0091(12)
C(11)	0.0390(13)	0.0443(15)	0.0311(13)	−0.0121(11)	0.0041(10)	−0.0046(11)
C(12)	0.0466(15)	0.0401(14)	0.0263(13)	−0.0034(11)	0.0110(11)	−0.0011(11)
C(13)	0.0424(13)	0.0305(12)	0.0241(12)	0.0005(9)	0.0022(10)	−0.0076(10)
C(14)	0.0403(13)	0.0369(13)	0.0323(13)	−0.0038(11)	0.0068(10)	−0.0066(11)
C(15)	0.0468(15)	0.0500(16)	0.0399(14)	−0.0066(13)	0.0159(12)	−0.0068(13)
C(16)	0.0430(15)	0.0617(19)	0.0376(15)	0.0059(13)	0.0115(12)	−0.0162(13)
C(17)	0.0554(17)	0.0508(18)	0.0400(15)	0.0067(13)	0.0027(12)	−0.0247(14)
C(18)	0.0549(15)	0.0341(14)	0.0315(13)	0.0031(11)	0.0032(11)	−0.0083(11)
C(19)	0.0413(14)	0.0376(14)	0.0424(15)	−0.0073(12)	0.0054(11)	−0.0015(11)
C(20)	0.037(3)	0.027(3)	0.030(3)	−0.004(3)	0.002(3)	0.005(2)

Table S11. Continued

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(21)	0.036(3)	0.044(3)	0.042(4)	−0.001(3)	0.012(3)	0.002(2)
C(22)	0.055(4)	0.028(2)	0.027(2)	−0.0029(19)	−0.004(2)	0.001(2)
C(23)	0.038(4)	0.041(4)	0.039(4)	0.008(3)	0.010(3)	−0.012(3)
C(20B)	0.038(4)	0.041(5)	0.016(3)	−0.001(3)	0.001(3)	−0.006(3)
C(21B)	0.032(3)	0.062(5)	0.053(5)	−0.017(4)	0.001(3)	0.006(3)
C(22B)	0.088(8)	0.054(4)	0.027(3)	−0.013(3)	0.005(4)	−0.018(5)
C(23B)	0.041(5)	0.077(9)	0.036(6)	−0.025(4)	0.006(4)	−0.001(4)
C(24)	0.034(3)	0.036(3)	0.018(3)	0.000(2)	−0.013(2)	−0.007(2)
C(25)	0.041(3)	0.065(4)	0.036(3)	−0.001(3)	−0.004(2)	−0.011(3)
C(26)	0.091(5)	0.048(3)	0.040(3)	−0.017(3)	0.001(3)	−0.021(3)
C(27)	0.033(3)	0.067(4)	0.058(4)	0.026(3)	−0.012(3)	−0.016(3)
C(24B)	0.056(4)	0.028(3)	0.008(4)	0.000(2)	−0.008(2)	0.002(3)
C(25B)	0.048(4)	0.062(4)	0.020(3)	−0.005(3)	0.004(2)	−0.009(3)
C(26B)	0.061(4)	0.039(4)	0.059(4)	−0.005(3)	0.008(3)	0.011(3)
C(27B)	0.059(6)	0.043(4)	0.056(5)	0.009(3)	0.013(4)	−0.002(4)
C(1S)	0.064(2)	0.0494(18)	0.093(3)	−0.0125(19)	0.0377(19)	−0.0019(15)
C(2S)	0.0379(14)	0.0554(18)	0.0471(16)	0.0025(14)	0.0080(12)	0.0029(12)
C(3S)	0.0592(19)	0.0463(16)	0.0440(16)	0.0041(14)	0.0058(14)	−0.0014(14)
N(3)	0.038(3)	0.0217(15)	0.012(4)	−0.0005(19)	−0.001(2)	0.002(2)
C(1)	0.032(3)	0.028(3)	0.020(3)	−0.002(2)	−0.003(2)	0.002(2)
N(4)	0.040(2)	0.0210(16)	0.027(4)	−0.0063(14)	0.016(4)	−0.004(2)
C(2)	0.035(3)	0.024(2)	0.028(3)	0.001(2)	0.002(2)	0.002(2)
C(3)	0.033(3)	0.021(2)	0.020(3)	0.0014(19)	−0.005(2)	0.002(2)
C(4)	0.040(3)	0.029(3)	0.045(3)	−0.018(2)	−0.003(2)	−0.004(2)
C(5)	0.087(7)	0.021(2)	0.052(7)	−0.010(2)	0.016(5)	−0.010(3)

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

The anisotropic displacement factor exponent takes the form: -2π [h^2 U_{11} +...+ 2 h k a* b* U_{12}].

Table S12. Hydrogen Atom Coordinates and Equivalent Isotropic Displacement Parameters
(Å^2) for $[\text{Co}(\text{TpivPP})(1\text{-EtIm})(\text{O}_2)]\cdot\text{C}_6\text{H}_6$ (100 K, $C2/c$ form)^a

atom	x	y	z	$U(\text{eq})$
H(5A)	0.6026	0.7553	0.9514	0.054
H(6A)	0.6931	0.7372	0.6302	0.054
H(BA	0.7155	0.8601	0.9240	0.049
H(BB	0.7707	0.8491	0.8012	0.046
H(BC	0.6705	0.8588	0.5313	0.043
H(BD	0.5498	0.8690	0.4759	0.041
H(8A)	0.6583	0.7754	1.1333	0.050
H(9A)	0.6631	0.8828	1.1927	0.052
H(10A)	0.6268	0.9844	1.1339	0.051
H(11A)	0.5841	0.9787	1.0139	0.046
H(15A)	0.8724	0.7572	0.5812	0.055
H(16A)	0.9375	0.8600	0.5886	0.057
H(17A)	0.8856	0.9606	0.6389	0.059
H(18A)	0.7669	0.9573	0.6775	0.048
H(21A)	0.6776	0.5675	0.9012	0.061
H(21B)	0.6996	0.5814	0.9845	0.061
H(21C)	0.7104	0.6414	0.9248	0.061
H(22A)	0.5663	0.6209	0.8504	0.055
H(22B)	0.6053	0.6938	0.8658	0.055
H(22C)	0.5262	0.6799	0.8968	0.055
H(23A)	0.5506	0.5367	0.9428	0.058
H(23B)	0.5124	0.5887	0.9989	0.058
H(23C)	0.5830	0.5468	1.0232	0.058
H(21D)	0.7288	0.6040	0.9675	0.073
H(21E)	0.6813	0.5384	0.9430	0.073
H(21F)	0.6841	0.5612	1.0270	0.073
H(22D)	0.6654	0.6774	0.8777	0.084
H(22E)	0.5794	0.6823	0.8788	0.084
H(22F)	0.6179	0.6117	0.8532	0.084
H(23D)	0.5519	0.5687	1.0287	0.077
H(23E)	0.5491	0.5459	0.9447	0.077
H(23F)	0.5107	0.6164	0.9703	0.077
H(25A)	0.6817	0.5378	0.7020	0.071
H(25B)	0.7067	0.6116	0.7341	0.071

Table S12. Continued

atom	x	y	z	$U(\text{eq})$
H(25C)	0.7652	0.5582	0.7031	0.071
H(26A)	0.6896	0.5180	0.5647	0.090
H(26B)	0.7735	0.5339	0.5759	0.090
H(26C)	0.7280	0.5770	0.5168	0.090
H(27A)	0.5996	0.5925	0.6110	0.079
H(27B)	0.6281	0.6574	0.5645	0.079
H(27C)	0.6189	0.6643	0.6511	0.079
H(25D)	0.6458	0.5769	0.7312	0.065
H(25E)	0.6487	0.6598	0.7214	0.065
H(25F)	0.7143	0.6197	0.7597	0.065
H(26D)	0.7198	0.5016	0.6616	0.079
H(26E)	0.7934	0.5412	0.6804	0.079
H(26F)	0.7695	0.5302	0.5971	0.079
H(27D)	0.6200	0.5722	0.5993	0.079
H(27E)	0.6785	0.5990	0.5419	0.079
H(27F)	0.6325	0.6540	0.5878	0.079
H(1SA)	0.9609	1.0592	0.8013	0.103
H(2SA)	0.9107	0.9541	0.8387	0.056
H(3SA)	0.9567	0.8503	0.7955	0.075
H(1A)	0.5591	1.0016	0.8195	0.032
H(2A)	0.4321	1.1144	0.6887	0.035
H(3A)	0.4162	0.9896	0.6593	0.030
H(4A)	0.5803	1.1383	0.8155	0.045
H(4B)	0.5039	1.1427	0.8551	0.045
H(5B)	0.5293	1.2484	0.7965	0.080
H(5C)	0.4599	1.2134	0.7597	0.080
H(5D)	0.5362	1.2088	0.7199	0.080

[a] $U(\text{eq})$ 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 S13. Complete Crystallographic Details for $[Co(TpivPP)(1\text{-}EtIm)(O_2)]\cdot C_6H_6$ (200 K, $C2/c$ form)

formula	$C_{75}H_{78}CoN_{10}O_6$
FW, amu	1274.40
a, Å	18.5681(7)
b, Å	19.2564(8)
c, Å	18.4497(7)
β, deg	90.169(2)
V, Å^3	6596.7(4)
space group	$C2/c$
Z	4
D_c, g/cm^3	1.283
F(000)	2692
μ, mm^{-1}	0.322
crystal dimensions, mm	$0.39 \times 0.26 \times 0.19$
radiation	MoKα, $\bar{\lambda} = 0.71073$ Å
temperature, K	200(2)
diffractometer	Bruker Apex CCD
θ range for collected data, deg	1.52–27.62
index range	$-24 \leq h \leq 18$
	$-25 \leq k \leq 24$
	$-24 \leq l \leq 23$
total data collected	27807
absorption correction	Semi-empirical from equiv
relative transmission coefficients (I)	0.9413 and 0.8847
unique data	7611 ($R_{\text{int}} = 0.0352$)
unique observed data [I > 2σ(I)]	4828
refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	7611/0/497
goodness-of-fit (pased on F^2)	1.013
final R indices [I > 2σ(I)]	$R_1 = 0.0486$, $wR_2 = 0.1266$
final R indices (all data)	$R_1 = 0.0911$, $wR_2 = 0.1498$

Table S14. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$) for $[Co(TpivPP)(1\text{-}EtIm)(O_2)]\cdot C_6H_6$ (200 K, $C2/c$ form)[a]

atom	x	y	z	U(eq)
Co(1)	0.5000	0.86278(2)	0.7500	0.0377(1)
N(1)	0.45623(10)	0.86207(8)	0.65227(9)	0.0391(4)
N(2)	0.40317(10)	0.86095(9)	0.79385(9)	0.0422(4)
N(5)	0.25915(11)	0.73366(11)	0.62992(13)	0.0647(6)
N(6)	0.38992(13)	0.75119(11)	0.99745(10)	0.0631(6)
O(1)	0.5000	0.76419(12)	0.7500	0.0565(6)
O(2a)	0.5435(4)	0.7286(2)	0.7715(4)	0.065(3)
O(2b)	0.493(3)	0.7276(11)	0.7972(14)	0.087(15)
O(3)	0.17142(12)	0.65428(12)	0.61620(15)	0.0962(8)
O(4)	0.36864(16)	0.67099(12)	1.08220(11)	0.1008(8)
C(a1)	0.49090(12)	0.86623(11)	0.58704(11)	0.0425(5)
C(a2)	0.38406(12)	0.85826(11)	0.63535(11)	0.0424(5)
C(a3)	0.33807(12)	0.85629(11)	0.75873(12)	0.0434(5)
C(a4)	0.38630(13)	0.86372(12)	0.86635(12)	0.0457(5)
C(b1)	0.43944(13)	0.86531(12)	0.52876(12)	0.0503(6)
C(b2)	0.37440(14)	0.85974(12)	0.55844(12)	0.0508(6)
C(b3)	0.28032(13)	0.85476(13)	0.81017(13)	0.0532(6)
C(b4)	0.31023(13)	0.86005(14)	0.87587(13)	0.0560(6)
C(m1)	0.32786(12)	0.85552(11)	0.68453(12)	0.0438(5)
C(m2)	0.43556(13)	0.86870(11)	0.92307(11)	0.0453(5)
C(6)	0.25225(13)	0.85532(12)	0.65615(12)	0.0481(5)
C(7)	0.21932(13)	0.79557(14)	0.62949(13)	0.0547(6)
C(8)	0.14860(15)	0.79849(17)	0.60380(15)	0.0709(8)
C(9)	0.11139(16)	0.85968(19)	0.60657(16)	0.0755(9)
C(10)	0.14254(17)	0.91810(19)	0.63345(16)	0.0755(9)
C(11)	0.21287(15)	0.91631(14)	0.65731(14)	0.0605(7)
C(12)	0.23457(15)	0.66810(15)	0.62664(15)	0.0625(7)
C(13)	0.40683(13)	0.87355(13)	0.99865(12)	0.0506(6)
C(14)	0.38530(13)	0.81439(14)	1.03526(12)	0.0529(6)
C(15)	0.35888(15)	0.81904(16)	1.10546(13)	0.0633(7)
C(16)	0.35533(15)	0.88395(19)	1.13807(15)	0.0704(8)
C(17)	0.37706(15)	0.94216(18)	1.10317(15)	0.0690(8)
C(18)	0.40268(14)	0.93739(15)	1.03312(14)	0.0603(7)
C(19)	0.38184(15)	0.68594(15)	1.01983(13)	0.0608(7)

Table S14. Continued

atom	x	y	z	U(eq)
N(3)	0.4915(3)	0.96753(9)	0.7584(3)	0.0351(10)
C(1)	0.5260(2)	1.01169(11)	0.7172(2)	0.0415(13)
N(4)	0.50588(15)	1.07753(9)	0.73352(14)	0.0447(15)
C(2)	0.45630(18)	1.07508(11)	0.78613(17)	0.0464(13)
C(3)	0.4474(2)	1.00721(12)	0.8022(2)	0.0408(13)
C(4)	0.5306(2)	1.13848(14)	0.6919(2)	0.0648(14)
C(5)	0.5154(3)	1.20588(10)	0.7328(3)	0.089(3)
C(1S)	0.4749(2)	0.4874(3)	0.2236(3)	0.1145(13)
C(2S)	0.44837(19)	0.5490(2)	0.19708(18)	0.0917(11)
C(3S)	0.4730(2)	0.6114(2)	0.22297(19)	0.0944(11)
C(21a)	0.3941(3)	0.6302(3)	0.9581(2)	0.0499(17)
C(22a)	0.4420(4)	0.5727(5)	0.9855(5)	0.081(2)
C(23a)	0.4241(8)	0.6586(3)	0.8884(3)	0.085(3)
C(24a)	0.3194(3)	0.6022(5)	0.9449(7)	0.099(3)
C(21b)	0.3786(7)	0.6298(6)	0.9659(4)	0.052(3)
C(22b)	0.4500(6)	0.5943(13)	0.9779(8)	0.118(7)
C(23b)	0.3730(15)	0.6532(6)	0.8881(5)	0.093(5)
C(24b)	0.3184(7)	0.5799(10)	0.9823(10)	0.097(6)
C(20a)	0.2894(4)	0.6110(3)	0.6469(3)	0.057(2)
C(25a)	0.3500(7)	0.6150(7)	0.5929(4)	0.099(4)
C(26a)	0.3193(5)	0.6192(4)	0.7225(3)	0.092(3)
C(27a)	0.2524(4)	0.5416(3)	0.6404(6)	0.114(4)
C(20b)	0.2903(3)	0.6107(2)	0.6250(3)	0.057(2)
C(25b)	0.3662(5)	0.6355(6)	0.6121(5)	0.143(6)
C(26b)	0.2850(4)	0.5801(5)	0.7000(3)	0.093(3)
C(27b)	0.2711(4)	0.5563(4)	0.5696(4)	0.113(3)

[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 S15. Bond Lengths for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (200 K, $C2/c$ form)^a

bond	length (Å)	bond	length (Å)
Co(1)–O(1)	1.899(2)	C(1)–H(1a)	0.9500
Co(1)–N(2)#1)	1.9741(18)	N(4)–C(2)	1.3405
Co(1)–N(2)	1.9741(18)	N(4)–C(4)	1.4763
Co(1)–N(1)	1.9757(16)	C(2)–C(3)	1.3503
Co(1)–N(1)#1	1.9757(16)	C(2)–H(2a)	0.9500
Co(1)–N(3)#1	2.0293(18)	C(3)–H(3a)	0.9500
Co(1)–N(3)	2.0293(18)	C(4)–C(5)	1.5273
N(1)–C(a1)	1.369(3)	C(4)–H(4a)	0.9900
N(1)–C(a2)	1.377(3)	C(4)–H(4b)	0.9900
N(2)–C(a3)	1.373(3)	C(5)–H(5b)	0.9800
N(2)–C(a4)	1.376(3)	C(5)–H(5C)	0.9800
N(5)–C(12)	1.344(3)	C(5)–H(5d)	0.9800
N(5)–C(7)	1.403(3)	C(1S)–C(1S)#2	1.346(8)
N(5)–H(5a)	0.8800	C(1S)–C(2S)	1.374(5)
N(6)–C(19)	1.331(3)	C(1S)–H(1Sa)	0.9500
N(6)–C(14)	1.406(3)	C(2S)–C(3S)	1.371(5)
N(6)–H(6a)	0.8800	C(2S)–H(2Sa)	0.9500
O(1)–O(2b)#1	1.13(2)	C(3S)–C(3S)#2	1.411(7)
O(1)–O(2b)	1.13(2)	C(3S)–H(3Sa)	0.9500
O(1)–O(2a)	1.131(5)	C(21a)–C(22a)	1.5069
O(1)–O(2a)#1	1.131(5)	C(21a)–C(24a)	1.5070
O(2a)–O(2a)#1	1.798(12)	C(21a)–C(23a)	1.5070
O(2b)–O(2b)#1	1.76(5)	C(22a)–H(22a)	0.9800
O(3)–C(12)	1.217(3)	C(22a)–H(22b)	0.9800
O(4)–C(19)	1.212(3)	C(22a)–H(22C)	0.9800
C(a1)–C(m2#1)	1.380(3)	C(23a)–H(23a)	0.9800
C(a1)–C(b1)	1.436(3)	C(23a)–H(23b)	0.9800
C(a2)–C(m1)	1.386(3)	C(23a)–H(23C)	0.9800
C(a2)–C(b2)	1.430(3)	C(24a)–H(24a)	0.9800
C(a3)–C(m1)	1.382(3)	C(24a)–H(24b)	0.9800
C(a3)–C(b3)	1.434(3)	C(24a)–H(24C)	0.9800
C(a4)–C(m2)	1.391(3)	C(21b)–C(24b)	1.5068
C(a4)–C(b4)	1.426(3)	C(21b)–C(22b)	1.5069
C(b1)–C(b2)	1.332(3)	C(21b)–C(23b)	1.5072

Table S15. Continued

bond	length (Å)	bond	length (Å)
C(b1)–H(ba)	0.9500	C(22b)–H(22d)	0.9800
C(b2)–H(bb)	0.9500	C(22b)–H(22e)	0.9800
C(b3)–C(b4)	1.336(3)	C(22b)–H(22F)	0.9800
C(b3)–H(bC)	0.9500	C(23b)–H(23d)	0.9800
C(b4)–H(bd)	0.9500	C(23b)–H(23e)	0.9800
C(m1)–C(6)	1.497(3)	C(23b)–H(23F)	0.9800
C(m2)–C(a1#1)	1.380(3)	C(24b)–H(24d)	0.9800
C(m2)–C(13)	1.497(3)	C(24b)–H(24e)	0.9800
C(6)–C(11)	1.384(3)	C(24b)–H(24F)	0.9800
C(6)–C(7)	1.392(3)	C(20a)–C(25a)	1.5069
C(7)–C(8)	1.396(3)	C(20a)–C(27a)	1.5070
C(8)–C(9)	1.367(4)	C(20a)–C(26a)	1.5070
C(8)–H(8a)	0.9500	C(25a)–H(25a)	0.9800
C(9)–C(10)	1.358(5)	C(25a)–H(25b)	0.9800
C(9)–H(9a)	0.9500	C(25a)–H(25C)	0.9800
C(10)–C(11)	1.377(4)	C(26a)–H(26a)	0.9800
C(10)–H(10a)	0.9500	C(26a)–H(26b)	0.9800
C(11)–H(11a)	0.9500	C(26a)–H(26C)	0.9800
C(12)–C(20b)	1.514(6)	C(27a)–H(27a)	0.9800
C(12)–C(20a)	1.544(7)	C(27a)–H(27b)	0.9800
C(13)–C(14)	1.384(4)	C(27a)–H(27C)	0.9800
C(13)–C(18)	1.386(3)	C(20b)–C(27b)	1.5068
C(14)–C(15)	1.389(3)	C(20b)–C(26b)	1.5069
C(15)–C(16)	1.389(4)	C(20b)–C(25b)	1.5072
C(15)–H(15a)	0.9500	C(25b)–H(25d)	0.9800
C(16)–C(17)	1.355(4)	C(25b)–H(25e)	0.9800
C(16)–H(16a)	0.9500	C(25b)–H(25F)	0.9800
C(17)–C(18)	1.381(4)	C(26b)–H(26d)	0.9800
C(17)–H(17a)	0.9500	C(26b)–H(26e)	0.9800
C(18)–H(18a)	0.9500	C(26b)–H(26F)	0.9800
C(19)–C(21b)	1.470(9)	C(27b)–H(27d)	0.9800
C(19)–C(21a)	1.581(6)	C(27b)–H(27e)	0.9800
N(3)–C(1)	1.3103	C(27b)–H(27F)	0.9800
N(3)–C(3)	1.3810		

Table S15. Continued

bond	length (Å)	bond	length (Å)
C(1)–N(4)	1.3561		

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

Table S16. Bond Angles for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (200 K, $C2/c$ form)^a

angle	degree	angle	degree
O(1)–Co(1)–N(2)#1	88.98(5)	N(4)–C(1)–H(1a)	125.0
O(1)–Co(1)–N(2)	88.98(5)	C(2)–N(4)–C(1)	108.6
N(2)#1–Co(1)–N(2)	177.95(10)	C(2)–N(4)–C(4)	128.3
O(1)–Co(1)–N(1)	89.60(5)	C(1)–N(4)–C(4)	122.8
N(2)#1–Co(1)–N(1)	89.92(7)	N(4)–C(2)–C(3)	106.1
N(2)–Co(1)–N(1)	90.07(7)	N(4)–C(2)–H(2a)	127.0
O(1)–Co(1)–N(1)#1	89.60(5)	C(3)–C(2)–H(2a)	127.0
N(2)#1–Co(1)–N(1)#1	90.07(7)	C(2)–C(3)–N(3)	109.6
N(2)–Co(1)–N(1)#1	89.92(7)	C(2)–C(3)–H(3a)	125.2
N(1)–Co(1)–N(1)#1	179.20(10)	N(3)–C(3)–H(3a)	125.2
O(1)–Co(1)–N(3)#1	173.71(8)	N(4)–C(4)–C(5)	111.2
N(2)#1–Co(1)–N(3)#1	85.12(12)	N(4)–C(4)–H(4a)	109.4
N(2)–Co(1)–N(3)#1	96.93(12)	C(5)–C(4)–H(4a)	109.4
N(1)–Co(1)–N(3)#1	88.23(19)	N(4)–C(4)–H(4b)	109.4
N(1)#1–Co(1)–N(3)#1	92.6(2)	C(5)–C(4)–H(4b)	109.4
O(1)–Co(1)–N(3)	173.71(8)	H(4a)–C(4)–H(4b)	108.0
N(2)#1–Co(1)–N(3)	96.93(12)	C(4)–C(5)–H(5b)	109.5
N(2)–Co(1)–N(3)	85.12(12)	C(4)–C(5)–H(5C)	109.5
N(1)–Co(1)–N(3)	92.56(19)	H(5b)–C(5)–H(5C)	109.5
N(1)#1–Co(1)–N(3)	88.23(19)	C(4)–C(5)–H(5d)	109.5
N(3)#1–Co(1)–N(3)	12.58(17)	H(5b)–C(5)–H(5d)	109.5
C(a1)–N(1)–C(a2)	105.29(17)	H(5C)–C(5)–H(5d)	109.5
C(a1)–N(1)–Co(1)	127.50(15)	C(1S)#2–C(1S)–C(2S)	120.3(2)
C(a2)–N(1)–Co(1)	127.21(14)	C(1S)#2–C(1S)–H(1Sa)	119.8
C(a3)–N(2)–C(a4)	105.00(18)	C(2S)–C(1S)–H(1Sa)	119.8
C(a3)–N(2)–Co(1)	127.55(15)	C(3S)–C(2S)–C(1S)	120.9(4)
C(a4)–N(2)–Co(1)	127.45(15)	C(3S)–C(2S)–H(2Sa)	119.6
C(12)–N(5)–C(7)	128.3(2)	C(1S)–C(2S)–H(2Sa)	119.6
C(12)–N(5)–H(5a)	115.9	C(2S)–C(3S)–C(3S)#2	118.8(2)
C(7)–N(5)–H(5a)	115.9	C(2S)–C(3S)–H(3Sa)	120.6
C(19)–N(6)–C(14)	131.0(2)	C(3S)#2–C(3S)–H(3Sa)	120.6
C(19)–N(6)–H(6a)	114.5	C(22a)–C(21a)–C(24a)	109.5
C(14)–N(6)–H(6a)	114.5	C(22a)–C(21a)–C(23a)	109.5
O(2b)#1–O(1)–O(2b)	103(3)	C(24a)–C(21a)–C(23a)	109.5

Table S16. Continued

angle	degree	angle	degree
O(2b)#1–O(1)–O(2a)	78.7(18)	C(22a)–C(21a)–C(19)	110.1(4)
O(2b)–O(1)–O(2a)	56(2)	C(24a)–C(21a)–C(19)	103.0(4)
O(2b)#1–O(1)–O(2a)#1	56(2)	C(23a)–C(21a)–C(19)	115.0(4)
O(2b)–O(1)–O(2a)#1	78.7(18)	C(21a)–C(22a)–H(22a)	109.5
O(2a)–O(1)–O(2a)#1	105.3(6)	C(21a)–C(22a)–H(22b)	109.5
O(2b)#1–O(1)–Co(1)	128.7(14)	H(22a)–C(22a)–H(22b)	109.5
O(2b)–O(1)–Co(1)	128.7(14)	C(21a)–C(22a)–H(22C)	109.5
O(2a)–O(1)–Co(1)	127.4(3)	H(22a)–C(22a)–H(22C)	109.5
O(2a)#1–O(1)–Co(1)	127.4(3)	H(22b)–C(22a)–H(22C)	109.5
O(1)–O(2a)–O(2a)#1	37.4(3)	C(21a)–C(23a)–H(23a)	109.5
O(1)–O(2b)–O(2b)#1	38.7(14)	C(21a)–C(23a)–H(23b)	109.5
N(1)–C(a1)–C(m2#1	126.10(19)	H(23a)–C(23a)–H(23b)	109.5
N(1)–C(a1)–C(b1)	110.1(2)	C(21a)–C(23a)–H(23C)	109.5
C(m2#1–C(a1)–C(b1)	123.8(2)	H(23a)–C(23a)–H(23C)	109.5
N(1)–C(a2)–C(m1)	126.00(19)	H(23b)–C(23a)–H(23C)	109.5
N(1)–C(a2)–C(b2)	110.1(2)	C(21a)–C(24a)–H(24a)	109.5
C(m1)–C(a2)–C(b2)	123.9(2)	C(21a)–C(24a)–H(24b)	109.5
N(2)–C(a3)–C(m1)	125.9(2)	H(24a)–C(24a)–H(24b)	109.5
N(2)–C(a3)–C(b3)	110.36(19)	C(21a)–C(24a)–H(24C)	109.5
C(m1)–C(a3)–C(b3)	123.7(2)	H(24a)–C(24a)–H(24C)	109.5
N(2)–C(a4)–C(m2)	125.7(2)	H(24b)–C(24a)–H(24C)	109.5
N(2)–C(a4)–C(b4)	110.27(19)	C(19)–C(21b)–C(24b)	111.2(8)
C(m2)–C(a4)–C(b4)	124.1(2)	C(19)–C(21b)–C(22b)	101.5(10)
C(b2)–C(b1)–C(a1)	107.2(2)	C(24b)–C(21b)–C(22b)	109.5
C(b2)–C(b1)–H(ba)	126.4	C(19)–C(21b)–C(23b)	115.4(7)
C(a1)–C(b1)–H(ba)	126.4	C(24b)–C(21b)–C(23b)	109.5
C(b1)–C(b2)–C(a2)	107.4(2)	C(22b)–C(21b)–C(23b)	109.5
C(b1)–C(b2)–H(bb)	126.3	C(21b)–C(22b)–H(22d)	109.5
C(a2)–C(b2)–H(bb)	126.3	C(21b)–C(22b)–H(22e)	109.5
C(b4)–C(b3)–C(a3)	106.8(2)	H(22d)–C(22b)–H(22e)	109.5
C(b4)–C(b3)–H(bC)	126.6	C(21b)–C(22b)–H(22F)	109.5
C(a3)–C(b3)–H(bC)	126.6	H(22d)–C(22b)–H(22f)	109.5
C(b3)–C(b4)–C(a4)	107.6(2)	H(22e)–C(22b)–H(22f)	109.5
C(b3)–C(b4)–H(bd)	126.2	C(21b)–C(23b)–H(23d)	109.5

Table S16. Continued

angle	degree	angle	degree
C(a4)–C(b4)–H(bd)	126.2	C(21b)–C(23b)–H(23e)	109.5
C(a3)–C(m1)–C(a2)	123.2(2)	H(23d)–C(23b)–H(23e)	109.5
C(a3)–C(m1)–C(6)	118.2(2)	C(21b)–C(23b)–H(23F)	109.5
C(a2)–C(m1)–C(6)	118.6(2)	H(23d)–C(23b)–H(23f)	109.5
C(a1#1–C(m2)–C(a4)	123.0(2)	H(23e)–C(23b)–H(23f)	109.5
C(a1#1–C(m2)–C(13)	118.91(19)	C(21b)–C(24b)–H(24d)	109.5
C(a4)–C(m2)–C(13)	118.0(2)	C(21b)–C(24b)–H(24e)	109.5
C(11)–C(6)–C(7)	118.4(2)	H(24d)–C(24b)–H(24e)	109.5
C(11)–C(6)–C(m1)	119.2(2)	C(21b)–C(24b)–H(24F)	109.5
C(7)–C(6)–C(m1)	122.4(2)	H(24d)–C(24b)–H(24f)	109.5
C(6)–C(7)–C(8)	119.9(3)	H(24e)–C(24b)–H(24f)	109.5
C(6)–C(7)–N(5)	118.0(2)	C(25a)–C(20a)–C(27a)	109.5
C(8)–C(7)–N(5)	122.1(2)	C(25a)–C(20a)–C(26a)	109.5
C(9)–C(8)–C(7)	119.8(3)	C(27a)–C(20a)–C(26a)	109.5
C(9)–C(8)–H(8a)	120.1	C(25a)–C(20a)–C(12)	107.3(7)
C(7)–C(8)–H(8a)	120.1	C(27a)–C(20a)–C(12)	108.1(5)
C(10)–C(9)–C(8)	120.9(3)	C(26a)–C(20a)–C(12)	113.0(5)
C(10)–C(9)–H(9a)	119.6	C(20a)–C(25a)–H(25a)	109.5
C(8)–C(9)–H(9a)	119.6	C(20a)–C(25a)–H(25b)	109.5
C(9)–C(10)–C(11)	119.9(3)	H(25a)–C(25a)–H(25b)	109.5
C(9)–C(10)–H(10a)	120.1	C(20a)–C(25a)–H(25C)	109.5
C(11)–C(10)–H(10a)	120.1	H(25a)–C(25a)–H(25C)	109.5
C(10)–C(11)–C(6)	121.1(3)	H(25b)–C(25a)–H(25C)	109.5
C(10)–C(11)–H(11a)	119.4	C(20a)–C(26a)–H(26a)	109.5
C(6)–C(11)–H(11a)	119.4	C(20a)–C(26a)–H(26b)	109.5
O(3)–C(12)–N(5)	122.6(3)	H(26a)–C(26a)–H(26b)	109.5
O(3)–C(12)–C(20b)	119.7(3)	C(20a)–C(26a)–H(26C)	109.5
N(5)–C(12)–C(20b)	117.0(3)	H(26a)–C(26a)–H(26C)	109.5
O(3)–C(12)–C(20a)	121.1(3)	H(26b)–C(26a)–H(26C)	109.5
N(5)–C(12)–C(20a)	115.8(3)	C(20a)–C(27a)–H(27a)	109.5
C(20b)–C(12)–C(20a)	15.2(3)	C(20a)–C(27a)–H(27b)	109.5
C(14)–C(13)–C(18)	119.3(2)	H(27a)–C(27a)–H(27b)	109.5
C(14)–C(13)–C(m2)	120.5(2)	C(20a)–C(27a)–H(27C)	109.5
C(18)–C(13)–C(m2)	120.2(2)	H(27a)–C(27a)–H(27C)	109.5

Table S16. Continued

angle	degree	angle	degree
C(13)–C(14)–C(15)	120.4(2)	H(27b)–C(27a)–H(27C)	109.5
C(13)–C(14)–N(6)	116.9(2)	C(27b)–C(20b)–C(26b)	109.5
C(15)–C(14)–N(6)	122.7(2)	C(27b)–C(20b)–C(25b)	109.5
C(16)–C(15)–C(14)	118.6(3)	C(26b)–C(20b)–C(25b)	109.5
C(16)–C(15)–H(15a)	120.7	C(27b)–C(20b)–C(12)	111.1(4)
C(14)–C(15)–H(15a)	120.7	C(26b)–C(20b)–C(12)	102.8(4)
C(17)–C(16)–C(15)	121.6(3)	C(25b)–C(20b)–C(12)	114.3(5)
C(17)–C(16)–H(16a)	119.2	C(20b)–C(25b)–H(25d)	109.5
C(15)–C(16)–H(16a)	119.2	C(20b)–C(25b)–H(25e)	109.5
C(16)–C(17)–C(18)	119.6(3)	H(25d)–C(25b)–H(25e)	109.5
C(16)–C(17)–H(17a)	120.2	C(20b)–C(25b)–H(25F)	109.5
C(18)–C(17)–H(17a)	120.2	H(25d)–C(25b)–H(25f)	109.5
C(17)–C(18)–C(13)	120.5(3)	H(25e)–C(25b)–H(25f)	109.5
C(17)–C(18)–H(18a)	119.7	C(20b)–C(26b)–H(26d)	109.5
C(13)–C(18)–H(18a)	119.7	C(20b)–C(26b)–H(26e)	109.5
O(4)–C(19)–N(6)	122.8(3)	H(26d)–C(26b)–H(26e)	109.5
O(4)–C(19)–C(21b)	117.4(5)	C(20b)–C(26b)–H(26F)	109.5
N(6)–C(19)–C(21b)	119.2(4)	H(26d)–C(26b)–H(26f)	109.5
O(4)–C(19)–C(21a)	123.5(3)	H(26e)–C(26b)–H(26f)	109.5
N(6)–C(19)–C(21a)	113.6(3)	C(20b)–C(27b)–H(27d)	109.5
C(21b)–C(19)–C(21a)	11.4(5)	C(20b)–C(27b)–H(27e)	109.5
C(1)–N(3)–C(3)	105.8	H(27d)–C(27b)–H(27e)	109.5
C(1)–N(3)–Co(1)	124.20(16)	C(20b)–C(27b)–H(27F)	109.5
C(3)–N(3)–Co(1)	129.87(15)	H(27d)–C(27b)–H(27f)	109.5
N(3)–C(1)–N(4)	110.0	H(27e)–C(27b)–H(27f)	109.5
N(3)–C(1)–H(1a)	125.0		

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

Table S17. Anisotropic Displacement Parameters (Å^2) for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (200 K, $C2/c$ form)[a]

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co(1)	0.0416(3)	0.0350(2)	0.0366(2)	0.000	−0.0025(2)	0.000
N(1)	0.0432(10)	0.0351(9)	0.0389(9)	−0.0002(7)	−0.0016(8)	−0.0017(8)
N(2)	0.0436(11)	0.0420(10)	0.0411(9)	−0.0062(8)	−0.0038(8)	0.0023(8)
N(5)	0.0413(12)	0.0592(14)	0.0934(16)	−0.0109(12)	−0.0124(11)	−0.0008(10)
N(6)	0.0937(17)	0.0625(14)	0.0332(9)	−0.0063(9)	0.0090(10)	−0.0013(12)
O(1)	0.0713(18)	0.0391(13)	0.0592(16)	0.000	0.0068(14)	0.000
O(2A)	0.077(5)	0.045(3)	0.072(5)	0.004(2)	−0.008(3)	0.011(3)
O(2B)	0.14(4)	0.045(13)	0.072(18)	0.037(11)	0.046(18)	0.017(15)
O(3)	0.0602(14)	0.0892(16)	0.139(2)	−0.0117(14)	−0.0176(13)	−0.0155(12)
O(4)	0.160(2)	0.0923(16)	0.0502(11)	0.0089(11)	0.0209(13)	−0.0018(16)
C(A1)	0.0485(13)	0.0409(11)	0.0381(11)	0.0038(9)	−0.0027(9)	−0.0058(10)
C(A2)	0.0464(13)	0.0388(11)	0.0420(11)	0.0007(9)	−0.0047(10)	0.0006(10)
C(A3)	0.0406(12)	0.0438(12)	0.0458(12)	−0.0066(9)	0.0002(9)	0.0027(10)
C(A4)	0.0464(13)	0.0495(13)	0.0411(11)	−0.0075(10)	0.0004(9)	0.0067(11)
C(B1)	0.0527(15)	0.0583(14)	0.0399(11)	0.0042(10)	−0.0026(10)	−0.0047(12)
C(B2)	0.0507(15)	0.0609(15)	0.0406(11)	−0.0002(10)	−0.0079(10)	−0.0028(12)
C(B3)	0.0403(13)	0.0688(17)	0.0504(13)	−0.0063(11)	0.0004(10)	0.0041(11)
C(B4)	0.0457(14)	0.0770(18)	0.0454(13)	−0.0123(12)	0.0051(11)	0.0056(12)
C(M1)	0.0429(13)	0.0430(12)	0.0455(12)	−0.0015(9)	−0.0039(10)	0.0005(10)
C(M2)	0.0501(14)	0.0470(13)	0.0387(11)	−0.0073(9)	−0.0004(10)	0.0058(10)
C(6)	0.0456(13)	0.0579(14)	0.0406(11)	0.0027(10)	−0.0023(10)	0.0048(11)
C(7)	0.0434(14)	0.0670(16)	0.0537(14)	−0.0033(12)	−0.0082(11)	0.0044(12)
C(8)	0.0482(16)	0.096(2)	0.0684(17)	−0.0047(15)	−0.0181(13)	0.0020(15)
C(9)	0.0517(17)	0.111(3)	0.0634(17)	0.0123(17)	−0.0134(13)	0.0192(18)
C(10)	0.065(2)	0.091(2)	0.0704(18)	0.0231(17)	0.0016(15)	0.0305(17)
C(11)	0.0585(16)	0.0610(16)	0.0621(15)	0.0083(12)	0.0005(12)	0.0119(13)
C(12)	0.0545(17)	0.0672(17)	0.0656(16)	−0.0123(14)	−0.0043(13)	−0.0031(14)
C(13)	0.0431(13)	0.0668(16)	0.0420(11)	−0.0131(11)	−0.0019(10)	0.0080(11)
C(14)	0.0518(15)	0.0700(17)	0.0367(11)	−0.0107(11)	0.0006(10)	0.0039(12)
C(15)	0.0614(17)	0.087(2)	0.0415(12)	−0.0126(13)	0.0037(11)	0.0023(14)
C(16)	0.0531(17)	0.112(3)	0.0459(14)	−0.0279(16)	0.0035(12)	0.0150(16)
C(17)	0.0603(18)	0.088(2)	0.0590(16)	−0.0361(16)	−0.0031(13)	0.0175(16)
C(18)	0.0583(16)	0.0669(16)	0.0555(14)	−0.0200(12)	−0.0035(12)	0.0102(13)
C(19)	0.0658(18)	0.0722(18)	0.0442(13)	0.0006(12)	−0.0035(12)	−0.0004(14)

Table S17. Continued

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(3)	0.033(3)	0.0417(16)	0.030(3)	−0.001(2)	0.0023(19)	−0.006(2)
C(1)	0.040(4)	0.049(3)	0.036(3)	0.004(2)	0.006(2)	−0.001(2)
N(4)	0.047(3)	0.0370(17)	0.050(4)	0.0089(16)	−0.004(3)	−0.004(2)
C(2)	0.053(3)	0.041(3)	0.046(3)	0.003(2)	−0.001(3)	0.001(2)
C(3)	0.043(4)	0.038(2)	0.041(3)	0.000(2)	0.008(2)	0.005(2)
C(4)	0.061(3)	0.051(3)	0.083(4)	0.023(3)	0.012(3)	−0.008(3)
C(5)	0.095(7)	0.046(3)	0.127(8)	0.027(4)	−0.005(5)	−0.006(3)
C(1S)	0.091(3)	0.118(3)	0.134(4)	−0.011(3)	−0.012(2)	−0.002(2)
C(2S)	0.071(2)	0.135(3)	0.069(2)	0.001(2)	−0.0036(16)	−0.015(2)
C(3S)	0.087(3)	0.115(3)	0.081(2)	0.012(2)	0.0015(18)	0.001(2)
C(21A)	0.042(3)	0.050(3)	0.057(4)	−0.004(3)	−0.001(2)	−0.002(2)
C(22A)	0.079(5)	0.077(4)	0.086(4)	−0.005(3)	−0.036(4)	0.029(3)
C(23A)	0.133(8)	0.063(3)	0.061(3)	−0.015(2)	0.029(4)	−0.003(4)
C(24A)	0.049(4)	0.126(6)	0.122(8)	−0.048(6)	−0.011(4)	−0.005(4)
C(21B)	0.045(6)	0.077(8)	0.033(5)	−0.004(5)	0.004(4)	0.009(5)
C(22B)	0.074(10)	0.188(19)	0.094(11)	−0.082(11)	0.013(8)	0.003(11)
C(23B)	0.134(15)	0.101(8)	0.043(5)	−0.026(5)	0.006(7)	−0.016(9)
C(24B)	0.073(8)	0.121(12)	0.098(10)	−0.060(9)	0.033(7)	−0.035(7)
C(20A)	0.078(5)	0.057(4)	0.035(5)	−0.004(3)	0.006(3)	−0.013(4)
C(25A)	0.116(9)	0.108(9)	0.075(5)	0.038(5)	0.056(5)	0.034(6)
C(26A)	0.099(7)	0.125(7)	0.053(4)	−0.010(4)	−0.007(4)	0.029(5)
C(27A)	0.120(7)	0.063(5)	0.158(12)	−0.014(5)	−0.002(7)	−0.018(5)
C(20B)	0.069(5)	0.063(4)	0.040(4)	0.000(2)	0.003(3)	0.004(3)
C(25B)	0.082(6)	0.100(8)	0.249(15)	0.061(8)	0.080(8)	0.053(5)
C(26B)	0.077(5)	0.139(8)	0.064(4)	0.012(5)	0.010(3)	0.024(5)
C(27B)	0.147(7)	0.093(5)	0.099(6)	−0.043(4)	−0.018(5)	0.039(5)

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

The anisotropic displacement factor exponent takes the form: -2π [h^2 U_{11} +...+ 2 h k a* b* U_{12}].

Table S18. Hydrogen Atom Coordinates and Equivalent Isotropic Displacement Parameters
(Å^2) for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (200 K, $C2/c$ form)^a

atom	x	y	z	U(eq)
H(5A)	0.3062	0.7384	0.6327	0.078
H(6A)	0.3998	0.7555	0.9511	0.076
H(BA	0.4499	0.8681	0.4785	0.060
H(BB	0.3298	0.8572	0.5332	0.061
H(BC	0.2304	0.8507	0.7996	0.064
H(BD	0.2853	0.8612	0.9208	0.067
H(8A)	0.1264	0.7581	0.5844	0.085
H(9A)	0.0631	0.8614	0.5895	0.091
H(10A)	0.1159	0.9601	0.6358	0.091
H(11A)	0.2347	0.9577	0.6749	0.073
H(15A)	0.3436	0.7786	1.1306	0.076
H(16A)	0.3372	0.8876	1.1860	0.085
H(17A)	0.3747	0.9860	1.1267	0.083
H(18A)	0.4176	0.9782	1.0084	0.072
H(1A)	0.5602	0.9994	0.6811	0.050
H(2A)	0.4323	1.1134	0.8078	0.056
H(3A)	0.4158	0.9895	0.8380	0.049
H(4A)	0.5057	1.1396	0.6444	0.078
H(4B)	0.5830	1.1345	0.6829	0.078
H(5B)	0.5323	1.2454	0.7040	0.134
H(5C)	0.5407	1.2052	0.7795	0.134
H(5D)	0.4635	1.2103	0.7410	0.134
H(1SA)	0.4577	0.4446	0.2047	0.172
H(2SA)	0.4125	0.5484	0.1603	0.110
H(3SA)	0.4542	0.6539	0.2048	0.142
H(22A)	0.4466	0.5369	0.9480	0.121
H(22B)	0.4209	0.5522	1.0292	0.121
H(22C)	0.4897	0.5915	0.9971	0.121
H(23A)	0.4292	0.6208	0.8532	0.128
H(23B)	0.4714	0.6795	0.8976	0.128
H(23C)	0.3913	0.6939	0.8689	0.128
H(24A)	0.3215	0.5650	0.9087	0.149
H(24B)	0.2883	0.6396	0.9270	0.149
H(24C)	0.2999	0.5838	0.9903	0.149

Table S18. Continued

atom	x	y	z	$U(\text{eq})$
H(22D)	0.4536	0.5792	1.0284	0.178
H(22E)	0.4891	0.6268	0.9671	0.178
H(22F)	0.4536	0.5539	0.9458	0.178
H(23D)	0.3266	0.6763	0.8803	0.139
H(23E)	0.3766	0.6128	0.8560	0.139
H(23F)	0.4122	0.6857	0.8774	0.139
H(24D)	0.2720	0.6030	0.9745	0.146
H(24E)	0.3220	0.5647	1.0329	0.146
H(24F)	0.3220	0.5395	0.9503	0.146
H(25A)	0.3740	0.6601	0.5971	0.149
H(25B)	0.3305	0.6096	0.5438	0.149
H(25C)	0.3847	0.5778	0.6026	0.149
H(26A)	0.2799	0.6167	0.7576	0.139
H(26B)	0.3434	0.6643	0.7267	0.139
H(26C)	0.3540	0.5820	0.7322	0.139
H(27A)	0.2130	0.5391	0.6756	0.171
H(27B)	0.2871	0.5044	0.6502	0.171
H(27C)	0.2329	0.5363	0.5913	0.171
H(25D)	0.3991	0.5957	0.6125	0.215
H(25E)	0.3801	0.6681	0.6505	0.215
H(25F)	0.3688	0.6589	0.5651	0.215
H(26D)	0.3218	0.5441	0.7060	0.140
H(26E)	0.2371	0.5595	0.7065	0.140
H(26F)	0.2924	0.6167	0.7361	0.140
H(27D)	0.3094	0.5213	0.5676	0.169
H(27E)	0.2657	0.5781	0.5220	0.169
H(27F)	0.2257	0.5340	0.5833	0.169

$^a U(\text{eq})$ 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 S19. Complete Crystallographic Details for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (300 K, $C2/c$ form)

formula	C$_{75}$H$_{78}$CoN$_{10}$O$_6$
FW, amu	1274.40
a, Å	18.711(2)
b, Å	19.566(3)
c, Å	18.725(3)
β, deg	90.824(5)
V, Å^3	6854.6(17)
space group	$C2/c$
Z	4
D$_c$, g/cm^3	1.235
F(000)	2692
μ, mm^{-1}	0.310
crystal dimensions, mm	0.39 × 0.26 × 0.19
radiation	MoKα, $\bar{\lambda} = 0.71073$ Å
temperature, K	300(2)
diffractometer	Bruker Apex CCD
θ range for collected data, deg	1.85–27.13
index range	$-22 \leq$ h ≤ 23
	$-24 \leq$ k ≤ 24
	$-20 \leq$ l ≤ 24
total data collected	29027
absorption correction	Semi-empirical from equiv
relative transmission coefficients (I)	0.9434 and 0.8887
unique data	7495 ($R_{\text{int}} = 0.0434$)
unique observed data [I $> 2\sigma$(I)]	4242
refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	7495/6/494
goodness-of-fit (pased on F^2)	1.023
final R indices [I $> 2\sigma$(I)]	$R_1 = 0.0606$, $wR_2 = 0.1755$
final R indices (all data)	$R_1 = 0.1091$, $wR_2 = 0.2052$

Table S20. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $[\text{Co(TpivPP)(1-EtIm)(O}_2)]\cdot\text{C}_6\text{H}_6$ (300 K, $C2/c$ form)[a]

atom	x	y	z	$U(\text{eq})$
Co(1)	0.5000	0.86313(2)	0.7500	0.0553(2)
O(1)	0.5000	0.76386(18)	0.7500	0.0941(10)
O(2a)	0.5430(7)	0.7283(4)	0.7710(7)	0.094(7)
O(2b)	0.4819(17)	0.7216(16)	0.7895(17)	0.263(16)
O(3)	0.17269(19)	0.6570(2)	0.6177(3)	0.1673(16)
O(4)	0.3643(3)	0.6780(2)	1.08029(19)	0.198(2)
N(1)	0.45629(12)	0.86168(10)	0.65308(12)	0.0578(5)
N(2)	0.40367(12)	0.86099(10)	0.79237(12)	0.0600(5)
N(5)	0.25852(14)	0.73505(16)	0.63319(17)	0.0953(9)
N(6)	0.38987(18)	0.75394(17)	0.99673(15)	0.1006(9)
C(a1)	0.49064(15)	0.86545(14)	0.58903(15)	0.0634(7)
C(a2)	0.38465(15)	0.85763(13)	0.63575(15)	0.0634(7)
C(a3)	0.33901(14)	0.85664(14)	0.75716(15)	0.0621(7)
C(a4)	0.38698(15)	0.86427(14)	0.86354(16)	0.0657(7)
C(b1)	0.44005(17)	0.86356(16)	0.53149(16)	0.0760(8)
C(b2)	0.37514(17)	0.85813(17)	0.55995(16)	0.0761(8)
C(b3)	0.28152(16)	0.85630(17)	0.80716(17)	0.0783(9)
C(b4)	0.31098(16)	0.86144(18)	0.87207(18)	0.0810(9)
C(m1)	0.32888(15)	0.85552(14)	0.68355(16)	0.0645(7)
C(m2)	0.43591(16)	0.86885(14)	0.92000(15)	0.0654(7)
C(6)	0.25330(16)	0.85553(17)	0.65462(17)	0.0737(8)
C(7)	0.21984(16)	0.7963(2)	0.63073(17)	0.0820(9)
C(8)	0.14953(19)	0.7989(3)	0.6059(2)	0.1103(13)
C(9)	0.1131(2)	0.8604(3)	0.6059(3)	0.1278(18)
C(10)	0.1449(3)	0.9179(3)	0.6299(3)	0.1246(17)
C(11)	0.2152(2)	0.9161(2)	0.6535(2)	0.0979(11)
C(12)	0.2352(2)	0.6704(2)	0.6295(2)	0.1011(12)
C(13)	0.40735(16)	0.87515(18)	0.99463(17)	0.0773(9)
C(14)	0.38519(17)	0.8178(2)	1.03205(16)	0.0804(9)
C(15)	0.35876(19)	0.8244(2)	1.10051(18)	0.1004(12)
C(16)	0.3555(2)	0.8895(3)	1.1310(2)	0.1097(14)
C(17)	0.3786(2)	0.9457(3)	1.0951(2)	0.1087(13)
C(18)	0.40357(19)	0.9390(2)	1.02663(19)	0.0920(10)
C(19)	0.3805(2)	0.6913(3)	1.0182(2)	0.1063(13)

Table S20. Continued

atom	x	y	z	U(eq)
C(20)	0.2973(9)	0.6141(5)	0.6399(7)	0.096(9)
C(21)	0.296(2)	0.5749(14)	0.5707(7)	0.26(3)
C(22)	0.3707(8)	0.6439(9)	0.653(2)	0.22(2)
C(23)	0.2793(10)	0.5666(13)	0.7005(9)	0.150(10)
C(20b)	0.2865(4)	0.6136(3)	0.6391(5)	0.107(5)
C(21b)	0.2523(6)	0.5463(5)	0.6198(13)	0.257(14)
C(22b)	0.3516(7)	0.6245(7)	0.5939(7)	0.170(7)
C(23b)	0.3084(9)	0.6130(9)	0.7168(4)	0.184(8)
C(24)	0.3840(5)	0.6345(5)	0.9649(4)	0.092(5)
C(25)	0.3238(6)	0.5862(7)	0.9817(8)	0.152(6)
C(26)	0.4545(5)	0.5989(11)	0.9773(8)	0.208(10)
C(27)	0.3781(11)	0.6565(5)	0.8879(4)	0.159(8)
C(24b)	0.3949(5)	0.6340(5)	0.9622(5)	0.093(6)
C(25b)	0.3222(6)	0.6159(12)	0.9321(11)	0.211(13)
C(26b)	0.4265(13)	0.5727(8)	0.9998(11)	0.219(13)
C(27b)	0.4431(13)	0.6553(6)	0.9024(11)	0.184(11)
C(1S)	0.9727(4)	0.8810(5)	0.7248(4)	0.184(3)
C(2S)	0.9481(4)	0.9442(8)	0.6991(4)	0.207(4)
C(3S)	0.9764(5)	1.0078(8)	0.7271(6)	0.262(6)
N(3)	0.5000	0.96770(12)	0.7500	0.0742(9)
C(1)	0.53113(14)	1.01384(15)	0.71360(15)	0.086(3)
N(4)	0.5085(2)	1.07727(13)	0.7318(3)	0.079(3)
C(2)	0.4579(2)	1.07118(14)	0.7813(3)	0.078(2)
C(3)	0.45089(16)	1.00354(15)	0.79369(19)	0.092(3)
C(4)	0.5322(3)	1.13965(17)	0.6947(5)	0.119(3)
C(5)	0.5138(4)	1.20371(12)	0.7372(6)	0.214(6)

$^a\,U$(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 S21. Bond Lengths for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (300 K, $C2/c$ form)^a

bond	length (Å)	bond	length (Å)
Co(1)–O(1)	1.942(4)	C(22)–H(22a)	0.9600
Co(1)–N(1)	1.980(2)	C(22)–H(22b)	0.9600
Co(1)–N(1)#1	1.980(2)	C(22)–H(22C)	0.9600
Co(1)–N(2)	1.980(2)	C(23)–H(23a)	0.9600
Co(1)–N(2)#1	1.980(2)	C(23)–H(23b)	0.9600
Co(1)–N(3)	2.046(2)	C(23)–H(23C)	0.9600
O(1)–O(2a)#1	1.129(9)	C(20b)–C(23b)	1.5070
O(1)–O(2a)	1.129(9)	C(20b)–C(21b)	1.5070
O(1)–O(2b)	1.16(2)	C(20b)–C(22b)	1.5072
O(1)–O(2b)#1	1.16(2)	C(21b)–H(21d)	0.9600
O(2a)–O(2a)#1	1.78(2)	C(21b)–H(21e)	0.9600
O(2b)–O(2b)#1	1.64(5)	C(21b)–H(21F)	0.9600
O(3)–C(12)	1.216(5)	C(22b)–H(22d)	0.9600
O(4)–C(19)	1.234(5)	C(22b)–H(22e)	0.9600
N(1)–C(a1)	1.371(4)	C(22b)–H(22F)	0.9600
N(1)–C(a2)	1.377(3)	C(23b)–H(23d)	0.9600
N(2)–C(a3)	1.372(3)	C(23b)–H(23e)	0.9600
N(2)–C(a4)	1.375(4)	C(23b)–H(23F)	0.9600
N(5)–C(12)	1.339(5)	C(24)–C(25)	1.5068
N(5)–C(7)	1.401(4)	C(24)–C(26)	1.5068
N(5)–H(5a)	0.8600	C(24)–C(27)	1.5071
N(6)–C(19)	1.303(5)	C(25)–H(25a)	0.9600
N(6)–C(14)	1.417(4)	C(25)–H(25b)	0.9600
N(6)–H(6a)	0.8600	C(25)–H(25C)	0.9600
C(a1)–C(m2#1)	1.389(4)	C(26)–H(26a)	0.9600
C(a1)–C(b1)	1.425(4)	C(26)–H(26b)	0.9600
C(a2)–C(m1)	1.385(4)	C(26)–H(26C)	0.9600
C(a2)–C(b2)	1.428(4)	C(27)–H(27a)	0.9600
C(a3)–C(m1)	1.389(4)	C(27)–H(27b)	0.9600
C(a3)–C(b3)	1.436(4)	C(27)–H(27C)	0.9600
C(a4)–C(m2)	1.391(4)	C(24b)–C(27b)	1.5068
C(a4)–C(b4)	1.434(4)	C(24b)–C(26b)	1.5070
C(b1)–C(b2)	1.338(5)	C(24b)–C(25b)	1.5070
C(b1)–H(ba)	0.9300	C(25b)–H(25d)	0.9600

bond	length (Å)	bond	length (Å)
C(b2)–H(bb)	0.9300	C(25b)–H(25e)	0.9600
C(b3)–C(b4)	1.331(5)	C(25b)–H(25F)	0.9600
C(b3)–H(bC)	0.9300	C(26b)–H(26d)	0.9600
C(b4)–H(bd)	0.9300	C(26b)–H(26e)	0.9600
C(m1)–C(6)	1.507(4)	C(26b)–H(26F)	0.9600
C(m2)–C(a1#1)	1.389(4)	C(27b)–H(27d)	0.9600
C(m2)–C(13)	1.508(4)	C(27b)–H(27e)	0.9600
C(6)–C(11)	1.383(5)	C(27b)–H(27F)	0.9600
C(6)–C(7)	1.388(5)	C(1S)–C(1S)#2	1.381(15)
C(7)–C(8)	1.390(5)	C(1S)–C(2S)	1.402(12)
C(8)–C(9)	1.382(7)	C(1S)–H(1Sa)	0.9300
C(8)–H(8a)	0.9300	C(2S)–C(3S)	1.447(14)
C(9)–C(10)	1.347(7)	C(2S)–H(2Sa)	0.9300
C(9)–H(9a)	0.9300	C(3S)–C(3S)#2	1.220(19)
C(10)–C(11)	1.381(6)	C(3S)–H(3Sa)	0.9300
C(10)–H(10a)	0.9300	N(3)–C(1)#1	1.277(2)
C(11)–H(11a)	0.9300	N(3)–C(1)	1.2769
C(12)–C(20b)	1.479(8)	N(3)–C(3)	1.4238
C(12)–C(20)	1.613(14)	N(3)–C(3)#1	1.4238(19)
C(13)–C(18)	1.388(5)	C(1)–N(4)	1.3563
C(13)–C(14)	1.389(5)	C(1)–H(1a)	0.9300
C(14)–C(15)	1.387(4)	N(4)–C(2)#1	0.688(6)
C(15)–C(16)	1.398(6)	N(4)–N(4)#1	0.757(9)
C(15)–H(15a)	0.9300	N(4)–C(2)	1.3405
C(16)–C(17)	1.362(6)	N(4)–C(4)	1.4762
C(16)–H(16a)	0.9300	N(4)–C(3)#1	1.7019(13)
C(17)–C(18)	1.377(5)	N(4)–C(1)#1	1.777(2)
C(17)–H(17a)	0.9300	C(2)–C(3)	1.3502
C(18)–H(18a)	0.9300	C(2)–H(2a)	0.9300
C(19)–C(24)	1.496(9)	C(3)–H(3a)	0.9300
C(19)–C(24b)	1.561(11)	C(4)–C(5)	1.5274
C(20)–C(21)	1.5068	C(4)–H(4a)	0.9700
C(20)–C(22)	1.5069	C(4)–H(4b)	0.9700
C(20)–C(23)	1.5070	C(5)–H(5b)	0.9600

Table S21. Continued

bond	length (Å)	bond	length (Å)
C(21)–H(21a)	0.9600	C(5)–H(5C)	0.9600
C(21)–H(21b)	0.9600	C(5)–H(5d)	0.9600
C(21)–H(21C)	0.9600		

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

Table S22. Bond Angles for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (300 K, $C2/c$ form)^a

angle	degree	angle	degree
O(1)–Co(1)–N(1)	89.18(6)	C(20)–C(23)–H(23C)	109.5
O(1)–Co(1)–N(1)#1	89.18(6)	H(23a)–C(23)–H(23C)	109.5
N(1)–Co(1)–N(1)#1	178.36(12)	H(23b)–C(23)–H(23C)	109.5
O(1)–Co(1)–N(2)	88.79(6)	C(12)–C(20b)–C(23b)	106.9(6)
N(1)–Co(1)–N(2)	90.03(9)	C(12)–C(20b)–C(21b)	110.8(6)
N(1)#1–Co(1)–N(2)	89.93(9)	C(23b)–C(20b)–C(21b)	109.5
O(1)–Co(1)–N(2)#1	88.79(6)	C(12)–C(20b)–C(22b)	110.7(6)
N(1)–Co(1)–N(2)#1	89.93(9)	C(23b)–C(20b)–C(22b)	109.5
N(1)#1–Co(1)–N(2)#1	90.03(9)	C(21b)–C(20b)–C(22b)	109.5
N(2)–Co(1)–N(2)#1	177.58(12)	C(20b)–C(21b)–H(21d)	109.5
O(1)–Co(1)–N(3)	180.000(1)	C(20b)–C(21b)–H(21e)	109.5
N(1)–Co(1)–N(3)	90.82(6)	H(21d)–C(21b)–H(21e)	109.5
N(1)#1–Co(1)–N(3)	90.82(6)	C(20b)–C(21b)–H(21F)	109.5
N(2)–Co(1)–N(3)	91.21(6)	H(21d)–C(21b)–H(21f)	109.5
N(2)#1–Co(1)–N(3)	91.21(6)	H(21e)–C(21b)–H(21f)	109.5
O(2a)#1–O(1)–O(2a)	104.0(11)	C(20b)–C(22b)–H(22d)	109.5
O(2a)#1–O(1)–O(2b)	64.7(18)	C(20b)–C(22b)–H(22e)	109.5
O(2a)–O(1)–O(2b)	63.4(13)	H(22d)–C(22b)–H(22e)	109.5
O(2a)#1–O(1)–O(2b)#1	63.4(13)	C(20b)–C(22b)–H(22F)	109.5
O(2a)–O(1)–O(2b)#1	64.7(18)	H(22d)–C(22b)–H(22f)	109.5
O(2b)–O(1)–O(2b)#1	89(3)	H(22e)–C(22b)–H(22f)	109.5
O(2a)#1–O(1)–Co(1)	128.0(6)	C(20b)–C(23b)–H(23d)	109.5
O(2a)–O(1)–Co(1)	128.0(6)	C(20b)–C(23b)–H(23e)	109.5
O(2b)–O(1)–Co(1)	135.3(17)	H(23d)–C(23b)–H(23e)	109.5
O(2b)#1–O(1)–Co(1)	135.3(17)	C(20b)–C(23b)–H(23F)	109.5
O(1)–O(2a)–O(2a)#1	38.0(6)	H(23d)–C(23b)–H(23f)	109.5
O(1)–O(2b)–O(2b)#1	45.3(17)	H(23e)–C(23b)–H(23f)	109.5
C(a1)–N(1)–C(a2)	105.3(2)	C(19)–C(24)–C(25)	106.6(6)
C(a1)–N(1)–Co(1)	127.47(19)	C(19)–C(24)–C(26)	106.7(7)
C(a2)–N(1)–Co(1)	127.22(19)	C(25)–C(24)–C(26)	109.5
C(a3)–N(2)–C(a4)	104.9(2)	C(19)–C(24)–C(27)	115.0(6)
C(a3)–N(2)–Co(1)	127.60(19)	C(25)–C(24)–C(27)	109.5
C(a4)–N(2)–Co(1)	127.46(19)	C(26)–C(24)–C(27)	109.5
C(12)–N(5)–C(7)	129.7(3)	C(24)–C(25)–H(25a)	109.5

Table S22. Continued

angle	degree	angle	degree
C(12)–N(5)–H(5a)	115.2	C(24)–C(25)–H(25b)	109.5
C(7)–N(5)–H(5a)	115.2	H(25a)–C(25)–H(25b)	109.5
C(19)–N(6)–C(14)	132.6(3)	C(24)–C(25)–H(25C)	109.5
C(19)–N(6)–H(6a)	113.7	H(25a)–C(25)–H(25C)	109.5
C(14)–N(6)–H(6a)	113.7	H(25b)–C(25)–H(25C)	109.5
N(1)–C(a1)–C(m2#1	125.9(3)	C(24)–C(26)–H(26a)	109.5
N(1)–C(a1)–C(b1)	110.2(3)	C(24)–C(26)–H(26b)	109.5
C(m2#1–C(a1)–C(b1)	123.9(3)	H(26a)–C(26)–H(26b)	109.5
N(1)–C(a2)–C(m1)	126.1(3)	C(24)–C(26)–H(26C)	109.5
N(1)–C(a2)–C(b2)	109.9(3)	H(26a)–C(26)–H(26C)	109.5
C(m1)–C(a2)–C(b2)	123.9(3)	H(26b)–C(26)–H(26C)	109.5
N(2)–C(a3)–C(m1)	125.8(3)	C(24)–C(27)–H(27a)	109.5
N(2)–C(a3)–C(b3)	110.5(3)	C(24)–C(27)–H(27b)	109.5
C(m1)–C(a3)–C(b3)	123.7(3)	H(27a)–C(27)–H(27b)	109.5
N(2)–C(a4)–C(m2)	125.7(3)	C(24)–C(27)–H(27C)	109.5
N(2)–C(a4)–C(b4)	110.2(3)	H(27a)–C(27)–H(27C)	109.5
C(m2)–C(a4)–C(b4)	124.1(3)	H(27b)–C(27)–H(27C)	109.5
C(b2)–C(b1)–C(a1)	107.3(3)	C(27b)–C(24b)–C(26b)	109.5
C(b2)–C(b1)–H(ba)	126.3	C(27b)–C(24b)–C(25b)	109.5
C(a1)–C(b1)–H(ba)	126.3	C(26b)–C(24b)–C(25b)	109.5
C(b1)–C(b2)–C(a2)	107.2(3)	C(27b)–C(24b)–C(19)	114.3(7)
C(b1)–C(b2)–H(bb)	126.4	C(26b)–C(24b)–C(19)	109.2(8)
C(a2)–C(b2)–H(bb)	126.4	C(25b)–C(24b)–C(19)	104.9(8)
C(b4)–C(b3)–C(a3)	106.9(3)	C(24b)–C(25b)–H(25d)	109.5
C(b4)–C(b3)–H(bC)	126.6	C(24b)–C(25b)–H(25e)	109.5
C(a3)–C(b3)–H(bC)	126.6	H(25d)–C(25b)–H(25e)	109.5
C(b3)–C(b4)–C(a4)	107.4(3)	C(24b)–C(25b)–H(25F)	109.5
C(b3)–C(b4)–H(bd)	126.3	H(25d)–C(25b)–H(25f)	109.5
C(a4)–C(b4)–H(bd)	126.3	H(25e)–C(25b)–H(25f)	109.5
C(a2)–C(m1)–C(a3)	123.2(3)	C(24b)–C(26b)–H(26d)	109.5
C(a2)–C(m1)–C(6)	118.7(3)	C(24b)–C(26b)–H(26e)	109.5
C(a3)–C(m1)–C(6)	118.1(3)	H(26d)–C(26b)–H(26e)	109.5
C(a1#1–C(m2)–C(a4)	123.1(3)	C(24b)–C(26b)–H(26F)	109.5
C(a1#1–C(m2)–C(13)	118.8(3)	H(26d)–C(26b)–H(26f)	109.5

angle	degree	angle	degree
C(a4)–C(m2)–C(13)	118.1(3)	H(26e)–C(26b)–H(26f)	109.5
C(11)–C(6)–C(7)	118.7(3)	C(24b)–C(27b)–H(27d)	109.5
C(11)–C(6)–C(m1)	119.1(3)	C(24b)–C(27b)–H(27e)	109.5
C(7)–C(6)–C(m1)	122.2(3)	H(27d)–C(27b)–H(27e)	109.5
C(6)–C(7)–C(8)	119.8(4)	C(24b)–C(27b)–H(27F)	109.5
C(6)–C(7)–N(5)	118.3(3)	H(27d)–C(27b)–H(27f)	109.5
C(8)–C(7)–N(5)	121.9(4)	H(27e)–C(27b)–H(27f)	109.5
C(9)–C(8)–C(7)	119.8(4)	C(1S)#2–C(1S)–C(2S)	118.0(6)
C(9)–C(8)–H(8a)	120.1	C(1S)#2–C(1S)–H(1Sa)	121.0
C(7)–C(8)–H(8a)	120.1	C(2S)–C(1S)–H(1Sa)	121.0
C(10)–C(9)–C(8)	120.7(4)	C(1S)–C(2S)–C(3S)	121.2(10)
C(10)–C(9)–H(9a)	119.6	C(1S)–C(2S)–H(2Sa)	119.4
C(8)–C(9)–H(9a)	119.6	C(3S)–C(2S)–H(2Sa)	119.4
C(9)–C(10)–C(11)	120.0(4)	C(3S)#2–C(3S)–C(2S)	120.8(7)
C(9)–C(10)–H(10a)	120.0	C(3S)#2–C(3S)–H(3Sa)	119.6
C(11)–C(10)–H(10a)	120.0	C(2S)–C(3S)–H(3Sa)	119.6
C(10)–C(11)–C(6)	121.0(4)	C(1)#1–N(3)–C(1)	90.01(10)
C(10)–C(11)–H(11a)	119.5	C(1)#1–N(3)–C(3)	16.64(14)
C(6)–C(11)–H(11a)	119.5	C(1)–N(3)–C(3)	105.2
O(3)–C(12)–N(5)	121.7(4)	C(1)#1–N(3)–C(3)#1	105.2
O(3)–C(12)–C(20b)	118.8(5)	C(1)–N(3)–C(3)#1	16.64(11)
N(5)–C(12)–C(20b)	119.5(4)	C(3)–N(3)–C(3)#1	121.0
O(3)–C(12)–C(20)	124.3(6)	C(1)#1–N(3)–Co(1)	135.0
N(5)–C(12)–C(20)	113.9(6)	C(1)–N(3)–Co(1)	135.00(10)
C(20b)–C(12)–C(20)	5.6(6)	C(3)–N(3)–Co(1)	119.51(9)
C(18)–C(13)–C(14)	119.4(3)	C(3)#1–N(3)–Co(1)	119.5
C(18)–C(13)–C(m2)	119.6(3)	N(3)–C(1)–N(4)	111.5
C(14)–C(13)–C(m2)	120.9(3)	N(3)–C(1)–H(1a)	124.3
C(15)–C(14)–C(13)	120.3(3)	N(4)–C(1)–H(1a)	124.3
C(15)–C(14)–N(6)	122.6(4)	C(2)#1–N(4)–N(4)#1	136.1(16)
C(13)–C(14)–N(6)	117.1(3)	C(2)#1–N(4)–C(2)	152.8(8)
C(14)–C(15)–C(16)	118.7(4)	N(4)#1–N(4)–C(2)	20.9(8)
C(14)–C(15)–H(15a)	120.6	C(2)#1–N(4)–C(1)	57.46(18)
C(16)–C(15)–H(15a)	120.6	N(4)#1–N(4)–C(1)	111.30(15)

angle	degree	angle	degree
C(17)–C(16)–C(15)	121.2(4)	C(2)–N(4)–C(1)	108.6
C(17)–C(16)–H(16a)	119.4	C(2)#1–N(4)–C(4)	72.1(3)
C(15)–C(16)–H(16a)	119.4	N(4)#1–N(4)–C(4)	123.90(7)
C(16)–C(17)–C(18)	119.8(4)	C(2)–N(4)–C(4)	128.3
C(16)–C(17)–H(17a)	120.1	C(1)–N(4)–C(4)	122.8
C(18)–C(17)–H(17a)	120.1	C(2)#1–N(4)–C(3)#1	48.68(12)
C(17)–C(18)–C(13)	120.5(4)	N(4)#1–N(4)–C(3)#1	116.6(3)
C(17)–C(18)–H(18a)	119.7	C(2)–N(4)–C(3)#1	116.19(7)
C(13)–C(18)–H(18a)	119.7	C(1)–N(4)–C(3)#1	8.80(13)
O(4)–C(19)–N(6)	121.7(4)	C(4)–N(4)–C(3)#1	115.50(8)
O(4)–C(19)–C(24)	119.1(5)	C(2)#1–N(4)–C(1)#1	118.4(4)
N(6)–C(19)–C(24)	119.1(4)	N(4)#1–N(4)–C(1)#1	45.32(11)
O(4)–C(19)–C(24b)	121.9(6)	C(2)–N(4)–C(1)#1	40.07(7)
N(6)–C(19)–C(24b)	116.3(5)	C(1)–N(4)–C(1)#1	68.89(7)
C(24)–C(19)–C(24b)	7.5(5)	C(4)–N(4)–C(1)#1	168.32(7)
C(21)–C(20)–C(22)	109.5	C(3)#1–N(4)–C(1)#1	76.2
C(21)–C(20)–C(23)	109.5	N(4)–C(2)–C(3)	106.1
C(22)–C(20)–C(23)	109.5	N(4)–C(2)–H(2a)	127.0
C(21)–C(20)–C(12)	104.0(10)	C(3)–C(2)–H(2a)	127.0
C(22)–C(20)–C(12)	114.1(9)	C(2)–C(3)–N(3)	108.6
C(23)–C(20)–C(12)	110.1(10)	C(2)–C(3)–H(3a)	125.7
C(20)–C(21)–H(21a)	109.5	N(3)–C(3)–H(3a)	125.7
C(20)–C(21)–H(21b)	109.5	N(4)–C(4)–C(5)	111.2
H(21a)–C(21)–H(21b)	109.5	N(4)–C(4)–H(4a)	109.4
C(20)–C(21)–H(21C)	109.5	C(5)–C(4)–H(4a)	109.4
H(21a)–C(21)–H(21C)	109.5	N(4)–C(4)–H(4b)	109.4
H(21b)–C(21)–H(21C)	109.5	C(5)–C(4)–H(4b)	109.4
C(20)–C(22)–H(22a)	109.5	H(4a)–C(4)–H(4b)	108.0
C(20)–C(22)–H(22b)	109.5	C(4)–C(5)–H(5b)	109.5
H(22a)–C(22)–H(22b)	109.5	C(4)–C(5)–H(5C)	109.5
C(20)–C(22)–H(22C)	109.5	H(5b)–C(5)–H(5C)	109.5
H(22a)–C(22)–H(22C)	109.5	C(4)–C(5)–H(5d)	109.5
H(22b)–C(22)–H(22C)	109.5	H(5b)–C(5)–H(5d)	109.5
C(20)–C(23)–H(23a)	109.5	H(5C)–C(5)–H(5d)	109.5

Table S22. Continued

angle	degree	angle	degree
C(20)–C(23)–H(23b)	109.5		
H(23a)–C(23)–H(23b)	109.5		

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

Table S23. Anisotropic Displacement Parameters ($Å^2$) for [Co(TpivPP)(1-EtIm)(O_2)]·C_6H_6 (300 K, $C2/c$ form)[a]

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co(1)	0.0569(3)	0.0537(3)	0.0554(3)	0.000	0.0015(2)	0.000
O(1)	0.111(3)	0.073(2)	0.098(3)	0.000	0.010(2)	0.000
O(2A)	0.113(10)	0.048(6)	0.121(12)	0.004(5)	−0.034(7)	0.023(5)
O(2B)	0.18(3)	0.36(4)	0.25(3)	0.21(3)	0.08(2)	0.02(2)
O(3)	0.099(2)	0.147(3)	0.255(5)	−0.016(3)	−0.029(3)	−0.037(2)
O(4)	0.334(6)	0.158(4)	0.103(2)	0.008(2)	0.071(3)	−0.041(4)
N(1)	0.0606(12)	0.0563(12)	0.0567(13)	0.0002(10)	0.0033(10)	−0.0020(10)
N(2)	0.0622(13)	0.0579(13)	0.0599(13)	−0.0038(10)	0.0031(10)	0.0023(10)
N(5)	0.0630(15)	0.094(2)	0.128(3)	−0.0170(18)	−0.0138(15)	−0.0083(15)
N(6)	0.149(3)	0.099(2)	0.0541(15)	−0.0012(16)	0.0243(16)	−0.013(2)
C(A1)	0.0701(17)	0.0618(16)	0.0582(16)	0.0022(13)	0.0000(13)	−0.0025(13)
C(A2)	0.0660(16)	0.0625(16)	0.0619(17)	−0.0009(13)	−0.0004(13)	−0.0002(13)
C(A3)	0.0571(15)	0.0656(17)	0.0637(17)	−0.0024(13)	0.0025(12)	0.0011(12)
C(A4)	0.0640(16)	0.0723(18)	0.0608(17)	−0.0078(14)	0.0063(13)	0.0029(13)
C(B1)	0.077(2)	0.097(2)	0.0542(17)	0.0024(15)	0.0015(14)	−0.0023(16)
C(B2)	0.0708(19)	0.097(2)	0.0598(18)	0.0004(15)	−0.0079(14)	−0.0032(16)
C(B3)	0.0571(16)	0.105(3)	0.073(2)	−0.0022(17)	0.0060(14)	0.0048(15)
C(B4)	0.0651(18)	0.113(3)	0.0656(19)	−0.0074(17)	0.0139(15)	0.0038(17)
C(M1)	0.0593(15)	0.0649(17)	0.0694(18)	0.0001(13)	−0.0016(13)	0.0006(13)
C(M2)	0.0704(17)	0.0695(17)	0.0566(16)	−0.0068(13)	0.0080(13)	0.0028(13)
C(6)	0.0642(17)	0.087(2)	0.0696(19)	0.0074(16)	−0.0020(14)	0.0063(16)
C(7)	0.0619(17)	0.105(3)	0.079(2)	−0.0013(19)	−0.0099(15)	0.0048(18)
C(8)	0.069(2)	0.147(4)	0.114(3)	−0.001(3)	−0.022(2)	0.001(2)
C(9)	0.075(3)	0.193(6)	0.115(4)	0.027(3)	−0.023(2)	0.016(3)
C(10)	0.093(3)	0.154(5)	0.127(4)	0.044(3)	0.003(3)	0.049(3)
C(11)	0.086(2)	0.101(3)	0.107(3)	0.020(2)	0.006(2)	0.020(2)
C(12)	0.083(3)	0.106(3)	0.114(3)	−0.022(2)	0.002(2)	−0.017(2)
C(13)	0.0652(17)	0.103(3)	0.0637(18)	−0.0210(18)	0.0021(14)	0.0068(16)
C(14)	0.079(2)	0.107(3)	0.0554(17)	−0.0112(18)	0.0074(14)	−0.0024(18)
C(15)	0.092(2)	0.146(4)	0.063(2)	−0.019(2)	0.0144(17)	−0.007(2)
C(16)	0.086(3)	0.173(4)	0.071(2)	−0.037(3)	0.0134(19)	0.013(3)
C(17)	0.101(3)	0.136(4)	0.089(3)	−0.052(3)	0.007(2)	0.015(3)
C(18)	0.093(2)	0.101(3)	0.082(2)	−0.026(2)	0.0047(18)	0.0084(19)
C(19)	0.127(3)	0.127(4)	0.066(2)	0.004(2)	0.010(2)	−0.022(3)

Table S23. Continued

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(20)	0.117(13)	0.060(11)	0.11(2)	−0.031(11)	0.025(12)	−0.002(9)
C(21)	0.48(7)	0.19(3)	0.104(13)	−0.025(15)	0.04(2)	0.16(4)
C(22)	0.091(11)	0.130(15)	0.43(6)	0.04(2)	0.07(2)	0.039(10)
C(23)	0.120(12)	0.15(2)	0.18(2)	0.054(16)	0.036(12)	−0.008(12)
C(20B)	0.091(6)	0.121(11)	0.108(11)	0.011(8)	0.012(6)	−0.012(6)
C(21B)	0.196(12)	0.092(7)	0.48(4)	−0.075(13)	−0.035(17)	−0.032(7)
C(22B)	0.167(12)	0.153(12)	0.192(13)	0.035(9)	0.094(11)	0.060(9)
C(23B)	0.228(18)	0.207(15)	0.117(8)	0.033(8)	0.043(8)	0.095(13)
C(24)	0.079(6)	0.117(12)	0.079(10)	−0.012(8)	0.013(6)	−0.016(6)
C(25)	0.127(9)	0.164(11)	0.166(12)	−0.068(9)	0.031(8)	−0.039(7)
C(26)	0.113(8)	0.34(3)	0.169(14)	−0.114(16)	−0.018(9)	0.082(13)
C(27)	0.27(2)	0.137(8)	0.067(5)	−0.027(5)	0.004(8)	−0.024(11)
C(24B)	0.107(11)	0.078(11)	0.093(14)	0.000(9)	−0.017(8)	−0.004(8)
C(25B)	0.099(10)	0.37(3)	0.17(2)	−0.12(2)	−0.038(11)	0.012(14)
C(26B)	0.32(3)	0.108(10)	0.23(2)	0.003(11)	−0.17(2)	0.028(14)
C(27B)	0.205(19)	0.130(10)	0.22(2)	−0.070(12)	0.129(17)	−0.041(12)
C(1S)	0.165(7)	0.254(9)	0.131(6)	−0.023(5)	0.008(4)	0.012(5)
C(2S)	0.124(6)	0.371(16)	0.124(5)	−0.003(8)	0.000(4)	0.045(7)
C(3S)	0.142(9)	0.387(17)	0.256(15)	0.038(12)	−0.006(7)	−0.003(8)
N(3)	0.081(2)	0.059(2)	0.082(2)	0.000	−0.0226(19)	0.000
C(1)	0.107(6)	0.046(4)	0.104(8)	0.001(4)	−0.035(5)	0.004(4)
N(4)	0.059(5)	0.056(3)	0.123(8)	0.011(3)	−0.006(5)	0.008(3)
C(2)	0.070(5)	0.068(5)	0.094(5)	0.005(4)	−0.014(4)	−0.004(3)
C(3)	0.129(7)	0.050(4)	0.096(7)	−0.004(4)	−0.022(5)	−0.004(5)
C(4)	0.113(6)	0.085(6)	0.159(9)	0.026(5)	0.037(6)	−0.020(4)
C(5)	0.259(14)	0.092(6)	0.292(15)	0.046(11)	−0.014(12)	−0.043(10)

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

The anisotropic displacement factor exponent takes the form: -2π [$h^2\ U_{11}$ +...+ 2 h k a* b* U_{12}].

Table S24. Hydrogen Atom Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $[\text{Co(TpivPP)(1-EtIm)(O}_2)]\cdot\text{C}_6\text{H}_6$ (300 K, $C2/c$ form)^a

atom	x	y	z	U(eq)
H(5A)	0.3041	0.7396	0.6378	0.114
H(6A)	0.4011	0.7572	0.9525	0.121
H(BA	0.4503	0.8657	0.4831	0.091
H(BB	0.3319	0.8552	0.5350	0.091
H(BC	0.2330	0.8531	0.7963	0.094
H(BD	0.2867	0.8629	0.9150	0.097
H(8A)	0.1271	0.7595	0.5893	0.132
H(9A)	0.0661	0.8620	0.5892	0.153
H(10A)	0.1196	0.9587	0.6305	0.150
H(11A)	0.2371	0.9562	0.6690	0.117
H(15A)	0.3435	0.7862	1.1257	0.120
H(16A)	0.3372	0.8946	1.1766	0.132
H(17A)	0.3775	0.9884	1.1167	0.130
H(18A)	0.4180	0.9776	1.0017	0.110
H(21A)	0.3348	0.5426	0.5707	0.386
H(21B)	0.3014	0.6060	0.5315	0.386
H(21C)	0.2516	0.5510	0.5657	0.386
H(22A)	0.3714	0.6688	0.6967	0.328
H(22B)	0.3821	0.6741	0.6140	0.328
H(22C)	0.4052	0.6076	0.6550	0.328
H(23A)	0.3168	0.5334	0.7064	0.226
H(23B)	0.2351	0.5437	0.6898	0.226
H(23C)	0.2747	0.5925	0.7437	0.226
H(21D)	0.2109	0.5393	0.6486	0.386
H(21E)	0.2858	0.5099	0.6282	0.386
H(21F)	0.2384	0.5466	0.5702	0.386
H(22D)	0.3734	0.6674	0.6062	0.255
H(22E)	0.3376	0.6249	0.5443	0.255
H(22F)	0.3851	0.5882	0.6023	0.255
H(23D)	0.2670	0.6060	0.7456	0.276
H(23E)	0.3302	0.6559	0.7291	0.276
H(23F)	0.3420	0.5767	0.7253	0.276
H(25A)	0.3276	0.5722	1.0307	0.228
H(25B)	0.3265	0.5468	0.9513	0.228

Table S24. Continued

atom	x	y	z	$U(\text{eq})$
H(25C)	0.2789	0.6089	0.9737	0.228
H(26A)	0.4929	0.6296	0.9666	0.311
H(26B)	0.4572	0.5595	0.9469	0.311
H(26C)	0.4583	0.5848	1.0264	0.311
H(27A)	0.4164	0.6873	0.8772	0.238
H(27B)	0.3332	0.6793	0.8800	0.238
H(27C)	0.3808	0.6172	0.8575	0.238
H(25D)	0.3268	0.5796	0.8980	0.317
H(25E)	0.3016	0.6552	0.9091	0.317
H(25F)	0.2919	0.6013	0.9701	0.317
H(26D)	0.4342	0.5368	0.9658	0.328
H(26E)	0.3942	0.5571	1.0357	0.328
H(26F)	0.4713	0.5851	1.0219	0.328
H(27D)	0.4494	0.6176	0.8703	0.276
H(27E)	0.4886	0.6690	0.9218	0.276
H(27F)	0.4218	0.6930	0.8769	0.276
H(1SA)	0.9529	0.8402	0.7082	0.275
H(2SA)	0.9130	0.9453	0.6635	0.248
H(3SA)	0.9585	1.0491	0.7101	0.392
H(1A)	0.5651	1.0051	0.6790	0.103
H(2A)	0.4327	1.1064	0.8029	0.093
H(3A)	0.4193	0.9837	0.8254	0.110
H(4A)	0.5093	1.1420	0.6479	0.143
H(4B)	0.5835	1.1376	0.6879	0.143
H(5B)	0.4683	1.1977	0.7594	0.322
H(5C)	0.5117	1.2424	0.7057	0.322
H(5D)	0.5498	1.2113	0.7734	0.322

[a] $U(\text{eq})$ 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 S25. Complete Crystallographic Details for $[Co(TpivPP)(2\text{-MeHIm})(O_2)]\cdot 1.8C_2H_5OH$ (100 K, $C2/c$ form)

formula	$C_{71.6}H_{80.8}CoN_{10}O_{7.8}$
FW, amu	1265.19
a, Å	18.7514(3)
b, Å	19.5309(3)
c, Å	17.8719(3)
β, deg	91.0650(10)
V, Å^3	6544.13(18)
space group	$C2/c$
Z	4
D_c, g/cm^3	1.284
F(000)	2679
μ, mm^{-1}	0.326
crystal dimensions, mm	$0.37 \times 0.21 \times 0.16$
radiation	MoKα, $\bar{\lambda} = 0.71073$ Å
temperature, K	100(2)
diffractometer	Bruker Apex CCD
θ range for collected data, deg	1.51–31.00
index range	$-27 \leq h \leq 27$
	$-28 \leq k \leq 28$
	$-25 \leq l \leq 25$
total data collected	68291
absorption correction	Semi-empirical from equiv
relative transmission coefficients (I)	0.9497 and 0.8889
unique data	10425 ($R_{\text{int}} = 0.028$)
unique observed data [I > 2σ(I)]	8732
refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	10425/1/521
goodness-of-fit (based on F^2)	1.057
final R indices [I > 2σ(I)]	$R_1 = 0.0559$, $wR_2 = 0.1591$
final R indices (all data)	$R_1 = 0.0676$, $wR_2 = 0.1703$

Table S26. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\mathring{A}^2$) for [Co(TpivPP)(2-MeHIm)(O$_2$)]·1.8C$_2$H$_5$OH^a (100 K, $C2/c$ form)^a

atom	x	y	z	U(eq)
Co(1)	0.5000	0.86363(1)	0.7500	0.0187(1)
O(1)	0.5000	0.76626(11)	0.7500	0.0463(5)
O(2)	0.5411(2)	0.73064(18)	0.7729(2)	0.0537(9)
N(3)	0.40332(7)	0.85847(7)	0.79322(7)	0.0222(2)
N(4)	0.54217(7)	0.86318(7)	0.85261(7)	0.0209(2)
N(5)	0.39145(10)	0.74530(9)	1.00339(10)	0.0379(4)
N(6)	0.72976(9)	0.73159(10)	0.87680(12)	0.0442(5)
C(a1)	0.33927(9)	0.85376(9)	0.75470(9)	0.0251(3)
C(a2)	0.38569(9)	0.85713(8)	0.86773(9)	0.0240(3)
C(a3)	0.50677(9)	0.86631(8)	0.91938(8)	0.0224(3)
C(a4)	0.61342(9)	0.86174(8)	0.87187(9)	0.0232(3)
C(b1)	0.28072(9)	0.84808(10)	0.80586(10)	0.0307(3)
C(b2)	0.30967(10)	0.85076(10)	0.87573(10)	0.0301(3)
C(b3)	0.55697(10)	0.86808(9)	0.98167(9)	0.0281(3)
C(b4)	0.62289(10)	0.86533(9)	0.95221(9)	0.0284(3)
C(m1)	0.43331(9)	0.86376(8)	0.92801(9)	0.0229(3)
C(m2)	0.66980(9)	0.85617(8)	0.82271(9)	0.0247(3)
C(5)	0.40459(9)	0.86729(9)	1.00560(9)	0.0254(3)
C(6)	0.38491(10)	0.80743(10)	1.04329(9)	0.0302(3)
C(7)	0.36010(11)	0.81110(14)	1.11670(10)	0.0424(5)
C(8)	0.35529(11)	0.87460(15)	1.15146(11)	0.0481(6)
C(9)	0.37426(11)	0.93364(14)	1.11522(12)	0.0439(5)
C(10)	0.39878(10)	0.93010(11)	1.04197(11)	0.0342(4)
C(11)	0.74394(9)	0.85264(10)	0.85481(10)	0.0287(3)
C(12)	0.77236(9)	0.79116(11)	0.88152(11)	0.0343(4)
C(13)	0.84146(11)	0.78952(14)	0.91287(13)	0.0455(5)
C(14)	0.88259(12)	0.84812(15)	0.91381(15)	0.0497(6)
C(15)	0.85590(12)	0.90859(14)	0.88579(16)	0.0515(6)
C(16)	0.78640(11)	0.91114(11)	0.85758(13)	0.0400(4)
C(17)	0.38421(12)	0.67976(12)	1.02561(15)	0.0468(5)
C(18)	0.39158(8)	0.62678(8)	0.9533(2)	0.0311(9)
C(19)	0.31901(9)	0.59453(14)	0.9434(3)	0.0367(10)
C(20)	0.44483(12)	0.57288(13)	0.9771(3)	0.0554(15)
C(21)	0.41401(19)	0.65798(17)	0.8803(2)	0.0449(12)

Table S26. Continued

atom	x	y	z	$U(\mathrm{eq})$
C(18b)	0.39085(10)	0.62423(9)	0.9800(2)	0.0316(13)
C(19b)	0.31610(8)	0.60046(15)	0.9616(3)	0.042(2)
C(20b)	0.43223(17)	0.56664(15)	1.0163(3)	0.070(3)
C(21b)	0.42699(14)	0.64562(14)	0.9091(2)	0.070(3)
C(22)	0.75276(11)	0.66667(12)	0.86379(11)	0.0380(4)
C(23)	0.69704(11)	0.61127(10)	0.85777(13)	0.0401(8)
C(25)	0.62095(14)	0.63477(18)	0.8653(2)	0.0634(12)
C(24)	0.71474(19)	0.56016(18)	0.91848(16)	0.0684(11)
C(26)	0.70609(17)	0.57822(17)	0.78235(14)	0.0585(10)
C(23b)	0.6986(5)	0.6052(4)	0.8378(6)	0.048(5)
C(25b)	0.6359(9)	0.6148(10)	0.8884(5)	0.071(6)
C(24b)	0.7297(8)	0.5349(6)	0.8496(10)	0.076(6)
C(26b)	0.6742(6)	0.6128(6)	0.7574(5)	0.041(3)
O(4a)	0.8149(6)	0.6602(5)	0.8511(12)	0.047(3)
O(3a)	0.3639(8)	0.6683(8)	1.0939(6)	0.0634(18)
O(4b)	0.8156(9)	0.6409(16)	0.8764(10)	0.048(4)
O(3b)	0.387(2)	0.6567(8)	1.0831(10)	0.058(5)
N(1)	0.4914(3)	0.96944(13)	0.7582(3)	0.0194(8)
C(1)	0.52580(17)	1.02084(16)	0.72458(18)	0.0228(6)
N(2)	0.4993(8)	1.08137(13)	0.7496(9)	0.0261(6)
C(2)	0.45019(17)	1.06984(18)	0.80131(18)	0.0256(6)
C(3)	0.44385(19)	1.00129(18)	0.80628(19)	0.0235(6)
C(4)	0.5824(2)	1.01717(18)	0.6676(2)	0.0319(7)
O(1S)	0.44760(18)	0.20174(16)	0.8100(2)	0.0504(9)
C(1S)	0.4728(3)	0.2604(2)	0.7812(3)	0.1109(18)
C(2S)	0.4639(7)	0.5566(5)	0.2252(5)	0.089(3)
C(3S)	0.5000	0.5094(7)	0.2500	0.137(4)
O(2S)	0.4494(7)	0.5446(4)	0.1601(6)	0.151(4)

$^{a}\,U(\mathrm{eq})$ 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 S27. Bond Lengths for [Co(TpivPP)(2-MeHIm)(O$_2$)]·1.8C$_2$H$_5$OH^a (100 K, $C2/c$ form)^a

bond	length (Å)	bond	length (Å)
Co(1)–O(1)	1.902(2)	C(19)–H(19C)	0.9800
Co(1)–N(4)	1.9836(13)	C(20)–H(20a)	0.9800
Co(1)–N(4)#1	1.9836(13)	C(20)–H(20b)	0.9800
Co(1)–N(3)	1.9863(14)	C(20)–H(20C)	0.9800
Co(1)–N(3)#1	1.9863(14)	C(21)–H(21a)	0.9800
Co(1)–N(1)	2.078(2)	C(21)–H(21b)	0.9800
Co(1)–N(1)#1	2.078(2)	C(21)–H(21C)	0.9800
O(1)–O(2)	1.110(4)	C(18b)–C(21b)	1.5069
O(1)–O(2)#1	1.111(4)	C(18b)–C(20b)	1.5069
O(2)–O(2)#1	1.731(7)	C(18b)–C(19b)	1.5069
N(3)–C(a1)	1.376(2)	C(19b)–H(19d)	0.9800
N(3)–C(a2)	1.378(2)	C(19b)–H(19e)	0.9800
N(4)–C(a4)	1.374(2)	C(19b)–H(19F)	0.9800
N(4)–C(a3)	1.3775(19)	C(20b)–H(20d)	0.9800
N(5)–C(17)	1.348(3)	C(20b)–H(20e)	0.9800
N(5)–C(6)	1.414(3)	C(20b)–H(20F)	0.9800
N(5)–H(5a)	0.8800	C(21b)–H(21d)	0.9800
N(6)–C(22)	1.361(3)	C(21b)–H(21e)	0.9800
N(6)–C(12)	1.413(3)	C(21b)–H(21F)	0.9800
N(6)–H(6a)	0.8800	C(22)–O(4a)	1.197(8)
C(a1)–C(m2#1)	1.392(2)	C(22)–O(4b)	1.298(7)
C(a1)–C(b1)	1.446(2)	C(22)–C(23)	1.507(3)
C(a2)–C(m1)	1.392(2)	C(22)–C(23b)	1.634(8)
C(a2)–C(b2)	1.441(2)	C(23)–C(24)	1.5068
C(a3)–C(m1)	1.390(2)	C(23)–C(26)	1.5070
C(a3)–C(b3)	1.445(2)	C(23)–C(25)	1.5073
C(a4)–C(m2)	1.391(2)	C(25)–H(25a)	0.9800
C(a4)–C(b4)	1.445(2)	C(25)–H(25b)	0.9800
C(b1)–C(b2)	1.353(2)	C(25)–H(25C)	0.9800
C(b1)–H(ba)	0.9500	C(24)–H(24a)	0.9800
C(b2)–H(bb)	0.9500	C(24)–H(24b)	0.9800
C(b3)–C(b4)	1.353(3)	C(24)–H(24C)	0.9800
C(b3)–H(bC)	0.9500	C(26)–H(26a)	0.9800
C(b4)–H(bd)	0.9500	C(26)–H(26b)	0.9800

bond	length (Å)	bond	length (Å)
C(m1)–C(5)	1.498(2)	C(26)–H(26C)	0.9800
C(m2)–C(a1#1)	1.392(2)	C(23b)–C(25b)	1.5070
C(m2)–C(11)	1.496(2)	C(23b)–C(24b)	1.5070
C(5)–C(10)	1.394(2)	C(23b)–C(26b)	1.5071
C(5)–C(6)	1.402(2)	C(25b)–H(25d)	0.9800
C(6)–C(7)	1.402(2)	C(25b)–H(25e)	0.9800
C(7)–C(8)	1.391(4)	C(25b)–H(25F)	0.9800
C(7)–H(7a)	0.9500	C(24b)–H(24d)	0.9800
C(8)–C(9)	1.373(4)	C(24b)–H(24e)	0.9800
C(8)–H(8a)	0.9500	C(24b)–H(24F)	0.9800
C(9)–C(10)	1.397(3)	C(26b)–H(26d)	0.9800
C(9)–H(9a)	0.9500	C(26b)–H(26e)	0.9800
C(10)–H(10a)	0.9500	C(26b)–H(26F)	0.9800
C(11)–C(16)	1.393(3)	N(1)–C(1)	1.341(4)
C(11)–C(12)	1.394(3)	N(1)–C(3)	1.396(4)
C(12)–C(13)	1.402(3)	C(1)–N(2)	1.361(7)
C(13)–C(14)	1.380(4)	C(1)–C(4)	1.486(5)
C(13)–H(13a)	0.9500	N(2)–C(2)	1.336(14)
C(14)–C(15)	1.374(4)	N(2)–H(2a)	0.8800
C(14)–H(14a)	0.9500	C(2)–C(3)	1.347(5)
C(15)–C(16)	1.389(3)	C(2)–H(2b)	0.9500
C(15)–H(15a)	0.9500	C(3)–H(3a)	0.9500
C(16)–H(16a)	0.9500	C(4)–H(4a)	0.9800
C(17)–O(3b)	1.122(13)	C(4)–H(4b)	0.9800
C(17)–O(3a)	1.304(12)	C(4)–H(4C)	0.9800
C(17)–C(18b)	1.364(4)	O(1S)–C(1S)	1.345(5)
C(17)–C(18)	1.663(4)	C(1S)–C(1S)#1)	1.525(7)
C(18)–C(21)	1.5069	C(2S)–O(2S)	1.213(12)
C(18)–C(19)	1.5069	C(2S)–C(3S)	1.222(13)
C(18)–C(20)	1.5070	C(2S)–C(2S)#2)	1.60(2)
C(19)–H(19a)	0.9800	C(3S)–C(2S)#2)	1.222(13)
C(19)–H(19b)	0.9800		

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

Table S28. Bond Angles for [Co(TpivPP)(2-MeHIm)(O$_2$)]·1.8C$_2$H$_5$OH^a (100 K, $C2/c$ form)^a

angle	degree	angle	degree
O(1)–Co(1)–N(4)	89.75(4)	H(19a)–C(19)–H(19C)	109.5
O(1)–Co(1)–N(4)#1	89.75(4)	H(19b)–C(19)–H(19C)	109.5
N(4)–Co(1)–N(4)#1	179.50(8)	C(18)–C(20)–H(20a)	109.5
O(1)–Co(1)–N(3)	87.09(4)	C(18)–C(20)–H(20b)	109.5
N(4)–Co(1)–N(3)	89.50(6)	H(20a)–C(20)–H(20b)	109.5
N(4)#1–Co(1)–N(3)	90.47(6)	C(18)–C(20)–H(20C)	109.5
O(1)–Co(1)–N(3)#1	87.10(4)	H(20a)–C(20)–H(20C)	109.5
N(4)–Co(1)–N(3)#1	90.48(6)	H(20b)–C(20)–H(20C)	109.5
N(4)#1–Co(1)–N(3)#1	89.50(6)	C(18)–C(21)–H(21a)	109.5
N(3)–Co(1)–N(3)#1	174.19(8)	C(18)–C(21)–H(21b)	109.5
O(1)–Co(1)–N(1)	173.93(8)	H(21a)–C(21)–H(21b)	109.5
N(4)–Co(1)–N(1)	88.2(2)	C(18)–C(21)–H(21C)	109.5
N(4)#1–Co(1)–N(1)	92.2(2)	H(21a)–C(21)–H(21C)	109.5
N(3)–Co(1)–N(1)	87.16(11)	H(21b)–C(21)–H(21C)	109.5
N(3)#1–Co(1)–N(1)	98.65(11)	C(17)–C(18b)–C(21b)	109.25(19)
O(1)–Co(1)–N(1)#1	173.93(8)	C(17)–C(18b)–C(20b)	112.8(2)
N(4)–Co(1)–N(1)#1	92.2(2)	C(21b)–C(18b)–C(20b)	109.5
N(4)#1–Co(1)–N(1)#1	88.3(2)	C(17)–C(18b)–C(19b)	106.3(2)
N(3)–Co(1)–N(1)#1	98.65(11)	C(21b)–C(18b)–C(19b)	109.5
N(3)#1–Co(1)–N(1)#1	87.16(11)	C(20b)–C(18b)–C(19b)	109.5
N(1)–Co(1)–N(1)#1	12.14(16)	C(18b)–C(19b)–H(19d)	109.5
O(2)–O(1)–O(2)#1	102.4(4)	C(18b)–C(19b)–H(19e)	109.5
O(2)–O(1)–Co(1)	128.8(2)	H(19d)–C(19b)–H(19e)	109.5
O(2)#1–O(1)–Co(1)	128.8(2)	C(18b)–C(19b)–H(19F)	109.5
O(1)–O(2)–O(2)#1	38.8(2)	H(19d)–C(19b)–H(19f)	109.5
C(a1)–N(3)–C(a2)	105.02(13)	H(19e)–C(19b)–H(19f)	109.5
C(a1)–N(3)–Co(1)	127.10(11)	C(18b)–C(20b)–H(20d)	109.5
C(a2)–N(3)–Co(1)	127.86(11)	C(18b)–C(20b)–H(20e)	109.5
C(a4)–N(4)–C(a3)	105.42(13)	H(20d)–C(20b)–H(20e)	109.5
C(a4)–N(4)–Co(1)	126.93(11)	C(18b)–C(20b)–H(20F)	109.5
C(a3)–N(4)–Co(1)	127.63(11)	H(20d)–C(20b)–H(20f)	109.5
C(17)–N(5)–C(6)	131.02(19)	H(20e)–C(20b)–H(20f)	109.5
C(17)–N(5)–H(5a)	114.5	C(18b)–C(21b)–H(21d)	109.5
C(6)–N(5)–H(5a)	114.5	C(18b)–C(21b)–H(21e)	109.5

Table S28. Continued

angle	degree	angle	degree
C(22)–N(6)–C(12)	126.64(17)	H(21d)–C(21b)–H(21e)	109.5
C(22)–N(6)–H(6a)	116.7	C(18b)–C(21b)–H(21F)	109.5
C(12)–N(6)–H(6a)	116.7	H(21d)–C(21b)–H(21f)	109.5
N(3)–C(a1)–C(m2#1	125.76(15)	H(21e)–C(21b)–H(21f)	109.5
N(3)–C(a1)–C(b1)	110.78(14)	O(4a)–C(22)–O(4b)	26.8(5)
C(m2#1–C(a1)–C(b1)	123.43(16)	O(4a)–C(22)–N(6)	116.3(4)
N(3)–C(a2)–C(m1)	125.72(15)	O(4b)–C(22)–N(6)	128.4(12)
N(3)–C(a2)–C(b2)	110.68(14)	O(4a)–C(22)–C(23)	125.9(3)
C(m1)–C(a2)–C(b2)	123.56(15)	O(4b)–C(22)–C(23)	111.1(15)
N(4)–C(a3)–C(m1)	126.08(14)	N(6)–C(22)–C(23)	117.38(18)
N(4)–C(a3)–C(b3)	110.55(14)	O(4a)–C(22)–C(23b)	118.1(5)
C(m1)–C(a3)–C(b3)	123.25(15)	O(4b)–C(22)–C(23b)	108.8(14)
N(4)–C(a4)–C(m2)	126.18(15)	N(6)–C(22)–C(23b)	122.4(4)
N(4)–C(a4)–C(b4)	110.41(14)	C(23)–C(22)–C(23b)	13.0(4)
C(m2)–C(a4)–C(b4)	123.40(15)	C(22)–C(23)–C(24)	106.33(18)
C(b2)–C(b1)–C(a1)	106.51(15)	C(22)–C(23)–C(26)	106.38(18)
C(b2)–C(b1)–H(ba)	126.7	C(24)–C(23)–C(26)	109.5
C(a1)–C(b1)–H(ba)	126.7	C(22)–C(23)–C(25)	115.55(19)
C(b1)–C(b2)–C(a2)	107.00(15)	C(24)–C(23)–C(25)	109.5
C(b1)–C(b2)–H(bb)	126.5	C(26)–C(23)–C(25)	109.5
C(a2)–C(b2)–H(bb)	126.5	C(23)–C(25)–H(25a)	109.5
C(b4)–C(b3)–C(a3)	106.61(14)	C(23)–C(25)–H(25b)	109.5
C(b4)–C(b3)–H(bC)	126.7	H(25a)–C(25)–H(25b)	109.5
C(a3)–C(b3)–H(bC)	126.7	C(23)–C(25)–H(25C)	109.5
C(b3)–C(b4)–C(a4)	106.99(15)	H(25a)–C(25)–H(25C)	109.5
C(b3)–C(b4)–H(bd)	126.5	H(25b)–C(25)–H(25C)	109.5
C(a4)–C(b4)–H(bd)	126.5	C(23)–C(24)–H(24a)	109.5
C(a3)–C(m1)–C(a2)	122.70(15)	C(23)–C(24)–H(24b)	109.5
C(a3)–C(m1)–C(5)	118.36(14)	H(24a)–C(24)–H(24b)	109.5
C(a2)–C(m1)–C(5)	118.94(15)	C(23)–C(24)–H(24C)	109.5
C(a4)–C(m2)–C(a1#1	123.38(15)	H(24a)–C(24)–H(24C)	109.5
C(a4)–C(m2)–C(11)	118.25(15)	H(24b)–C(24)–H(24C)	109.5
C(a1#1–C(m2)–C(11)	118.38(15)	C(23)–C(26)–H(26a)	109.5
C(10)–C(5)–C(6)	119.10(16)	C(23)–C(26)–H(26b)	109.5

Table S28. Continued

angle	degree	angle	degree
C(10)–C(5)–C(m1)	120.31(16)	H(26a)–C(26)–H(26b)	109.5
C(6)–C(5)–C(m1)	120.57(15)	C(23)–C(26)–H(26C)	109.5
C(7)–C(6)–C(5)	120.12(19)	H(26a)–C(26)–H(26C)	109.5
C(7)–C(6)–N(5)	123.31(19)	H(26b)–C(26)–H(26C)	109.5
C(5)–C(6)–N(5)	116.56(15)	C(25b)–C(23b)–C(24b)	109.5
C(8)–C(7)–C(6)	119.3(2)	C(25b)–C(23b)–C(26b)	109.5
C(8)–C(7)–H(7a)	120.4	C(24b)–C(23b)–C(26b)	109.5
C(6)–C(7)–H(7a)	120.4	C(25b)–C(23b)–C(22)	103.1(10)
C(9)–C(8)–C(7)	121.24(18)	C(24b)–C(23b)–C(22)	113.1(8)
C(9)–C(8)–H(8a)	119.4	C(26b)–C(23b)–C(22)	112.0(7)
C(7)–C(8)–H(8a)	119.4	C(23b)–C(25b)–H(25d)	109.5
C(8)–C(9)–C(10)	119.6(2)	C(23b)–C(25b)–H(25e)	109.5
C(8)–C(9)–H(9a)	120.2	H(25d)–C(25b)–H(25e)	109.5
C(10)–C(9)–H(9a)	120.2	C(23b)–C(25b)–H(25F)	109.5
C(5)–C(10)–C(9)	120.7(2)	H(25d)–C(25b)–H(25f)	109.5
C(5)–C(10)–H(10a)	119.7	H(25e)–C(25b)–H(25f)	109.5
C(9)–C(10)–H(10a)	119.7	C(23b)–C(24b)–H(24d)	109.5
C(16)–C(11)–C(12)	118.66(17)	C(23b)–C(24b)–H(24e)	109.5
C(16)–C(11)–C(m2)	120.16(17)	H(24d)–C(24b)–H(24e)	109.5
C(12)–C(11)–C(m2)	121.17(16)	C(23b)–C(24b)–H(24F)	109.5
C(11)–C(12)–C(13)	120.1(2)	H(24d)–C(24b)–H(24f)	109.5
C(11)–C(12)–N(6)	118.47(16)	H(24e)–C(24b)–H(24f)	109.5
C(13)–C(12)–N(6)	121.48(19)	C(23b)–C(26b)–H(26d)	109.5
C(14)–C(13)–C(12)	119.9(2)	C(23b)–C(26b)–H(26e)	109.5
C(14)–C(13)–H(13a)	120.1	H(26d)–C(26b)–H(26e)	109.5
C(12)–C(13)–H(13a)	120.1	C(23b)–C(26b)–H(26F)	109.5
C(15)–C(14)–C(13)	120.6(2)	H(26d)–C(26b)–H(26f)	109.5
C(15)–C(14)–H(14a)	119.7	H(26e)–C(26b)–H(26f)	109.5
C(13)–C(14)–H(14a)	119.7	C(1)–N(1)–C(3)	105.1(3)
C(14)–C(15)–C(16)	119.7(2)	C(1)–N(1)–Co(1)	132.4(2)
C(14)–C(15)–H(15a)	120.1	C(3)–N(1)–Co(1)	122.5(2)
C(16)–C(15)–H(15a)	120.1	N(1)–C(1)–N(2)	108.8(6)
C(15)–C(16)–C(11)	121.0(2)	N(1)–C(1)–C(4)	128.8(3)
C(15)–C(16)–H(16a)	119.5	N(2)–C(1)–C(4)	122.4(6)

Table S28. Continued

angle	degree	angle	degree
C(11)–C(16)–H(16a)	119.5	C(2)–N(2)–C(1)	109.9(6)
O(3b)–C(17)–O(3a)	23.3(14)	C(2)–N(2)–H(2a)	125.0
O(3b)–C(17)–N(5)	130.4(8)	C(1)–N(2)–H(2a)	125.0
O(3a)–C(17)–N(5)	118.1(8)	N(2)–C(2)–C(3)	106.0(3)
O(3b)–C(17)–C(18b)	103.1(11)	N(2)–C(2)–H(2b)	127.0
O(3a)–C(17)–C(18b)	117.1(7)	C(3)–C(2)–H(2b)	127.0
N(5)–C(17)–C(18b)	124.6(3)	C(2)–C(3)–N(1)	110.1(3)
O(3b)–C(17)–C(18)	117.4(11)	C(2)–C(3)–H(3a)	124.9
O(3a)–C(17)–C(18)	130.6(7)	N(1)–C(3)–H(3a)	124.9
N(5)–C(17)–C(18)	110.6(2)	C(1)–C(4)–H(4a)	109.5
C(18b)–C(17)–C(18)	14.29(6)	C(1)–C(4)–H(4b)	109.5
C(21)–C(18)–C(19)	109.5	H(4a)–C(4)–H(4b)	109.5
C(21)–C(18)–C(20)	109.5	C(1)–C(4)–H(4C)	109.5
C(19)–C(18)–C(20)	109.5	H(4a)–C(4)–H(4C)	109.5
C(21)–C(18)–C(17)	116.72(15)	H(4b)–C(4)–H(4C)	109.5
C(19)–C(18)–C(17)	105.27(16)	O(1S)–C(1S)–C(1S)#1	121.6(2)
C(20)–C(18)–C(17)	106.20(17)	O(2S)–C(2S)–C(3S)	108.3(10)
C(18)–C(19)–H(19a)	109.5	O(2S)–C(2S)–C(2S)#2	134.6(16)
C(18)–C(19)–H(19b)	109.5	C(3S)–C(2S)–C(2S)#2	49.0(7)
H(19a)–C(19)–H(19b)	109.5	C(2S)#2–C(3S)–C(2S)	82.0(14)
C(18)–C(19)–H(19C)	109.5		

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

Table S29. Anisotropic Displacement Parameters ($Å^2$) for [Co(TpivPP)(2-MeHIm)(O$_2$)]·1.8C$_2$H$_5$OH[a] (100 K, $C2/c$ form)[a]

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co(1)	0.0220(1)	0.0199(1)	0.0143(1)	0.000	−0.0002(1)	0.000
O(1)	0.0656(15)	0.0234(9)	0.0504(13)	0.000	0.0112(11)	0.000
O(2)	0.060(2)	0.0375(16)	0.064(2)	0.0044(15)	−0.0085(17)	0.0081(15)
N(3)	0.0244(6)	0.0260(6)	0.0161(5)	−0.0003(4)	0.0002(4)	−0.0006(5)
N(4)	0.0241(6)	0.0227(6)	0.0160(5)	0.0010(4)	−0.0003(4)	0.0014(4)
N(5)	0.0528(10)	0.0316(8)	0.0295(8)	0.0056(6)	0.0079(7)	−0.0022(7)
N(6)	0.0238(7)	0.0433(9)	0.0650(12)	0.0242(9)	−0.0066(7)	0.0007(6)
C(A1)	0.0248(7)	0.0296(8)	0.0209(7)	−0.0006(6)	0.0011(5)	−0.0018(6)
C(A2)	0.0262(7)	0.0271(7)	0.0187(7)	0.0002(5)	0.0027(5)	−0.0007(6)
C(A3)	0.0283(7)	0.0228(7)	0.0160(6)	0.0007(5)	−0.0001(5)	0.0010(5)
C(A4)	0.0265(7)	0.0255(7)	0.0175(6)	0.0026(5)	−0.0022(5)	0.0017(5)
C(B1)	0.0253(7)	0.0431(9)	0.0238(8)	0.0001(7)	0.0023(6)	−0.0036(7)
C(B2)	0.0275(8)	0.0405(9)	0.0224(7)	0.0012(6)	0.0041(6)	−0.0029(7)
C(B3)	0.0318(8)	0.0362(9)	0.0162(6)	0.0004(6)	−0.0019(6)	0.0012(6)
C(B4)	0.0295(8)	0.0375(9)	0.0180(7)	0.0017(6)	−0.0037(6)	0.0015(6)
C(M1)	0.0283(7)	0.0241(7)	0.0163(6)	0.0003(5)	0.0018(5)	0.0003(5)
C(M2)	0.0242(7)	0.0281(7)	0.0217(7)	0.0022(5)	−0.0021(5)	0.0018(6)
C(5)	0.0264(7)	0.0331(8)	0.0166(6)	−0.0027(6)	0.0015(5)	0.0006(6)
C(6)	0.0331(8)	0.0395(9)	0.0182(7)	0.0017(6)	0.0020(6)	−0.0031(7)
C(7)	0.0374(10)	0.0715(15)	0.0184(7)	0.0041(8)	0.0042(7)	−0.0117(10)
C(8)	0.0298(9)	0.0936(19)	0.0210(8)	−0.0173(10)	0.0055(7)	−0.0097(10)
C(9)	0.0315(9)	0.0662(14)	0.0341(10)	−0.0267(10)	0.0008(7)	0.0020(9)
C(10)	0.0342(9)	0.0377(9)	0.0309(9)	−0.0110(7)	0.0006(7)	0.0009(7)
C(11)	0.0244(7)	0.0399(9)	0.0219(7)	−0.0003(6)	−0.0016(6)	0.0008(6)
C(12)	0.0244(7)	0.0451(10)	0.0331(9)	0.0101(8)	−0.0043(6)	0.0012(7)
C(13)	0.0288(9)	0.0624(14)	0.0448(11)	0.0058(10)	−0.0112(8)	0.0054(9)
C(14)	0.0286(9)	0.0690(15)	0.0511(13)	−0.0176(12)	−0.0125(9)	0.0014(9)
C(15)	0.0342(10)	0.0517(13)	0.0683(16)	−0.0236(12)	−0.0064(10)	−0.0068(9)
C(16)	0.0343(9)	0.0384(10)	0.0470(11)	−0.0120(8)	−0.0042(8)	−0.0008(8)
C(17)	0.0389(10)	0.0380(10)	0.0630(15)	0.0155(10)	−0.0093(10)	−0.0091(8)
C(18)	0.0332(17)	0.0316(16)	0.028(2)	0.0046(12)	−0.0079(12)	−0.0003(12)
C(19)	0.032(2)	0.034(2)	0.044(2)	0.0011(14)	−0.0084(14)	−0.0029(15)
C(20)	0.039(2)	0.051(2)	0.075(4)	0.009(2)	−0.018(2)	−0.0004(18)
C(21)	0.065(3)	0.0354(19)	0.034(2)	−0.0065(15)	0.0096(17)	−0.0043(18)

Table S29. Continued

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(18B)	0.026(2)	0.032(2)	0.037(3)	−0.0021(19)	−0.0036(18)	−0.0032(17)
C(19B)	0.027(3)	0.053(4)	0.045(3)	−0.019(3)	0.004(2)	0.009(3)
C(20B)	0.052(4)	0.029(3)	0.128(9)	−0.008(4)	−0.056(5)	0.007(3)
C(21B)	0.070(5)	0.050(4)	0.089(7)	−0.034(4)	0.036(5)	−0.009(4)
C(22)	0.0315(9)	0.0535(12)	0.0289(9)	0.0036(8)	0.0035(7)	0.0001(8)
C(23)	0.0374(16)	0.0433(16)	0.0401(17)	0.0055(12)	0.0120(11)	−0.0079(12)
C(25)	0.0320(15)	0.079(3)	0.079(3)	−0.021(2)	0.0071(17)	−0.0165(16)
C(24)	0.084(3)	0.058(2)	0.063(2)	0.0232(18)	0.0159(19)	−0.0090(19)
C(26)	0.062(2)	0.066(2)	0.0483(18)	−0.0126(16)	0.0058(15)	−0.0223(17)
C(23B)	0.040(7)	0.064(10)	0.040(8)	0.030(7)	0.019(5)	0.024(7)
C(25B)	0.075(13)	0.104(16)	0.034(7)	0.021(8)	−0.005(7)	0.011(11)
C(24B)	0.062(10)	0.047(8)	0.121(18)	0.015(9)	−0.015(10)	0.011(7)
C(26B)	0.037(6)	0.054(7)	0.033(5)	0.001(5)	0.003(4)	−0.006(5)
O(4A)	0.032(2)	0.032(2)	0.077(7)	−0.010(3)	0.018(3)	0.0005(14)
O(3A)	0.069(4)	0.049(4)	0.073(3)	0.024(2)	0.020(3)	−0.010(3)
O(4B)	0.037(3)	0.059(8)	0.048(5)	−0.011(5)	−0.012(3)	0.022(4)
O(3B)	0.088(11)	0.050(4)	0.036(5)	0.017(3)	−0.005(4)	0.004(5)
N(1)	0.020(3)	0.0244(10)	0.014(3)	0.0012(10)	0.0008(15)	−0.0017(10)
C(1)	0.0229(14)	0.0239(14)	0.0218(14)	−0.0016(11)	0.0004(13)	−0.0044(11)
N(2)	0.0280(12)	0.0237(11)	0.0265(11)	−0.007(5)	0.0005(9)	0.011(4)
C(2)	0.0256(14)	0.0287(15)	0.0226(14)	−0.0013(11)	0.0009(11)	0.0014(12)
C(3)	0.0224(14)	0.0293(16)	0.0189(14)	0.0006(13)	0.0037(12)	0.0025(13)
C(4)	0.0363(18)	0.0231(15)	0.0370(19)	−0.0008(14)	0.0155(17)	−0.0074(13)
O(1S)	0.0472(17)	0.0320(14)	0.073(2)	−0.0060(14)	0.0304(16)	−0.0009(13)
C(1S)	0.144(4)	0.065(2)	0.127(4)	−0.020(2)	0.083(3)	−0.031(2)
C(2S)	0.140(10)	0.071(6)	0.056(5)	−0.004(4)	−0.023(5)	−0.023(6)
C(3S)	0.089(6)	0.159(11)	0.165(11)	0.000	0.036(7)	0.000
O(2S)	0.261(13)	0.064(4)	0.125(7)	0.028(5)	−0.077(8)	−0.010(6)

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

The anisotropic displacement factor exponent takes the form: -2π [h^2 U_{11} +...+ 2 h k a* b* U_{12}].

Table S30. Hydrogen Atom Coordinates and Equivalent Isotropic Displacement Parameters
(Å^2) for [Co(TpivPP)(2-MeHIm)(O$_2$)]·1.8C$_2$H$_5$OH^a (100 K, $C2/c$ form)^a

atom	x	y	z	U(eq)
H(5A)	0.4021	0.7503	0.9559	0.045
H(6A)	0.6836	0.7370	0.8829	0.053
H(BA	0.2316	0.8434	0.7930	0.037
H(BB	0.2846	0.8488	0.9214	0.036
H(BC	0.5459	0.8707	1.0332	0.034
H(BD	0.6670	0.8657	0.9792	0.034
H(7A)	0.3467	0.7707	1.1424	0.051
H(8A)	0.3386	0.8772	1.2012	0.058
H(9A)	0.3707	0.9766	1.1398	0.053
H(10A)	0.4116	0.9710	1.0167	0.041
H(13A)	0.8599	0.7482	0.9334	0.055
H(14A)	0.9298	0.8466	0.9340	0.060
H(15A)	0.8848	0.9485	0.8857	0.062
H(16A)	0.7676	0.9534	0.8399	0.048
H(19A)	0.3196	0.5625	0.9012	0.055
H(19B)	0.2834	0.6303	0.9335	0.055
H(19C)	0.3068	0.5698	0.9891	0.055
H(20A)	0.4504	0.5396	0.9366	0.083
H(20B)	0.4278	0.5494	1.0219	0.083
H(20C)	0.4909	0.5946	0.9884	0.083
H(21A)	0.4154	0.6224	0.8417	0.067
H(21B)	0.4615	0.6784	0.8865	0.067
H(21C)	0.3797	0.6935	0.8651	0.067
H(19D)	0.2926	0.5866	1.0077	0.062
H(19E)	0.3179	0.5615	0.9272	0.062
H(19F)	0.2892	0.6379	0.9379	0.062
H(20D)	0.4808	0.5821	1.0283	0.105
H(20E)	0.4340	0.5276	0.9819	0.105
H(20F)	0.4087	0.5527	1.0624	0.105
H(21D)	0.4756	0.6611	0.9210	0.104
H(21E)	0.4001	0.6831	0.8854	0.104
H(21F)	0.4288	0.6066	0.8747	0.104
H(25A)	0.6094	0.6680	0.8258	0.095
H(25B)	0.6151	0.6563	0.9144	0.095

Table S30. Continued

atom	x	y	z	$U(\mathrm{eq})$
H(25C)	0.5889	0.5953	0.8607	0.095
H(24A)	0.7642	0.5449	0.9136	0.103
H(24B)	0.6827	0.5207	0.9138	0.103
H(24C)	0.7088	0.5817	0.9675	0.103
H(26A)	0.6946	0.6115	0.7429	0.088
H(26B)	0.6740	0.5388	0.7777	0.088
H(26C)	0.7556	0.5629	0.7774	0.088
H(25D)	0.6014	0.5779	0.8795	0.107
H(25E)	0.6132	0.6590	0.8777	0.107
H(25F)	0.6524	0.6136	0.9407	0.107
H(24D)	0.6933	0.5002	0.8383	0.115
H(24E)	0.7460	0.5301	0.9018	0.115
H(24F)	0.7702	0.5285	0.8164	0.115
H(26D)	0.6405	0.5761	0.7446	0.062
H(26E)	0.7155	0.6100	0.7247	0.062
H(26F)	0.6507	0.6572	0.7506	0.062
H(2A)	0.5126	1.1221	0.7340	0.031
H(2B)	0.4249	1.1032	0.8289	0.031
H(3A)	0.4117	0.9780	0.8379	0.028
H(4A)	0.5930	0.9691	0.6567	0.048
H(4B)	0.6256	1.0398	0.6870	0.048
H(4C)	0.5659	1.0402	0.6217	0.048

[a] $U(\mathrm{eq})$ 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 S31. Complete Crystallographic Details for [Co(TpivPP)(2-MeHIm)0.4(O$_2$)]·2C$_2$H$_5$OH (100 K, $C2/c$ form)

formula	C$_{72}$H$_{82}$CoN$_{10}$O$_{6.8}$
FW, amu	1255.21
a, Å	18.5678(7)
b, Å	19.5594(8)
c, Å	17.8219(6)
β, deg	90.954(2)
V, Å^3	6471.6(4)
space group	$C2/c$
Z	4
D$_c$, g/cm^3	1.288
F(000)	2662
μ, mm^{-1}	0.328
crystal dimensions, mm	0.50 × 0.22 × 0.21
radiation	MoKα, $\bar{\lambda} = 0.71073$ Å
temperature, K	100(2)
diffractometer	Bruker Apex CCD
θ range for collected data, deg	1.51–27.28
index range	$-23 \leq$ h ≤ 23
	$-25 \leq$ k ≤ 25
	$-19 \leq$ l ≤ 22
total data collected	79057
absorption correction	Semi-empirical from equiv
relative transmission coefficients (I)	0.9343 and 0.8532
unique data	7227 ($R_{\text{int}} = 0.0265$)
unique observed data [I > 2σ(I)]	6388
refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	7227/0/453
goodness-of-fit (based on F^2)	1.078
final R indices [I > 2σ(I)]	$R_1 = 0.0509$, $wR_2 = 0.1399$
final R indices (all data)	$R_1 = 0.0593$, $wR_2 = 0.1512$

Table S32. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for [Co(TpivPP)(2-MeHIm)0.4(O$_2$)]·2C$_2$H$_5$OH^a (100 K, $C2/c$ form)^a

atom	x	y	z	U(eq)
Co(1)	0.5000	0.86468(2)	0.7500	0.0167(1)
N(1)	0.45824(9)	0.86145(8)	0.64747(9)	0.0191(3)
N(2)	0.40274(9)	0.85694(8)	0.79257(9)	0.0197(3)
N(5)	0.61102(12)	0.74416(10)	0.49953(11)	0.0343(4)
N(6)	0.27034(10)	0.73201(11)	0.62130(12)	0.0354(5)
O(1)	0.5000	0.7658(3)	0.7500	0.0390(14)
O(2)	0.4589(6)	0.7305(5)	0.7273(6)	0.047(2)
O(3)	0.62257(18)	0.66155(13)	0.41310(14)	0.0801(9)
O(4)	0.18435(11)	0.65489(13)	0.63957(17)	0.0721(8)
C(a1)	0.49405(11)	0.86482(10)	0.58069(11)	0.0213(4)
C(a2)	0.38679(11)	0.86074(10)	0.62759(11)	0.0208(4)
C(a3)	0.33846(11)	0.85274(10)	0.75383(11)	0.0218(4)
C(a4)	0.38443(11)	0.85603(10)	0.86706(11)	0.0214(4)
C(b1)	0.44388(12)	0.86729(11)	0.51848(11)	0.0266(4)
C(b2)	0.37773(12)	0.86479(11)	0.54725(11)	0.0262(4)
C(b3)	0.27932(11)	0.84762(12)	0.80473(12)	0.0268(4)
C(b4)	0.30793(11)	0.85019(11)	0.87466(12)	0.0262(4)
C(m1)	0.56797(11)	0.86254(10)	0.57259(11)	0.0207(4)
C(m2)	0.32985(11)	0.85550(10)	0.67652(11)	0.0211(4)
C(5)	0.59710(11)	0.86527(11)	0.49483(11)	0.0239(4)
C(6)	0.61675(12)	0.80526(12)	0.45819(12)	0.0290(5)
C(7)	0.64108(13)	0.80781(16)	0.38461(13)	0.0416(6)
C(8)	0.64522(13)	0.86938(18)	0.34862(13)	0.0463(7)
C(9)	0.62646(13)	0.92911(16)	0.38373(14)	0.0432(7)
C(10)	0.60269(12)	0.92692(13)	0.45724(13)	0.0326(5)
C(11)	0.61379(14)	0.67860(14)	0.47819(16)	0.0422(6)
C(12)	0.25537(11)	0.85213(12)	0.64401(11)	0.0253(4)
C(13)	0.22716(11)	0.79110(12)	0.61663(12)	0.0286(4)
C(14)	0.15797(13)	0.78917(15)	0.58546(14)	0.0379(5)
C(15)	0.11664(14)	0.84743(16)	0.58450(16)	0.0454(7)
C(16)	0.14310(14)	0.90751(15)	0.61289(18)	0.0480(7)
C(17)	0.21250(13)	0.91013(13)	0.64154(15)	0.0365(5)
C(18)	0.24763(12)	0.66798(13)	0.63516(13)	0.0326(5)
C(19)	0.60814(14)	0.62634(13)	0.54197(19)	0.0448(7)

Table S32. Continued

atom	x	y	z	$U(\text{eq})$
C(20)	0.68312(14)	0.59515(14)	0.55078(18)	0.0458(7)
C(21)	0.55410(18)	0.57142(17)	0.5184(3)	0.0851(15)
C(22)	0.58529(19)	0.65642(16)	0.6177(2)	0.0571(8)
C(23)	0.30428(13)	0.61227(14)	0.64464(15)	0.0382(5)
C(24)	0.2889(2)	0.5618(2)	0.5809(2)	0.0707(10)
C(25)	0.29259(17)	0.57880(17)	0.71910(18)	0.0550(8)
C(26)	0.38123(15)	0.63853(17)	0.6393(2)	0.0561(8)
O(1S)	0.0522(2)	0.70269(19)	0.6897(2)	0.0470(10)
C(1S)	0.0271(3)	0.7606(2)	0.7190(3)	0.0978(18)
N(3)	0.5093(5)	0.97182(17)	0.7419(6)	0.0209(15)
C(1)	0.5566(3)	1.0034(3)	0.6938(3)	0.0242(9)
C(2)	0.5508(2)	1.0713(2)	0.6986(2)	0.0254(8)
N(4)	0.5000	1.08274(13)	0.7500	0.0245(5)
C(3)	0.4753(2)	1.0223(2)	0.7755(3)	0.0221(8)
C(4)	0.4189(3)	1.0175(2)	0.8320(3)	0.0294(10)
O(2S)	0.5476(4)	0.5427(3)	0.3445(3)	0.0827(17)
C(2S)	0.5411(5)	0.5586(4)	0.2734(4)	0.070(2)
C(3S)	0.5000	0.5127(7)	0.2500	0.153(4)

[a] $U(\text{eq})$ 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 S33. Bond Lengths for [Co(TpivPP)(2-MeHIm)0.4(O$_2$)]·2C$_2$H$_5$OH^a (100 K, $C2/c$ form)^a

bond	length (Å)	bond	length (Å)
Co(1)–O(1)	1.934(6)	C(14)–C(15)	1.374(4)
Co(1)–N(1)#1)	1.9741(16)	C(14)–H(14a)	0.9500
Co(1)–N(1)	1.9741(16)	C(15)–C(16)	1.367(4)
Co(1)–N(2)	1.9761(17)	C(15)–H(15a)	0.9500
Co(1)–N(2)#1)	1.9762(17)	C(16)–C(17)	1.379(4)
Co(1)–N(3)	2.108(3)	C(16)–H(16a)	0.9500
Co(1)–N(3)#1)	2.108(3)	C(17)–H(17a)	0.9500
N(1)–C(a2)	1.367(3)	C(18)–C(23)	1.522(3)
N(1)–C(a1)	1.374(3)	C(19)–C(21)	1.524(4)
N(2)–C(a3)	1.371(3)	C(19)–C(20)	1.526(3)
N(2)–C(a4)	1.376(2)	C(19)–C(22)	1.538(5)
N(5)–C(11)	1.339(3)	C(20)–H(20a)	0.9800
N(5)–C(6)	1.409(3)	C(20)–H(20b)	0.9800
N(5)–H(5a)	0.8800	C(20)–H(20C)	0.9800
N(6)–C(18)	1.346(3)	C(21)–H(21a)	0.9800
N(6)–C(13)	1.408(3)	C(21)–H(21b)	0.9800
N(6)–H(6a)	0.8800	C(21)–H(21C)	0.9800
O(1)–O(2)#1	1.100(9)	C(22)–H(22a)	0.9800
O(1)–O(2)	1.100(9)	C(22)–H(22b)	0.9800
O(2)–O(2)#1	1.71(2)	C(22)–H(22C)	0.9800
O(3)–C(11)	1.221(4)	C(23)–C(25)	1.499(4)
O(4)–C(18)	1.206(3)	C(23)–C(26)	1.523(4)
C(a1)–C(m1)	1.383(3)	C(23)–C(24)	1.529(4)
C(a1)–C(b1)	1.437(3)	C(24)–H(24a)	0.9800
C(a2)–C(m2)	1.385(3)	C(24)–H(24b)	0.9800
C(a2)–C(b2)	1.441(3)	C(24)–H(24C)	0.9800
C(a3)–C(m2)	1.385(3)	C(25)–H(25a)	0.9800
C(a3)–C(b3)	1.440(3)	C(25)–H(25b)	0.9800
C(a4)–C(m1#1)	1.387(3)	C(25)–H(25C)	0.9800
C(a4)–C(b4)	1.434(3)	C(26)–H(26a)	0.9800
C(b1)–C(b2)	1.340(3)	C(26)–H(26b)	0.9800
C(b1)–H(ba)	0.9500	C(26)–H(26C)	0.9800
C(b2)–H(bb)	0.9500	O(1S)–C(1S)	1.335(5)
C(b3)–C(b4)	1.348(3)	C(1S)–C(1S)#2	1.507(7)

Table S33. Continued

bond	length (Å)	bond	length (Å)
C(b3)–H(bC)	0.9500	N(3)–C(3)	1.322(6)
C(b4)–H(bd)	0.9500	N(3)–C(1)	1.383(7)
C(m1)–C(a4#1)	1.387(3)	C(1)–C(2)	1.336(7)
C(m1)–C(5)	1.497(3)	C(1)–H(1a)	0.9500
C(m2)–C(12)	1.492(3)	C(2)–N(4)	1.345(4)
C(5)–C(10)	1.384(3)	C(2)–H(2a)	0.9500
C(5)–C(6)	1.395(3)	N(4)–C(2)#1	1.345(4)
C(6)–C(7)	1.395(3)	N(4)–C(3)#1	1.349(5)
C(7)–C(8)	1.367(4)	N(4)–C(3)	1.349(5)
C(7)–H(7a)	0.9500	N(4)–H(4a)	0.8800
C(8)–C(9)	1.373(4)	C(3)–C(4)	1.468(7)
C(8)–H(8a)	0.9500	C(4)–H(4b)	0.9800
C(9)–C(10)	1.390(3)	C(4)–H(4C)	0.9800
C(9)–H(9a)	0.9500	C(4)–H(4d)	0.9800
C(10)–H(10a)	0.9500	O(2S)–C(2S)	1.308(8)
C(11)–C(19)	1.534(4)	C(2S)–C(3S)	1.245(11)
C(12)–C(17)	1.386(3)	C(3S)–C(2S)#3	1.245(11)
C(12)–C(13)	1.389(3)		
C(13)–C(14)	1.392(3)		

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

Table S34. Bond Angles for [Co(TpivPP)(2-MeHIm)0.4(O$_2$)]·2C$_2$H$_5$OH^a (100 K, $C2/c$ form)^a

angle	degree	angle	degree
O(1)–Co(1)–N(1)#1	88.17(5)	C(13)–C(14)–H(14a)	120.2
O(1)–Co(1)–N(1)	88.17(5)	C(16)–C(15)–C(14)	120.7(2)
N(1)#1–Co(1)–N(1)	176.33(9)	C(16)–C(15)–H(15a)	119.6
O(1)–Co(1)–N(2)	85.61(5)	C(14)–C(15)–H(15a)	119.6
N(1)#1–Co(1)–N(2)	89.40(7)	C(15)–C(16)–C(17)	119.8(3)
N(1)–Co(1)–N(2)	90.32(7)	C(15)–C(16)–H(16a)	120.1
O(1)–Co(1)–N(2)#1	85.61(5)	C(17)–C(16)–H(16a)	120.1
N(1)#1–Co(1)–N(2)#1	90.32(7)	C(16)–C(17)–C(12)	120.9(3)
N(1)–Co(1)–N(2)#1	89.40(7)	C(16)–C(17)–H(17a)	119.5
N(2)–Co(1)–N(2)#1	171.21(9)	C(12)–C(17)–H(17a)	119.5
O(1)–Co(1)–N(3)	173.81(15)	O(4)–C(18)–N(6)	121.2(2)
N(1)#1–Co(1)–N(3)	93.7(4)	O(4)–C(18)–C(23)	120.9(2)
N(1)–Co(1)–N(3)	90.0(4)	N(6)–C(18)–C(23)	117.9(2)
N(2)–Co(1)–N(3)	100.30(18)	C(21)–C(19)–C(20)	110.0(2)
N(2)#1–Co(1)–N(3)	88.48(18)	C(21)–C(19)–C(11)	108.6(3)
O(1)–Co(1)–N(3)#1	173.81(14)	C(20)–C(19)–C(11)	105.6(2)
N(1)#1–Co(1)–N(3)#1	90.0(4)	C(21)–C(19)–C(22)	108.7(3)
N(1)–Co(1)–N(3)#1	93.7(4)	C(20)–C(19)–C(22)	109.1(3)
N(2)–Co(1)–N(3)#1	88.48(18)	C(11)–C(19)–C(22)	114.7(2)
N(2)#1–Co(1)–N(3)#1	100.30(18)	C(19)–C(20)–H(20a)	109.5
N(3)–Co(1)–N(3)#1	12.4(3)	C(19)–C(20)–H(20b)	109.5
C(a2)–N(1)–C(a1)	104.92(16)	H(20a)–C(20)–H(20b)	109.5
C(a2)–N(1)–Co(1)	127.19(13)	C(19)–C(20)–H(20C)	109.5
C(a1)–N(1)–Co(1)	127.72(14)	H(20a)–C(20)–H(20C)	109.5
C(a3)–N(2)–C(a4)	104.95(16)	H(20b)–C(20)–H(20C)	109.5
C(a3)–N(2)–Co(1)	127.20(13)	C(19)–C(21)–H(21a)	109.5
C(a4)–N(2)–Co(1)	127.84(14)	C(19)–C(21)–H(21b)	109.5
C(11)–N(5)–C(6)	131.3(2)	H(21a)–C(21)–H(21b)	109.5
C(11)–N(5)–H(5a)	114.3	C(19)–C(21)–H(21C)	109.5
C(6)–N(5)–H(5a)	114.3	H(21a)–C(21)–H(21C)	109.5
C(18)–N(6)–C(13)	126.50(19)	H(21b)–C(21)–H(21C)	109.5
C(18)–N(6)–H(6a)	116.8	C(19)–C(22)–H(22a)	109.5
C(13)–N(6)–H(6a)	116.8	C(19)–C(22)–H(22b)	109.5
O(2)#1–O(1)–O(2)	102.4(11)	H(22a)–C(22)–H(22b)	109.5

Table S34. Continued

angle	degree	angle	degree
O(2)#1–O(1)–Co(1)	128.8(6)	C(19)–C(22)–H(22C)	109.5
O(2)–O(1)–Co(1)	128.8(6)	H(22a)–C(22)–H(22C)	109.5
O(1)–O(2)–O(2)#1	38.8(6)	H(22b)–C(22)–H(22C)	109.5
N(1)–C(a1)–C(m1)	125.74(18)	C(25)–C(23)–C(18)	107.5(2)
N(1)–C(a1)–C(b1)	110.67(18)	C(25)–C(23)–C(26)	110.6(3)
C(m1)–C(a1)–C(b1)	123.51(19)	C(18)–C(23)–C(26)	113.5(2)
N(1)–C(a2)–C(m2)	125.80(18)	C(25)–C(23)–C(24)	110.4(3)
N(1)–C(a2)–C(b2)	110.71(18)	C(18)–C(23)–C(24)	105.1(2)
C(m2)–C(a2)–C(b2)	123.48(19)	C(26)–C(23)–C(24)	109.6(3)
N(2)–C(a3)–C(m2)	125.69(18)	C(23)–C(24)–H(24a)	109.5
N(2)–C(a3)–C(b3)	110.71(17)	C(23)–C(24)–H(24b)	109.5
C(m2)–C(a3)–C(b3)	123.56(19)	H(24a)–C(24)–H(24b)	109.5
N(2)–C(a4)–C(m1#1	125.64(19)	C(23)–C(24)–H(24C)	109.5
N(2)–C(a4)–C(b4)	110.69(17)	H(24a)–C(24)–H(24C)	109.5
C(m1#1–C(a4)–C(b4)	123.62(19)	H(24b)–C(24)–H(24C)	109.5
C(b2)–C(b1)–C(a1)	106.87(18)	C(23)–C(25)–H(25a)	109.5
C(b2)–C(b1)–H(ba)	126.6	C(23)–C(25)–H(25b)	109.5
C(a1)–C(b1)–H(ba)	126.6	H(25a)–C(25)–H(25b)	109.5
C(b1)–C(b2)–C(a2)	106.83(19)	C(23)–C(25)–H(25C)	109.5
C(b1)–C(b2)–H(bb)	126.6	H(25a)–C(25)–H(25C)	109.5
C(a2)–C(b2)–H(bb)	126.6	H(25b)–C(25)–H(25C)	109.5
C(b4)–C(b3)–C(a3)	106.69(18)	C(23)–C(26)–H(26a)	109.5
C(b4)–C(b3)–H(bC)	126.7	C(23)–C(26)–H(26b)	109.5
C(a3)–C(b3)–H(bC)	126.7	H(26a)–C(26)–H(26b)	109.5
C(b3)–C(b4)–C(a4)	106.95(18)	C(23)–C(26)–H(26C)	109.5
C(b3)–C(b4)–H(bd)	126.5	H(26a)–C(26)–H(26C)	109.5
C(a4)–C(b4)–H(bd)	126.5	H(26b)–C(26)–H(26C)	109.5
C(a1)–C(m1)–C(a4#1	122.87(18)	O(1S)–C(1S)–C(1S)#2	121.9(2)
C(a1)–C(m1)–C(5)	118.03(18)	C(3)–N(3)–C(1)	105.1(4)
C(a4#1–C(m1)–C(5)	119.08(18)	C(3)–N(3)–Co(1)	132.2(4)
C(a3)–C(m2)–C(a2)	123.51(19)	C(1)–N(3)–Co(1)	122.7(3)
C(a3)–C(m2)–C(12)	118.39(18)	C(2)–C(1)–N(3)	110.6(5)
C(a2)–C(m2)–C(12)	118.10(18)	C(2)–C(1)–H(1a)	124.7
C(10)–C(5)–C(6)	119.0(2)	N(3)–C(1)–H(1a)	124.7

Table S34. Continued

angle	degree	angle	degree
C(10)–C(5)–C(m1)	120.7(2)	C(1)–C(2)–N(4)	105.4(4)
C(6)–C(5)–C(m1)	120.32(18)	C(1)–C(2)–H(2a)	127.3
C(5)–C(6)–C(7)	120.1(2)	N(4)–C(2)–H(2a)	127.3
C(5)–C(6)–N(5)	116.52(18)	C(2)#1–N(4)–C(2)	160.9(4)
C(7)–C(6)–N(5)	123.4(2)	C(2)#1–N(4)–C(3)#1	109.3(3)
C(8)–C(7)–C(6)	119.6(3)	C(2)–N(4)–C(3)#1	51.6(3)
C(8)–C(7)–H(7a)	120.2	C(2)#1–N(4)–C(3)	51.6(3)
C(6)–C(7)–H(7a)	120.2	C(2)–N(4)–C(3)	109.3(3)
C(7)–C(8)–C(9)	121.3(2)	C(3)#1–N(4)–C(3)	57.7(4)
C(7)–C(8)–H(8a)	119.4	C(2)#1–N(4)–H(4a)	73.7
C(9)–C(8)–H(8a)	119.4	C(2)–N(4)–H(4a)	125.3
C(8)–C(9)–C(10)	119.4(2)	C(3)#1–N(4)–H(4a)	176.9
C(8)–C(9)–H(9a)	120.3	C(3)–N(4)–H(4a)	125.3
C(10)–C(9)–H(9a)	120.3	N(3)–C(3)–N(4)	109.5(4)
C(5)–C(10)–C(9)	120.7(2)	N(3)–C(3)–C(4)	127.9(4)
C(5)–C(10)–H(10a)	119.7	N(4)–C(3)–C(4)	122.6(4)
C(9)–C(10)–H(10a)	119.7	C(3)–C(4)–H(4b)	109.5
O(3)–C(11)–N(5)	122.5(3)	C(3)–C(4)–H(4C)	109.5
O(3)–C(11)–C(19)	122.3(3)	H(4b)–C(4)–H(4C)	109.5
N(5)–C(11)–C(19)	115.1(2)	C(3)–C(4)–H(4d)	109.5
C(17)–C(12)–C(13)	118.6(2)	H(4b)–C(4)–H(4d)	109.5
C(17)–C(12)–C(m2)	120.3(2)	H(4C)–C(4)–H(4d)	109.5
C(13)–C(12)–C(m2)	121.07(19)	C(3S)–C(2S)–O(2S)	101.5(6)
C(12)–C(13)–C(14)	120.2(2)	C(3S)–C(2S)–C(2S)#3	46.1(6)
C(12)–C(13)–N(6)	118.27(19)	O(2S)–C(2S)–C(2S)#3	122.4(10)
C(14)–C(13)–N(6)	121.5(2)	C(2S)–C(3S)–C(2S)#3	87.8(11)
C(15)–C(14)–C(13)	119.6(2)		
C(15)–C(14)–H(14a)	120.2		

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

Table S35. Anisotropic Displacement Parameters (Å^2) for [Co(TpivPP)(2-MeHIm)0.4(O$_2$)]·2C$_2$H$_5$OH[a] (100 K, $C2/c$ form)[a]

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co(1)	0.0189(2)	0.0186(2)	0.0127(2)	0.000	0.0001(1)	0.000
N(1)	0.0212(8)	0.0197(8)	0.0163(8)	−0.0005(6)	0.0006(6)	−0.0010(6)
N(2)	0.0224(8)	0.0215(8)	0.0151(7)	0.0000(6)	0.0007(6)	−0.0006(6)
N(5)	0.0470(12)	0.0326(10)	0.0234(9)	−0.0066(8)	0.0047(8)	0.0031(9)
N(6)	0.0189(8)	0.0367(11)	0.0505(12)	−0.0171(9)	−0.0030(8)	−0.0012(7)
O(1)	0.058(4)	0.016(3)	0.044(3)	0.000	0.010(3)	0.000
O(2)	0.053(6)	0.028(4)	0.058(6)	−0.007(4)	−0.009(5)	−0.007(4)
O(3)	0.124(2)	0.0603(15)	0.0548(14)	−0.0324(12)	−0.0232(15)	0.0379(15)
O(4)	0.0277(10)	0.0670(15)	0.122(2)	0.0533(15)	0.0090(12)	−0.0030(9)
C(A1)	0.0261(10)	0.0217(9)	0.0160(9)	−0.0007(7)	0.0001(7)	−0.0007(7)
C(A2)	0.0237(9)	0.0216(9)	0.0170(9)	−0.0012(7)	−0.0016(7)	0.0000(7)
C(A3)	0.0221(9)	0.0235(9)	0.0198(9)	0.0002(7)	0.0003(7)	−0.0013(7)
C(A4)	0.0242(10)	0.0227(9)	0.0174(9)	0.0003(7)	0.0030(7)	0.0005(7)
C(B1)	0.0293(11)	0.0348(11)	0.0157(9)	0.0007(8)	−0.0009(8)	−0.0010(8)
C(B2)	0.0275(10)	0.0339(11)	0.0170(9)	0.0000(8)	−0.0033(8)	−0.0002(8)
C(B3)	0.0223(10)	0.0361(11)	0.0221(10)	0.0016(8)	0.0021(8)	−0.0018(8)
C(B4)	0.0247(10)	0.0334(11)	0.0207(10)	0.0012(8)	0.0042(8)	−0.0018(8)
C(M1)	0.0264(10)	0.0207(9)	0.0150(9)	0.0002(7)	0.0024(7)	−0.0004(7)
C(M2)	0.0212(9)	0.0217(9)	0.0203(9)	−0.0005(7)	−0.0022(7)	−0.0007(7)
C(5)	0.0216(9)	0.0347(11)	0.0155(9)	0.0036(8)	0.0014(7)	0.0000(8)
C(6)	0.0284(10)	0.0419(12)	0.0168(9)	−0.0013(8)	0.0019(8)	0.0025(9)
C(7)	0.0324(12)	0.0754(19)	0.0170(10)	−0.0043(11)	0.0026(9)	0.0122(12)
C(8)	0.0259(11)	0.095(2)	0.0182(11)	0.0162(12)	0.0040(9)	0.0102(12)
C(9)	0.0260(11)	0.0699(18)	0.0337(13)	0.0298(13)	0.0015(9)	0.0003(11)
C(10)	0.0284(11)	0.0407(13)	0.0288(11)	0.0117(9)	0.0007(8)	0.0003(9)
C(11)	0.0375(13)	0.0399(13)	0.0487(15)	−0.0164(11)	−0.0142(11)	0.0125(11)
C(12)	0.0215(10)	0.0361(11)	0.0182(9)	0.0022(8)	−0.0006(7)	0.0002(8)
C(13)	0.0219(10)	0.0397(12)	0.0242(10)	−0.0046(9)	−0.0025(8)	−0.0008(9)
C(14)	0.0264(11)	0.0532(15)	0.0340(12)	−0.0009(11)	−0.0087(9)	−0.0053(10)
C(15)	0.0256(12)	0.0623(17)	0.0477(15)	0.0220(13)	−0.0127(10)	−0.0024(11)
C(16)	0.0328(13)	0.0463(15)	0.0648(18)	0.0228(14)	−0.0064(12)	0.0068(11)
C(17)	0.0312(12)	0.0352(12)	0.0430(13)	0.0111(10)	−0.0026(10)	0.0014(9)
C(18)	0.0256(11)	0.0473(14)	0.0248(10)	−0.0003(9)	0.0035(8)	−0.0002(9)
C(19)	0.0297(12)	0.0290(12)	0.075(2)	−0.0019(12)	−0.0152(12)	0.0011(9)

Table S35. Continued

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(20)	0.0305(12)	0.0397(14)	0.0666(18)	−0.0042(13)	−0.0142(12)	0.0032(10)
C(21)	0.0469(18)	0.0423(17)	0.164(4)	0.005(2)	−0.057(2)	−0.0047(14)
C(22)	0.0605(19)	0.0417(15)	0.070(2)	0.0213(15)	0.0183(16)	0.0068(14)
C(23)	0.0321(12)	0.0410(13)	0.0417(13)	−0.0097(11)	0.0076(10)	0.0032(10)
C(24)	0.077(2)	0.066(2)	0.069(2)	−0.0314(19)	0.0100(19)	0.0035(19)
C(25)	0.0514(17)	0.0589(19)	0.0549(18)	0.0152(14)	0.0067(14)	0.0185(14)
C(26)	0.0302(14)	0.063(2)	0.075(2)	0.0114(16)	0.0087(14)	0.0125(12)
O(1S)	0.042(2)	0.0317(18)	0.069(3)	0.0082(17)	0.0283(19)	0.0038(15)
C(1S)	0.130(4)	0.055(2)	0.112(4)	0.019(2)	0.080(3)	0.029(2)
N(3)	0.017(5)	0.0284(15)	0.017(5)	−0.0019(17)	0.000(3)	0.0016(16)
C(1)	0.019(2)	0.036(3)	0.017(2)	−0.001(2)	0.0061(19)	−0.002(2)
C(2)	0.0228(19)	0.032(2)	0.0211(19)	0.0032(16)	0.0003(15)	−0.0011(16)
N(4)	0.0235(12)	0.0240(12)	0.0260(12)	0.000	0.0010(9)	0.000
C(3)	0.0180(18)	0.028(2)	0.0196(19)	−0.0015(18)	−0.0021(16)	0.0031(18)
C(4)	0.030(3)	0.022(2)	0.037(3)	0.0034(19)	0.015(2)	0.0044(18)
O(2S)	0.136(5)	0.054(3)	0.058(3)	−0.004(2)	−0.012(3)	−0.013(3)
C(2S)	0.117(7)	0.052(4)	0.039(3)	0.000(3)	−0.024(4)	0.018(4)
C(3S)	0.084(6)	0.164(10)	0.211(13)	0.000	0.030(7)	0.000

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

The anisotropic displacement factor exponent takes the form: -2π [h^2 U_{11} +...+ 2 h k a* b* U_{12}].

Table S36. Hydrogen Atom Coordinates and Equivalent Isotropic Displacement Parameters ($\mathring{A}^2$) for [Co(TpivPP)(2-MeHIm)0.4(O$_2$)]·2C$_2$H$_5$OH^a (100 K, $C2/c$ form)

atom	x	y	z	$U(\text{eq})$
H(5A)	0.6045	0.7501	0.5479	0.041
H(6A)	0.3168	0.7375	0.6145	0.042
H(BA	0.4554	0.8702	0.4668	0.032
H(BB	0.3334	0.8655	0.5199	0.031
H(BC	0.2297	0.8433	0.7916	0.032
H(BD	0.2823	0.8485	0.9203	0.031
H(7A)	0.6547	0.7670	0.3597	0.050
H(8A)	0.6614	0.8709	0.2983	0.056
H(9A)	0.6297	0.9715	0.3580	0.052
H(10A)	0.5902	0.9682	0.4819	0.039
H(14A)	0.1394	0.7478	0.5650	0.046
H(15A)	0.0692	0.8460	0.5639	0.054
H(16A)	0.1138	0.9473	0.6129	0.058
H(17A)	0.2312	0.9523	0.6598	0.044
H(20A)	0.6980	0.5760	0.5027	0.069
H(20B)	0.6821	0.5588	0.5886	0.069
H(20C)	0.7174	0.6306	0.5668	0.069
H(21A)	0.5680	0.5520	0.4701	0.128
H(21B)	0.5060	0.5917	0.5136	0.128
H(21C)	0.5535	0.5352	0.5564	0.128
H(22A)	0.6196	0.6919	0.6333	0.086
H(22B)	0.5846	0.6201	0.6556	0.086
H(22C)	0.5371	0.6764	0.6124	0.086
H(24A)	0.2394	0.5450	0.5843	0.106
H(24B)	0.3224	0.5231	0.5849	0.106
H(24C)	0.2952	0.5847	0.5325	0.106
H(25A)	0.2430	0.5617	0.7212	0.083
H(25B)	0.3008	0.6122	0.7593	0.083
H(25C)	0.3263	0.5406	0.7254	0.083
H(26A)	0.3909	0.6711	0.6801	0.084
H(26B)	0.3875	0.6614	0.5909	0.084
H(26C)	0.4149	0.6000	0.6436	0.084
H(1A)	0.5888	0.9800	0.6618	0.029
H(2A)	0.5771	1.1046	0.6714	0.031

Table S36. Continued

atom	x	y	z	$U(\mathrm{eq})$
H(4A)	0.4852	1.1233	0.7647	0.029
H(4B)	0.4089	0.9692	0.8426	0.044
H(4C)	0.3749	1.0396	0.8129	0.044
H(4D)	0.4351	1.0403	0.8782	0.044

Supporting Information

Table S37. Complete Crystallographic Details for [Co(TpivPP)(2-MeHIm)0.3(O$_2$)]·1.8C$_2$H$_5$OH (300 K, $C2/c$ form)

formula	C$_{71.6}$H$_{80.8}$CoN$_{10}$O$_{6.4}$
FW, amu	1242.79
a, Å	18.9063(5)
b, Å	19.6633(5)
c, Å	18.3473(5)
β, deg	91.6660(10)
V, Å^3	6817.9(3)
space group	$C2/c$
Z	4
D$_c$, g/cm^3	1.211
F(000)	2634
μ, mm^{-1}	0.310
crystal dimensions, mm	0.37 × 0.21 × 0.16
radiation	MoKα, $\bar{\lambda} = 0.71073$ Å
temperature, K	300(2)
diffractometer	Bruker Apex CCD
θ range for collected data, deg	1.49–30.65
index range	$-26 \leq$ h ≤ 26
	$-28 \leq$ k ≤ 28
	$-26 \leq$ l ≤ 26
total data collected	59647
absorption correction	Semi-empirical from equiv
relative transmission coefficients (I)	0.9520 and 0.8939
unique data	10430 ($R_{\text{int}} = 0.044$)
unique observed data [I $> 2\sigma$(I)]	6200
refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	10430/39/456
goodness-of-fit (based on F^2)	1.024
final R indices [I $> 2\sigma$(I)]	$R_1 = 0.0758$, $wR_2 = 0.2301$
final R indices (all data)	$R_1 = 0.1219$, $wR_2 = 0.2646$

Table S38. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for [Co(TpivPP)(2-MeHIm)0.3(O_2)]·1.8$C_2H_5OH^a$ (300 K, $C2/c$ form)[a]

atom	x	y	z	U(eq)
Co(1)	0.5000	0.86465(2)	0.7500	0.0455(2)
O(1)	0.5000	0.7633(5)	0.7500	0.062(2)
O(2)	0.523(2)	0.7254(10)	0.7760(14)	0.206(19)
N(3)	0.45761(12)	0.86017(10)	0.64970(11)	0.0464(4)
N(4)	0.40456(12)	0.85608(10)	0.79113(11)	0.0491(5)
N(5)	0.6105(2)	0.74871(17)	0.49836(16)	0.0963(11)
N(6)	0.26761(15)	0.73281(16)	0.6269(2)	0.0873(9)
O(3)	0.6261(4)	0.6726(3)	0.4110(3)	0.234(4)
O(4)	0.1830(2)	0.6566(2)	0.6385(4)	0.197(3)
C(a1)	0.49237(15)	0.86294(13)	0.58508(13)	0.0512(6)
C(a2)	0.38710(14)	0.85849(12)	0.63055(13)	0.0500(6)
C(a3)	0.34044(14)	0.85256(14)	0.75358(15)	0.0537(6)
C(a4)	0.38704(15)	0.85648(14)	0.86366(14)	0.0538(6)
C(b1)	0.44263(17)	0.86370(17)	0.52447(15)	0.0643(7)
C(b2)	0.37750(17)	0.86118(16)	0.55256(15)	0.0638(7)
C(b3)	0.28302(16)	0.84872(19)	0.80324(17)	0.0682(8)
C(b4)	0.31178(16)	0.85203(19)	0.87062(17)	0.0705(8)
C(m1)	0.56523(15)	0.86246(13)	0.57737(14)	0.0538(6)
C(m2)	0.33149(15)	0.85472(13)	0.67810(15)	0.0537(6)
C(5)	0.59352(15)	0.86935(16)	0.50226(14)	0.0593(7)
C(6)	0.61467(18)	0.81258(19)	0.46302(15)	0.0717(8)
C(7)	0.6393(2)	0.8202(3)	0.39303(18)	0.0932(13)
C(8)	0.6421(2)	0.8853(3)	0.3624(2)	0.1037(15)
C(9)	0.6211(2)	0.9393(3)	0.3993(2)	0.0978(14)
C(10)	0.5965(2)	0.9329(2)	0.4695(2)	0.0811(10)
C(11)	0.25712(15)	0.85243(16)	0.64644(16)	0.0604(7)
C(12)	0.22671(16)	0.79246(19)	0.62260(18)	0.0719(8)
C(13)	0.1573(2)	0.7929(3)	0.5941(2)	0.0951(12)
C(14)	0.1192(2)	0.8520(3)	0.5915(3)	0.1096(16)
C(15)	0.1490(2)	0.9105(3)	0.6152(3)	0.1059(15)
C(16)	0.21699(19)	0.9117(2)	0.6422(2)	0.0822(10)
C(17)	0.6152(3)	0.6857(3)	0.4766(3)	0.1161(16)
C(18)	0.2461(2)	0.6700(2)	0.6378(2)	0.0892(11)
C(19)	0.6104(3)	0.6304(2)	0.5308(3)	0.1000(13)

Table S38. Continued

atom	x	y	z	U(eq)
C(20)	0.6815(3)	0.6038(4)	0.5475(5)	0.187(4)
C(21)	0.5619(5)	0.5729(4)	0.5019(6)	0.218(4)
C(22)	0.5813(7)	0.6517(4)	0.6018(6)	0.243(6)
C(23)	0.3017(3)	0.6143(2)	0.6484(3)	0.0961(12)
C(24)	0.2859(6)	0.5652(5)	0.5849(6)	0.242(5)
C(25)	0.2902(4)	0.5780(5)	0.7150(5)	0.232(6)
C(26)	0.3733(4)	0.6354(4)	0.6390(8)	0.273(8)
N(2)	0.5000	1.0840(2)	0.7500	0.0751(10)
N(1)	0.4892(6)	0.9733(3)	0.7584(7)	0.0554(19)
C(1)	0.5233(4)	1.0238(3)	0.7275(4)	0.0598(13)
C(3)	0.4416(5)	1.0050(4)	0.8050(5)	0.0677(19)
C(2)	0.4481(4)	1.0710(4)	0.8020(4)	0.0758(17)
C(4)	0.5776(6)	1.0200(5)	0.6711(7)	0.096(3)
O(1S)	0.4464(6)	0.2033(5)	0.7974(7)	0.187(5)
C(1S)	0.4725(5)	0.2633(4)	0.7731(6)	0.211(4)
C(2S)	0.0000	1.0039(13)	0.7500	0.268(10)
C(3S)	−0.0319(15)	0.9432(11)	0.7265(14)	0.225(10)
O(2Sb)	−0.0960(15)	0.9452(17)	0.6914(18)	0.201(9)
O(2Sa)	−0.0373(19)	0.9613(16)	0.6554(14)	0.201(9)

[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 S39. Bond Lengths for [Co(TpivPP)(2-MeHIm)0.3(O$_2$)]·1.8C$_2$H$_5$OH^a (300 K, $C2/c$ form)^a

bond	length (Å)	bond	length (Å)
Co(1)–N(4)	1.983(2)	C(14)–C(15)	1.348(7)
Co(1)–N(4)#1	1.983(2)	C(14)–H(14a)	0.9300
Co(1)–N(3)#1	1.988(2)	C(15)–C(16)	1.364(6)
Co(1)–N(3)	1.988(2)	C(15)–H(15a)	0.9300
Co(1)–O(1)	1.993(9)	C(16)–H(16a)	0.9300
Co(1)–N(1)	2.153(5)	C(17)–C(19)	1.477(7)
Co(1)–N(1)#1	2.153(5)	C(18)–C(23)	1.527(6)
O(1)–O(2)	0.98(2)	C(19)–C(20)	1.466(7)
O(1)–O(2)#1	0.98(2)	C(19)–C(22)	1.489(10)
O(2)–O(2)#1	1.28(5)	C(19)–C(21)	1.539(8)
N(3)–C(a2)	1.369(3)	C(20)–H(20a)	0.9600
N(3)–C(a1)	1.373(3)	C(20)–H(20b)	0.9600
N(4)–C(a3)	1.379(3)	C(20)–H(20C)	0.9600
N(4)–C(a4)	1.381(3)	C(21)–H(21a)	0.9600
N(5)–C(17)	1.306(6)	C(21)–H(21b)	0.9600
N(5)–C(6)	1.417(5)	C(21)–H(21C)	0.9600
N(5)–H(5a)	0.8600	C(22)–H(22a)	0.9600
N(6)–C(18)	1.317(5)	C(22)–H(22b)	0.9600
N(6)–C(12)	1.406(5)	C(22)–H(22C)	0.9600
N(6)–H(6a)	0.8600	C(23)–C(26)	1.431(8)
O(3)–C(17)	1.253(6)	C(23)–C(25)	1.437(8)
O(4)–C(18)	1.221(5)	C(23)–C(24)	1.536(10)
C(a1)–C(m1)	1.389(4)	C(24)–H(24a)	0.9600
C(a1)–C(b1)	1.435(4)	C(24)–H(24b)	0.9600
C(a2)–C(m2)	1.388(4)	C(24)–H(24C)	0.9600
C(a2)–C(b2)	1.438(4)	C(25)–H(25a)	0.9600
C(a3)–C(m2)	1.391(4)	C(25)–H(25b)	0.9600
C(a3)–C(b3)	1.439(4)	C(25)–H(25C)	0.9600
C(a4)–C(m1#1)	1.394(4)	C(26)–H(26a)	0.9600
C(a4)–C(b4)	1.435(4)	C(26)–H(26b)	0.9600
C(b1)–C(b2)	1.350(4)	C(26)–H(26C)	0.9600
C(b1)–H(ba)	0.9300	N(2)–C(1)#1	1.332(8)
C(b2)–H(bb)	0.9300	N(2)–C(1)	1.332(8)
C(b3)–C(b4)	1.337(4)	N(2)–C(2)#1	1.412(8)

Table S39. Continued

bond	length (Å)	bond	length (Å)
C(b3)–H(bC)	0.9300	N(2)–C(2)	1.412(8)
C(b4)–H(bd)	0.9300	N(2)–H(2a)	0.8600
C(m1)–C(a4#1)	1.394(4)	N(1)–C(1)	1.319(8)
C(m1)–C(5)	1.499(4)	N(1)–C(3)	1.405(11)
C(m2)–C(11)	1.506(4)	C(1)–C(4)	1.481(11)
C(5)–C(10)	1.388(5)	C(3)–C(2)	1.304(12)
C(5)–C(6)	1.393(5)	C(3)–H(3a)	0.9300
C(6)–C(7)	1.387(4)	C(2)–H(2b)	0.9300
C(7)–C(8)	1.400(7)	C(4)–H(4a)	0.9600
C(7)–H(7a)	0.9300	C(4)–H(4b)	0.9600
C(8)–C(9)	1.326(7)	C(4)–H(4C)	0.9600
C(8)–H(8a)	0.9300	O(1S)–C(1S)	1.358(11)
C(9)–C(10)	1.389(5)	C(1S)–C(1S)#1	1.360(14)
C(9)–H(9a)	0.9300	C(2S)–C(3S)#2	1.400(17)
C(10)–H(10a)	0.9300	C(2S)–C(3S)	1.400(17)
C(11)–C(12)	1.378(5)	C(3S)–O(2Sa)	1.353(18)
C(11)–C(16)	1.392(5)	C(3S)–O(2Sb)	1.356(18)
C(12)–C(13)	1.398(5)	C(3S)–C(3S)#2	1.46(5)
C(13)–C(14)	1.366(7)		
C(13)–H(13a)	0.9300		

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

Table S40. Bond Angles for [Co(TpivPP)(2-MeHIm)0.3(O$_2$)]·1.8C$_2$H$_5$OH^a (300 K, $C2/c$ form)^a

angle	degree	angle	degree
N(4)–Co(1)–N(4)#1	170.26(12)	C(14)–C(15)–C(16)	120.8(4)
N(4)–Co(1)–N(3)#1	89.47(9)	C(14)–C(15)–H(15a)	119.6
N(4)#1–Co(1)–N(3)#1	90.10(9)	C(16)–C(15)–H(15a)	119.6
N(4)–Co(1)–N(3)	90.10(9)	C(15)–C(16)–C(11)	120.8(4)
N(4)#1–Co(1)–N(3)	89.47(9)	C(15)–C(16)–H(16a)	119.6
N(3)#1–Co(1)–N(3)	174.92(12)	C(11)–C(16)–H(16a)	119.6
N(4)–Co(1)–O(1)	85.13(6)	O(3)–C(17)–N(5)	120.2(5)
N(4)#1–Co(1)–O(1)	85.13(6)	O(3)–C(17)–C(19)	120.6(5)
N(3)#1–Co(1)–O(1)	87.46(6)	N(5)–C(17)–C(19)	119.1(4)
N(3)–Co(1)–O(1)	87.46(6)	O(4)–C(18)–N(6)	120.7(4)
N(4)–Co(1)–N(1)	88.2(2)	O(4)–C(18)–C(23)	120.8(4)
N(4)#1–Co(1)–N(1)	101.6(2)	N(6)–C(18)–C(23)	118.5(4)
N(3)#1–Co(1)–N(1)	90.8(4)	C(20)–C(19)–C(17)	109.2(5)
N(3)–Co(1)–N(1)	94.2(4)	C(20)–C(19)–C(22)	106.1(7)
O(1)–Co(1)–N(1)	173.10(16)	C(17)–C(19)–C(22)	114.4(4)
N(4)–Co(1)–N(1)#1	101.6(2)	C(20)–C(19)–C(21)	110.1(6)
N(4)#1–Co(1)–N(1)#1	88.2(2)	C(17)–C(19)–C(21)	110.9(5)
N(3)#1–Co(1)–N(1)#1	94.2(4)	C(22)–C(19)–C(21)	106.0(7)
N(3)–Co(1)–N(1)#1	90.8(4)	C(19)–C(20)–H(20a)	109.5
O(1)–Co(1)–N(1)#1	173.10(16)	C(19)–C(20)–H(20b)	109.5
N(1)–Co(1)–N(1)#1	13.8(3)	H(20a)–C(20)–H(20b)	109.5
O(2)–O(1)–O(2)#1	81(3)	C(19)–C(20)–H(20C)	109.5
O(2)–O(1)–Co(1)	139.3(16)	H(20a)–C(20)–H(20C)	109.5
O(2)#1–O(1)–Co(1)	139.3(16)	H(20b)–C(20)–H(20C)	109.5
O(1)–O(2)–O(2)#1	49.3(16)	C(19)–C(21)–H(21a)	109.5
C(a2)–N(3)–C(a1)	105.4(2)	C(19)–C(21)–H(21b)	109.5
C(a2)–N(3)–Co(1)	127.02(18)	H(21a)–C(21)–H(21b)	109.5
C(a1)–N(3)–Co(1)	127.40(18)	C(19)–C(21)–H(21C)	109.5
C(a3)–N(4)–C(a4)	104.5(2)	H(21a)–C(21)–H(21C)	109.5
C(a3)–N(4)–Co(1)	127.64(18)	H(21b)–C(21)–H(21C)	109.5
C(a4)–N(4)–Co(1)	127.78(18)	C(19)–C(22)–H(22a)	109.5
C(17)–N(5)–C(6)	134.1(3)	C(19)–C(22)–H(22b)	109.5
C(17)–N(5)–H(5a)	112.9	H(22a)–C(22)–H(22b)	109.5
C(6)–N(5)–H(5a)	112.9	C(19)–C(22)–H(22C)	109.5

Table S40. Continued

angle	degree	angle	degree
C(18)–N(6)–C(12)	128.2(3)	H(22a)–C(22)–H(22C)	109.5
C(18)–N(6)–H(6a)	115.9	H(22b)–C(22)–H(22C)	109.5
C(12)–N(6)–H(6a)	115.9	C(26)–C(23)–C(25)	114.4(7)
N(3)–C(a1)–C(m1)	126.1(2)	C(26)–C(23)–C(18)	115.3(4)
N(3)–C(a1)–C(b1)	110.5(2)	C(25)–C(23)–C(18)	110.2(4)
C(m1)–C(a1)–C(b1)	123.4(3)	C(26)–C(23)–C(24)	104.7(8)
N(3)–C(a2)–C(m2)	126.1(2)	C(25)–C(23)–C(24)	107.5(8)
N(3)–C(a2)–C(b2)	110.4(2)	C(18)–C(23)–C(24)	103.7(5)
C(m2)–C(a2)–C(b2)	123.5(3)	C(23)–C(24)–H(24a)	109.5
N(4)–C(a3)–C(m2)	125.2(2)	C(23)–C(24)–H(24b)	109.5
N(4)–C(a3)–C(b3)	110.8(2)	H(24a)–C(24)–H(24b)	109.5
C(m2)–C(a3)–C(b3)	124.0(3)	C(23)–C(24)–H(24C)	109.5
N(4)–C(a4)–C(m1#1	125.5(3)	H(24a)–C(24)–H(24C)	109.5
N(4)–C(a4)–C(b4)	110.6(2)	H(24b)–C(24)–H(24C)	109.5
C(m1#1–C(a4)–C(b4)	123.9(3)	C(23)–C(25)–H(25a)	109.5
C(b2)–C(b1)–C(a1)	106.8(2)	C(23)–C(25)–H(25b)	109.5
C(b2)–C(b1)–H(ba)	126.6	H(25a)–C(25)–H(25b)	109.5
C(a1)–C(b1)–H(ba)	126.6	C(23)–C(25)–H(25C)	109.5
C(b1)–C(b2)–C(a2)	106.9(2)	H(25a)–C(25)–H(25C)	109.5
C(b1)–C(b2)–H(bb)	126.5	H(25b)–C(25)–H(25C)	109.5
C(a2)–C(b2)–H(bb)	126.5	C(23)–C(26)–H(26a)	109.5
C(b4)–C(b3)–C(a3)	106.8(3)	C(23)–C(26)–H(26b)	109.5
C(b4)–C(b3)–H(bC)	126.6	H(26a)–C(26)–H(26b)	109.5
C(a3)–C(b3)–H(bC)	126.6	C(23)–C(26)–H(26C)	109.5
C(b3)–C(b4)–C(a4)	107.3(3)	H(26a)–C(26)–H(26C)	109.5
C(b3)–C(b4)–H(bd)	126.3	H(26b)–C(26)–H(26C)	109.5
C(a4)–C(b4)–H(bd)	126.3	C(1)#1–N(2)–C(1)	54.7(7)
C(a1)–C(m1)–C(a4#1	122.9(2)	C(1)#1–N(2)–C(2)#1	106.9(5)
C(a1)–C(m1)–C(5)	118.3(2)	C(1)–N(2)–C(2)#1	52.2(4)
C(a4#1–C(m1)–C(5)	118.8(3)	C(1)#1–N(2)–C(2)	52.2(4)
C(a2)–C(m2)–C(a3)	123.7(3)	C(1)–N(2)–C(2)	106.9(5)
C(a2)–C(m2)–C(11)	118.4(2)	C(2)#1–N(2)–C(2)	159.1(7)
C(a3)–C(m2)–C(11)	117.9(3)	C(1)#1–N(2)–H(2a)	178.5
C(10)–C(5)–C(6)	118.8(3)	C(1)–N(2)–H(2a)	126.6

angle	degree	angle	degree
C(10)–C(5)–C(m1)	120.0(3)	C(2)#1–N(2)–H(2a)	74.3
C(6)–C(5)–C(m1)	121.2(3)	C(2)–N(2)–H(2a)	126.6
C(7)–C(6)–C(5)	120.1(4)	C(1)–N(1)–C(3)	104.9(6)
C(7)–C(6)–N(5)	123.0(4)	C(1)–N(1)–Co(1)	131.9(5)
C(5)–C(6)–N(5)	117.0(3)	C(3)–N(1)–Co(1)	123.1(5)
C(6)–C(7)–C(8)	119.2(4)	N(1)–C(1)–N(2)	111.4(7)
C(6)–C(7)–H(7a)	120.4	N(1)–C(1)–C(4)	128.3(7)
C(8)–C(7)–H(7a)	120.4	N(2)–C(1)–C(4)	120.2(6)
C(9)–C(8)–C(7)	120.8(3)	C(2)–C(3)–N(1)	110.6(8)
C(9)–C(8)–H(8a)	119.6	C(2)–C(3)–H(3a)	124.7
C(7)–C(8)–H(8a)	119.6	N(1)–C(3)–H(3a)	124.7
C(8)–C(9)–C(10)	120.9(4)	C(3)–C(2)–N(2)	106.1(7)
C(8)–C(9)–H(9a)	119.5	C(3)–C(2)–H(2b)	127.0
C(10)–C(9)–H(9a)	119.5	N(2)–C(2)–H(2b)	127.0
C(5)–C(10)–C(9)	120.2(4)	C(1)–C(4)–H(4a)	109.5
C(5)–C(10)–H(10a)	119.9	C(1)–C(4)–H(4b)	109.5
C(9)–C(10)–H(10a)	119.9	H(4a)–C(4)–H(4b)	109.5
C(12)–C(11)–C(16)	118.5(3)	C(1)–C(4)–H(4C)	109.5
C(12)–C(11)–C(m2)	121.6(3)	H(4a)–C(4)–H(4C)	109.5
C(16)–C(11)–C(m2)	119.8(3)	H(4b)–C(4)–H(4C)	109.5
C(11)–C(12)–C(13)	119.5(4)	O(1S)–C(1S)–C(1S)#1	119.8(5)
C(11)–C(12)–N(6)	118.2(3)	C(3S)#2–C(2S)–C(3S)	63(2)
C(13)–C(12)–N(6)	122.3(3)	O(2Sa)–C(3S)–O(2Sb)	60(2)
C(14)–C(13)–C(12)	120.4(4)	O(2Sa)–C(3S)–C(2S)	95.3(19)
C(14)–C(13)–H(13a)	119.8	O(2Sb)–C(3S)–C(2S)	119(2)
C(12)–C(13)–H(13a)	119.8	O(2Sa)–C(3S)–C(3S)#2	127(4)
C(15)–C(14)–C(13)	120.0(4)	O(2Sb)–C(3S)–C(3S)#2	172(4)
C(15)–C(14)–H(14a)	120.0	C(2S)–C(3S)–C(3S)#2	58.5(12)
C(13)–C(14)–H(14a)	120.0		

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

Table S41. Anisotropic Displacement Parameters ($Å^2$) for [Co(TpivPP)(2-MeHIm)0.3(O$_2$)]·1.8C$_2$H$_5$OH[a] (300 K, $C2/c$ form)[a]

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co(1)	0.0439(3)	0.0519(3)	0.0405(2)	0.000	0.0005(2)	0.000
O(1)	0.075(6)	0.044(5)	0.067(5)	0.000	−0.002(5)	0.000
O(2)	0.43(6)	0.048(10)	0.13(2)	0.024(11)	−0.12(3)	0.021(18)
N(3)	0.0479(11)	0.0467(11)	0.0445(10)	−0.0012(8)	0.0005(8)	−0.0027(8)
N(4)	0.0479(11)	0.0554(12)	0.0439(9)	0.0016(8)	−0.0001(8)	−0.0020(9)
N(5)	0.154(3)	0.079(2)	0.0579(15)	−0.0116(14)	0.0275(18)	0.001(2)
N(6)	0.0553(16)	0.081(2)	0.126(3)	−0.0165(18)	−0.0026(15)	−0.0101(14)
O(3)	0.427(11)	0.168(5)	0.109(3)	−0.040(3)	0.023(5)	0.078(6)
O(4)	0.084(2)	0.126(3)	0.383(8)	0.072(4)	0.046(4)	−0.018(2)
C(A1)	0.0565(15)	0.0541(14)	0.0428(11)	0.0013(10)	−0.0016(10)	−0.0021(11)
C(A2)	0.0514(14)	0.0522(14)	0.0461(11)	0.0001(10)	−0.0042(10)	−0.0033(11)
C(A3)	0.0473(14)	0.0611(16)	0.0529(13)	0.0012(11)	0.0034(10)	−0.0039(11)
C(A4)	0.0495(14)	0.0642(16)	0.0481(12)	0.0008(11)	0.0061(10)	−0.0015(11)
C(B1)	0.0642(17)	0.087(2)	0.0411(12)	0.0004(12)	−0.0026(11)	−0.0042(15)
C(B2)	0.0554(16)	0.088(2)	0.0472(13)	−0.0003(13)	−0.0074(11)	−0.0054(14)
C(B3)	0.0464(15)	0.098(2)	0.0602(16)	0.0048(15)	0.0063(12)	−0.0063(15)
C(B4)	0.0534(16)	0.105(3)	0.0538(15)	0.0009(15)	0.0121(12)	−0.0021(16)
C(M1)	0.0592(15)	0.0595(15)	0.0428(11)	0.0011(10)	0.0053(10)	−0.0019(12)
C(M2)	0.0479(13)	0.0582(15)	0.0546(13)	0.0012(11)	−0.0037(11)	−0.0038(11)
C(5)	0.0528(15)	0.0800(19)	0.0453(12)	0.0082(12)	0.0043(11)	−0.0032(13)
C(6)	0.075(2)	0.097(2)	0.0444(13)	0.0018(14)	0.0090(13)	0.0038(17)
C(7)	0.088(3)	0.143(4)	0.0496(16)	0.005(2)	0.0166(16)	0.016(2)
C(8)	0.075(2)	0.180(5)	0.0571(18)	0.038(3)	0.0136(17)	0.008(3)
C(9)	0.082(3)	0.128(4)	0.083(2)	0.051(3)	0.008(2)	−0.007(2)
C(10)	0.081(2)	0.090(2)	0.0729(19)	0.0215(18)	0.0064(16)	−0.0041(19)
C(11)	0.0480(14)	0.0769(19)	0.0559(14)	0.0054(12)	−0.0046(11)	0.0011(13)
C(12)	0.0504(16)	0.089(2)	0.0752(19)	−0.0081(16)	−0.0087(13)	−0.0039(15)
C(13)	0.060(2)	0.119(3)	0.105(3)	−0.004(2)	−0.0187(19)	−0.012(2)
C(14)	0.058(2)	0.157(5)	0.113(3)	0.031(3)	−0.024(2)	0.007(3)
C(15)	0.069(2)	0.119(4)	0.129(4)	0.042(3)	−0.006(2)	0.026(2)
C(16)	0.069(2)	0.079(2)	0.099(3)	0.0130(19)	−0.0021(18)	0.0098(17)
C(17)	0.143(5)	0.114(4)	0.091(3)	−0.010(3)	−0.007(3)	0.034(3)
C(18)	0.073(2)	0.089(3)	0.106(3)	0.000(2)	0.015(2)	−0.012(2)
C(19)	0.087(3)	0.090(3)	0.122(4)	0.003(2)	−0.008(3)	0.011(2)

Table S41. Continued

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(20)	0.087(4)	0.209(7)	0.263(9)	0.115(7)	−0.031(5)	0.000(4)
C(21)	0.195(7)	0.160(6)	0.291(10)	0.032(7)	−0.127(7)	−0.035(5)
C(22)	0.382(15)	0.131(5)	0.226(10)	0.093(6)	0.150(10)	0.035(8)
C(23)	0.103(3)	0.083(3)	0.104(3)	−0.006(2)	0.030(2)	0.002(2)
C(24)	0.301(11)	0.204(8)	0.221(9)	−0.083(7)	0.000(8)	0.093(8)
C(25)	0.192(8)	0.313(13)	0.196(8)	0.144(8)	0.077(7)	0.108(8)
C(26)	0.101(5)	0.184(8)	0.54(2)	0.170(11)	0.109(9)	0.056(5)
N(2)	0.075(2)	0.063(2)	0.087(3)	0.000	−0.003(2)	0.000
N(1)	0.048(7)	0.064(3)	0.053(6)	0.002(3)	−0.001(3)	−0.003(3)
C(1)	0.061(4)	0.052(3)	0.066(4)	−0.002(3)	−0.003(3)	−0.004(3)
C(3)	0.082(6)	0.058(5)	0.064(4)	0.004(3)	0.015(4)	0.001(4)
C(2)	0.078(5)	0.072(4)	0.077(4)	−0.004(3)	0.005(3)	0.011(4)
C(4)	0.101(7)	0.068(6)	0.122(9)	0.009(5)	0.048(6)	−0.015(4)
O(1S)	0.209(10)	0.095(6)	0.263(12)	−0.015(6)	0.120(9)	0.012(6)
C(1S)	0.236(10)	0.140(6)	0.264(11)	−0.067(6)	0.133(8)	−0.052(6)
C(2S)	0.30(2)	0.193(18)	0.30(2)	0.000	−0.065(19)	0.000
C(3S)	0.28(3)	0.183(18)	0.21(2)	0.085(17)	0.037(18)	0.089(18)
O(2SB)	0.24(3)	0.177(17)	0.189(19)	−0.016(15)	0.018(16)	0.067(19)
O(2SA)	0.24(3)	0.177(17)	0.189(19)	−0.016(15)	0.018(16)	0.067(19)

[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 S42. Hydrogen Atom Coordinates and Equivalent Isotropic Displacement Parameters
(Å^2) for [Co(TpivPP)(2-MeHIm)0.3(O$_2$)]·1.8C$_2$H$_5$OH^a (300 K, $C2/c$ form)

atom	x	y	z	U(eq)
H(5A)	0.6034	0.7522	0.5443	0.116
H(6A)	0.3124	0.7380	0.6219	0.105
H(BA	0.4532	0.8656	0.4753	0.077
H(BB	0.3346	0.8612	0.5265	0.077
H(BC	0.2352	0.8447	0.7909	0.082
H(BD	0.2875	0.8515	0.9140	0.085
H(7A)	0.6539	0.7825	0.3668	0.112
H(8A)	0.6588	0.8907	0.3156	0.124
H(9A)	0.6230	0.9821	0.3778	0.117
H(10A)	0.5819	0.9712	0.4947	0.097
H(13A)	0.1369	0.7527	0.5769	0.114
H(14A)	0.0728	0.8518	0.5733	0.132
H(15A)	0.1229	0.9506	0.6131	0.127
H(16A)	0.2367	0.9526	0.6580	0.099
H(20A)	0.7021	0.5878	0.5035	0.281
H(20B)	0.6784	0.5670	0.5816	0.281
H(20C)	0.7104	0.6393	0.5683	0.281
H(21A)	0.5785	0.5571	0.4559	0.327
H(21B)	0.5145	0.5897	0.4956	0.327
H(21C)	0.5626	0.5360	0.5362	0.327
H(22A)	0.6096	0.6878	0.6222	0.365
H(22B)	0.5820	0.6137	0.6347	0.365
H(22C)	0.5335	0.6672	0.5943	0.365
H(24A)	0.3184	0.5277	0.5876	0.364
H(24B)	0.2912	0.5887	0.5395	0.364
H(24C)	0.2384	0.5485	0.5878	0.364
H(25A)	0.3032	0.6063	0.7558	0.348
H(25B)	0.3187	0.5375	0.7161	0.348
H(25C)	0.2412	0.5657	0.7174	0.348
H(26A)	0.3859	0.6690	0.6750	0.409
H(26B)	0.3779	0.6544	0.5912	0.409
H(26C)	0.4042	0.5969	0.6445	0.409
H(2A)	0.5139	1.1233	0.7356	0.090
H(3A)	0.4097	0.9821	0.8339	0.081

Table S42. Continued

atom	x	y	z	$U(\text{eq})$
H(2B)	0.4235	1.1029	0.8288	0.091
H(4A)	0.5877	0.9732	0.6607	0.144
H(4B)	0.6200	1.0421	0.6886	0.144
H(4C)	0.5603	1.0421	0.6275	0.144

Supporting Information

Table S43. Complete Crystallographic Details for [Co(TpivPP)(2-MeHIm)]·1.8C$_2$H$_5$OH (100 K, $C2/c$ form)

formula	C$_{71.6}$H$_{82}$CoN$_{10}$O$_{5.8}$
FW, amu	1234.40
a, Å	18.6326(3)
b, Å	19.6158(3)
c, Å	17.9050(3)
β, deg	90.8790(10)
V, Å^3	6543.39(18)
space group	$C2/c$
Z	4
D$_c$, g/cm^3	1.253
F(000)	2620
μ, mm^{-1}	0.322
crystal dimensions, mm	0.37 × 0.21 × 0.16
radiation	MoKα, $\bar{\lambda} = 0.71073$ Å
temperature, K	100(2)
diffractometer	Bruker Apex CCD
θ range for collected data, deg	1.51–30.56
index range	$-26 \leq h \leq 26$
	$-28 \leq k \leq 28$
	$-25 \leq l \leq 25$
total data collected	66118
absorption correction	Semi-empirical from equiv
relative transmission coefficients (I)	0.9503 and 0.8901
unique data	9999 ($R_{\text{int}} = 0.0288$)
unique observed data [I > 2σ(I)]	7966
refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	9999/1/450
goodness-of-fit (based on F^2)	1.072
final R indices [I > 2σ(I)]	$R_1 = 0.0572$, $wR_2 = 0.1633$
final R indices (all data)	$R_1 = 0.0733$, $wR_2 = 0.1776$

Table S44. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for [Co(TpivPP)(2-MeHIm)]·1.8C_2H_5OH[a] (100 K, $C2/c$ form)[a]

atom	x	y	z	U(eq)
Co(1)	0.5000	0.86671(2)	0.7500	0.0209(1)
O(1)	0.38012(19)	0.66005(14)	1.08391(14)	0.0919(9)
O(2)	0.1844(3)	0.6617(5)	0.6471(10)	0.052(3)
O(2b)	0.1889(8)	0.6393(12)	0.6195(8)	0.043(4)
N(3)	0.45849(8)	0.86164(7)	0.64770(8)	0.0227(3)
N(4)	0.40257(8)	0.85723(7)	0.79238(8)	0.0237(3)
N(5)	0.27041(9)	0.73264(10)	0.62083(12)	0.0410(4)
N(6)	0.38711(12)	0.74436(10)	0.99891(10)	0.0446(5)
C(a1)	0.49443(10)	0.86470(9)	0.58091(9)	0.0244(3)
C(a2)	0.38685(10)	0.86083(9)	0.62767(9)	0.0248(3)
C(a3)	0.33799(10)	0.85322(9)	0.75387(9)	0.0252(3)
C(a4)	0.38403(10)	0.85704(9)	0.86681(9)	0.0252(3)
C(b1)	0.44455(11)	0.86690(10)	0.51860(10)	0.0304(4)
C(b2)	0.37788(11)	0.86443(10)	0.54745(10)	0.0303(4)
C(b3)	0.27876(11)	0.84873(11)	0.80462(10)	0.0313(4)
C(b4)	0.30723(11)	0.85175(11)	0.87450(11)	0.0314(4)
C(m1)	0.32974(10)	0.85584(9)	0.67648(10)	0.0256(3)
C(m2)	0.43165(10)	0.86326(9)	0.92710(9)	0.0248(3)
C(5)	0.25527(10)	0.85267(11)	0.64417(10)	0.0303(4)
C(6)	0.22700(11)	0.79173(12)	0.61652(11)	0.0353(4)
C(7)	0.15763(12)	0.79003(15)	0.58559(14)	0.0485(6)
C(8)	0.11603(13)	0.84858(17)	0.58560(16)	0.0551(7)
C(9)	0.14249(14)	0.90835(16)	0.61456(17)	0.0551(7)
C(10)	0.21224(13)	0.91099(13)	0.64223(14)	0.0423(5)
C(11)	0.40232(10)	0.86601(10)	1.00477(10)	0.0282(4)
C(12)	0.38204(12)	0.80569(12)	1.04099(10)	0.0357(4)
C(13)	0.35822(14)	0.80743(16)	1.11461(11)	0.0497(6)
C(14)	0.35463(12)	0.86940(17)	1.15129(12)	0.0522(7)
C(15)	0.37369(12)	0.92907(15)	1.11666(13)	0.0477(6)
C(16)	0.39742(12)	0.92745(12)	1.04289(12)	0.0373(4)
C(17)	0.24847(12)	0.66843(13)	0.63420(12)	0.0387(5)
C(18)	0.38752(15)	0.67857(14)	1.01884(15)	0.0496(6)
C(19)	0.30547(12)	0.61338(12)	0.64387(13)	0.0400(5)
C(20)	0.2923(2)	0.56210(19)	0.5799(2)	0.0757(10)

Table S44. Continued

atom	x	y	z	$U(\text{eq})$
C(21)	0.29197(15)	0.57786(15)	0.71869(16)	0.0522(6)
C(22)	0.38211(14)	0.64000(14)	0.64225(19)	0.0540(7)
C(23)	0.39279(13)	0.62754(12)	0.95483(16)	0.0461(6)
C(24)	0.44898(16)	0.57332(16)	0.9761(2)	0.0696(9)
C(25)	0.31802(14)	0.59490(14)	0.94817(18)	0.0534(6)
C(26)	0.41362(17)	0.65809(14)	0.87909(16)	0.0544(6)
C(1S)	0.0272(4)	0.7630(2)	0.7192(4)	0.150(3)
O(1S)	0.0501(2)	0.70638(19)	0.6866(3)	0.0712(14)
N(2)	0.5000	1.08722(11)	0.7500	0.0284(4)
C(1)	0.4768(2)	1.02648(18)	0.7759(2)	0.0258(7)
N(1)	0.5105(3)	0.97599(15)	0.7415(3)	0.0240(9)
C(3)	0.5576(2)	1.0079(2)	0.6931(2)	0.0275(7)
C(2)	0.5519(2)	1.0759(2)	0.6986(2)	0.0292(7)
C(4)	0.4207(3)	1.0205(2)	0.8338(3)	0.0358(9)
O(2S)	0.4521(3)	0.5424(3)	0.1557(3)	0.0680(15)
C(2S)	0.4574(5)	0.5600(4)	0.2252(4)	0.065(2)
C(3S)	0.5000	0.5144(7)	0.2500	0.142(4)

[a] $U(\text{eq})$ 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 S45. Bond Lengths for [Co(TpivPP)(2-MeHIm)]·1.8C₂H₅OH^a (100 K, $C2/c$ form)^a

bond	length (Å)	bond	length (Å)
Co(1)–N(3)#1)	1.9799(14)	C(14)–H(14a)	0.9500
Co(1)–N(3)	1.9799(14)	C(15)–C(16)	1.400(3)
Co(1)–N(4)#1)	1.9869(15)	C(15)–H(15a)	0.9500
Co(1)–N(4)	1.9869(15)	C(16)–H(16a)	0.9500
Co(1)–N(1)	2.158(3)	C(17)–C(19)	1.523(3)
Co(1)–N(1)#1	2.158(3)	C(18)–C(23)	1.526(4)
O(1)–C(18)	1.230(3)	C(19)–C(22)	1.521(3)
O(2)–C(17)	1.226(4)	C(19)–C(21)	1.534(4)
O(2b)–C(17)	1.272(7)	C(19)–C(20)	1.541(4)
N(3)–C(a2)	1.377(2)	C(20)–H(20a)	0.9800
N(3)–C(a1)	1.381(2)	C(20)–H(20b)	0.9800
N(4)–C(a3)	1.380(2)	C(20)–H(20C)	0.9800
N(4)–C(a4)	1.382(2)	C(21)–H(21a)	0.9800
N(5)–C(17)	1.347(3)	C(21)–H(21b)	0.9800
N(5)–C(6)	1.415(3)	C(21)–H(21C)	0.9800
N(5)–H(5a)	0.8800	C(22)–H(22a)	0.9800
N(6)–C(18)	1.339(3)	C(22)–H(22b)	0.9800
N(6)–C(12)	1.423(3)	C(22)–H(22C)	0.9800
N(6)–H(6a)	0.8800	C(23)–C(25)	1.536(3)
C(a1)–C(m2#1)	1.387(3)	C(23)–C(24)	1.536(4)
C(a1)–C(b1)	1.442(2)	C(23)–C(26)	1.538(4)
C(a2)–C(m1)	1.391(3)	C(24)–H(24a)	0.9800
C(a2)–C(b2)	1.445(2)	C(24)–H(24b)	0.9800
C(a3)–C(m1)	1.393(2)	C(24)–H(24C)	0.9800
C(a3)–C(b3)	1.443(3)	C(25)–H(25a)	0.9800
C(a4)–C(m2)	1.392(2)	C(25)–H(25b)	0.9800
C(a4)–C(b4)	1.443(3)	C(25)–H(25C)	0.9800
C(b1)–C(b2)	1.354(3)	C(26)–H(26a)	0.9800
C(b1)–H(ba)	0.9500	C(26)–H(26b)	0.9800
C(b2)–H(bb)	0.9500	C(26)–H(26C)	0.9800
C(b3)–C(b4)	1.353(3)	C(1S)–O(1S)	1.327(6)
C(b3)–H(bC)	0.9500	C(1S)–C(1S)#2	1.510(9)
C(b4)–H(bd)	0.9500	N(2)–C(1)#1	1.352(4)
C(m1)–C(5)	1.496(3)	N(2)–C(1)	1.352(4)

Table S45. Continued

bond	length (Å)	bond	length (Å)
C(m2)–C(a1#1)	1.387(3)	N(2)–C(2)#1	1.363(4)
C(m2)–C(11)	1.503(2)	N(2)–C(2)	1.363(4)
C(5)–C(6)	1.394(3)	N(2)–H(2a)	0.8800
C(5)–C(10)	1.397(3)	C(1)–N(1)	1.329(5)
C(6)–C(7)	1.399(3)	C(1)–C(4)	1.488(6)
C(7)–C(8)	1.386(4)	N(1)–C(3)	1.391(6)
C(7)–H(7a)	0.9500	C(3)–C(2)	1.342(6)
C(8)–C(9)	1.371(4)	C(3)–H(3a)	0.9500
C(8)–H(8a)	0.9500	C(2)–H(2b)	0.9500
C(9)–C(10)	1.385(3)	C(4)–H(4a)	0.9800
C(9)–H(9a)	0.9500	C(4)–H(4b)	0.9800
C(10)–H(10a)	0.9500	C(4)–H(4C)	0.9800
C(11)–C(16)	1.389(3)	O(2S)–C(2S)	1.292(9)
C(11)–C(12)	1.404(3)	C(2S)–C(3S)	1.271(10)
C(12)–C(13)	1.398(3)	C(2S)–C(2S)#3	1.808(17)
C(13)–C(14)	1.384(4)	C(3S)–C(2S)#3	1.271(10)
C(13)–H(13a)	0.9500		
C(14)–C(15)	1.374(4)		

^{a}The estimated standard deviations of the least significant digits are given in parentheses.

Table S46. Bond Angles for [Co(TpivPP)(2-MeHIm)]·1.8C$_2$H$_5$OH^a (100 K, $C2/c$ form)^a

angle	degree	angle	degree
N(3)#1–Co(1)–N(3)	174.24(8)	C(15)–C(16)–H(16a)	119.7
N(3)#1–Co(1)–N(4)#1	90.13(6)	O(2)–C(17)–O(2b)	30.9(4)
N(3)–Co(1)–N(4)#1	89.33(6)	O(2)–C(17)–N(5)	115.6(4)
N(3)#1–Co(1)–N(4)	89.33(6)	O(2b)–C(17)–N(5)	130.5(9)
N(3)–Co(1)–N(4)	90.13(6)	O(2)–C(17)–C(19)	125.6(3)
N(4)#1–Co(1)–N(4)	169.26(9)	O(2b)–C(17)–C(19)	108.1(12)
N(3)#1–Co(1)–N(1)	94.60(19)	N(5)–C(17)–C(19)	118.05(19)
N(3)–Co(1)–N(1)	91.13(19)	O(1)–C(18)–N(6)	122.5(3)
N(4)#1–Co(1)–N(1)	88.94(10)	O(1)–C(18)–C(23)	121.8(3)
N(4)–Co(1)–N(1)	101.79(10)	N(6)–C(18)–C(23)	115.6(2)
N(3)#1–Co(1)–N(1)#1	91.13(19)	C(22)–C(19)–C(17)	114.1(2)
N(3)–Co(1)–N(1)#1	94.60(19)	C(22)–C(19)–C(21)	109.8(2)
N(4)#1–Co(1)–N(1)#1	101.79(10)	C(17)–C(19)–C(21)	107.33(18)
N(4)–Co(1)–N(1)#1	88.95(10)	C(22)–C(19)–C(20)	110.4(2)
N(1)–Co(1)–N(1)#1	13.29(15)	C(17)–C(19)–C(20)	106.0(2)
C(a2)–N(3)–C(a1)	104.84(14)	C(21)–C(19)–C(20)	109.0(2)
C(a2)–N(3)–Co(1)	127.23(12)	C(19)–C(20)–H(20a)	109.5
C(a1)–N(3)–Co(1)	127.68(12)	C(19)–C(20)–H(20b)	109.5
C(a3)–N(4)–C(a4)	104.64(15)	H(20a)–C(20)–H(20b)	109.5
C(a3)–N(4)–Co(1)	127.54(12)	C(19)–C(20)–H(20C)	109.5
C(a4)–N(4)–Co(1)	127.73(12)	H(20a)–C(20)–H(20C)	109.5
C(17)–N(5)–C(6)	126.94(19)	H(20b)–C(20)–H(20C)	109.5
C(17)–N(5)–H(5a)	116.5	C(19)–C(21)–H(21a)	109.5
C(6)–N(5)–H(5a)	116.5	C(19)–C(21)–H(21b)	109.5
C(18)–N(6)–C(12)	132.4(2)	H(21a)–C(21)–H(21b)	109.5
C(18)–N(6)–H(6a)	113.8	C(19)–C(21)–H(21C)	109.5
C(12)–N(6)–H(6a)	113.8	H(21a)–C(21)–H(21C)	109.5
N(3)–C(a1)–C(m2#1	125.73(16)	H(21b)–C(21)–H(21C)	109.5
N(3)–C(a1)–C(b1)	110.86(16)	C(19)–C(22)–H(22a)	109.5
C(m2#1–C(a1)–C(b1)	123.36(16)	C(19)–C(22)–H(22b)	109.5
N(3)–C(a2)–C(m1)	125.82(16)	H(22a)–C(22)–H(22b)	109.5
N(3)–C(a2)–C(b2)	110.80(16)	C(19)–C(22)–H(22C)	109.5
C(m1)–C(a2)–C(b2)	123.36(17)	H(22a)–C(22)–H(22C)	109.5
N(4)–C(a3)–C(m1)	125.25(17)	H(22b)–C(22)–H(22C)	109.5

angle	degree	angle	degree
N(4)–C(a3)–C(b3)	111.00(15)	C(18)–C(23)–C(25)	105.2(2)
C(m1)–C(a3)–C(b3)	123.70(17)	C(18)–C(23)–C(24)	108.6(2)
N(4)–C(a4)–C(m2)	125.58(17)	C(25)–C(23)–C(24)	110.1(2)
N(4)–C(a4)–C(b4)	110.79(15)	C(18)–C(23)–C(26)	115.3(2)
C(m2)–C(a4)–C(b4)	123.60(16)	C(25)–C(23)–C(26)	109.6(2)
C(b2)–C(b1)–C(a1)	106.74(16)	C(24)–C(23)–C(26)	108.0(3)
C(b2)–C(b1)–H(ba)	126.6	C(23)–C(24)–H(24a)	109.5
C(a1)–C(b1)–H(ba)	126.6	C(23)–C(24)–H(24b)	109.5
C(b1)–C(b2)–C(a2)	106.75(16)	H(24a)–C(24)–H(24b)	109.5
C(b1)–C(b2)–H(bb)	126.6	C(23)–C(24)–H(24C)	109.5
C(a2)–C(b2)–H(bb)	126.6	H(24a)–C(24)–H(24C)	109.5
C(b4)–C(b3)–C(a3)	106.67(17)	H(24b)–C(24)–H(24C)	109.5
C(b4)–C(b3)–H(bC)	126.7	C(23)–C(25)–H(25a)	109.5
C(a3)–C(b3)–H(bC)	126.7	C(23)–C(25)–H(25b)	109.5
C(b3)–C(b4)–C(a4)	106.87(16)	H(25a)–C(25)–H(25b)	109.5
C(b3)–C(b4)–H(bd)	126.6	C(23)–C(25)–H(25C)	109.5
C(a4)–C(b4)–H(bd)	126.6	H(25a)–C(25)–H(25C)	109.5
C(a2)–C(m1)–C(a3)	123.63(17)	H(25b)–C(25)–H(25C)	109.5
C(a2)–C(m1)–C(5)	118.29(16)	C(23)–C(26)–H(26a)	109.5
C(a3)–C(m1)–C(5)	118.08(17)	C(23)–C(26)–H(26b)	109.5
C(a1#1–C(m2)–C(a4)	122.93(16)	H(26a)–C(26)–H(26b)	109.5
C(a1#1–C(m2)–C(11)	118.07(16)	C(23)–C(26)–H(26C)	109.5
C(a4)–C(m2)–C(11)	118.96(17)	H(26a)–C(26)–H(26C)	109.5
C(6)–C(5)–C(10)	118.66(19)	H(26b)–C(26)–H(26C)	109.5
C(6)–C(5)–C(m1)	121.07(18)	O(1S)–C(1S)–C(1S)#2	123.0(3)
C(10)–C(5)–C(m1)	120.27(19)	C(1)#1–N(2)–C(1)	56.4(3)
C(5)–C(6)–C(7)	120.2(2)	C(1)#1–N(2)–C(2)#1	108.8(3)
C(5)–C(6)–N(5)	118.06(17)	C(1)–N(2)–C(2)#1	52.5(2)
C(7)–C(6)–N(5)	121.7(2)	C(1)#1–N(2)–C(2)	52.5(2)
C(8)–C(7)–C(6)	119.6(2)	C(1)–N(2)–C(2)	108.8(3)
C(8)–C(7)–H(7a)	120.2	C(2)#1–N(2)–C(2)	161.2(4)
C(6)–C(7)–H(7a)	120.2	C(1)#1–N(2)–H(2a)	176.5
C(9)–C(8)–C(7)	120.7(2)	C(1)–N(2)–H(2a)	125.6
C(9)–C(8)–H(8a)	119.6	C(2)#1–N(2)–H(2a)	73.1

Table S46. Continued

angle	degree	angle	degree
C(7)–C(8)–H(8a)	119.6	C(2)–N(2)–H(2a)	125.6
C(8)–C(9)–C(10)	119.8(2)	N(1)–C(1)–N(2)	110.0(3)
C(8)–C(9)–H(9a)	120.1	N(1)–C(1)–C(4)	127.3(3)
C(10)–C(9)–H(9a)	120.1	N(2)–C(1)–C(4)	122.7(3)
C(9)–C(10)–C(5)	120.9(2)	C(1)–N(1)–C(3)	105.1(3)
C(9)–C(10)–H(10a)	119.6	C(1)–N(1)–Co(1)	131.6(3)
C(5)–C(10)–H(10a)	119.6	C(3)–N(1)–Co(1)	123.3(2)
C(16)–C(11)–C(12)	118.96(18)	C(2)–C(3)–N(1)	110.5(4)
C(16)–C(11)–C(m2)	120.90(18)	C(2)–C(3)–H(3a)	124.8
C(12)–C(11)–C(m2)	120.10(17)	N(1)–C(3)–H(3a)	124.8
C(13)–C(12)–C(11)	120.4(2)	C(3)–C(2)–N(2)	105.6(3)
C(13)–C(12)–N(6)	123.0(2)	C(3)–C(2)–H(2b)	127.2
C(11)–C(12)–N(6)	116.57(17)	N(2)–C(2)–H(2b)	127.2
C(14)–C(13)–C(12)	119.2(2)	C(1)–C(4)–H(4a)	109.5
C(14)–C(13)–H(13a)	120.4	C(1)–C(4)–H(4b)	109.5
C(12)–C(13)–H(13a)	120.4	H(4a)–C(4)–H(4b)	109.5
C(15)–C(14)–C(13)	121.3(2)	C(1)–C(4)–H(4C)	109.5
C(15)–C(14)–H(14a)	119.3	H(4a)–C(4)–H(4C)	109.5
C(13)–C(14)–H(14a)	119.3	H(4b)–C(4)–H(4C)	109.5
C(14)–C(15)–C(16)	119.6(2)	C(3S)–C(2S)–O(2S)	100.8(6)
C(14)–C(15)–H(15a)	120.2	C(3S)–C(2S)–C(2S)#3	44.6(6)
C(16)–C(15)–H(15a)	120.2	O(2S)–C(2S)–C(2S)#3	121.7(9)
C(11)–C(16)–C(15)	120.5(2)	C(2S)#3–C(3S)–C(2S)	90.7(11)
C(11)–C(16)–H(16a)	119.7		

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

Table S47. Anisotropic Displacement Parameters (Å^2) for [Co(TpivPP)(2-MeHIm)]·1.8C$_2$H$_5$OH^a (100 K, $C2/c$ form)^a

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co(1)	0.0232(2)	0.0244(2)	0.0150(2)	0.000	−0.0009(1)	0.000
O(1)	0.145(3)	0.0750(16)	0.0546(13)	0.0301(12)	−0.0190(15)	−0.0350(16)
O(2)	0.0293(14)	0.040(3)	0.088(6)	0.015(4)	0.015(2)	0.0002(14)
O(2B)	0.035(3)	0.049(7)	0.044(5)	0.007(4)	−0.008(3)	−0.014(4)
N(3)	0.0252(7)	0.0256(7)	0.0172(6)	0.0000(5)	−0.0009(5)	−0.0004(5)
N(4)	0.0261(7)	0.0283(7)	0.0165(6)	0.0003(5)	−0.0010(5)	0.0000(5)
N(5)	0.0218(8)	0.0447(10)	0.0564(11)	−0.0188(9)	−0.0031(7)	−0.0021(7)
N(6)	0.0693(14)	0.0403(10)	0.0243(8)	0.0062(7)	0.0018(8)	−0.0060(9)
C(A1)	0.0294(8)	0.0265(8)	0.0172(7)	0.0005(6)	−0.0019(6)	−0.0012(6)
C(A2)	0.0277(8)	0.0284(8)	0.0182(7)	0.0001(6)	−0.0028(6)	−0.0002(6)
C(A3)	0.0247(8)	0.0300(8)	0.0210(7)	0.0009(6)	−0.0006(6)	−0.0001(6)
C(A4)	0.0271(8)	0.0299(8)	0.0186(7)	0.0008(6)	0.0018(6)	0.0010(6)
C(B1)	0.0328(9)	0.0419(10)	0.0164(7)	0.0022(6)	−0.0023(6)	−0.0011(8)
C(B2)	0.0310(9)	0.0419(10)	0.0180(7)	0.0010(7)	−0.0047(6)	0.0001(7)
C(B3)	0.0254(9)	0.0436(10)	0.0248(8)	0.0011(7)	0.0015(7)	−0.0007(7)
C(B4)	0.0283(9)	0.0429(10)	0.0230(8)	0.0010(7)	0.0034(7)	−0.0013(8)
C(M1)	0.0254(8)	0.0294(8)	0.0218(7)	0.0001(6)	−0.0033(6)	0.0008(6)
C(M2)	0.0297(8)	0.0279(8)	0.0169(7)	−0.0004(6)	0.0017(6)	0.0008(6)
C(5)	0.0243(8)	0.0438(10)	0.0227(8)	0.0014(7)	−0.0028(6)	0.0024(7)
C(6)	0.0245(9)	0.0498(12)	0.0315(9)	−0.0083(8)	−0.0044(7)	0.0019(8)
C(7)	0.0297(11)	0.0708(17)	0.0445(12)	−0.0074(11)	−0.0119(9)	−0.0021(10)
C(8)	0.0300(11)	0.0801(19)	0.0549(15)	0.0186(14)	−0.0148(10)	0.0032(12)
C(9)	0.0369(12)	0.0610(16)	0.0673(17)	0.0210(13)	−0.0076(11)	0.0133(11)
C(10)	0.0375(11)	0.0430(11)	0.0464(12)	0.0107(9)	−0.0038(9)	0.0057(9)
C(11)	0.0283(8)	0.0398(10)	0.0166(7)	−0.0037(6)	0.0016(6)	0.0004(7)
C(12)	0.0388(10)	0.0497(12)	0.0187(8)	0.0011(7)	0.0017(7)	−0.0050(9)
C(13)	0.0451(13)	0.0848(19)	0.0194(8)	0.0023(10)	0.0042(8)	−0.0181(12)
C(14)	0.0304(10)	0.105(2)	0.0209(9)	−0.0159(11)	0.0044(8)	−0.0106(12)
C(15)	0.0315(10)	0.0781(17)	0.0335(10)	−0.0290(11)	−0.0020(8)	0.0038(11)
C(16)	0.0345(10)	0.0468(11)	0.0305(9)	−0.0123(8)	−0.0008(8)	0.0026(9)
C(17)	0.0302(10)	0.0568(13)	0.0291(9)	0.0047(9)	0.0014(7)	−0.0068(9)
C(18)	0.0495(14)	0.0520(14)	0.0469(13)	0.0113(11)	−0.0141(11)	−0.0091(11)
C(19)	0.0379(11)	0.0446(11)	0.0378(11)	−0.0085(9)	0.0085(9)	−0.0033(9)
C(20)	0.088(2)	0.077(2)	0.0629(19)	−0.0338(17)	0.0149(17)	−0.0118(19)

Table S47. Continued

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(21)	0.0477(14)	0.0580(15)	0.0511(14)	0.0115(11)	0.0028(11)	0.0077(11)
C(22)	0.0317(11)	0.0564(15)	0.0743(19)	0.0027(13)	0.0115(12)	0.0055(10)
C(23)	0.0364(11)	0.0414(12)	0.0599(15)	0.0005(10)	−0.0161(10)	−0.0011(9)
C(24)	0.0452(15)	0.0549(16)	0.108(3)	0.0021(16)	−0.0345(16)	0.0023(12)
C(25)	0.0355(12)	0.0503(14)	0.0740(18)	0.0035(13)	−0.0133(12)	−0.0012(10)
C(26)	0.0597(16)	0.0479(14)	0.0556(15)	−0.0173(12)	0.0020(12)	0.0001(12)
C(1S)	0.211(7)	0.070(3)	0.174(6)	0.032(3)	0.133(5)	0.045(3)
O(1S)	0.073(3)	0.0363(18)	0.106(4)	−0.001(2)	0.056(3)	−0.0042(17)
N(2)	0.0271(10)	0.0269(10)	0.0313(11)	0.000	0.0007(8)	0.000
C(1)	0.0237(16)	0.0291(17)	0.0246(15)	0.0012(13)	−0.0032(14)	0.0035(14)
N(1)	0.021(3)	0.0308(12)	0.020(3)	−0.0016(12)	−0.0013(17)	0.0010(12)
C(3)	0.028(2)	0.035(2)	0.0189(17)	−0.0029(15)	0.0026(15)	−0.0012(16)
C(2)	0.0264(17)	0.0347(18)	0.0265(16)	0.0030(13)	−0.0012(13)	−0.0025(14)
C(4)	0.038(2)	0.030(2)	0.040(2)	0.0036(17)	0.015(2)	0.0054(17)
O(2S)	0.097(4)	0.057(3)	0.049(3)	0.014(2)	−0.003(3)	0.016(3)
C(2S)	0.102(6)	0.054(4)	0.038(3)	−0.007(3)	−0.018(4)	−0.020(4)
C(3S)	0.076(6)	0.165(11)	0.185(12)	0.000	0.046(7)	0.000

[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 S48. Hydrogen Atom Coordinates and Equivalent Isotropic Displacement Parameters
(Å^2) for $[\text{Co(TpivPP)(2-MeHIm)}] \cdot 1.8\text{C}_2\text{H}_5\text{OH}^a$ (100 K, $C2/c$ form)

atom	x	y	z	$U(\text{eq})$
H(5A)	0.3167	0.7385	0.6141	0.049
H(6A)	0.3907	0.7509	0.9505	0.054
H(BA	0.4562	0.8696	0.4672	0.036
H(BB	0.3337	0.8650	0.5202	0.036
H(BC	0.2294	0.8445	0.7915	0.038
H(BD	0.2816	0.8506	0.9199	0.038
H(7A)	0.1392	0.7490	0.5647	0.058
H(8A)	0.0686	0.8473	0.5653	0.066
H(9A)	0.1131	0.9479	0.6156	0.066
H(10A)	0.2311	0.9530	0.6601	0.051
H(13A)	0.3447	0.7666	1.1392	0.060
H(14A)	0.3387	0.8707	1.2014	0.063
H(15A)	0.3708	0.9712	1.1426	0.057
H(16A)	0.4103	0.9687	1.0187	0.045
H(20A)	0.3011	0.5844	0.5319	0.114
H(20B)	0.2425	0.5461	0.5811	0.114
H(20C)	0.3248	0.5232	0.5860	0.114
H(21A)	0.3012	0.6099	0.7597	0.078
H(21B)	0.3241	0.5386	0.7240	0.078
H(21C)	0.2420	0.5624	0.7202	0.078
H(22A)	0.3904	0.6626	0.5943	0.081
H(22B)	0.4157	0.6019	0.6484	0.081
H(22C)	0.3896	0.6727	0.6830	0.081
H(24A)	0.4369	0.5531	1.0244	0.104
H(24B)	0.4965	0.5946	0.9798	0.104
H(24C)	0.4494	0.5377	0.9378	0.104
H(25A)	0.2825	0.6300	0.9352	0.080
H(25B)	0.3056	0.5740	0.9960	0.080
H(25C)	0.3183	0.5599	0.9091	0.080
H(26A)	0.3756	0.6890	0.8615	0.082
H(26B)	0.4198	0.6213	0.8427	0.082
H(26C)	0.4587	0.6835	0.8848	0.082
H(2A)	0.4842	1.1274	0.7640	0.034
H(3A)	0.5894	0.9848	0.6608	0.033

Table S48. Continued

atom	x	y	z	$U(\text{eq})$
H(2B)	0.5784	1.1092	0.6722	0.035
H(4A)	0.4120	0.9722	0.8445	0.054
H(4B)	0.3762	1.0417	0.8155	0.054
H(4C)	0.4371	1.0435	0.8795	0.054

Supporting Information Figure Captions

Figure S1. Chemdraw of picket fence porphyrin

Figure S2. A top view thermal ellipsoid diagram of [Co(TpivPP)(1-EtIm)(O$_2$)] (C2/c) (100K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure S3. A edge-on thermal ellipsoid diagram of [Co(TpivPP)(1-EtIm)(O$_2$)] (C2/c) (100K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure S4. A top view thermal ellipsoid diagram of [Co(TpivPP)(1-EtIm)(O$_2$)] ($P\bar{1}$) (100K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure S5. A edge-on thermal ellipsoid diagram of [Co(TpivPP)(1-EtIm)(O$_2$)] ($P\bar{1}$) (100K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure S6. A top view thermal ellipsoid diagram of [Co(TpivPP)(1-EtIm)(O$_2$)] (200K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure S7. A edge-on thermal ellipsoid diagram of [Co(TpivPP)(1-EtIm)(O$_2$)] (200K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure S8. A top view thermal ellipsoid diagram of [Co(TpivPP)(1-EtIm)(O$_2$)] (300K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure S9. A edge-on thermal ellipsoid diagram of [Co(TpivPP)(1-EtIm)(O$_2$)] (300K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure S10. A scheme showing the temperature-dependent structure determination of the second [Co(TpivPP)(1-EtIm)(O$_2$)] crystal. The annealing experiments are described. The temperatures, corresponding space groups, unit cell parameters, and observed R factors are given in highlighted boxes.

Figure S11. A edge-on thermal ellipsoid diagram of the second [Co(TpivPP)(1-EtIm)(O$_2$)] crystal structure at 80K displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure S12. Formal diagram of the porphyrin cores of [Co(TpivPP)(1-EtIm)(O$_2$)] structure at 100, 200 and 300K. Averaged values of the chemically unique bond distances (in Å) and angles (in degrees) are shown. The numbers in parentheses are the esd's calculated on the assumption that the averaged values were all drawn from the same population. The perpendicular displacements (in units of 0.01 Å) of the porphyrin core atoms from the 24-atom mean plane are also displayed.

Figure S13. Packing diagrams of [Co(TpivPP)(2-MeHIm)] and the oxygen adduct [Co(TpivPP)(2-MeHIm)(O$_2$)], showing the unit cell. Hydrogens omitted for clarity.

Figure S14. A edge-on thermal ellipsoid diagram of [Co(TpivPP)(2-MeHIm)(O$_2$)] (100K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure S15. A top view thermal ellipsoid diagram of [Co(TpivPP)(2-MeHIm)(O$_2$)] (100K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure S16. A edge-on thermal ellipsoid diagram of [Co(TpivPP)(2-MeHIm)0.4(O$_2$)] (100K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure S17. A top view thermal ellipsoid diagram of [Co(TpivPP)(2-MeHIm)0.4(O$_2$)] (100K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure S18. A edge-on thermal ellipsoid diagram of [Co(TpivPP)(2-MeHIm)0.3(O$_2$)] (300K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure S19. A top view thermal ellipsoid diagram of [Co(TpivPP)(2-MeHIm)0.3(O$_2$)] (300K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure S20. A edge-on thermal ellipsoid diagram of [Co(TpivPP)(2-MeHIm)] (100K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure S21. A top view thermal ellipsoid diagram of [Co(TpivPP)(2-MeHIm)] (100K) displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured

at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure S22. Formal diagram of the porphyrin cores of [Co(TpivPP)(2-MeHIm)] and oxygen adducts structure. Averaged values of the chemically unique bond distances (in Å) and angles (in degrees) are shown. The numbers in parentheses are the esd's calculated on the assumption that the averaged values were all drawn from the same population. The perpendicular displacements (in units of 0.01 Å) of the porphyrin core atoms from the 24-atom mean plane are also displayed (positive to hindered porphyrin side).

Supporting Information Table Captions

Table S1. Complete Crystallographic Details for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (100K, $P\bar{1}$).

Table S2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (100K, $P\bar{1}$).

Table S3. Bond Lengths for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (100K, $P\bar{1}$).

Table S4. Bond Angles for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (100K, $P\bar{1}$).

Table S5. Anisotropic Isotropic Displacement Parameters for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (100K, $P\bar{1}$).

Table S6. Hydrogen Coordinates and Isotropic Displacement Parameters for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (100K, $P\bar{1}$).

Table S7. Complete Crystallographic Details for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (100K, C2/c).

Table S8. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (100K, C2/c).

Table S9. Bond Lengths for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (100K, C2/c).

Table S10. Bond Angles for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (100K, C2/c).

Table S11. Anisotropic Isotropic Displacement Parameters for [Co(TpivPP)(1-EtIm)(O$_2$)]·C$_6$H$_6$ (100K, C2/c).

Table S24. Hydrogen Coordinates and Isotropic Displacement Parameters for [Co(TpivPP)(1-
    EtIm)(O$_2$)]·C$_6$H$_6$ (300K).

Table S25. Complete Crystallographic Details for [Co(TpivPP)(2-MeHIm)(O$_2$)]·1.8C$_2$H$_5$OH.

Table S26. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for
    [Co(TpivPP)(2-MeHIm)(O$_2$)]·1.8C$_2$H$_5$OH.

Table S27. Bond Lengths for [Co(TpivPP)(2-MeHIm)(O$_2$)]·1.8C$_2$H$_5$OH.

Table S28. Bond Angles for [Co(TpivPP)(2-MeHIm)(O$_2$)]·1.8C$_2$H$_5$OH.

Table S29. Anisotropic Isotropic Displacement Parameters for [Co(TpivPP)(2-MeHIm)(O$_2$)]·1.8C$_2$H$_5$OH.

Table S30. Hydrogen Coordinates and Isotropic Displacement Parameters for [Co(TpivPP)(2-
    MeHIm)(O$_2$)]·1.8C$_2$H$_5$OH.

Table S31. Complete Crystallographic Details for [Co(TpivPP)(2-MeHIm)0.4(O$_2$)]·2C$_2$H$_5$OH.

Table S32. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for
    [Co(TpivPP)(2-MeHIm)0.4(O$_2$)]·2C$_2$H$_5$OH.

Table S33. Bond Lengths for [Co(TpivPP)(2-MeHIm)0.4(O$_2$)]·2C$_2$H$_5$OH.

Table S34. Bond Angles for [Co(TpivPP)(2-MeHIm)0.4(O$_2$)]·2C$_2$H$_5$OH.

Table S35. Anisotropic Isotropic Displacement Parameters for [Co(TpivPP)(2-MeHIm)0.4(O$_2$)]·2C$_2$H$_5$OH.

Table S48. Hydrogen Coordinates and Isotropic Displacement Parameters for [Co(TpivPP)(2-MeHIm)]·1.8C$_2$H$_5$OH.