Activation of Molecular Oxygen by a Cobalt(II) Tetra-NHC Complex**

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** Supporting Information
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Experimental procedures

General procedures and analytical methods

Unless otherwise stated, all manipulations were performed under an argon atmosphere using standard Schlenk and glovebox techniques. Solvents were obtained water- and oxygen-free from a MBraun solvent purification system, degassed by three freeze-pump-thaw cycles and stored over molecular sieves. The ligand precursor \( [\text{H}_2(\text{CCl}_3)\text{PF}_6]_2 \) was synthesized according to known literature procedure.[1] Anhydrous cobalt(II) chloride was obtained by heating of CoCl\(_2\cdot\)H\(_2\)O at 550 °C in vacuo until the purple color entirely changed to light blue applying a modified literature procedure.[2] Quantofix® peroxide test strips were applied to detect hydrogen peroxide as reported in literature.[3] All other reagents were purchased from commercial suppliers and used without further purification. NMR spectra were recorded on a Bruker Avance DPX 400 (\(^1\)H-NMR, 400.13 MHz; \(^13\)C-NMR, 100.53 MHz; \(^31\)P-NMR, 162 MHz) and chemical shifts are reported relative to the residual signal of the deuterated solvent.[4] Elemental analyses (C/H/N) were obtained by the microanalytical laboratory at Technische Universität München. Electrospray ionization mass spectrometry (ESI-MS) data were acquired on a Thermo Fisher Ultimate 3000.

DFT

DFT calculations were performed with Gaussian-16[5] and processed using GaussView-6.[6] Calculations were performed in a gas atmosphere, initial parameters were imported from crystal structures. Geometry optimizations were obtained without using constraint coordinates. The obtained structures are true ground states as no negative eigenvalues were found during vibrational analysis. Calculations applying various functionals were performed on 1 to determine the best suited functional for the following investigation of 2. The basis set def2-SVP was applied to small atoms.[7] Co is treated by the Stuttgart/Dresden 1997 SDD relativistic effective core potential (ECP) and its respective basis set.[8] The pure density functionals M06L[9] and B97D3[10] as well as the hybrid density functionals B3LYP[11], M06L[12] and wB97XD[13] were tested. Of these, wB97XD gave the most reliable and rational results according to a vibrational analysis and electronic structure (see SI), in line with calculations of comparable complexes.[14] Further single point calculations were performed for wB97XD using the def2-TZVP basis set to determine a high quality electronic structure. From these, TD-DFT calculations were performed using the TD(50-50, NStates=25) keyword as well as the according NTO calculations. EPR calculations of 1 and the corresponding superoxo species were performed with ORCA version 4.2.1, built with support for libXC version 4.2.3,[15] starting from the structures obtained from Gaussian-16. The libint2 library for the computation of 2-electron integrals was used.[16] Quasirelativistic calculations (ZORA with one-center approximation) were performed using the PBE0 functional[17] and the ZORA-def2-SVP basis set applied to all atoms.[18] In order to speed up calculations, the RIJCOSX approximation was used in combination with a grid of 6 and the auxiliary basis SARC/J.[19] Numerical precision was ensured by using grid 6 for all atoms, an integration accuracy of 6 for H, C, N, O and an increased integration accuracy of 10 for Co. Final grids were suppressed using the keywords nofinalgrid and nofinalgridx. Solvation in MeCN was mimicked by the SMD model.[20] For property calculations, picturechange is set as true. EPR tensors are obtained using the integrated nmrepr utility with the keywords Aiso, Adip, Aorb and fgrad. The center of origin was set to the center of the electric field.

EPR

EPR spectra were recorded on a JEOL JES-FA 200 at X-Band frequency (approx. 9.27 GHz). The microwave frequency was measured via a microwave frequency counter Advantest R5372. Temperature was controlled using an ES-DVT4 variable temperature control unit. The measurements were performed at 173 K, achieved by cooling with liquid nitrogen with a microwave power of 5 mW. The values for g and A were determined using a Mn\(^{2+}\) \((I = 5/2)\) standard embedded in MnO\(_2\). The fourth low field line is taken as reference signal set to \( g = 1.981 \). The measured EPR spectra were simulated using EasySpin 5.2.28[21] and Matlab R2019b[22] for determining the presented g and A values.

XRD

Data were collected on a single crystal X-ray diffractometer equipped with a CCD detector (APEX II, \( \kappa \)-CCD), a fine-focus sealed tube with MoK\(_\alpha\) radiation \((\lambda = 0.7073 \ \text{Å})\) and a graphite monochromator (2) or a single crystal X-ray diffractometer equipped with a CCD detector (APEX II, \( \kappa \)-CCD), an FR591 rotating anode with MoK\(_\alpha\) radiation \((\lambda = 0.71073 \ \text{Å})\) and a MONTEL mirror optic \((1,3)\) using the APEX2 software package.[23] Measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on top of a glass fiber or cactus spine and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were corrected for Lorentz and polarization effects, scan speed, and background using SAINT.[24] Absorption correction, including odd and even ordered spherical harmonics was performed using SADABS.[25] Space group assignment was based upon systematic absences, E statistics, and successful refinement of the structures. The structures were solved using SHELXS1997 with the aid of successive difference Fourier maps, and were refined against all data using SHELXL2014 in conjunction with SHELXL.[26] Hydrogen atoms were calculated in ideal positions as follows: Methyl hydrogen atoms were refined as part of rigid rotating groups with a C–H distance of 0.98 Å and \( U_{iso}(\text{H}) = 1.5 \times U_{eq}(\text{C}) \). Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 Å and 0.95 Å, respectively, and other C–H distances of 1.00 Å, all with \( U_{iso}(\text{H}) = 1.2 \times U_{eq}(\text{C}) \). Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing \( \Sigma w(F_o^2 - F_c^2)^2 \) with the SHELXL weighting scheme.[27] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.[27] A split layer refinement was used for disordered groups and additional restraints on geometries and anisotropic displacement parameters were used, if necessary. Images of the crystal structures were generated with PLATON.[28] CCDC 2032593-
Synthetic procedures

\[ \text{[Co(cCCC)](MeCN)}_{2}(PF_{6})_{2} \]: 1: \( H_{2}(cCCC) \) (200 mg, 221 µmol, 1.00 eq.) and anhydrous CoCl\(_2\) (28.7 mg, 221 µmmol, 1.00 eq.) and anhydrous Cs\(_2\)CO\(_3\) (360 mg, 1.11 mmol, 5.00 eq.) are suspended in 8 mL MeCN in a Schlenk tube. The mixture is heated to 75 °C and stirred for 18 h. After cooling to room temperature, the suspension is filtered. The yellow filtrate is treated with 14 mL Et\(_2\)O. The white precipitate is filtered off. After treatment of the solution with additional 30 mL Et\(_2\)O a yellow precipitate is formed. The solid is redissolved in 5 mL MeCN and layered with 30 mL Et\(_2\)O. The mixture is stored at -40 °C for 2 d. After filtering off the yellow precipitate is washed with 10 mL Et\(_2\)O three times. After drying in vacuo 111 mg 1 are obtained as a yellow solid (157 µmol, 71%). Single crystals suitable for SC-XRD were obtained by slow vapor diffusion of Et\(_2\)O to a solution of 1 in MeCN at room temperature.

\(^{1}\)H-NMR (400 MHz, CD\(_3\)CN, 298 K): \( \delta \) (ppm) = 27.17 (br. s, 8H, H\(_{\text{Me}}\)), 6.54-5.99 (m, 16H, CH\(_{2}\)), 1.96 (s, 6H, H\(_{2}\)CCN).

31P-NMR (162 MHz, CD\(_3\)CN, 298 K): \( \delta \) (ppm) = -144.6 (hept, PF\(_6\)).

Anal. calcd. for C\(_{30}\)H\(_{36}\)CoP\(_6\)N\(_3\)F\(_{12}\): C 30.44; H 2.70; N 17.75. Found: C 30.38; H 2.62; N 17.64.

ESI-MS (m/z): [H\(_{2}(cCCC)-2PF\(_6\)]^{2+} \text{calcd.}, 189.54; found, 189.59; [H\(_{2}(cCCC)-2PF\(_6\)]^{+} \text{calcd.}, 524.05; found, 523.92; [2-1-2MeCN-2PF\(_6\)]^{+} \text{calcd.}, 1193.06; found, 1192.51.

\[ \text{[Co}_{2}(cCCC)_{2}(µ-\text{O}_2)\text{(MeCN)}_{2}\}(PF_{6})_{2} \]: 2: A solution of 1 (60.0 mg, 84.7 µmol, 1.00 eq.) in 2 mL MeCN is exposed to air under vigorous stirring at room temperature. The color of the solution gradually changes from yellow to brown. After stirring for 2 h and addition of 20 mL Et\(_2\)O a green precipitate is formed. After centrifugation, the precipitate is washed twice with 5 mL Et\(_2\)O and dried in vacuo yielding 59.9 mg 2 as a light green powder (41.4 µmol, 98%). Single crystals suitable for SC-XRD were obtained by slow vapor diffusion of Et\(_2\)O to a solution of 2 in MeCN at room temperature.

\(^{1}\)H-NMR (400 MHz, CD\(_3\)CN, 298 K): \( \delta \) (ppm) = 7.76-7.44 (m, 16H, H\(_{\text{Me}}\)), 6.54-5.99 (m, 16H, CH\(_{2}\)), 1.96 (s, 6H, H\(_{2}\)CCN).

31P-NMR (162 MHz, CD\(_3\)CN, 298 K): \( \delta \) (ppm) = -144.6 (hept, PF\(_6\)).

Anal. calcd. for C\(_{30}\)H\(_{36}\)Co\(_2\)P\(_4\)N\(_3\)F\(_{12}\): C 30.18; H 2.68; N 17.30. Found: C 30.17; H 2.77; N 17.36.

ESI-MS (m/z): [2-2H\(_2\)O-Na\(^+\)-2MeCN-2PF\(_6\)]^{2+} \text{calcd.}, 379.70; found, 380.26; [2+2H\(_2\)O-2PF\(_6\)]^{2+} \text{calcd.}, 599.08; found, 599.68.

\[ \text{[Co(cCCC)](MeCN)(OAc)}\}(PF_{6})_{2} \]: 3: In air a solution of 2 (30.0 mg, 20.7 µmol, 1.00 eq.) in 1 mL acetonitrile is treated with 0.1 mL of glacial acetic acid (105 mg, 1.75 mmol, 84.5 eq.). The mixture is stirred at room temperature for 30 min. The addition of 10 mL Et\(_2\)O results in a green precipitate. The precipitate is washed twice with 5 mL diethyl ether. After drying in vacuo 3 is obtained as a green powder in a yield of 30.5 mg (39.7 mmol, 96%). Single crystals suitable for SC-XRD were obtained by slow vapor diffusion of Et\(_2\)O to a solution of 3 in MeCN at room temperature.

\(^{1}\)H-NMR (400 MHz, CD\(_3\)CN, 298 K): \( \delta \) (ppm) = 7.74 (s, 8H, H\(_{\text{Me}}\)), 6.45 (d, J = 12.93 Hz, 4H, CH\(_{2}\)), 6.26 (d, J = 12.93 Hz, 4H, CH\(_{2}\)), 1.69 (s, 3H, H\(_{2}\)CCN), 1.07 (s, 3H, H\(_{2}\)CO\(_2\)).

\(^{13}\)C-NMR (126 MHz, CD\(_3\)CN, 298 K): \( \delta \) (ppm) = 177.3 (C\(_{\text{carbene}}\)), 176.2 (CH\(_{3}\)COO\(_{-}\)), 130.3 (H\(_{2}\)CN), 123.9 (CH\(_{2}\)CN), 63.4 (CH\(_{3}\)), 21.8 (CH\(_{2}\)COO\(_{-}\)), 5.1 (CH\(_{3}\)CN).

31P-NMR (162 MHz, CD\(_3\)CN, 298 K): \( \delta \) (ppm) = -144.6 (hept, PF\(_6\)).

Anal. calcd. for C\(_{30}\)H\(_{36}\)Co\(_2\)P\(_4\)N\(_3\)F\(_{12}\)O\(_2\): C 29.18; H 3.43; N 15.31.

ESI-MS (m/z): [3-3MeCN-2PF\(_6\)]^{2+} \text{calcd.}, 219.15; found, 218.84; [3-OAc\(^-\)-MeCN-2PF\(_6\)]^{+} \text{calcd.}, 497.11; found, 497.11; [3-PF\(_6\)]^{+} \text{calcd.}, 624.09; found, 623.42.

Control reactions of 1 and 2 with electron-rich substrates

All batch reactions were conducted in a cryostat (Julabo FP-50) with a total reaction volume of 4.0 mL and a reaction time of 16 h at 20 °C and 60 °C, respectively. Acetonitrile (HPLC-grade) was applied as solvent for all experiments. The respective complex (5 mol% with regard to Co) was added from a preformed stock solution (4.2 µmol/L) according to the appropriate stoichiometry to a solution of substrate (100 mol%, 269 µmol). After filtration over activated neutral alumina, two GC samples were prepared for cis-cyclooctene as substrate using 200 µL filtrate, 500 µL external standard (p-xylene, 4.0 mg/mL in i-PrOH) and 800 µL n-hexane, respectively. Evaluation of other substrates besides cis-cyclooctene was performed by \(^{1}\)H-NMR spectroscopy using stock solutions in CD\(_3\)CN in the same concentration and H\(_{2}\)O as external standard in a total reaction volume of 1 mL. Further experiments applying additional 100 mol% of acetic acid were performed and analyzed.

Solutions of cis-cyclooctene, cyclohexane and n-hexane, respectively, are stirred at room temperature and 60 °C in presence of 5 mol% 2 in air, respectively. However, even after prolonged reaction times of 16 h no formation of oxidized products is observed, in line with the assigned nucleophilic reactivity of 2 by DFT. Attempts to utilize superoxo compound 4\(^{\text{oxo}}\) in situ, by performing the above reactions in presence of 5 mol% 1, were also unsuccessful.
Characterization of 3

The $^1$H-NMR spectrum of 3 shows two doublets at 6.45 ppm and 6.26 ppm with a relative integral of 4 each, corresponding to the methylene protons. The sharp singlet at 7.74 ppm with a relative integral of 8 is assignable to the imidazole backbone protons. A singlet at 1.69 ppm with an integral of 1 refers to coordinating MeCN. Another singlet at 1.96 ppm with a relative integral of 2 belongs to non-coordinating MeCN. The amount of coordinating and non-coordinating MeCN sums up to one equivalent per complex. The NMR spectrum indicates that the exchange with deuterated solvent molecules proceeds comparably slow. Octahedral complexes of d$^6$-metals such as 3 are known to be inert to ligand substitution reactions explaining the slow substitution with deuterated solvent.$^{[29]}$ In addition, 3 was characterized by SC-XRD (Figure 5). Suitable single crystals were obtained by slow vapor diffusion of Et$_2$O into a solution of 3 in MeCN. The Co–C distances between 1.889(2) Å and 1.902(2) Å are accord with of other Co(III) NHC complexes reported in literature and similar to those of compound 2.$^{[30]}$ The Co–O bond length of 1.9282(17) Å is in good accord with other Co(III) η$^1$-acetate complexes reported in literature.$^{[31]}$ ESI-MS is also in alignment with a composition of [Co(cCCCC)(MeCN)(OAc)](PF$_6$)$_2$. The elemental analysis suggests, that 3 contains 3 eq. of H$_2$O, which probably originate from the glacial acetic acid that was applied within synthesis and not dried prior to the reaction.
Crystallographic data

Compound 1 (CCDC 2032593)

Figure S1. ORTEP-style representation of the cationic fragment of compound 1. Hydrogen atoms, co-crystallized solvent molecules and hexafluorophosphate anions are omitted for clarity. Thermal ellipsoids are shown at a 50% probability.

Diffraeomter operator C. Jandl
scanspeed 5 s per frame
dx 60 mm
4991 frames measured in 13 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5

Crystal data

\[ \text{C}_{18}\text{H}_{19}\text{CoN}_9 \cdot 2(\text{F}_6\text{P}) \cdot \text{C}_2\text{H}_3\text{N} \]

\[ M_r = 751.35 \quad D_x = 1.732 \text{ Mg m}^{-3} \]

Monoclinic, \( P2_1/c \)

Hall symbol: \(-P 2ybc\)

\[ a = 10.1164 \ (5) \ \text{Å} \]

\[ b = 14.6804 \ (7) \ \text{Å} \]

\[ c = 19.7553 \ (9) \ \text{Å} \]

\[ \beta = 100.872 \ (2) ^\circ \]

\[ V = 2881.3 \ (2) \ \text{Å}^3 \]

\[ Z = 4 \]

\[ F(000) = 1508 \]

Data collection

Bruker APEX-II CCD
diffractometer

Radiation source: rotating anode FR591

\[ 5278 \text{ independent reflections} \]

\[ 4842 \text{ reflections with } I > 2\sigma(I) \]

\[ \text{MONTEL optic monochromator} \]

\[ R_{int} = 0.048 \]

Detector resolution: 16 pixels mm\(^{-1}\)

\[ \theta_{max} = 25.4^\circ, \ \theta_{min} = 1.7^\circ \]

\[ h = -12 \quad 12 \]

\[ k = -17 \quad 17 \]

Absorption correction: multi-scan
\[ \text{SADABS (Bruker, 2014)} \]
Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.115$

$S = 1.03$

5278 reflections

408 parameters

0 restraints

0 constraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$W = 1/[\sum \sigma^2(FO^2) + (0.0672P)^2 + 3.7476P]$ WHERE $P = (FO^2 + 2FC^2)/3$

$(\Delta/\sigma)_{max} = 0.006$

$\Delta rho_{max} = 0.74 \text{ e \AA}^{-3}$

$\Delta rho_{min} = -0.50 \text{ e \AA}^{-3}$

Extinction correction: none

Extinction coefficient: -

64322 measured reflections
Compound 2 (CCDC 2032594)

Figure S2. ORTEP-style representation of the cationic fragment of compound 2. Hydrogen atoms, co-crystallized solvent molecules and hexafluorophosphate anions are omitted for clarity. Thermal ellipsoids are shown at a 50% probability.

Diffraction operator C. Jandl
scanspeed 60 s per frame
dx 40 mm
2355 frames measured in 7 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5

Crystal data

\[ \text{C}_{36}\text{H}_{38}\text{Co}_{2}\text{N}_{18}\text{O}_{2} \cdot 4(\text{F}_6\text{P}) \cdot 3(\text{C}_2\text{H}_3\text{N}) \]  
\[ F(000) = 1584 \]
\[ M_r = 1575.75 \]

Triclinic, \( \text{P} \)
Hall symbol: \(-\text{P} 1\)

\[ a = 12.0232 (4) \text{ Å} \]
\[ b = 12.8760 (5) \text{ Å} \]
\[ c = 19.5407 (8) \text{ Å} \]
\[ \alpha = 99.325 (2)^\circ \]
\[ \beta = 102.207 (2)^\circ \]
\[ \gamma = 90.676 (2)^\circ \]

\[ V = 2914.31 (19) \text{ Å}^3 \]
\[ Z = 2 \]

Data collection
Bruker APEX-II CCD diffractometer

10524 independent reflections

Radiation source: fine-focus sealed tube

7602 reflections with $I > 2\sigma(I)$

Graphite monochromator

$R_{int} = 0.065$

Detector resolution: 16 pixels mm$^{-1}$

$\theta_{max} = 25.3^\circ$, $\theta_{min} = 1.6^\circ$

phi– and $\omega$–rotation scans

$h = -14$ 14

Absorption correction: multi-scan

$SADABS$ (Bruker, 2014)

$k = -15$ 15

$T_{\text{min}} = 0.553$, $T_{\text{max}} = 0.745$

$l = -22$ 23

51756 measured reflections

Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.060$

$wR(F^2) = 0.152$

$S = 1.08$

10524 reflections

989 parameters

600 restraints

0 constraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$W = 1/[\Sigma^2(FO^2) + (0.0532P)^2 + 9.8778P] \text{ WHERE } P = (FO^2 + 2FC^2)/3$

$\langle \Delta/\sigma \rangle_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 1.36$ e Å$^{-3}$

$\Delta\rho_{\text{min}} = -0.65$ e Å$^{-3}$

Extinction correction: none

Extinction coefficient: -
Compound 3 (CCDC 2032595)

Figure S3. ORTEP-style representation of the cationic fragment of compound 3. Hydrogen atoms, co-crystallized solvent molecules and hexafluorophosphate anions are omitted for clarity. Thermal ellipsoids are shown at a 50% probability.

Diffractometer operator C. Jandl
scanspeed 10 s per frame
dx 50 mm
4132 frames measured in 10 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5

Crystal data

(C_{20}H_{22}CoN_9O_2)·2(F_6P)·0.5(C_2H_3N)

\( M_r = 789.84 \)

Monoclinic, C2/c

Hall symbol: -C 2yc

\( a = 22.6716 (6) \) Å

\( b = 11.3153 (3) \) Å

\( c = 23.3894 (6) \) Å

\( \beta = 97.787 (2)^\circ \)

\( V = 5944.9 (3) \) Å³

\( Z = 8 \)

\( F(000) = 3176 \)

Data collection

Bruker APEX-II CCD
diffractometer

5457 independent reflections

Radiation source: rotating anode FR591

4943 reflections with \( i > 2\sigma(i) \)

MONTEL optic monochromator

\( R_{int} = 0.028 \)

Detector resolution: 16 pixels mm⁻¹

\( \theta_{max} = 25.4^\circ, \theta_{min} = 1.8^\circ \)

phi- and ω-rotation scans

\( h = -27 \quad 27 \)
Absorption correction: multi-scan

SADABS (Bruker, 2014)

\[ k = -13 \quad \frac{13}{13} \]

\[ T_{\text{min}} = 0.700, \quad T_{\text{max}} = 0.746 \]

\[ l = -28 \quad \frac{28}{28} \]

71810 measured reflections

Refinement

Refinement on \( F^2 \)

Least-squares matrix: full

\[ R(F^2 > 2\sigma(F^2)) = 0.037 \]

\[ wR(F^2) = 0.098 \]

\[ S = 1.04 \]

5457 reflections

453 parameters

9 restraints

0 constraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

\( H \) atoms treated by a mixture of independent and constrained refinement

\[ W = 1/\left[ \Sigma^2(FO^2) + (0.0446P)^2 + 18.6342P \right] \]

WHERE \( P = (FO^2 + 2FC^2)/3 \)

\( (\Delta/\sigma)_{\text{max}} = 0.043 \)

\( \Delta\rho_{\text{max}} = 1.05 \) e Å\(^{-3}\)

\( \Delta\rho_{\text{min}} = -0.47 \) e Å\(^{-3}\)

Extinction correction: none

Extinction coefficient: -
EPR spectroscopy

Regarding possible coordination of the oxygen in form of a superoxo species, two main coordination modes are feasible: end-on with trans MeCN coordination (4end-on) or side-on without any MeCN coordination (4side-on). The possibility of side-on with a MeCN as well as end-on without any MeCN coordination were also considered, yet ruled out, since no feasible doublet ground state has been obtained using DFT calculations. The calculated values for 4side-on follow the trend of $g_x < g_y < g_z$ and large $A$ values, which would be more in-line with a rhombic symmetry of the spin density strongly localized on the Co center in contrast to the observed spectra. In contrast, the g and A values of 4end-on correspond well with those achieved during simulation, with $g_x ~ g_y ~ g_z$, an inversed trend compared to 1 (Table S1). The spin density is located mainly in the π surface of the superoxo unit, corresponding to the O-centered radical. Hence, the signal observed by EPR spectroscopy can be assigned to the end-on, trans MeCN superoxo species (4end-on). This is supported by the simulation of the EPR spectrum during the conversion of 1 (Figure S5, left bottom), which corresponds to the experiment when using the values for 1 and 4end-on, showing that both paramagnetic species are present simultaneously.

For the EPR simulation of 1, $A_z$ could be correctly fit to the spectrum according to line splitting, whilst the $A_x$ and $A_y$ are chosen as best-fit. Line broadening for all spectra was applied as HStrain.

| Compound | Method | $g_x$ | $g_y$ | $g_z$ | $A_x$ | $A_y$ | $A_z$ | $Q_x$ | $Q_y$ | $Q_z$ |
|----------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1        | Simulated | 2.230 | 2.225 | 2.015 | 70.01 | 69.99 | 405.0 | -     | -     | -     |
| 1        | Calculated | 2.166 | 2.162 | 2.008 | 56.21 | 59.95 | 456.3 | -1.385| -1.634| 3.019 |
| 1+MeCN   | Calculated | 2.148 | 2.146 | 2.008 | 84.34 | 89.66 | 507.1 | -1.489| -1.623| 3.112 |
| 4end-on  | Simulated | 2.005 | 2.005 | 2.079 | 25.36 | 36.49 | 42.70 | -     | -     | -     |
| 4end-on  | Calculated | 1.994 | 2.005 | 2.058 | 28.20 | 31.33 | 53.04 | -2.055| -2.288| 4.342 |
| 4side-on | Calculated | 2.025 | 2.045 | 2.200 | -395.9| 419.0 | 163.9 | -5.549| 4.770 | 0.778 |

Figure S4. Top left: Spin density of 1, Gaussian SP calculation. Top center: Spin density of 1 from Orca. Top right: Spin density of 1 with additional MeCN from Orca. Bottom left: Spin density of side-on 4 from Orca. Bottom right: Spin density of end-on 4 from Orca. Density Matrix = SCF (Isovalues: MO = 0.02, Density = 0.0004, Laplacian = 0.00).
Figure S5. EPR spectra of 1 (left) and the mixture of 1 and 4-end-on (right). Experimental (black), simulated (red) and calculated (blue).
Electronic structures

Figure S6. Calculated electronic structures (HOMO and LUMO) of complexes 1 and 2 applying various functionals at the def2-SVP theory level (Isovalues: MO = 0.02, Density = 0.0004, Laplacian = 0.00).

Figure S7. Calculated SP electronic structures (HOMO and LUMO) of complexes 1 and 2 at wB97XD and def2-TZVP theory level (Isovalues: MO = 0.02, Density = 0.0004, Laplacian = 0.00).
The corresponding quartet ($E_{\text{Quart}} = -1334.196154 \, \text{h}$) and triplet ($E_{\text{Trip}} = -2818.461135 \, \text{h}$) structures of 1 and 2 ($E_1 = -1335.512631 \, \text{h}$, $E_2 = -2821.141165 \, \text{h}$) were obtained with a residual NIMA-1 (CH$_3$ rotation of MeCN) and as a true ground state and can therefore be eliminated as possible electronic structures.

The HOMO ($E_{\text{HOMO}} = -16.3 \, \text{eV}$) of 2 is of $\pi^*$ character and predominantly located on the O–O bond (Figure S7), thus rationalizing the reaction with electrophiles like H$^+$. The LUMO ($E_{\text{LUMO}} = -8.5 \, \text{eV}$) on the other hand, has a Co-centered $d_{z^2}$ character with only marginal $\pi$ character located on the O–O bond (Figure S7). No higher oxygen centered frontier orbitals are found either, analyzed for $\Delta = 2 \, \text{eV}$ between LUMO and LUMO$_{26}$, $E_{\text{LUMO}_{26}} = -6.4 \, \text{eV}$. Therefore the peroxo unit is nucleophilic accounting for both the lack of reactivity towards the electron rich substrates cis-cyclooctene and cyclohexane as well as the successful hydrogen peroxide formation.
# DFT coordinate tables

Table S2. Coordinates of 1 calculated with M06L/def2-SVP (charge 2, multiplicity 2, SCF: E = -1334.521802 h).

| Atom | X Coordinate [Å] | Y Coordinate [Å] | Z Coordinate [Å] |
|------|------------------|------------------|------------------|
| Co   | -0.000348        | -0.000040        | -0.141222        |
| N    | -2.672901        | 1.204123         | -0.072951        |
| C    | -3.248333        | -0.000037        | 0.496338         |
| H    | -4.328129        | -0.000034        | 0.307471         |
| H    | -3.094345        | -0.000072        | 1.587200         |
| N    | -1.213939        | 2.636890         | -0.718189        |
| C    | -1.343771        | 1.348815         | -0.311041        |
| N    | 1.212989         | 2.636877         | -0.718850        |
| C    | -3.363076        | 2.380828         | -0.318528        |
| H    | -4.435183        | 2.479767         | -0.177064        |
| N    | 2.672208         | 1.204098         | -0.074025        |
| C    | -2.440909        | 3.286291         | -0.733623        |
| H    | -2.556441        | 4.321230         | -1.041539        |
| N    | 2.672298         | -1.204261        | -0.073956        |
| C    | -0.000625        | 3.226332         | -1.252750        |
| H    | -0.000556        | 4.299008         | -1.018890        |
| H    | -0.000915        | 3.126067         | -2.351031        |
| N    | 1.212947         | -2.637026        | -0.718701        |
| C    | 1.343031         | 1.348814         | -0.311708        |
| N    | -1.213958        | -2.637011        | -0.718031        |
| C    | 2.439970         | 3.286233         | -0.735089        |
| H    | 2.555348         | 4.321138         | -1.043180        |
| N    | -2.672920        | -1.204225        | -0.072481        |
| C    | 3.362367         | 2.380759         | -0.320513        |
| H    | 4.434572         | 2.479657         | -0.179750        |
| N    | 0.000594         | 0.000644         | 2.005341         |
| C    | 3.248120         | -0.000076        | 0.494509         |
| H    | 4.327776         | -0.000086        | 0.304858         |
| H    | 3.094915         | -0.000114        | 1.585467         |
| C    | 1.343009         | -1.348962        | -0.311553        |
| C    | 3.362343         | -2.380917        | -0.320459        |
| H    | 4.434543         | -2.479830        | -0.179677        |
| C    | 2.439928         | -3.286386        | -0.735006        |
| H    | 2.555290         | -4.321289        | -1.043107        |
| C    | -0.000664        | -3.226427        | -1.252652        |
| H    | -0.000957        | -3.126066        | -2.350925        |
| H    | -0.000607        | -4.299127        | -1.018898        |
| C    | 0.002658         | 0.000801         | 3.167332         |
| C    | -3.363105        | -2.380916        | -0.318449        |
| H    | -4.435208        | -2.479850        | -0.176958        |
| C    | -2.440939        | -3.286395        | -0.733510        |
| H    | -2.556474        | -4.321333        | -1.041425        |
| C    | -1.343784        | -1.348928        | -0.310885        |
| C    | 0.006230         | 0.0000054        | 4.607856         |
| H    | 0.720497         | 0.739517         | 4.991540         |
| H    | 0.287686         | -0.988734        | 4.991635         |
| H    | -0.989045        | 0.251161         | 4.995835         |
| Atom | X Coordinate [Å] | Y Coordinate [Å] | Z Coordinate [Å] |
|------|------------------|------------------|------------------|
| Co   | 0.000347         | 0.000149         | -0.120581        |
| N    | 2.669989         | -1.205361        | -0.028241        |
| C    | 3.230774         | 0.000001         | 0.574176         |
| H    | 4.320631         | 0.000024         | 0.424467         |
| H    | 3.015832         | -0.000168        | 1.657464         |
| N    | 1.215376         | -2.623924        | -0.748750        |
| C    | 1.338773         | -1.339109        | -0.303765        |
| N    | -1.214254        | -2.623918        | -0.749692        |
| C    | 3.369403         | -2.383670        | -0.291757        |
| H    | 4.441866         | -2.489483        | -0.127173        |
| N    | -2.669435        | -1.205320        | -0.030371        |
| C    | 2.448366         | -3.282138        | -0.754093        |
| H    | 2.569202         | -4.312515        | -1.088937        |
| N    | -2.669418        | 1.205683         | -0.029876        |
| C    | 0.000794         | -3.183048        | -1.334998        |
| H    | 0.000728         | -4.272404        | -1.171834        |
| H    | 0.001207         | -2.989903        | -2.424463        |
| N    | -1.214197        | 2.624494         | -0.748663        |
| C    | -1.337984        | -1.339108        | -0.304776        |
| N    | 1.215423         | 2.624458         | -0.747697        |
| C    | -2.447262        | -3.282082        | -0.756112        |
| H    | -2.567658        | -4.312426        | -1.091148        |
| N    | 2.670013         | 1.205620         | -0.027715        |
| C    | -3.368662        | -2.383590        | -0.294527        |
| H    | -4.441278        | -2.489349        | -0.130899        |
| N    | -0.000822        | -0.001080        | 1.943412         |
| C    | -3.230751        | 0.000071         | 0.571564         |
| H    | -4.320465        | 0.000110         | 0.420831         |
| H    | -3.016780        | -0.000084        | 1.655016         |
| C    | -1.337946        | 1.339554         | -0.304111        |
| C    | -3.368639        | 2.384010         | -0.293746        |
| H    | -4.441257        | 2.489724         | -0.130108        |
| C    | -2.447213        | 3.282645         | -0.755004        |
| H    | -2.567792        | 4.313086         | -1.089746        |
| C    | 0.000861         | 3.183795         | -1.333774        |
| H    | 0.001283         | 2.991006         | -2.423303        |
| H    | 0.000813         | 4.273100         | -1.170265        |
| C    | -0.002915        | -0.001856        | 3.110005         |
| C    | 3.369470         | 2.383962         | -0.290929        |
| H    | 4.441937         | 2.489687         | -0.126322        |
| C    | 2.448448         | 3.282610         | -0.752945        |
| H    | 2.569310         | 4.313081         | -1.087488        |
| C    | 1.338784         | 1.339506         | -0.303083        |
| C    | -0.006794        | -0.002124        | 4.565988         |
| H    | -0.693850        | -0.778879        | 4.945991         |
| H    | -0.333670        | 0.981580         | 4.947102         |
| H    | 1.007025         | -0.211339        | 4.950984         |
Table S4. Coordinates of 1 calculated with M06/def2-SVP (charge 2, multiplicity 2, SCF: E = -1333.793156 h).

| Atom | X Coordinate [Å] | Y Coordinate [Å] | Z Coordinate [Å] |
|------|------------------|------------------|------------------|
| Co   | 0.000489         | 0.000040         | -0.156667        |
| N    | 2.664925         | -1.203137        | -0.058371        |
| C    | 3.234719         | 0.000016         | 0.517235         |
| H    | 4.319780         | 0.000014         | 0.337278         |
| H    | 3.067315         | 0.000034         | 1.608245         |
| N    | 1.212358         | -2.627749        | -0.732812        |
| C    | 1.344711         | -1.348212        | -0.316777        |
| N    | -1.210797        | -2.627740        | -0.734141        |
| C    | 3.356815         | -2.382506        | -0.303249        |
| H    | 4.429415         | -2.483648        | -0.147779        |
| N    | -2.664119        | -1.203113        | -0.061326        |
| C    | 2.440022         | -3.281799        | -0.734256        |
| H    | 2.555902         | -4.318470        | -1.045446        |
| N    | -2.664118        | 1.203257         | -0.061218        |
| C    | 0.001087         | -3.208612        | -1.280732        |
| H    | 0.000964         | -4.288288        | -1.063917        |
| H    | 0.001679         | -3.086008        | -2.378797        |
| N    | -1.210760        | 2.627915         | -0.733849        |
| C    | -1.343602        | -1.348208        | -0.318217        |
| N    | 1.212379         | 2.627898         | -0.732506        |
| C    | -2.438474        | -3.281752        | -0.737051        |
| H    | -2.554024        | -4.318395        | -1.048462        |
| N    | 2.664950         | 1.203222         | -0.058245        |
| C    | -3.355749        | -2.382450        | -0.307074        |
| H    | -4.428541        | -2.483555        | -0.152898        |
| N    | -0.001233        | -0.000792        | 2.021694         |
| C    | -3.234635        | 0.000055         | 0.513579         |
| H    | -4.319459        | 0.000063         | 0.332202         |
| H    | -3.068671        | 0.000082         | 1.604803         |
| C    | -1.343583        | 1.348361         | -0.317981        |
| C    | -3.355739        | 2.382593         | -0.306944        |
| H    | -4.28532         | 2.483694         | -0.152780        |
| C    | -2.438442        | 3.281919         | -0.736825        |
| H    | -2.553977        | 4.318574         | -1.048202        |
| C    | 0.001125         | 3.208785         | -1.280427        |
| H    | 0.000172         | 3.086196         | -2.378495        |
| C    | 0.001012         | 4.288462         | -1.063610        |
| C    | -0.004278        | -0.000872        | 3.179266         |
| C    | 3.356855         | 2.382580         | -0.303086        |
| H    | 4.429457         | 2.483697         | -0.147619        |
| C    | 2.440061         | 3.281917         | -0.733999        |
| H    | 2.555948         | 4.318601         | -1.045146        |
| C    | 1.344722         | 1.348334         | -0.316535        |
| C    | -0.008964        | 0.000016         | 4.625249         |
| H    | -0.716138        | -0.751415        | 5.005767         |
| H    | -0.304808        | 0.988525         | 5.005893         |
| H    | 0.992780         | -0.238546        | 5.011333         |
Table S5. Coordinates of 1 calculated with wB97XD/def2-SVP (charge 2, multiplicity 2, SCF: E = -1334.258258 hartrees).

| Atom | X Coordinate [Å]     | Y Coordinate [Å]     | Z Coordinate [Å]     |
|------|----------------------|----------------------|----------------------|
| Co   | -0.000950            | -0.000286            | -0.194050            |
| N    | -2.665718            | 1.206903             | -0.064951            |
| C    | -3.232468            | 0.000020             | 0.514390             |
| H    | -4.314844            | -0.000022            | 0.337142             |
| H    | -3.050068            | 0.000389             | 1.599316             |
| N    | -1.216508            | 2.635593             | -0.729853            |
| C    | -1.351044            | 1.352831             | -0.334148            |
| N    | 1.213605             | 2.635529             | -0.732569            |
| C    | -3.355562            | 2.391055             | -0.282994            |
| H    | -4.424480            | 2.497537             | -0.117497            |
| N    | 2.664178             | 1.206763             | -0.070765            |
| C    | -2.439897            | 3.293988             | -0.708606            |
| H    | -2.560050            | 4.333966             | -1.000741            |
| N    | 2.664118             | -1.207420            | -0.069867            |
| C    | -0.002057            | 3.215771             | -1.282347            |
| H    | -0.001786            | 4.291487             | -1.063930            |
| H    | -0.003277            | 3.081023             | -2.375315            |
| N    | 1.213474             | -2.636519            | -0.730766            |
| C    | 1.348921             | 1.352776             | -0.337100            |
| N    | -1.216633            | -2.636462            | -0.728052            |
| C    | 2.437093             | 3.293824             | -0.714068            |
| H    | 2.555692             | 4.333749             | -1.006624            |
| N    | -2.665774            | -1.207299            | -0.064047            |
| C    | 3.353629             | 2.390842             | -0.290412            |
| H    | 4.422927             | 2.497236             | -0.127322            |
| N    | 0.002495             | 0.001365             | 2.033964             |
| C    | 3.232043             | -0.000139            | 0.507496             |
| H    | 4.314066             | -0.000233            | 0.328122             |
| H    | 3.051731             | 0.000233             | 1.592774             |
| C    | 1.348841             | -1.353546            | -0.336019            |
| C    | 3.353533             | -2.391630            | -0.288896            |
| H    | 4.422827             | -2.497972            | -0.125748            |
| C    | 2.436949             | -3.294829            | -0.711982            |
| H    | 2.555607             | -4.334920            | -1.003960            |
| C    | -0.002213            | -3.217027            | -1.280197            |
| H    | -0.003425            | -3.082916            | -2.373245            |
| H    | -0.001993            | -4.292617            | -1.061162            |
| C    | 0.008195             | 0.002814             | 3.188138             |
| C    | -3.355699            | -2.391511            | -0.281487            |
| H    | -4.424623            | -2.497838            | -0.115932            |
| C    | -2.440074            | -3.294749            | -0.708533            |
| H    | -2.560285            | -4.334881            | -0.998094            |
| C    | -1.351093            | -1.353471            | -0.333056            |
| C    | 0.017179             | 0.004423             | 4.643922             |
| H    | 0.630196             | 0.838129             | 5.012928             |
| H    | 0.432202             | -0.942240            | 5.016113             |
| H    | -1.006980            | 0.119778             | 5.024265             |
Table S6. Coordinates of 1 calculated with B3LYP/def2-SVP (charge 2, multiplicity 2, SCF: E = -1334.631079 h).

| Atom | X Coordinate [Å] | Y Coordinate [Å] | Z Coordinate [Å] |
|------|------------------|------------------|------------------|
| Co   | -0.000777        | -0.000042        | -0.156318        |
| N    | -2.686464        | 1.211267         | -0.078056        |
| C    | -3.270643        | 0.000027         | 0.487869         |
| H    | -4.348558        | 0.000017         | 0.280374         |
| H    | -3.122826        | 0.000134         | 1.579431         |
| N    | -1.222268        | 2.646871         | -0.721743        |
| C    | -1.358731        | 1.359127         | -0.317869        |
| N    | 1.219620         | 2.646865         | -0.724220        |
| C    | -3.377790        | 2.395301         | -0.320703        |
| H    | -4.451054        | 2.499319         | -0.179317        |
| N    | 2.685101         | 1.211255         | -0.083442        |
| C    | -2.453049        | 3.302297         | -0.732419        |
| H    | -2.571070        | 4.340285         | -1.034620        |
| N    | 2.685093         | -1.211291        | -0.083307        |
| C    | -0.001877        | 3.237094         | -1.263099        |
| H    | -0.001635        | 4.310543         | -1.027616        |
| H    | -0.002982        | 3.124757         | -2.360595        |
| N    | 1.219620         | -2.646954        | -0.724018        |
| C    | 1.356882         | 1.359128         | -0.320594        |
| N    | -1.222287        | -2.646950        | -0.721544        |
| C    | 2.450390         | 3.302263         | -0.737428        |
| H    | 2.567622         | 4.340222         | -1.039961        |
| N    | -2.686466        | -1.211282        | -0.077926        |
| C    | 3.375953         | 2.395263         | -0.327553        |
| H    | 4.449513         | 2.499247         | -0.188400        |
| N    | 0.002536         | 0.000054         | 2.066569         |
| C    | 3.270414         | 0.000016         | 0.481359         |
| H    | 4.347909         | 0.000001         | 0.271703         |
| H    | 3.124752         | 0.000125         | 1.573210         |
| C    | 1.356872         | -1.359200        | -0.320451        |
| C    | 3.375957         | -2.395299        | -0.327401        |
| H    | 4.449525         | -2.499261        | -0.188286        |
| C    | 2.450397         | -3.302334        | -0.737210        |
| H    | 2.567637         | -4.340309        | -1.039668        |
| C    | -0.001888        | -3.237247        | -1.262813        |
| H    | -0.002991        | -3.125053        | -2.360324        |
| H    | -0.001651        | -4.310663        | -1.027183        |
| C    | 0.007241         | 0.000181         | 3.224610         |
| C    | -3.377811        | -2.395314        | -0.320553        |
| H    | -4.451083        | -2.499303        | -0.179205        |
| C    | -2.453080        | -3.302350        | -0.732204        |
| H    | -2.571116        | -4.340354        | -1.034346        |
| C    | -1.358732        | -1.359187        | -0.317729        |
| C    | 0.014585         | 0.000570         | 4.681912         |
| H    | 0.390538         | 0.964189         | 5.058866         |
| H    | 0.661021         | -0.807296        | 5.057833         |
| H    | -1.004916        | -0.156322        | 5.066358         |
Table S7. Coordinates of 2 calculated with wB97XD/def2-SVP (charge 4, multiplicity 1, SCF: E = -2818.465738 h).

| Atom | X Coordinate [Å] | Y Coordinate [Å] | Z Coordinate [Å] |
|------|------------------|------------------|------------------|
| Co   | -2.193666        | 0.000980         | -0.231417        |
| Co   | 2.274404         | -0.000552        | 0.256152         |
| O    | -0.453417        | 0.001040         | 0.507654         |
| O    | 0.545622         | -0.001091        | -0.499774        |
| N    | -2.528307        | 1.216955         | 2.396890         |
| N    | -2.819709        | 2.657225         | 0.837037         |
| N    | -2.169762        | 2.650583         | -1.490362        |
| N    | -1.154391        | 1.207245         | -2.707287        |
| N    | -1.155884        | -1.215068        | -2.703060        |
| N    | -2.173697        | -2.652816        | -1.481494        |
| N    | -2.823666        | -2.650769        | 0.845929         |
| N    | -2.529866        | -1.205697        | 2.400912         |
| N    | 1.614290         | 1.198732         | 2.841096         |
| N    | 1.398641         | 2.599026         | 1.231550         |
| N    | 2.240916         | 2.606566         | -1.042414        |
| N    | 3.443434         | 1.210729         | -2.141645        |
| N    | 3.445786         | -1.201924        | -2.145534        |
| N    | 2.245775         | -2.603578        | -1.050973        |
| N    | 1.402529         | -2.604784        | 1.222731         |
| N    | 1.615626         | -1.209552        | 2.836986         |
| N    | -4.105887        | 0.000361         | -0.816684        |
| N    | 4.137883         | 0.000027         | 0.949302         |
| C    | -2.093299        | 0.006461         | 3.075035         |
| C    | -2.553085        | 1.358542         | 1.061473         |
| C    | -2.781710        | 2.432283         | 3.024199         |
| C    | -2.971323        | 3.342921         | 2.039550         |
| C    | -3.062146        | 3.213052         | -0.484051        |
| C    | -1.801384        | 1.353169         | -1.538177        |
| C    | -1.750174        | 3.324761         | -2.632263        |
| C    | -1.103446        | 2.412246         | -3.397226        |
| C    | -0.475868        | -0.005066        | -3.139199        |
| C    | -1.803160        | -1.356159        | -1.533483        |
| C    | -1.106978        | -2.422362        | -3.389137        |
| C    | -1.755235        | -3.331337        | -2.621216        |
| C    | -3.066802        | -3.210801        | -0.473269        |
| C    | -2.554752        | -1.351810        | 1.065968         |
| C    | -2.976414        | -3.332115        | 2.050742         |
| C    | -2.785323        | -2.418475        | 3.032327         |
| C    | 1.999215         | -0.006437        | 3.561869         |
| C    | 1.755272         | -1.342391        | 1.506530         |
| C    | 1.157957         | -2.396697        | 3.400351         |
| C    | 1.018114         | -3.276033        | 2.378154         |
| C    | 1.236713         | -3.107014        | -0.131772        |
| C    | 2.702567         | -1.341164        | -1.032959        |
| C    | 2.705332         | -3.273320        | -2.180563        |
| C    | 3.467231         | -2.389746        | -2.870957        |
| C    | 4.199650         | 0.005658         | -2.460838        |
| C    | 2.700131         | 1.344994         | -1.028531        |
| C    | 3.462442         | 2.400910         | -2.863293        |
| C    | 2.698967         | 3.280789         | -2.169949        |
| C    | 1.231072         | 3.104984         | -0.121354        |
| C    | 1.753447         | 1.336266         | 1.511063         |
| C    | 1.013168         | 3.265731         | 2.389213         |
| C    | 1.154763         | 2.383278         | 3.408487         |
| C          | -5.214439 | -0.002078 | -1.135337  |
| C          | -6.612050 | -0.007545 | -1.535133  |
| C          | 5.224340  | 0.000575  | 1.335989   |
| C          | 6.595423  | 0.000844  | 1.818736   |
| H          | -0.994015 | 0.005935  | 3.108992   |
| H          | -2.503049 | 0.008407  | 4.092890   |
| H          | -2.827329 | 2.547202  | 4.104546   |
| H          | -3.227682 | 4.398419  | 2.095858   |
| H          | -2.909745 | 4.298989  | -0.444505  |
| H          | -4.105015 | 3.022208  | -0.777974  |
| H          | -1.967598 | 4.374078  | -2.819187  |
| H          | -0.635617 | 2.519812  | -4.372914  |
| H          | 0.536348  | -0.004863 | -2.713974  |
| H          | -0.443587 | -0.007027 | -4.236115  |
| H          | -0.639306 | -2.533817 | -4.364471  |
| H          | -1.974215 | -4.380949 | -2.804659  |
| H          | -4.109438 | -3.019691 | -0.767901  |
| H          | -2.915646 | -4.296766 | -0.430028  |
| H          | -3.234434 | -4.387059 | 2.110617   |
| H          | -2.831101 | -2.529710 | 4.113054   |
| H          | 1.507417  | -0.008380 | 4.542552   |
| H          | 3.086895  | -0.006168 | 3.723502   |
| H          | 1.015615  | -2.533216 | 4.469879   |
| H          | 0.712194  | -4.319162 | 2.387364   |
| H          | 0.247674  | -2.791876 | -0.493767  |
| H          | 1.299057  | -4.202193 | -0.110670  |
| H          | 2.474626  | -4.314798 | -2.391433  |
| H          | 4.034218  | -2.317059 | -3.795535  |
| H          | 5.14150   | 0.005606  | -1.898256  |
| H          | 4.433763  | 0.007603  | -3.532451  |
| H          | 4.028978  | 2.532241  | -3.782581  |
| H          | 2.466175  | 4.322466  | -2.377497  |
| H          | 0.242595  | 2.788460  | -0.483755  |
| H          | 1.299053  | 4.200230  | -0.096975  |
| H          | 0.705407  | 4.302827  | 2.401919   |
| H          | 1.012634  | 2.516052  | 4.478522   |
| H          | -6.702370 | -0.354386 | -2.574482  |
| H          | -7.026903 | 1.007636  | -1.458335  |
| H          | -7.185492 | -0.675876 | -0.876833  |
| H          | 7.137636  | 0.861058  | 1.400582   |
| H          | 7.097530  | -0.929163 | 1.515737   |
| H          | 6.606043  | 0.072014  | 2.915668   |
Table S8. SP Coordinates of 1 with wB97XD/def2-TZVP (charge 2, multiplicity 2, SCF: E = -1335.512631 h).

| Atom | X Coordinate [Å] | Y Coordinate [Å] | Z Coordinate [Å] |
|------|------------------|------------------|------------------|
| Co   | -0.000950        | -0.00286         | -0.194050        |
| N    | -2.665718        | 1.206903         | -0.064951        |
| C    | -3.232468        | 0.000020         | 0.514391         |
| H    | -4.314845        | -0.000022        | 0.337142         |
| H    | -3.050068        | 0.000389         | 1.599316         |
| N    | -1.216509        | 2.635593         | -0.729853        |
| C    | -1.351044        | 1.352831         | -0.334148        |
| N    | 1.213605         | 2.635529         | -0.732569        |
| C    | -3.355562        | 2.391055         | -0.282994        |
| H    | -4.424481        | 2.497537         | -0.117497        |
| N    | 2.664178         | 1.206763         | -0.070765        |
| C    | -2.439898        | 3.293988         | -0.708606        |
| H    | -2.560050        | 4.333966         | -1.000741        |
| N    | 2.664118         | -1.207420        | -0.069867        |
| C    | -0.002057        | 3.215772         | -1.282347        |
| H    | -0.001786        | 4.291488         | -1.063930        |
| H    | -0.003277        | 3.081024         | -2.375315        |
| N    | 1.213474         | -2.636519        | -0.730766        |
| C    | 1.348921         | 1.352776         | -0.337100        |
| N    | -1.216633        | -2.636462        | -0.728052        |
| C    | 2.437093         | 3.293824         | -0.714068        |
| H    | 2.555692         | 4.333749         | -1.006624        |
| N    | -2.665774        | -1.207299        | -0.064047        |
| C    | 3.353630         | 2.390843         | -0.290412        |
| H    | 4.422928         | 2.497236         | -0.127322        |
| N    | 0.002495         | 0.001365         | 2.033964         |
| C    | 3.232043         | -0.000139        | 0.507496         |
| H    | 4.314666         | -0.00233         | 0.328122         |
| H    | 3.051732         | 0.000233         | 1.592775         |
| C    | 1.348841         | -1.353546        | -0.336019        |
| C    | 3.353533         | -2.391630        | -0.288896        |
| H    | 4.422827         | -2.497972        | -0.125748        |
| C    | 2.436949         | -3.294829        | -0.711982        |
| H    | 2.555607         | -4.334921        | -1.003960        |
| C    | -0.002213        | -3.217027        | -1.280198        |
| H    | -0.003425        | -3.082916        | -2.373245        |
| H    | -0.001993        | -4.292618        | -1.061162        |
| C    | 0.008195         | 0.002814         | 3.188138         |
| C    | -3.355699        | -2.391511        | -0.281487        |
| H    | -4.424623        | -2.497838        | -0.115932        |
| C    | -2.440074        | -3.294749        | -0.708534        |
| H    | -2.560285        | -4.334881        | -0.998094        |
| C    | -1.351093        | -1.353471        | -0.333056        |
| C    | 0.017179         | 0.004423         | 4.643922         |
| H    | 0.630197         | 0.838129         | 5.012929         |
| H    | 0.432202         | -0.942240        | 5.016113         |
| H    | -1.006980        | 0.119778         | 5.024265         |
Table S9. SP Coordinates of 2 with wB97XD/def2-TZVP (charge 4, multiplicity 1, SCF: E = -2821.141165 h).

| Atom | X Coordinate [Å]   | Y Coordinate [Å]   | Z Coordinate [Å]   |
|------|--------------------|--------------------|--------------------|
| Co   | -2.193666          | 0.000980           | -0.231417          |
| Co   | 2.274404           | -0.000552          | 0.256152           |
| O    | -0.453417          | 0.001040           | 0.507654           |
| O    | 0.545622           | -0.001091          | -0.499774          |
| N    | -2.528307          | 1.216955           | 2.396890           |
| N    | -2.819709          | 2.657225           | 0.837037           |
| N    | -2.169762          | 2.650583           | -1.490362          |
| N    | -1.154391          | 1.207245           | -2.707287          |
| N    | -1.155884          | -1.215068          | -2.703060          |
| N    | -2.173697          | -2.652816          | -1.481494          |
| N    | -2.823666          | -2.650769          | 0.845929           |
| N    | -2.529866          | -1.205697          | 2.400912           |
| N    | 1.614290           | 1.198732           | 2.841096           |
| N    | 1.398641           | 2.590026           | 1.231550           |
| N    | 2.240916           | 2.606566           | -1.042414          |
| N    | 3.443434           | 1.210729           | -2.141645          |
| N    | 3.445786           | -1.201924          | -2.145534          |
| N    | 2.245775           | -2.603578          | -1.050973          |
| N    | 1.402529           | -2.604784          | 1.222731           |
| N    | 1.615626           | -1.209552          | 2.836986           |
| N    | -4.105887          | 0.000361           | -0.816684          |
| N    | 4.137883           | 0.000027           | 0.949302           |
| C    | -2.093299          | 0.006461           | 3.075035           |
| C    | -2.553085          | 1.358542           | 1.061473           |
| C    | -2.781710          | 2.432283           | 3.024199           |
| C    | -2.971323          | 3.342921           | 2.039550           |
| C    | -3.062146          | 3.213052           | -0.484051          |
| C    | -1.801384          | 1.353169           | -1.538177          |
| C    | -1.750174          | 3.324761           | -2.632263          |
| C    | -1.103446          | 2.412246           | -3.397226          |
| C    | -0.475868          | -0.005066          | -3.139199          |
| C    | -1.803160          | -1.356159          | -1.533483          |
| C    | -1.106878          | -2.422362          | -3.389137          |
| C    | -1.755235          | -3.331337          | -2.621216          |
| C    | -3.066802          | -3.210801          | -0.473269          |
| C    | -2.554752          | -1.351810          | 1.065968           |
| C    | -2.976414          | -3.322115          | 2.050742           |
| C    | -2.785323          | -2.418475          | 3.032237           |
| C    | 1.999215           | -0.006437          | 3.561869           |
| C    | 1.755272           | -1.342391          | 1.506530           |
| C    | 1.157957           | -2.396697          | 3.400351           |
| C    | 1.018114           | -3.276033          | 2.378154           |
| C    | 1.236713           | -3.107014          | -0.131772          |
| C    | 2.702567           | -1.341164          | -1.032959          |
| C    | 2.705332           | -3.273320          | -2.180563          |
| C    | 3.467231           | -2.389746          | -2.870957          |
| C    | 4.199650           | 0.005658           | -2.460838          |
| C    | 2.700131           | 1.344994           | -1.028531          |
| C    | 3.462442           | 2.400910           | -2.863293          |
| C    | 2.698967           | 3.280799           | -2.169949          |
| C    | 1.231072           | 3.104984           | -0.121354          |
| C    | 1.753447           | 1.336266           | 1.511063           |
| C    | 1.013168           | 3.265731           | 2.389213           |
| C    | 1.154763           | 2.383278           | 3.408487           |
| | C   | C   | C   | H   | H   | H   | H   | H   | H   | H   | H   | H   | H   | H   | H   | H   | H   | H   | H   | H   | H   | H   |
|---|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|   | -5.214439 | -6.612050 | 5.224340 | 6.595423 | -0.994015 | -2.303049 | -2.827329 | -3.227882 | -2.909745 | -4.105015 | -1.967598 | -0.635617 | 0.536348 | -0.443587 | -0.639306 | -1.974215 | -4.109438 | -2.915646 | -3.234434 | -2.831101 | 1.507417 | 3.086895 | 1.015615 | 0.712194 | 0.247674 | 1.299057 | 2.474626 | 4.034218 | 5.144150 | 4.433763 | 4.028978 | 2.466175 | 0.242595 | 1.290953 | 0.705407 | 1.012634 | -6.702370 | -7.026903 | -7.185493 | 7.137637 | 7.097530 | 6.606043 | -0.02078 | -0.007545 | 0.000575 | 0.000844 | 0.005935 | 0.008407 | 2.547202 | 4.398419 | 4.298989 | 3.022208 | 4.374078 | 2.519812 | -0.004863 | -0.007027 | -2.533817 | -4.380949 | -3.019691 | -4.296766 | -4.387059 | -2.529710 | -0.008380 | -0.006168 | -2.533216 | -4.319162 | -2.791876 | -4.202193 | -4.314798 | -2.517059 | 0.005606 | 0.007603 | 2.532241 | 4.322466 | 2.788460 | 4.200230 | 4.308278 | 2.516052 | -0.354386 | 1.007636 | -0.675876 | 0.861058 | -0.929163 | 0.072014 | 2.401919 | 4.478522 | 2.574482 | 1.458335 | -0.876833 | 1.400582 | 1.515737 | 2.915668 |
Table S10. Coordinates of 1 calculated by Orca (charge 2, multiplicity 0, SCF: E = -2591.211783 h).

| Atom | X Coordinate [Å] | Y Coordinate [Å] | Z Coordinate [Å] |
|------|------------------|------------------|------------------|
| Co   | 0.002573         | 0.010022         | -0.145886        |
| N    | -2.641949        | 1.206825         | -0.030056        |
| C    | -3.201024        | 0.013392         | 0.575502         |
| H    | -4.278865        | 0.012439         | 0.421423         |
| H    | -2.987075        | 0.019029         | 1.647205         |
| N    | -1.204644        | 2.615983         | -0.737326        |
| C    | -1.329618        | 1.343088         | -0.310889        |
| N    | 1.206474         | 2.615692         | -0.745304        |
| C    | -3.333806        | 2.377715         | -0.270493        |
| H    | -4.394846        | 2.471900         | -0.093472        |
| N    | 2.647391         | 1.206562         | -0.045331        |
| C    | -2.423685        | 3.270487         | -0.724827        |
| H    | -2.533736        | 4.296207         | -1.044037        |
| N    | 2.647408         | -1.186107        | -0.305153        |
| C    | -0.000947        | 3.181437         | -1.316501        |
| H    | -0.000458        | 4.256142         | -1.138378        |
| H    | -0.004669        | 2.997531         | -2.396363        |
| N    | 1.206188         | -2.602140        | -0.720210        |
| C    | 1.333698         | 1.343020         | -0.319185        |
| N    | -1.204459        | -2.602548        | -0.711298        |
| C    | 2.425731         | 3.269725         | -0.740203        |
| H    | 2.533856         | 4.295753         | -1.059144        |
| N    | -2.641602        | -1.186587        | -0.017404        |
| C    | 3.338245         | 2.377048         | -0.290527        |
| H    | 4.400286         | 2.471614         | -0.119650        |
| N    | 0.008903         | -0.004967        | 1.946891         |
| C    | 3.208744         | 0.012912         | 0.557468         |
| H    | 4.286122         | 0.012325         | 0.400194         |
| H    | 2.997672         | 0.017295         | 1.629661         |
| C    | 1.334531         | -1.323573        | -0.312468        |
| C    | 3.336363         | -2.361917        | -0.258941        |
| H    | 4.397354         | -2.456490        | -0.081691        |
| C    | 2.423752         | -3.259065        | -0.699381        |
| H    | 2.530841         | -4.290085        | -1.002243        |
| C    | -0.001185        | -3.172815        | -1.288512        |
| H    | -0.005532        | -2.998207        | -2.367860        |
| H    | -0.000586        | -4.245863        | -1.098907        |
| C    | 0.002034         | -0.028676        | 3.096220         |
| C    | -3.331482        | -2.363036        | -0.235656        |
| H    | -4.391293        | -2.457272        | -0.051231        |
| C    | -2.421484        | -3.260165        | -0.881787        |
| H    | -2.530561        | -4.290894        | -0.984826        |
| C    | -1.330434        | -1.323856        | -0.303312        |
| C    | -0.007828        | -0.061368        | 4.538626         |
| H    | 0.601446         | 0.757138         | 4.930880         |
| H    | 0.398771         | -1.013494        | 4.889558         |
| H  | -1.032720 | 0.047342 | 4.903057 |
Table S11. Coordinates of end-on 4 calculated by Orca (charge 2, multiplicity 0, SCF: E = -2741.577482 h).

| Atom | X Coordinate [Å] | Y Coordinate [Å] | Z Coordinate [Å] |
|------|------------------|------------------|------------------|
| Co   | -0.022809        | -0.003922        | -0.495782        |
| N    | 2.623275         | -1.211687        | -0.437345        |
| C    | 3.236260         | -0.014093        | 0.110150         |
| H    | 4.295052         | -0.016916        | -0.143010        |
| H    | 3.123559         | -0.014443        | 1.196876         |
| N    | 1.132738         | -2.612426        | -1.054809        |
| C    | 1.305507         | -1.344153        | -0.653301        |
| N    | -1.267057        | -2.603459        | -0.852417        |
| C    | 3.286110         | -2.397176        | -0.699483        |
| H    | 4.353766         | -2.502234        | -0.577594        |
| N    | -2.627477        | -1.196655        | 0.003511         |
| C    | 2.342726         | -3.283410        | -1.094611        |
| H    | 2.421666         | -4.315240        | -1.402876        |
| N    | -2.620377        | 1.202214         | 0.008139         |
| C    | -0.120730        | -3.141816        | -1.563594        |
| H    | -0.115203        | -4.224657        | -1.448513        |
| H    | -0.209457        | -2.885870        | -2.62360         |
| N    | -1.251926        | 2.604974         | -0.641583        |
| C    | -1.363498        | -1.335595        | -0.424367        |
| N    | 1.147685         | 2.600170         | -1.046075        |
| C    | -2.473586        | -3.264980        | -0.702897        |
| H    | -2.609070        | -4.294161        | -1.000094        |
| N    | 2.630296         | 1.188183         | -0.435285        |
| C    | -3.334519        | -2.374519        | -0.157619        |
| H    | -4.369090        | -2.472705        | 0.135232         |
| N    | 0.145406         | 0.000888         | 1.421218         |
| C    | -3.135016        | 0.002984         | 0.644251         |
| H    | -4.221035        | 0.006446         | 0.568413         |
| H    | -2.846138        | 0.000349         | 1.698022         |
| C    | -1.356290        | 1.335093         | -0.421400        |
| C    | -3.319050        | 2.386445         | -0.142990        |
| H    | -4.352228        | 2.490089         | 0.153083         |
| C    | -2.453095        | 3.274482         | -0.684541        |
| H    | -2.581767        | 4.306741         | -0.974006        |
| C    | -0.102869        | 3.140960         | -1.550115        |
| H    | -0.194064        | 2.894287         | -2.610821        |
| H    | -0.090225        | 4.222818         | -1.426250        |
| C    | 0.244378         | 0.013756         | 2.563498         |
| C    | 3.299549         | 2.371757         | -0.689608        |
| H    | 4.367530         | 2.470698         | -0.565388        |
| C    | 2.360986         | 3.265030         | -1.080397        |
| H    | 2.445555         | 4.298452         | -1.381823        |
| C    | 1.313428         | 1.328878         | -0.651823        |
| C    | 0.368720         | 0.032017         | 3.997525         |
| H    | -0.164514        | -0.822918        | 4.421531         |
| H    | -0.058239        | 0.959046         | 4.389001         |
|   |         |         |         |
|---|---------|---------|---------|
| H | 1.42477 | -0.025957 | 4.273926 |
| O | -0.096209 | -0.001199 | -2.392942 |
| O | -1.260478 | -0.016345 | -2.937305 |
Table S12. Coordinates of side-on 4 calculated by Orca (charge 2, multiplicity 0, SCF: E = -2608.820169 h).

| Atom | X Coordinate [Å] | Y Coordinate [Å] | Z Coordinate [Å] |
|------|------------------|------------------|------------------|
| Co   | 0.002213         | 0.000389         | 0.336643         |
| N    | -1.489787        | 2.491147         | 0.317126         |
| C    | -2.651495        | 1.793339         | 0.821489         |
| H    | -3.532549        | 2.412800         | 0.668383         |
| H    | -2.511911        | 1.575978         | 1.880955         |
| N    | 0.488101         | 2.826720         | -0.401555        |
| C    | -0.315206        | 1.876461         | 0.102321         |
| N    | 2.448273         | 1.433952         | -0.500959        |
| C    | -1.429551        | 3.822906         | -0.033082        |
| H    | -2.269950        | 4.490713         | 0.083152         |
| N    | 2.840632         | -0.535219        | 0.231231         |
| C    | -0.173464        | 4.036821         | -0.489310        |
| H    | 0.304195         | 4.927824         | -0.868778        |
| N    | 1.494746         | -2.489806        | 0.323769         |
| C    | 1.784614         | 2.612209         | -1.017264        |
| H    | 2.415870         | 3.476433         | -0.813673        |
| H    | 1.646893         | 2.505104         | -2.095944        |
| N    | -0.444496        | -2.804461        | -0.503176        |
| C    | 1.846127         | 0.318258         | -0.066322        |
| N    | -2.397430        | -1.406789        | -0.683643        |
| C    | 3.820629         | 1.283232         | -0.489606        |
| H    | 4.488120         | 2.063539         | -0.822928        |
| N    | -2.827724        | 0.540722         | 0.103729         |
| C    | 4.067210         | 0.036592         | -0.020409        |
| H    | 4.995434         | -0.485212        | 0.158064         |
| C    | 2.629733         | -1.806996        | 0.904393         |
| H    | 3.517948         | -2.422561        | 0.779555         |
| H    | 2.438006         | -1.618349        | 1.961134         |
| C    | 0.332734         | -1.868222        | 0.063945         |
| C    | 1.451096         | -3.812701        | -0.060203        |
| H    | 2.284595         | -4.484017        | 0.082523         |
| C    | 0.219857         | -4.013671        | -0.584956        |
| H    | -0.236779        | -4.894173        | -1.011460        |
| C    | -1.707659        | -2.570978        | -1.178554        |
| H    | -1.514723        | -2.433281        | -2.245186        |
| H    | -2.347963        | -3.440079        | -1.032276        |
| C    | -4.039643        | -0.021818        | -0.227762        |
| H    | -4.976233        | 0.495430         | -0.082968        |
| C    | -3.768544        | -1.254808        | -0.718809        |
| H    | -4.417626        | -2.025172        | -1.107117        |
| C    | -1.818872        | -0.304903        | -0.166336        |
| O    | 0.611057         | 0.037305         | 2.196028         |
| O    | -0.694614        | -0.089781        | 2.166023         |
NMR spectroscopy

Figure S8. Paramagnetic $^1$H-NMR Spectrum of 1 in CD$_3$CN.

Figure S9. $^{31}$P-NMR Spectrum of 1 in CD$_3$CN.
Figure S10. $^1$H-NMR Spectrum of 2 in CD$_3$CN. Note: the C1–O1 (3.033 Å) and C29–O2 (3.103 Å) distances are remarkably short going along with hydrogen bonds between one methylene group of each tetra-NHC ligand with one of the oxygen atoms of the bridging peroxo ligand (Figure 5). These donor-acceptor distances correspond to “moderate, mostly electrostatic” hydrogen bonds (4-15 kJ/mol) and provide an explanation for the low symmetry and splitting patterns observed in the $^1$H-NMR spectrum.[32]

Figure S11. COSY-$^1$H-NMR Spectrum of 2 in CD$_3$CN. The spectrum shows couplings within each multiplet originating from germinal coupling of the methylene protons and $^3$J-couplings for the backbone signals of the ligand cCCCC.
Figure S12. HSQC NMR Spectrum of 2 in CD₃CN. The higher shifted signal set is attributable to the methylene protons and the downfield shifted multiplet is attributable to the imidazole backbone protons.

Figure S13. ³¹P-NMR Spectrum of 2 in CD₃CN.
Figure S14. $^1$H-NMR Spectrum of 3 in CD$_3$CN.

Figure S15. $^{13}$C-NMR Spectrum of 3 in CD$_3$CN.
Figure S16. $^{31}$P-NMR Spectrum of 3 in CD$_3$CN.
Author Contributions

Jonas F. Schlagintweit: lead synthetic work, writing of original draft; Philipp J. Allmann: lead synthetic work, supporting writing of original draft; Alexander D. Böth and Benjamin J. Hofmann: equal EPR measurements, DFT calculations; Christian Jandi: X-ray diffraction; Clemens Käufler: supporting synthetic work, supporting reactivity studies, preliminary DFT testing; Linda Nguyen: supporting synthetic work; Robert M. Reich: project administration; Alexander Pöthig: project administration, supporting writing of original draft; Fritz E. Kühn: lead project administration.

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