Supporting Information

Spectroscopic Evidence for a Cobalt-Bound Peroxyhemiacetal Intermediate

Yeongjin Son,†‡ Kyungmin Kim,†‡ Seonghan Kim,†‡ Guilherme L. Tripodi,§
Aleksandr Pereverzev,§ Jana Roithová*,§ and Jaeheung Cho*,†

†Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST),
Ulsan 44919, Korea
‡Department of Emerging Materials Science, Daegu Gyeongbuk Institute of Science and
Technology (DGIST), Daegu 42988, Korea
§Department of Spectroscopy and Catalysis, Institute for Molecules and Materials, Radboud
University, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands

*Corresponding author: jaeheung@unist.ac.kr, J.Roithova@science.ru.nl
Experimental Section

Materials. All chemicals obtained from Aldrich Chemical Co. were the best available purity and used without further purification unless otherwise indicated. The solvents acetonitrile (MeCN) and diethyl ether (Et₂O) were passed through solvent purification columns (JC Meyer Solvent Systems) prior to use. H₂¹⁸O₂ (95% ¹⁸O-enriched, 2.2% H₂¹⁸O₂ in water) was purchased from ICON Services Inc. (Summit, NJ, USA). The 3,6,9-trimethyl-3,6,9-triaza-1(2,6)-pyridinacyclodecapane (Me₃-TPADP) ligand, [Co⁰(Me₃-TPADP)(MeCN)₂](ClO₄)₂, and [Co³⁺(Me₃-TPADP)(O₂)]⁺ were synthesized according to literature methods.¹¹

Instrumentation. UV-vis spectra were recorded on a Hewlett Packard 8454 diode array spectrophotometer equipped with a UNISOKU Scientific Instruments for low-temperature experiments or with a circulating water bath. Electrospray ionization mass (ESI-MS) spectra were collected on a Waters (Milford, MA, USA) Acquity SQD quadrupole Mass instrument, by infusing samples directly into the source using a manual method. The spray voltage was set at 2.5 kV and the capillary temperature at 80 °C. Cold spray ionization mass spectra (CSI-MS) were collected on a JEOL JMS-T100LP 4G spectrometer. The spray voltage was set at 4.2 kV and the capillary temperature at 80 °C. Electron paramagnetic resonance (EPR) spectra were obtained on a JEOL JES-FA200 spectrometer. ¹H, ¹³C, ¹H-¹³C HSQC, ¹H-¹H COSY NMR spectra were recorded on a VNMRS 600 (600 MHz for proton, 150 MHz for carbon). Chemical shifts are given on the δ-scale in ppm, and residual solvent peaks were used as internal standards. IRPD spectra were measured with home-built instrument ISORI (see below). The crystallographic analysis was conducted with a SMART APEX II CCD equipped with a Mo X-ray tube at CCRF in DGIST. Product analysis was performed on a Thermo Fisher Trace 1310 gas chromatograph (GC) system equipped with a flame ionization detector (FID).

Generation and Characterization of [Co(Me₃-TPADP)(O₂CH(O)CH(CH₃)C₆H₅)]⁺ (2). [Co(Me₃-TPADP)(O₂CH(O)CH(CH₃)C₆H₅)]⁺ (2) was generated by the reaction of [Co(Me₃-TPADP)(O₂)]⁺ (1) (0.5 mM) with 200 equiv of 2-phenylpropionaldehyde (2-PPA) in MeCN at 0 °C, where the color of the solution changed from purple to green. [Co(Me₃-TPADP)(¹⁸O₂CH(O)CH(CH₃)C₆H₅)]⁺ (2-¹⁸O) was also prepared by reacting [Co(Me₃-TPADP)(¹⁸O)₂]⁺ (1-¹⁸O) with MeCN (2.0 mL) in the presence of 2-PPA at 0 °C. UV-vis in
MeCN: The weak UV–vis absorption bands at 400 nm ($\varepsilon = 616$ M$^{-1}$ cm$^{-1}$) and 680 nm ($\varepsilon = 174$ M$^{-1}$ cm$^{-1}$) (see Figure 3a), CSI-MS in MeCN (see Figure 3b and SI, Figure S4): $m/z = 473.3$ for [Co(Me$_3$-TPADP)(O$_2$CH(O)CH(CH$_3$)C$_6$H$_5$)]$^+$ (calculated $m/z = 473.2$). Elemental analysis of 2 was not carried out due to the thermal instability at room temperature.

**Isolation of [Co(Me$_3$-TPADP)(O$_2$CH(O)CH(CH$_3$)C$_6$H$_5$)]$^+$ (2).**

[Co(Me$_3$-TPADP)(O$_2$CH(O)CH(CH$_3$)C$_6$H$_5$)]$^+$ (2) was isolated from the reaction solution of 1 (25 mM) with excess amount of 2-PPA (1.0 M) in CH$_3$CN at −40 °C to yield a green powder. The green powder was washed with Et$_2$O several times, and dried in vacuo. During the isolation process of 2, excess 2-PPA was eliminated.

**Generation and Characterization of [Co(Me$_3$-TPADP)(O$_2$CH(O)C(CH$_3$)$_3$H$_11$)]$^+$ ($2^{CCA}$).**

[Co(Me$_3$-TPADP)(O$_2$CH(O)C(CH$_3$)$_3$H$_11$)]$^+$ ($2^{CCA}$) was generated by the reaction of [Co(Me$_3$-TPADP)(O)$_2$]$^+$ (1) (0.5 mM) with 200 equiv of cyclohexanecarboxaldehyde (CCA) in MeCN at 0 °C. UV-vis in MeCN: The weak UV–vis absorption bands at 400 nm ($\varepsilon = 506$ M$^{-1}$ cm$^{-1}$) and 665 nm ($\varepsilon = 506$ M$^{-1}$ cm$^{-1}$) (see Figure S17), CSI-MS in MeCN (see Figure S18): $m/z = 451.3$ for [Co(Me$_3$-TPADP)(O$_2$CH(O)C$_6$H$_11$)]$^+$ (calculated $m/z = 451.3$). Elemental analysis of $2^{CCA}$ was not carried out due to the thermal instability at room temperature.

**Generation and Characterization of [Co(Me$_3$-TPADP)(O$_2$CH(O)C(CH$_3$)$_3$)]$^+$ ($2^{PA}$).**

[Co(Me$_3$-TPADP)(O$_2$CH(O)C(CH$_3$)$_3$)]$^+$ ($2^{PA}$) was generated by the reaction of [Co(Me$_3$-TPADP)(O)$_2$]$^+$ (1) (0.5 mM) with 200 equiv of pivalaldehyde in MeCN at 0 °C. UV-vis in MeCN: The weak UV–vis absorption bands at 400 nm ($\varepsilon = 496$ M$^{-1}$ cm$^{-1}$) and 675 nm ($\varepsilon = 140$ M$^{-1}$ cm$^{-1}$) (see Figure S21), CSI-MS in MeCN (see Figure S22): $m/z = 425.2$ for [Co(Me$_3$-TPADP)(O$_2$CH(O)C(CH$_3$)$_3$)]$^+$ (calculated $m/z = 425.2$). Elemental analysis of $2^{PA}$ was not carried out due to the thermal instability at room temperature.

**Generation and Characterization of [Co(Me$_3$-TPADP)(O$_2$C(O)C$_6$H$_5$)]$^{2+}$ (3).**

[Co(Me$_3$-TPADP)(O$_2$C(O)C$_6$H$_5$)]$^{2+}$ (3) was generated by the reaction of [Co(Me$_3$-TPADP)(O)$_2$]$^+$ (1) (0.5 mM) with 50 equiv of benzoyl chloride in MeCN at 0 °C. UV-vis in MeCN: The weak UV–vis absorption bands at 575 nm ($\varepsilon = 174$ M$^{-1}$ cm$^{-1}$) (see Figure 5a), CSI-MS in MeCN (see Figure S26): $m/z = 222.2$ for [Co(Me$_3$-TPADP)(O$_2$C(O)C$_6$H$_5$)]$^{2+}$.
(calculated $m/z = 222.08$). Elemental analysis of 3 was not carried out due to the thermal instability at room temperature.

**Isolation of \([\text{Co(Me}_3\text{-TPADP})(\text{O}_2\text{C(O)}\text{C}_6\text{H}_5)]^{2+} (3)\).**

\([\text{Co(Me}_3\text{-TPADP})(\text{O}_2\text{C(O)}\text{C}_6\text{H}_5)]^{2+} (3)\) was isolated from the reaction solution of the Co(III)-peroxo species (1) (25 mM) with 1 equiv of benzoyl chloride (25 mM) in CH$_3$CN at −40 °C to yield a light purple powder. The light purple powder was washed with Et$_2$O several times, and dried in vacuo.

**NMR experiments.**

**Characterization of isolated \([\text{Co(Me}_3\text{-TPADP})(\text{O}_2\text{CH(O)}\text{CH(CH}_3\text{)}\text{C}_6\text{H}_5)]^{+} (2)\).**

The $^1$H NMR spectrum of 2 in acetonitrile-$d_3$ at −40 °C exhibits the complicated signals of the mixture of 1, 2-PPA, and 2, which is consistent with the equilibrium of 1 and 2 (Scheme 2 in the Text). In order to assign the complicated spectrum, additional NMR experiments for 1 and 2 were performed. At first, complex 1 was characterized by $^1$H NMR, $^{13}$C NMR, and $^1$H-$^{13}$C heteronuclear single quantum coherence (HSQC) spectroscopy (Figures S5-S6). $^{13}$C NMR (acetonitrile-$d_3$, 150 MHz, 233K) δ, ppm: 162.80 (pyC$_a$), 139.80 (pyC$_γ$), 120.24 (pyC$_β$), 72.31 (py-CH$_2$), 66.63 (N-CH$_2$-CH$_2$), 58.47 (N-CH$_2$-CH$_2$), 46.49 (N-CH$_3$), 45.58 (N-CH$_3$); $^1$H NMR (acetonitrile-$d_3$, 600 MHz, 233K) δ, ppm: 8.12 (t, 1H, pyH$_γ$), 7.55 (d, 2H, pyH$_β$), 3.81-3.60 (m, 4H, py-CH$_2$), 3.32 (s, 3H, N-CH$_3$), 2.87-2.38 (m, 8H, N-CH$_2$-CH$_2$), 1.37 (s, 6H, N-CH$_3$). Secondly, 2-PPA was characterized by $^1$H NMR (Figure S7). $^1$H NMR (acetonitrile-$d_3$, 600 MHz, 233K) δ, ppm: $^1$H NMR (acetonitrile-$d_3$, 600 MHz, 233K) δ 9.63 (s, 1H, -CHO), 7.42-7.25 (m, 5H, -C$_6$H$_5$), 3.76 (q, 1H, -CH$_γ$), 1.36 (d, 3H, -CH$_3$). Based on the NMR data of 1 and 2-PPA, the characteristic peaks of 2 were distinguished and assigned by using $^1$H NMR, $^{13}$C NMR, $^1$H-$^{13}$C HSQC, and $^1$H-$^1$H homonuclear correlation spectroscopy (COSY) (Figures S8-S11). $^1$H NMR (acetonitrile-$d_3$, 600 MHz, 233K) δ, ppm: 8.18 (t, 1H, pyH$_γ$), 7.60 (d, 2H, pyH$_β$), 7.26-7.14 (m, 5H, -C$_6$H$_5$), 5.51-5.30 (m, 1H, C$_{peroxyhemiacetal}$-H), 4.22-4.01 (m, 4H, py-CH$_2$), 3.56-3.49 (m, 6H, N-CH$_3$), 3.06-2.26 (m, N-CH$_2$-CH$_2$), 2.75-2.70 (m, -OCH(O)-CH$_β$), 1.58 (d, 3H, N-CH$_3$), 1.34-1.23 (m, 3H, -CH$_3$); where the spectrum also showed the signals of 1 (8.13, 7.55, 3.80-3.57, 3.36, 3.06-2.26, 1.37 ppm) and 2-PPA (9.65, 7.41-7.29, 3.75-3.70 and 1.39-1.37 ppm). Especially, the single C$_{peroxyhemiacetal}$-H bond of 2 was observed in the $^1$H-$^{13}$C HSQC
spectrum with a $^{13}$C chemical shifts at 107.88 and 108.91 ppm, correlated with $^1$H signals at 5.51 and 5.30 ppm, respectively, which clearly indicated the generation of 2 with two diastereomers.

**Characterization of isolated [Co(Me$_3$-TPADP)(O$_2$CH(O)C$_6$H$_{11}$)]$^+$ (2$^{\text{CCA}}$).**
The $^1$H NMR spectrum of 2$^{\text{CCA}}$ in acetonitrile-$d_3$ at $-40 \, ^\circ\text{C}$ exhibits the complicated signals of the mixture of 1, CCA, and 2$^{\text{CCA}}$, which is consistent with the equilibrium of 1 and 2$^{\text{CCA}}$. At first, CCA was characterized by $^1$H NMR (Figure S19). $^1$H NMR (acetonitrile-$d_3$, 600 MHz, 233K) δ, ppm: $^1$H NMR (acetonitrile-$d_3$, 600 MHz, 233K) δ 9.55 (s, 1H, -CHO), 2.27-1.19 (m, 11H, -C$_6$H$_{11}$). Based on the NMR data of 1 and CCA, the characteristic peaks of 2$^{\text{CCA}}$ were distinguished and assigned by using $^1$H NMR (Figure S20). $^1$H NMR (acetonitrile-$d_3$, 600 MHz, 233K) δ, ppm: 8.16 (t, 1H, py$_H$), 7.58 (d, 2H, py$_H$), 4.93 (s, 1H, C$_{\text{peroxyhemiacetal}}$-H), 4.17-4.03 (m, 4H, py-CH$_2$), 3.57-3.50 (m, 6H, N-CH$_3$), 3.00-2.10 (m, N-CH$_2$-CH$_2$); where the spectrum also showed the signals of 1 (8.13, 7.55, 3.81-3.61, 3.32, 3.00-2.10, 1.37 ppm) and CCA (9.55, 2.27-1.19 ppm). Especially, the single C$_{\text{peroxyhemiacetal}}$-H bond of 2$^{\text{CCA}}$ was observed in the $^1$H NMR spectrum with $^1$H signals at 4.93 ppm, which clearly indicated the generation of 2$^{\text{CCA}}$.

**Characterization of isolated [Co(Me$_3$-TPADP)(O$_2$CH(O)C(CH$_3$)$_3$)]$^+$ (2$^{\text{PA}}$).**
The $^1$H NMR spectrum of 2$^{\text{PA}}$ in acetonitrile-$d_3$ at $-40 \, ^\circ\text{C}$ exhibits the complicated signals of the mixture of 1, pivalaldehyde, and 2$^{\text{PA}}$, which is consistent with the equilibrium of 1 and 2$^{\text{PA}}$. At first, pivalaldehyde was characterized by $^1$H NMR (Figure S23). $^1$H NMR (acetonitrile-$d_3$, 600 MHz, 233K) δ, ppm: $^1$H NMR (acetonitrile-$d_3$, 600 MHz, 233K) δ 9.44 (s, 1H, -CHO), 1.04 (s, 9H, C(CH$_3$)$_3$). Based on the NMR data of 1 and pivalaldehyde, the characteristic peaks of 2$^{\text{PA}}$ were distinguished and assigned by using $^1$H NMR (Figure S24). $^1$H NMR (acetonitrile-$d_3$, 600 MHz, 233K) δ, ppm: 8.19 (t, 1H, py$_H$), 7.60 (d, 2H, py$_H$), 4.91 (s, 1H, C$_{\text{peroxyhemiacetal}}$-H), 4.15-4.06 (m, 4H, py-CH$_2$), 3.57-3.50 (m, 6H, N-CH$_3$), 3.04-2.09 (m, N-CH$_2$-CH$_2$); where the spectrum also showed the signals of 1 (8.12, 7.55, 3.81-3.60, 3.32, 3.04-2.09, 1.37 ppm) and pivalaldehyde (9.44, 1.04 ppm). Especially, the single C$_{\text{peroxyhemiacetal}}$-H bond of 2$^{\text{PA}}$ was observed in the $^1$H NMR spectrum with $^1$H signals at 4.91 ppm, which clearly indicated the generation of 2$^{\text{PA}}$. 
X-ray crystallography. Single crystal of [Co(Me$_7$TPADP)(O$_2$)](ClO$_4$)(MeCN) (1-(ClO$_4$)(MeCN)) was picked from solutions by a nylon loop (Hampton Research Co.) on a handmade copper plate mounted inside a liquid N$_2$ Dewar vessel at ca. -40 °C and mounted on a goniometer head in a N$_2$ cryostream. Data collections were carried out on a Bruker SMART APEX II CCD diffractometer equipped with a monochromator in the Mo Kα (λ = 0.71073 Å) incident beam. The CCD data were integrated and scaled using the Bruker-SAINT software package, and the structure was solved and refined using SHELXTL V 6.12.$^5$ Hydrogen atoms were located in the calculated positions. All non-hydrogen atoms were refined with anisotropic thermal parameters. The crystallographic data with the selected bond distance s and angles for 1-(ClO$_4$)(MeCN) are listed in Tables S1 and S2. Crystal data for 1-(ClO$_4$)(MeCN): C$_{16}$H$_{27}$ClCoN$_5$O$_6$, monoclinic, P2$_1$/c, Z = 4, a = 9.238(2), b = 22.883(4), c = 9.472(3) Å, β = 98.354(13)$^\circ$, V = 1981.1(9) Å$^3$, μ = 1.046 mm$^{-1}$, ρ$_{calc}$ = 1.609 g/cm$^3$, R$_1$ = 0.0283, wR$_2$ = 0.0993 for 3886 unique reflections, 266 variables. CCDC-2074524 for 1-(ClO$_4$)(MeCN) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Helium tagging IR photodissociation (IRPD) spectroscopy. The IR spectra of mass-selected ions were measured with ISORI (Ion Spectroscopy of Reactive Intermediates) instrument described in detail elsewhere.$^{53-55}$ The instrument is equipped with an electrospray ionization source, the ionization conditions were analogous as for the rest of MS experiments (spray voltage 3.8 kV, sheath gas~ 30 psi, capillary temperature 80 °C) and the solutions of the complexes were prepared in the very same way. The ions of interest were mass-selected with the first quadrupole and guided by a quadrupole bender and an octopole into a wire quadrupole ion trap operated at 2.6 K. The ions were trapped and cooled by collisions with helium buffer gas (100 ms). The cooled ions formed complexes with helium (20 % conversion). The ions in the trap were irradiated by IR OPO (pulses at 10 Hz frequence for 2 s) and the resulting mixture of the ions was extracted and the number of helium complexes was counted with a Daly type detector after the mass analysis with the second quadrupole. The spectra were measured with
0.5 Hz frequency with alternating irradiation. The number of helium complexes with and without irradiation is N(v) and N₀, respectively. The intensity of IR absorption at a given wavenumber is determined as 1 - N(v)/N₀.

**Computational details.** Theoretical calculations were carried out with Density Functional Theory (DFT)⁶⁶ using the Gaussian 16 package.⁵⁷ The unrestricted B3LYP-D3 functional was employed for all optimizations and frequency calculations with 6-31G* level of theory for all atoms.⁵⁸ All calculations were performed in solvent (acetonitrile) using the SMD continuum solvation model.⁵⁹ Optimized geometries were visualized with Gaussview 6. In order to gauge the credibility of the DFT calculations, we compared optimized geometry of [Co(Me₃-TPADP)(O₂)]⁺ (1) to the crystal structure of [Co(Me₃-TPADP)(O₂)]⁺. The root mean square deviation (RMSD) value of 0.10 Å without hydrogen atoms was obtained giving credibility to the subsequent calculations. Following each geometry optimization, harmonic frequency analysis was carried out to confirm the nature of the stationary point as an equilibrium structure (all real frequencies) or a transition structure (one imaginary frequency). Populations were obtained from a Mulliken Analysis.

**Equilibrium constant.** The expression used for determination of $K_{eq}$ was derived according to a literature method.⁶⁰ The equation of equilibrium is provided below. The $K_{eq}$ value of 288 M⁻¹ is determined from the slope of the linear plot $(α^{-1}-1)^{-1}$ against $[1]₀-α[2-PPA]₀$ (see Figure S14 in the Text).

$$K_{eq} = \frac{[[\text{Co}(\text{Me}_3\text{-TPADP})(\text{O}_2\text{CH(O)CH(CH}_3\text{)C}_6\text{H}_5)]^+] \cdot \text{[2-PPA]}_0}{[[\text{Co}(\text{Me}_3\text{-TPADP})(\text{OO})]^+] \cdot \text{[2-PPA]}_0}$$

$$\frac{1}{K_{eq}} = \frac{[[\text{Co}(\text{Me}_3\text{-TPADP})(\text{OO})]^+]_0 \cdot \text{[2-PPA]}_0}{[[\text{Co}(\text{Me}_3\text{-TPADP})(\text{O}_2\text{CH(O)CH(CH}_3\text{)C}_6\text{H}_5)]^+]^{-1} \cdot \text{[2-PPA]}_0}$$

$$α = \frac{[[\text{Co}(\text{Me}_3\text{-TPADP})(\text{O}_2\text{CH(O)CH(CH}_3\text{)C}_6\text{H}_5)]^+] \cdot \text{[2-PPA]}_0}{[[\text{Co}(\text{Me}_3\text{-TPADP})(\text{OO})]^+]_0 \cdot \text{[2-PPA]}_0}$$

$$(α^{-1}-1)^{-1} = K_{eq} \cdot ([[\text{Co}(\text{Me}_3\text{-TPADP})(\text{OO})]^+]_0-α\cdot\text{[2-PPA]}_0) = K_{eq} \cdot ([1]₀-α[2-PPA]₀)$$
Reactivity Studies. All reactions were run in a 1-cm UV cuvette by monitoring UV-vis spectral changes of reaction solutions, and rate constants were determined by fitting the changes in absorbance at 340 nm for the decay of 1. Reactions were run at least in triplicate, and the data reported represent the average of these reactions. Isolated 1 (0.5 mM) was used in reactivity studies, such as the oxidation of 2-phenylpropionaldehyde (see Figure 3a in the Text), cyclohexanecarboxaldehyde (see Figure S17) and pivalaldehyde (see Figure S21) in MeCN at 0 °C. The reactivity of 1 was further investigated using para-substituted benzoylchlorides \( \text{para-}X\text{-PhC(O)Cl; } X = \text{CH}_3, \text{F, H, Cl, Br} \) in MeCN at 0 °C (see Figure 5b in the Text). After the completion of reactions, pseudo-first-order fitting of the kinetic data allowed us to determine \( k_{obs} \) values. Products formed in the thermal decomposition of the isolated intermediate 2 (0.5 mM) in the presence of excess aldehydes in MeCN at 70 °C was analyzed by injecting the reaction mixture directly into GC. Products were identified by comparing with authentic samples, and product yields were determined by comparison against standard areas prepared with authentic samples as an internal standard (see Table S7).
Table S1. Crystal Data and Structural Refinements for [Co(Me₃-TPADP)(O₂)][ClO₄](MeCN) (1-(ClO₄)(MeCN)).

|                              | 1-(ClO₄)(MeCN)                                      |
|------------------------------|---------------------------------------------------|
| Empirical formula            | C₁₆H₂₇ClCoN₅O₆                                    |
| Formula weight               | 479.80                                            |
| Temperature (K)              | 153.0(2)                                          |
| Wavelength (Å)               | 0.71073                                           |
| Crystal system/space group   | Monoclinic, P2₁/c                                 |
| Unit cell dimensions         |                                                   |
| a (Å)                        | 9.238(2)                                          |
| b (Å)                        | 22.883(4)                                         |
| c (Å)                        | 9.472(3)                                          |
| α (°)                        | 90.00                                             |
| β (°)                        | 98.354(13)                                        |
| γ (°)                        | 90.00                                             |
| Volume (Å³)                  | 1981.1(9)                                         |
| Z                            | 4                                                 |
| Calculated density (g/cm⁻³)  | 1.609                                             |
| Absorption coefficient (mm⁻¹)| 1.046                                             |
| Reflections collected        | 57275                                             |
| Independent reflections [R(int)] | 3886 [0.0356]                             |
| Refinement method            | Full-matrix least-squares on F²                   |
| Data/restraints/parameters    | 3886/0/266                                        |
| Goodness-of-fit on F²         | 0.840                                             |
| Final R indices [I > 2σ(I)]  | R₁ = 0.0283, wR₂ = 0.0993                         |
| R indices (all data)         | R₁ = 0.0317, wR₂ = 0.1043                         |
**Table S2.** Selected Bond Distances (Å) and Angles (°) for [Co(Me3-TPADP)(O2)][ClO4](MeCN) (1·(ClO4)(MeCN)).

| Bond Distances (Å)          |     |
|-----------------------------|-----|
| Co-O1                       | 1.8666(14) |
| Co-O2                       | 1.8476(13) |
| Co-N1                       | 1.9939(16) |
| Co-N2                       | 1.8977(16) |
| Co-N3                       | 2.0026(16) |
| Co-N4                       | 1.9976(16) |
| O1-O2                       | 1.4611(19) |

| Bond Angles (°)            |    |
|---------------------------|----|
| O2-Co-O1                  | 46.33(6) |
| O2-Co-N2                  | 155.95(6) |
| O1-Co-N2                  | 109.62(6) |
| O2-Co-N1                  | 96.38(6) |
| O1-Co-N1                  | 97.17(6) |
| N2-Co-N1                  | 86.01(7) |
| O2-Co-N4                  | 98.69(6) |
| O1-Co-N4                  | 95.20(6) |
| N2-Co-N4                  | 81.34(7) |
| N1-Co-N4                  | 164.68(6) |
| O2-Co-N3                  | 105.69(7) |
| O1-Co-N3                  | 98.35(7) |
| N2-Co-N3                  | 95.09(8) |
| N1-Co-N3                  | 85.31(7) |
| N4-Co-N3                  | 88.00(6) |
| O1-O2-Co                  | 67.52(7) |
| O2-O1-Co                  | 66.15(7) |
**Table S3.** Selected bond distances (Å) and bond angle (°) from the obtained crystal structure and the DFT calculations of [Co(Me₃-TPADP)(O₂)]⁺ (1).

| Bond distances (Å) | 1 (exp.) | 1 (cal.) |
|--------------------|----------|----------|
| Co-N1              | 1.998    | 2.046    |
| Co-N2              | 1.898    | 1.903    |
| Co-N3              | 2.003    | 2.019    |
| Co-N4              | 1.994    | 2.054    |
| Co-O1              | 1.848    | 1.832    |
| Co-O2              | 1.866    | 1.834    |
| O1-O2              | 1.461    | 1.441    |

| Bond angle (°) | 1 (exp.) | 1 (cal.) |
|----------------|----------|----------|
| N1-Co-N4       | 164.68   | 164.86   |
| N2-Co-N3       | 98.35    | 97.73    |
| O1-Co-O2       | 46.33    | 46.27    |
Table S4. Selected bond distances (Å) and bond angle (°) from the DFT calculations of [Co(Me3-TPADP)(O2CH(O)CH(CH3)C6H5)]+ (2).

| Bond distances (Å) | 2 (S = 0) | 2 (S = 1) | 2 (S = 2) |
|--------------------|-----------|-----------|-----------|
| Co-N1              | 2.092     | 2.274     | 2.259     |
| Co-N2              | 1.922     | 1.966     | 2.076     |
| Co-N3              | 2.047     | 2.136     | 2.243     |
| Co-N4              | 2.074     | 2.264     | 2.249     |
| Co-O2              | 1.849     | 1.837     | 1.970     |
| Co-O3              | 1.870     | 1.822     | 1.944     |
| O1-O2              | 1.463     | 1.458     | 1.343     |
| C1-O1              | 1.432     | 1.416     | 1.563     |
| C1-O3              | 1.387     | 1.402     | 1.325     |

| Bond angle (°) | 2 (S = 0) | 2 (S = 1) | 2 (S = 2) |
|----------------|-----------|-----------|-----------|
| N1-Co-N4       | 162.48    | 153.59    | 150.59    |
| N2-Co-N3       | 94.11     | 91.83     | 91.05     |
| O2-Co-O3       | 86.69     | 86.52     | 81.57     |
| Co-O3-C1       | 109.13    | 110.57    | 117.06    |
| O1-C1-O3       | 109.16    | 108.16    | 111.31    |
| C1-O1-O2       | 104.79    | 103.93    | 111.70    |
| O1-O2-Co       | 106.20    | 105.56    | 116.10    |
Table S5. Calculated energy and energy difference ($\Delta E$) between different spin states of the electronic structure models of $[\text{Co(Me}_3\text{-TPADP})(\text{O}_2\text{CH(O)CH(CH}_3\text{)C}_6\text{H}_5)]^+$ (2) at the uB3LYP/6-31g* level of theory.

| Complex   | E (Hartree) | $\Delta E$ (kcal/mol) |
|-----------|-------------|-----------------------|
| 2 (S = 0) | -2724.112   | 0.00                  |
| 2 (S = 1) | -2724.101   | 7.02                  |
| 2 (S = 2) | -2724.088   | 15.03                 |
Table S6. Mulliken charge distribution of $[\text{Co(Me}_3\text{-TPADP})(\text{O}_2\text{CH(O)CH(CH}_3\text{)C}_6\text{H}_5])^+ (2)$.

| Orbital | Co    | O1    | O2    | O3    | 2-PPA | Me$_3$-TPADP |
|---------|-------|-------|-------|-------|-------|-------------|
|         | 0.98  | -0.32 | -0.45 | -0.65 | 0.49  | 0.96        |
Table S7. Oxidative reaction of [Co(Me₃-TPADP)(O₂)]⁺ (1) with substrates.

| Substrate                                      | $k_2$ (M⁻¹ s⁻¹) | Product            | Yield [%] |
|------------------------------------------------|-----------------|--------------------|-----------|
| 2-phenylpropionaldehyde (2-PPA)                | 3.4(2) × 10⁻²    | acetophenone       | 83(3)     |
| cyclohexanecarboxaldehyde (CCA)               | 2.7(1) × 10⁻²    | cyclohexanone      | 46(6)     |
| pivalaldehyde (PA)                             | 2.8(1) × 10⁻³    | pivalic acid       | 87(2)     |
| 2-cyclohexylaldehyde                          | 2.7(1) × 10⁻²    | cyclohexanol       | 18(2)     |
| 2-cyclohexylaldehyde                          | 2.7(1) × 10⁻²    | cyclohexane        | 12(1)     |
Scheme S1. Formation of [Co(Me₃-TPADP)(O₂C(C₆H₅))²⁺ (3) from the reaction of [Co(Me₃-TPADP)(O₂)]⁺ (1) with benzoylchloride.
Figure S1. Collision induced dissociation of mass-selected [Co(Me₃-TPADP)(O₂CH(O)CH(CH₃)C₆H₅)]⁺ (2) (m/z 473).
Figure S2. Top: Helium tagging IRPD spectra of mass-selected [Co(Me₃-TPADP)(O₂)]⁺ (1) (m/z 339 - unlabeled = black trace, m/z 443 - ¹⁸O labeled = red trace). Bottom: B3LYP-D3/6-31G* calculated IR spectra 1 (black line) and 1-¹⁸O (red line).
**Figure S3.** Top spectrum in every block: Helium tagging IRPD spectra of mass-selected [Co(Me$_3$-TPADP)(O$_2$CH(O)CH(CH$_3$)C$_6$H$_5$)]$^+$ (2) (m/z 473 - unlabeled = black trace, m/z 447 - $^{18}$O labeled = red trace). Bottom three spectra: B3LYP/6-311++G** calculated IR spectra 2 (black line) and $^2$-$^{18}$O (red line). The blocks show the IR spectra of the 4 diastereoisomers of 2 (2 can have 8 stereoisomers because of the two chiral carbons and the chiral cobalt atom), the energies are the relative energies of the selected diastereoisomers with respect to the structure depicted in c) (bottom left). The absolute configuration of the chiral carbons is depicted in the figure.

**Discussion:** The comparison of the experimental and theoretical spectra clearly suggests that the isotopic labelling affects the C-O(Co) stretching band. No isotopic shifts in the 1000 – 1100 cm$^{-1}$ range are expected for the isomers that would result from a nucleophilic attack of aldehyde at the cobalt center (the top theoretical spectra in all blocks). The bottom theoretical spectra in all blocks are added for the sake of completeness; however, $^2$-$^{18}$O$_2$ eliminates exclusively $^1$-$^{16}$O, therefore these isotopomers are not present among experimentally detected $^2$-$^{18}$O$_2$.

The O-O vibration of 2 is an extremely weak band that should be located at ~870 cm$^{-1}$. Given the small abundance of 2 because of the equilibrium with 1, the detection of such a weak band is beyond the current instrumentation reach. The spectra thus clearly suggest that the aldehyde reacts by the insertion between the two oxygen atoms of 1.
Figure S4. CSI-MS spectra of the reaction solution obtained in the reaction of [Co(Me3-TPADP)(O)]2+ (1) (0.5 mM) with 2-PPA (0.1 M) in CH3CN at 0 °C. (a) The mass peak for [Co(Me3-TPADP)(O2CH(O)CH(CH3)C6H5)]+ (2-16O) at m/z 473.3 with isotope distribution pattern. (b) The mass peak for [Co(Me3-TPADP)(18O2CH(O)CH(CH3)C6H5)]+ (2-18O) at m/z 477.3 with isotope distribution pattern; the reaction was conducted with isotopically labeled [Co(Me3-TPADP)(18O2)]+ (1-18O).
Figure S5. (a) The $^{13}$C NMR spectrum of [Co$^{III}$($Me_3$-TPADP)(O$_2$)]$^+$ (1) (8 mM) in acetonitrile-$d_3$ at −40 °C. (b) The $^1$H NMR spectrum of 1 (8 mM) in diamagnetic region at −40 °C acetonitrile-$d_3$. The peaks marked with ‘s’ are ascribed to solvents. The 2 – 3 ppm region shows the multiplet singals of $H_e$ and $H_f$. 
Figure S6. $^1$H-$^{13}$C HSQC spectrum of [Co$^{III}$($\text{Me}_3$-TPADP)($O_2$)]$^+$ (I) (8 mM) in acetonitrile-$d_3$ at –40 °C. The inset shows the zoomed-in spectrum. The peaks marked with ‘s’ are ascribed to solvents.
**Figure S7.** The $^1$H NMR spectrum of 2-phenylpropionaldehyde (25 mM) in acetonitrile-$d_3$ at $-40 \, ^\circ\text{C}$. The peaks marked with ‘s’ are ascribed to solvents.
Figure S8. The $^1$H NMR spectrum of the isolated $[\text{Co(Me}_3\text{-TPADP})(\text{O}_2\text{CH(O)CH(CH}_3\text{)C}_6\text{H}_5)]^+$ (2) (8 mM) in acetonitrile-$d_3$ at −40 °C showed complicated signals because 2 is in equilibrium with $[\text{Co}^{III}\text{(Me}_3\text{-TPADP})(\text{O}_2)]^+$ (1) and 2-PPA (purple rectangle: 1; green rectangle: 2; red rectangle: 2-PPA). The multiplet signals (m) in the region at 2.0–3.0 ppm were derived from the N–CH$_2$–CH$_2$ moiety in 1 and 2. The peaks marked with ‘s’ are ascribed to solvents. Inset showed the zoom in spectrum, which exhibits the coupling between H$_o$ and H$_p$.
Figure S9. The $^{13}$C NMR spectrum of the isolated [Co(Me$_3$-TPADP)(O$_2$CH(O)CH(CH$_3$)C$_6$H$_5$)]$^+$ (2) (8 mM) in acetonitrile-$d_3$ at −40 °C showed complicated signals because 2 is in equilibrium with [Co$^{lll}$(Me$_3$-TPADP)(O$_2$)]$^+$ (1) and 2-PPA. The peaks marked with ‘s’ are ascribed to solvents.
Figure S10. The $^1$H-$^1$H COSY NMR spectrum of the isolated [Co(Me$_3$-TPADP)(O$_2$CH(O)CH(CH$_3$)C$_6$H$_5$)]$^+$ (2) (8 mM) in acetonitrile-$d_3$ at $-40$ °C.
Figure S11. The $^{1}$H-$^{13}$C COSY NMR spectrum of the isolated $[\text{Co(Me}_{3}\text{-TPADP})(\text{O}_{2}\text{CH(O)CH(CH}_{3}\text{)C}_{6}\text{H}_{5})]^{+}$ (2) (8 mM) in acetonitrile-$d_{3}$ at $-40$ °C.
Figure S12. X-band EPR spectrum of [Co(Me$_3$-TPADP)(O$_2$CH(O)CH(CH$_3$)C$_6$H$_5$)]$^+$ (2) (4.0 mM) in frozen CH$_3$CN at 113 K. Spectroscopic settings: frequency = 9.152 GHz, microwave power = 0.995mW, modulation frequency=100 kHz, and modulation amplitude = 0.6 mT.
Figure S13. (a) Plot of $k_{obs}$ against 2-PPA concentration obtained in the reaction of 1 with 2-PPA in CH$_3$CN at 0 °C to determine a second-order rate constant ($k_2$). (b) Plot of ln($k_2/T$) against $1/T$ obtained in the reaction of 1 with 2-PPA in CH$_3$CN at various temperatures to determine the activation parameters.
Figure S14. Plot of ($\alpha^{-1}$-1)$^{-1}$ vs $[1]_0$-$\alpha[2$-$PPA]_0$ to determine the equilibrium constant ($K_{eq}$) between $[\text{Co(Me}_3\text{-TPADP)}(\text{O}_2)]^+$ (1) and $[\text{Co(Me}_3\text{-TPADP)}(\text{O}_2\text{CH(OCCH}_3\text{C}_6\text{H}_5)])^+$ (2) in CH$_3$CN at 0 °C.
Figure S15. (a) UV−vis spectral changes observed upon natural decay of [Co(Me$_3$-TPADP)(O$_2$CH(O)CH(CH$_3$)C$_6$H$_5$)]$^+$ (2) (0.5 mM) in CH$_3$CN at 70 °C in the presence of an excess amount of 2-PPA (0.2 M). (b) The time course of the absorbance at 680 nm and its first-order fitting (red line).
Figure S16. ESI-MS taken after natural decay of \([\text{Co}(\text{Me}_3\text{-TPADP})(\text{O}_2\text{CH(O)CH(CH}_3\text{)C}_6\text{H}_5)]^+\) (2) in CH$_3$CN at 70 °C in the presence of an excess amount of 2-PPA (0.2 M), showing the formation of a Co(II) precursor: Mass peaks at \(m/z\) of 174.1, 194.6 and 406.1 are assigned to \([\text{Co}^{II}(\text{Me}_3\text{-TPADP})(\text{CH}_3\text{CN})]^2^+\), \([\text{Co}^{II}(\text{Me}_3\text{-TPADP})(\text{CH}_3\text{CN})_2]^2^+\) and \([\text{Co}^{II}(\text{Me}_3\text{-TPADP})(\text{ClO}_4)]^+\), respectively. Mass peak at \(m/z\) 352.1 corresponds to Co(II)-formato complex, \([\text{Co}^{II}(\text{Me}_3\text{-TPADP})(\text{HCOO})]^+\).
Figure S17. (a) UV–vis spectral changes observed upon addition of CCA (0.1 M) to the solution [Co$^{III}$($\text{Me}_3$-TPADP)(O$_2$)]$^+$ (1) to afford the [Co$^{III}$($\text{Me}_3$-TPADP)(O$_2$CH(O)C$_6$H$_{11}$)]$^+$ (2$^{\text{CCA}}$) (0.5 mM) in CH$_3$CN at 0 °C. (b) The time course of the absorbance at 340 nm and its first-order fitting (red line).
Figure S18. (a) CSI-MS spectrum of the reaction solution obtained in the oxidation reaction of CCA (0.1 M) by [Co^{III}(Me_3-TPADP)(O_2)]^+ (1) (0.5 mM) in CH\textsubscript{3}CN at 0 °C, showing the formation of the 2\textsuperscript{CCA}: Mass peak at \textit{m}/\textit{z} of 451.3 is assigned to [Co^{III}(Me_3-TPADP)(O_2CH(O)C_6H_{11})]^+. The peak at \textit{m}/\textit{z} of 339.2 corresponds to 1 due to an equilibrium between 1 and 2\textsuperscript{CCA}. Mass peaks at \textit{m}/\textit{z} of 419.2 and 434.3 are assigned to [Co^{I}(Me_3-TPADP)(C_6H_{11}CHO)]^+ and [Co^{I}(Me_3-TPADP)(C_6H_{11}CHO)(H_2O)]^+, respectively. Asterisks are some unidentified species. (b) The mass peak for 2\textsuperscript{CCA} at \textit{m}/\textit{z} 451.3 with isotope distribution pattern.
Figure S19. The $^1$H NMR spectrum of cyclohexanecarboxaldehyde (CCA) (25 mM) in acetonitrile-$d_3$ at $-40$ °C. The peaks marked with ‘s’ are ascribed to solvents.
Figure S20. The $^1$H NMR spectrum of the isolated [Co(Me$_3$-TPADP)(O$_2$CH(O)C$_6$H$_{11}$)]$^+$ (2$^{\text{CCA}}$) (8mM) in CD$_3$CN at 0 °C showed complicated signals because 2$^{\text{CCA}}$ is in equilibrium with [Co$^{\text{III}}$(Me$_3$-TPADP)(O$_2$)]$^+$ (1) and CCA (purple circles: 1; green circles: 2$^{\text{CCA}}$; cyan circles: CCA). The multiplet signals (m) in the region at 2.0–3.0 ppm were derived from the N–CH$_2$–CH$_2$ moiety in 1 and 2$^{\text{CCA}}$. The peaks marked with ‘s’ are ascribed to solvents.
Figure S21. (a) UV−vis spectral changes observed upon addition of pivaldehyde (0.1 M) to the solution [Co(Me$_3$-TPADP)(O$_2$)]$^+$ (1) to afford the [Co$^{III}$(Me$_3$-TPADP)(O$_2$CH(O)C(CH$_3$)$_3$]$^+$ (2$^{PA}$) (0.5 mM) in CH$_3$CN at 0 °C. (b) The time course of the absorbance at 340 nm and its first-order fitting (red line).
Figure S22. (a) CSI-MS spectrum of the reaction solution obtained in the oxidation reaction of pivalaldehyde (0.1 M) by [Co^{III}(Me$_3$-TPADP)(O$_2$)]$^+$ (1) (0.5 mM) in CH$_3$CN at 0 °C, showing the formation of the 2$^{PA}$. Mass peak at $m/z$ of 425.2 is assigned to [Co^{III}(Me$_3$-TPADP)(O$_2$CH(O)C(CH$_3$)$_3$]$^+$. The peak at $m/z$ of 339.2 corresponds to 1 due to an equilibrium between 1 and 2$^{PA}$. Mass peaks at $m/z$ of 393.2 and 411.2 are assigned to [Co$^I$(Me$_3$-TPADP)((CH$_3$)$_3$CCHO)$]^+$ and [Co$^I$(Me$_3$-TPADP)((CH$_3$)$_3$CCHO)(H$_2$O)]$^+$, respectively. Asterisks are some unidentified species. (b) The mass peak for 2$^{PA}$ at $m/z$ 425.2 with isotope distribution pattern.
Figure S23. The $^1$H NMR spectrum of pivalaldehyde (25 mM) in acetonitrile-$d_3$ at –40 °C. The peaks marked with ‘s’ are ascribed to solvents.
Figure S24. The $^1$H NMR spectrum of the isolated $[\text{Co(Me}_3\text{-TPADP})(\text{O}_2\text{CH(O)C(CH}_3)_3])^+$ ($2^\text{PA}$) (8mM) in CD$_3$CN at 0 °C showed complicated signals because $2^\text{PA}$ is in equilibrium with $[\text{Co}^{\text{III}}(\text{Me}_3\text{-TPADP})(\text{O}_2)]^+$ ($1$) and pivalaldehyde (purple circles: $1$; green circles: $2^\text{PA}$; cyan circles: pivalaldehyde). The multiplet signals (m) in the region at 2.0–3.0 ppm were derived from the N–CH$_2$–CH$_2$ moiety in $1$ and $2^\text{PA}$. The peaks marked with ‘s’ are ascribed to solvents.
Figure S25. Plots of pseudo-first-order rate constants ($k_{obs}$) against the concentration of (a) cyclohexanecarboxaldehyde (CCA) and (b) pivalaldehyde (PA) to obtain second-order rate constants ($k_2$) in CH$_3$CN at 0 °C.
Figure S26. CSI-MS spectrum of the reaction solution obtained in the oxidation reaction of benzoylchloride (25 mM) by [Co$^{III}$(Me$_3$-TPADP)(O$_2$)]$^+$ (1) (0.5 mM) in CH$_3$CN at 0 °C. (a) The mass peak $m/z$ of 222.2, 342.2, 445.3 and 479.3 is assigned to [Co$^{III}$(Me$_3$-TPADP)(O$_2$C(O)(C$_6$H$_5$))]$^{2+}$, [Co$^{II}$(Me$_3$-TPADP)(Cl)]$^{2+}$, [Co$^{III}$(Me$_3$-TPADP)(OC(O)(C$_6$H$_5$))(OH)]$^+$ and [Co$^{III}$(Me$_3$-TPADP)(O$_2$C(O)(Cl))C$_6$H$_5$]$^+$, respectively. Asterisks are some unidentified species. (b) The mass peak for 3 at $m/z$ 222.2 with isotope distribution patterns.
Figure S27. UV-vis spectral change was not observed during the incubation of 3 in CH$_3$CN at 0 °C. The inset shows the time course of the absorbance at 560 nm.
Figure S28. Time dependant ESI-MS spectra were obtained during the incubation of the isolated [Co$^{III}$$(Me_3$-TPADP$)$($O_2$C(O)$C_6$H$_5$)]$^+$ (3) (0.5 mM) in CH$_3$CN at 0 °C at (a) 5 min. and (b) 35 min. The mass peak m/z of 182.6, 191.6, 222.1, 242.6, 342.2 and 445.3 is assigned to [Co$^{III}$$(Me_3$-TPADP$)$($OH$)($CH_3$CN)]$^{2+}$, [Co$^{III}$$(Me_3$-TPADP$)$($Cl$)($CH_3$CN)]$^{2+}$, [Co$^{III}$$(Me_3$-TPADP$)$($O_2$C(O)$C_6$H$_5$)]$^{2+}$, [Co$^{III}$$(Me_3$-TPADP$)$($O_2$C(O)$C_6$H$_5$)($CH_3$CN)]$^{2+}$, [Co$^{III}$$(Me_3$-TPADP$)$($Cl$)]$^{2+}$ and [Co$^{III}$$(Me_3$-TPADP$)$($OC(O)$C$_6$H$_5$)($OH$)]$^+$, respectively.
Figure S29. Top: Helium tagging IRPD spectrum of [Co\textsuperscript{III}(Me\textsubscript{3}-TPADP)(O\textsubscript{2}C(O)C\textsubscript{6}H\textsubscript{5})\textsubscript{2}+] (m/z 222) formed from the reaction of benzoylchloride with [Co\textsuperscript{III}(Me\textsubscript{3}-TPADP)(O\textsubscript{2})\textsuperscript{+}] (black) and [Co\textsuperscript{III}(Me\textsubscript{3}-TPADP)(\textsuperscript{18}O\textsubscript{2})\textsuperscript{+}] (red). Bottom: Theoretical (B3LYP-D3/6-311++G**) IR spectra of the most stable localized isomer of [Co\textsuperscript{III}(Me\textsubscript{3}-TPADP)(O\textsubscript{2}C(O)C\textsubscript{6}H\textsubscript{5})\textsubscript{2}+] (in black). The theoretical IR spectra of different \textsuperscript{18}O isotopomers (in red).

**Discussion:** The comparison of the experimental and theoretical spectra clearly suggests that the isotopic labelling affects the C-O(O) stretching band consistent with the upper theoretical isotopomer (the bottom isotopomer is given for the sake of completeness, but it’s formation can be excluded). The detected isotopomer is consistent with the nucleophilic attack of benzoylchloride at the cobalt center. The alternative pathway of the insertion into O-O bond can be excluded, because this would not lead to the isotopic shift of the band at ~1360 cm\textsuperscript{-1} observed experimentally.
The O-O vibration is a weak band theoretically predicted at 862 cm⁻¹ (note that the theoretical spectra are 5 times enhanced in this range) and it is out of the detectable range of our spectrometer. The band at 1147 cm⁻¹ is associated to the O₂C-C(Ph) stretching mode and it is coupled to the C-O stretching modes. The experimental spectrum contains the isotopically sensitive bands, but the signal to noise ratio is rather poor; hence, it should be taken only as a tentative assignment.
**XYZ Coordinates from DFT optimized structures**

1  S=0  b3lyp-d3/6-31+G*  SMD-acetonitrile-solvation

| Atom | Coordinates | SMD-acetonitrile-solvation |
|------|-------------|-----------------------------|
| Co   | -0.620465000 | 0.000018000 -0.470245000 |
| O    | -2.184028000 | 0.000078000 -1.448747000 |
| O    | -1.007495000 | 0.000058000 -2.276635000 |
| N    | 1.271100000  | -0.000045000 -0.233073000 |
| N    | -0.411100000 | 2.032752000 -0.287581000 |
| N    | -0.411234000 | -2.032738000 -0.287617000 |
| N    | -1.118176000 | 0.000028000 1.478278000 |
| C    | 3.956861000  | -0.000100000 0.292525000 |
| C    | 3.277987000  | -1.129740000 0.134535000 |
| C    | 3.278061000  | 1.212802000  0.134416000 |
| C    | 1.915053000  | 1.174359000  0.145560000 |
| C    | -0.826280000 | 2.390050000  1.114009000 |
| C    | 1.043826000  | 2.346198000  0.217717000 |
| C    | -1.216675000 | 2.817800000 -0.038228000 |
| C    | -1.216734000 | -2.816606000 0.217717000 |
| C    | 1.043704000  | -2.346198000 0.217717000 |
| C    | 1.914980000  | 1.174359000  0.145560000 |
| C    | -0.537481000 | -1.238237000 2.061635000 |
| C    | -2.599931000 | 0.000121000 -0.499182000 |
| C    | -0.826685000 | -2.390050000 0.217717000 |
| H    | 5.018693000  | -0.000121000 0.521601000 |
| H    | 3.792647000  | 2.164688000  0.217717000 |
| H    | -0.313189000 | 3.301846000  1.438749000 |
| H    | 0.538056000  | 1.085102000  2.173291000 |
| H    | 1.327064000  | 3.257348000  0.217717000 |
| H    | 1.183630000  | 2.533780000 -1.568755000 |
| H    | -1.035379000 | 3.892292000 -1.148360000 |
| H    | -0.943821000 | 2.511488000 -2.264209000 |
| H    | -1.035579000 | -3.892217000 -1.114962000 |
| H    | -0.943647000 | -2.511444000 -2.264390000 |
| H    | -0.313863000 | -3.301957000 1.438647000 |
| H    | 1.326809000  | -3.257378000 0.038228000 |
| H    | 1.183886000  | -2.536132000 -1.568477000 |
| H    | 3.792647000  | 2.164688000  0.217717000 |
| H    | -1.894856000 | 2.605365000  1.090772000 |
| H    | -0.958819000 | 1.439526000  3.054906000 |
| H    | -0.959143000 | -1.439578000 3.054844000 |
| H    | 0.537837000  | -1.085379000 2.173310000 |
| H    | -0.872906000 | 0.000206000  2.684041000 |
| H    | -3.020492000 | -0.877753000 1.133137000 |
| H    | -3.020321000 | 0.878173000  1.133125000 |
| H    | -2.770005000 | -2.588940000 -1.097803000 |
| H    | -1.895313000 | -2.605059000 1.090496000 |
| H    | -2.269958000 | 2.589170000 -1.097431000 |

1  S=0  b3lyp-d3/6-31+G*  gas phase

| Atom | Coordinates | Gas phase |
|------|-------------|-----------|
| Co   | -0.606567000 | 0.000024000 -0.458255000 |
| O    | -2.175529000 | 0.000010000 -1.395143000 |
| O    | -1.027442000 | 0.000050000 -2.240668000 |
| N    | 1.283544000  | -0.000046000 -0.225010000 |
| N    | -0.407728000 | 2.026557000  0.297366000 |
| N    | -1.131323000 | 0.000028000  1.493570000 |
| C    | 3.967618000  | -0.000136000 0.306877000 |
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | 3.289247000 | -1.213805000 | 0.144427000 |
| C    | 3.289335000 | 1.213576000 | 0.144424000 |
| C    | 1.926789000 | 1.174699000 | -0.139882000 |
| C    | -0.827936000 | 2.390445000 | 1.097942000 |
| C    | 1.045519000 | 2.338095000 | -0.518140000 |
| C    | -1.229038000 | 2.779674000 | -1.289090000 |
| C    | -1.229195000 | -2.779545000 | -1.289196000 |
| C    | 1.045350000 | -2.338202000 | -0.518031000 |
| C    | 1.926704000 | -1.174841000 | -0.139865000 |
| C    | -0.554283000 | 1.242812000 | 2.065745000 |
| C    | -0.554434000 | -1.242831000 | 2.065720000 |
| C    | -2.616730000 | 0.000100000 | 1.608548000 |
| C    | -0.828267000 | -2.390390000 | 1.097882000 |
| H    | 5.028918000 | -0.000178000 | 0.536714000 |
| H    | 3.811106000 | 2.162114000 | 0.223553000 |
| H    | -0.322851000 | 3.306216000 | 1.428839000 |
| H    | 0.521090000 | 1.089897000 | 2.187205000 |
| H    | 1.330497000 | 3.268602000 | -0.012749000 |
| H    | 1.176897000 | 2.496568000 | -1.593985000 |
| H    | -1.074186000 | 3.859675000 | -1.172501000 |
| H    | -0.952308000 | 2.443918000 | -2.287788000 |
| H    | -1.074469000 | -3.859562000 | -1.172595000 |
| H    | -0.952606000 | -2.443809000 | -2.287862000 |
| H    | -0.323380000 | -3.306269000 | 1.428779000 |
| H    | 1.330221000 | -3.268650000 | -0.012473000 |
| H    | 1.176792000 | -2.496874000 | -1.593837000 |
| H    | 3.810965000 | -2.162373000 | 0.223553000 |
| H    | -1.895528000 | 2.611055000 | 1.065720000 |
| H    | -0.976774000 | 1.465424000 | 3.055453000 |
| H    | -0.976945000 | -1.465400000 | 3.055428000 |
| H    | 0.520963000 | -1.090063000 | 2.187155000 |
| H    | -2.919350000 | 0.000216000 | 2.664412000 |
| H    | -3.027499000 | -0.870957000 | 1.101882000 |
| H    | -3.027499000 | 0.871075000 | 1.101701000 |
| H    | -2.275381000 | -2.516847000 | -1.139322000 |
| H    | -1.895904000 | -2.610788000 | 1.065596000 |
| H    | -2.275237000 | 2.517088000 | -1.139121000 |

1 S=1 b3lyp-d3/6-31+G* SMD-acetonitrile-solvation

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| Co   | -0.732212000 | -0.000436000 | -0.533559000 |
| O    | -2.303859000 | -0.001502000 | -1.377836000 |
| O    | -1.280481000 | -0.000869000 | -2.323098000 |
| N    | 1.258981000 | 0.000959000 | -0.311791000 |
| N    | -0.357934000 | 2.209580000 | -0.259106000 |
| N    | -0.354851000 | -2.209957000 | -0.259019000 |
| N    | -1.083978000 | -0.000833000 | 1.480052000 |
| C    | 3.963309000 | 0.002558000 | 0.222098000 |
| C    | 3.277299000 | -1.204759000 | 0.077074000 |
| C    | 3.275673000 | 1.209040000 | 0.078016000 |
| C    | 1.910566000 | 1.172964000 | -0.198309000 |
| C    | -0.762257000 | 2.442424000 | 1.154057000 |
| C    | 1.093746000 | 2.414745000 | -0.467690000 |
| C    | -1.136356000 | 3.065923000 | -1.174690000 |
| C    | -1.136342000 | -3.067526000 | -1.173642000 |
| C    | 1.096864000 | -2.412858000 | -0.469418000 |
| C    | 1.912167000 | -1.170287000 | -0.199201000 |
| C    | -0.464902000 | 1.234763000 | 2.040523000 |
| C    | -0.461640000 | -1.234805000 | 2.040490000 |
| C    | -2.551847000 | -0.002750000 | 1.719528000 

S48
| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| Co      | 0.774814 | -0.000060 | 0.346882 |
| O       | 2.607892 | -0.000263 | -1.437987 |
| O       | 1.661617 | -0.000256 | -2.398508 |
| N       | -1.292736 | 0.000122 | -1.437987 |
| N       | 0.349333 | 2.164427 | 0.212313 |
| N       | 0.960730 | 0.000054 | 1.624333 |
| C       | -3.976640 | 0.000301 | 0.346882 |
| C       | -3.291680 | 1.209249 | 0.346882 |
| C       | -3.291840 | 1.209249 | 0.346882 |
| C       | -1.933090 | 1.699020 | 0.346882 |
| C       | -0.624710 | -2.426381 | 0.346882 |
| C       | -1.077417 | -2.395231 | -0.574862 |
| C       | -1.220474 | -3.014771 | -1.055127 |
| C       | -1.220850 | 3.014516 | -1.055448 |
| C       | -1.077063 | 2.395471 | -0.574604 |
| C       | -1.932900 | 1.693270 | -0.360999 |
| C       | 0.271729 | -1.227123 | 2.102899 |
| C       | 0.272229 | 1.227300 | 2.102899 |
| C       | 2.386770 | -0.000310 | 2.018081 |
| C       | 0.625514 | 2.426350 | 1.229143 |
| C       | -5.033949 | 0.000371 | 0.346882 |
| H       | -3.794040 | -2.162444 | 0.081998 |
| H       | 0.073955 | -3.312430 | 1.574246 |
| H       | -0.803981 | -1.040231 | 2.068208 |
| H       | -1.488652 | -3.257692 | -0.035695 |
| H       | -1.109118 | -2.633909 | -1.643745 |
| H       | 1.014614 | -4.082792 | -0.892081 |
| H       | 1.053634 | -2.771069 | -2.106949 |
| H       | 1.015249 | 4.082587 | -0.892403 |
| H       | 1.053709 | 2.770827 | -2.107219 |

**1 S=2** b3lyp-d3/6-31+G* SMD-acetonitrile-solvation
|    |    |    |    |
|----|----|----|----|
| H  | 0.075233000 | 3.312652000 | 1.574131000 |
| H  | -1.488068000 | 3.257865000 | -0.035140000 |
| H  | -1.108957000 | 2.634409000 | -1.643422000 |
| H  | -3.792691000 | 2.163014000 | 0.082264000 |
| H  | 1.690183000  | -2.648859000 | 1.318195000 |
| H  | 0.537538000  | -1.441325000 | 3.148174000 |
| H  | 0.538260000  | 1.441492000  | 3.148114000 |
| H  | -0.803550000 | 1.042578000  | 2.068377000 |
| H  | 2.491891000  | -0.000415000 | 3.113402000 |
| H  | 2.883126000  | -0.881705000 | 1.608969000 |
| H  | 2.265169000  | 2.807817000  | -0.811622000 |
| H  | 1.691099000  | 2.648396000  | 1.317788000 |
| H  | 2.264777000  | -2.808277000 | -0.811064000 |
| 2  | S=0 | b3lyp-d3/6-311++G** | gas phase | RS |
| a) |     |                           |             |     |
| Co | -0.835742000 | -0.407098000 | 0.065332000 |
| O  | 1.739504000  | -0.873439000 | -0.272244000 |
| O  | 0.589788000  | -1.555901000 | 0.282313000 |
| O  | 0.416305000  | 0.972444000  | 0.024195000 |
| N  | -2.207506000 | 0.940145000  | -0.081713000 |
| N  | -0.999715000 | -0.447922000 | -1.990594000 |
| N  | -1.269514000 | -0.242532000 | 2.097864000 |
| N  | -2.158868000 | -1.976969000 | 0.055087000 |
| C  | 5.988782000  | 0.071884000  | 1.303351000 |
| C  | 6.109410000  | 0.325432000  | 1.030519000 |
| C  | 4.858078000  | -1.234487000 | 0.076532000 |
| C  | 4.740727000  | 0.653611000  | 1.092796000 |
| C  | 4.269154000  | 2.736489000  | 0.446130000 |
| C  | 2.789069000  | 1.274618000  | -0.415212000 |
| C  | 1.686464000  | 0.442632000  | 0.265399000 |
| C  | -2.758006000 | 2.836341000  | -0.325432000 |
| C  | -3.750130000 | 2.413709000  | 0.940850000 |
| C  | -3.519370000 | 2.341970000  | -1.466310000 |
| C  | -2.520517000 | 1.391244000  | -1.301773000 |
| C  | -1.927744000 | -1.574033000 | -2.338011000 |
| C  | -1.588703000 | 0.876450000  | -2.363248000 |
| C  | 0.273521000  | -0.627870000 | -2.737985000 |
| C  | -0.081121000 | -0.238259000 | 2.988779000 |
| C  | -2.034713000 | 1.031623000  | 2.283770000 |
| C  | -2.740656000 | 1.461136000  | 1.025397000 |
| C  | -2.917730000 | -1.841473000 | -1.214935000 |
| C  | -3.613771000 | -1.795510000 | 1.256986000 |
| C  | -3.351380000 | -3.306895000 | 0.106899000 |
| C  | -2.115380000 | -1.431768000 | 2.427252000 |
| H  | 1.897257000  | 0.371892000  | 1.340669000 |
| H  | 6.389922000  | -0.956106000 | -1.863906000 |
| H  | 4.419528000  | 0.062472000  | -2.227271000 |
| H  | 6.425839000  | 0.078131000  | 2.295668000 |
| H  | 7.652292000  | -0.958980000 | 0.402950000 |
| H  | 4.222962000  | 1.109393000  | 1.929950000 |
| H  | 2.581208000  | 1.243841000  | -1.489651000 |
| H  | 2.845556000  | 2.821607000  | 1.128566000 |
| H  | 3.466114000  | 3.336576000  | -0.440350000 |
| H  | 1.714368000  | 3.149510000  | -0.189218000 |
| H  | -4.943654000 | 3.572049000  | -0.422648000 |
| H  | -3.783015000 | 2.695588000  | -2.453561000 |
| H  | -2.451212000 | -1.363604000 | -3.275853000 |
| Atom | x       | y       | z       |
|------|---------|---------|---------|
| H    | -3.619066000 | -1.014622000 | -1.109137000 |
| H    | -2.050631000  | 0.837701000  | -3.354322000 |
| H    | -0.757205000  | 1.584255000  | -2.395952000 |
| H    | 0.075671000   | -0.657281000 | -3.815275000 |
| H    | 0.935754000   | 0.195445000  | -2.493717000 |
| H    | -0.387672000  | -0.263294000 | 4.040145000  |
| H    | 0.496440000   | 0.661415000  | 2.794745000  |
| H    | -2.703921000  | -1.246888000 | 3.332029000  |
| H    | -2.710728000  | 0.963210000  | 3.141723000  |
| H    | -1.305120000  | 1.815413000  | 2.499449000  |
| H    | -4.194407000  | 2.827526000  | 1.837352000  |
| H    | -1.311235000  | -2.454716000 | -2.506962000 |
| H    | -3.498953000  | -2.745699000 | -1.427696000 |
| H    | -3.584660000  | -2.703805000 | 1.478286000  |
| H    | -3.728196000  | -0.997229000 | 1.054951000  |
| H    | -2.236544000  | -4.102309000 | 0.078374000  |
| H    | -0.885977000  | -3.386306000 | 1.008723000  |
| H    | -0.790443000  | -3.404558000 | -0.720329000 |
| H    | 0.531402000   | -1.103283000 | 2.743103000  |
| H    | -1.436480000  | -2.254016000 | 2.646811000  |
| H    | 0.749756000   | -1.545712000 | -2.405396000 |

2 S=0 b3lyp-d3/6-311++G** gas phase  SS  b)

Co  -0.867117000  -0.480758000  0.130184000
O   0.440322000  -2.608932000  -0.658707000
O   -0.255725000  -2.172645000  0.533458000
O   0.668262000  -0.325854000  -0.905472000
N   -1.260733000  1.348437000  -0.353126000
N   -2.107991000  -0.909084000  -1.490943000
N   -0.041897000  0.446686000  1.807848000
N   -2.537073000  -0.690740000  1.293391000
C   4.261659000  1.696183000  -1.189597000
C   3.147007000  1.876713000  -0.127529000
C   5.219933000  0.908814000  0.872946000
C   4.408025000  -0.222207000  0.807700000
C   3.449611000  0.564015000  -1.248587000
C   3.505622000  -0.412998000  -0.247060000
C   3.467712000  -2.855269000  -0.871275000
C   2.667646000  -1.678860000  -0.280585000
C   1.328998000  -1.546933000  -1.039964000
C   -1.765507000  3.944427000  -1.030322000
C   -0.905688000  3.657982000  0.032170000
C   -2.314062000  2.909317000  -1.785169000
C   -2.015681000  1.598995000  -1.422968000
C   -3.373645000  -1.411515000  -0.875252000
C   -2.347721000  -0.376522000  -2.233080000
C   -1.626993000  -1.919490000  -2.473716000
C   1.144871000  -0.214097000  2.406368000
C   0.351649000  1.801076000  1.315470000
C   -0.659548000  2.326951000  0.337454000
C   -3.702812000  -0.616012000  0.373471000
C   -2.507190000  0.442373000  2.253516000
C   -2.548706000  -1.989695000  2.025817000
C   -1.114302000  0.527867000  2.857432000
H   1.506588000  -1.759034000  -2.107796000
H   5.911709000  1.030168000  1.699315000
H   4.478474000  -0.974824000  1.587975000
H   4.205873000  2.437603000  -1.979344000
H   5.779319000  2.756127000  -0.085114000
H   2.756562000  0.452842000  -2.072465000

SS1
H 2.401935000 -1.947763000 0.744584000
H 3.774672000 -2.636387000 -1.898548000
H 4.371168000 -3.042670000 -0.287553000
H 2.861842000 -3.764524000 -0.873560000
H -1.984323000 4.974308000 -1.286156000
H -2.939581000 3.114074000 -2.645008000
H -4.197266000 -1.371554000 -1.596521000
H -3.879220000 0.431919000 0.126567000
H -3.367020000 0.406793000 -2.630396000
H -1.984323000 1.444604000 -1.286156000
H -3.764524000 2.487610000 2.146988000
H -4.371168000 1.667329000 0.750516000
H -2.636387000 4.448907000 0.596075000
H -2.372168000 -2.050441000 -3.266671000
H -0.688399000 -1.571889000 -2.895725000
H 1.397558000 0.254173000 3.363763000
H 1.983453000 1.729024000 2.146988000
H -1.941422000 -2.856806000 -1.960341000

2 S=0
b3lyp-d3/6-311++G** gas phase SS c)

Co -0.717013000 -0.027014000 -0.091639000
O 0.641227000 -1.453745000 -1.861106000
O 1.311455000 -0.128741000 -0.055681000
O -0.614397000 -0.729964000 -1.800998000
N -2.627162000 -0.022838000 -0.281371000
N -1.068163000 -1.801650000 0.854626000
N -0.896238000 1.918497000 -0.788588000
N -0.737422000 0.802462000 1.796763000
C 5.266927000 1.533618000 -0.145992000
C 5.586143000 1.200731000 1.170275000
C 5.064323000 0.034589000 1.727410000
C 4.224465000 -0.784401000 0.973862000
C 4.430447000 0.708341000 -0.895104000
C 3.893072000 -0.460922000 -0.344782000
C 3.480538000 -1.779949000 -2.495835000
C 2.939556000 -1.331947000 -1.133537000
C 1.603496000 -0.569855000 -1.285910000
C -5.345516000 -0.032732000 -0.533519000
C -4.613018000 1.079439000 -0.947847000
C -4.687946000 -1.166318000 -0.052884000
C -3.303318000 -1.132154000 0.043998000
C -1.113106000 -1.545557000 2.328453000
C -2.398227000 -2.291948000 0.351600000
C -0.060272000 -2.896381000 0.609624000
C 0.115121000 2.301531000 -1.806058000
C -2.262650000 2.045010000 -1.390529000
C -3.229012000 1.049020000 -0.823232000
C -1.562197000 -0.120530000 2.612850000
C -1.352839000 2.143083000 1.640124000
C 0.628407000 0.933200000 2.390054000

SS2
|     |     |     |
|-----|-----|-----|
| C   | -0.749459000 | 2.801437000 | 0.410596000 |
| H   | 1.744767000  | 0.262998000  | -1.990944000 |
| H   | 5.319066000  | -0.242276000 | 2.744639000  |
| H   | 3.824667000  | -1.692449000 | 1.414376000  |
| H   | 5.679312000  | 2.431393000  | -0.593243000 |
| H   | 6.245118000  | 1.836687000  | 1.750181000  |
| H   | 4.200525000  | 0.978347000  | -1.920177000 |
| H   | 2.710853000  | -2.220533000 | -0.534932000 |
| H   | 3.661337000  | -0.926292000 | -3.154313000 |
| H   | 4.427191000  | -2.309242000 | -2.369067000 |
| H   | 2.771234000  | -2.441608000 | -2.996275000 |
| H   | -6.426908000 | -0.207724000 | -0.612412000 |
| H   | -5.236790000 | -2.058047000 | 0.222004000  |
| H   | -1.761742000 | -2.266695000 | 2.835623000  |
| H   | -2.607570000 | 0.020710000  | 2.340110000  |
| H   | -2.852445000 | -3.014543000 | 1.036468000  |
| H   | -2.214926000 | -2.791918000 | -0.602771000 |
| H   | -0.316715000 | -3.796187000 | 1.179569000  |
| H   | -0.017766000 | -3.105489000 | -0.454473000 |
| H   | -0.048449000 | 3.330864000  | -2.143354000 |
| H   | 0.037517000  | 1.608095000  | -2.640225000 |
| H   | -1.202295000 | 3.781082000  | 0.225349000  |
| H   | -2.631274000 | 3.072142000  | -1.313500000 |
| H   | -2.169638000 | 1.805646000  | -2.453271000 |
| H   | -5.103126000 | 1.945706000  | -1.373970000 |
| H   | -0.106049000 | -1.696366000 | 2.711604000  |
| H   | -1.465819000 | 0.098398000  | 3.682458000  |
| H   | -1.187684000 | 2.764071000  | 2.527429000  |
| H   | -2.429575000 | 2.016358000  | 1.521915000  |
| H   | 0.550176000  | 1.346936000  | 3.401164000  |
| H   | 1.249082000  | 1.563559000  | 1.763166000  |
| H   | 1.122769000  | -0.031748000 | 2.405538000  |
| H   | 1.102240000  | 2.208376000  | -1.339249000 |
| H   | 0.317024000  | 2.958514000  | 0.559890000  |
| H   | 0.910653500  | -2.513909000 | 0.913693000  |

|     |     |     |
|-----|-----|-----|
| C   | -0.845625000 | 0.208781000 | -0.075766000 |
| O   | 1.540474000  | -0.862020000 | 0.244726000  |
| O   | 0.703304000  | 1.098438000  | -0.605903000 |
| O   | 0.256638000  | -0.899924000 | 0.906278000  |
| N   | -2.319000000 | -0.849475000 | 0.550976000  |
| N   | -1.304271000 | 1.371200000  | 1.577665000  |
| N   | -0.986687000 | -1.034633000 | -1.724545000 |
| N   | -2.032928000 | 1.515690000  | -1.145744000 |
| C   | 5.884822000  | -0.124342000 | 1.656628000  |
| C   | 6.422128000  | -1.300156000 | 1.134240000  |
| C   | 5.877926000  | -1.846678000 | -0.026017000 |
| C   | 4.803198000  | -1.220956000 | -0.655331000 |
| C   | 4.813911000  | 0.499471000  | 1.020730000  |
| C   | 4.256369000  | -0.041102000 | -0.143995000 |
| C   | 3.344781000  | 2.089242000  | -1.201666000 |
| C   | 3.078478000  | 0.621144000  | -0.835220000 |
| C   | 1.805653000  | 0.523098000  | 0.024532000  |
| C   | -4.406583000 | -2.374653000 | 1.429777000  |
| C   | -3.719574000 | -2.738117000 | 0.270474000  |
| C   | -3.985717000 | -1.274534000 | 2.177218000  |
| C   | -2.900587600 | -0.534068000 | 1.709980000  |
| C   | -2.036960000 | 2.564445000  | 1.051096000  |
| C   | -2.183411000 | 0.546312000  | 2.467836000  |
S 54

C  -0.119757000      1.819606000      2.352692000
C   0.300256000     -1.417850000     -2.364969000
C  -1.669162000     -2.268160000     -1.228343000
C  -2.650695000     -1.950730000     -0.135706000
C  -2.899082000      2.182468000     -0.140757000
C  -2.796773000      0.657117000     -2.085237000
C  -1.246469000      2.531688000     -1.900920000
C  -1.830547000    -0.318645000     -2.739977000
H   1.994322000      0.981938000     -1.006348000
H  6.290384000      -2.758913000      -0.442316000
H  4.382972000     -1.656143000     -1.557488000
H   6.304461000      0.310449000      2.556959000
H   7.258670000     -1.783377000      1.625230000
H   4.415396000      1.418352000      1.437313000
H   2.869499000      2.166811000     -1.822391000
H   2.495322000      2.505892000     -1.745798000
H  -5.249843000     -2.965235000      1.766395000
H  -4.470812000    -1.011835000     -3.108440000
H  -2.637904000     -3.027585000     -1.556519000
H  -2.862741000     -3.027585000     -1.556519000
H   -1.531488000     -0.037293000      3.178540000
H   -0.428294000      2.412464000      3.220551000
H   0.434234000      0.937976000      2.666524000
H   0.112377000    -2.046412000     -3.242428000
H   0.917388000    -1.935010000     -1.637126000
H  -2.369811000    -1.039444000     -3.362548000
H  -2.117842000     -2.832523000     -2.051613000
H  -0.896310000     -2.887825000     -0.766473000
H  -3.996675000    -3.621154000     -0.291130000
H  -1.284028000     -3.289997000      0.747912000
H  -3.387636000     -3.068590000     -0.560722000
H  -3.302695000     -1.256452000     -2.850970000
H  -3.563448000     -0.127414000     -1.521388000
H   -1.923533000      3.170086000     -2.477889000
H   -0.533674000      2.038214000     -2.551738000
H   -0.654298000      3.125183000     -0.766473000
H   0.816375000    -0.505296000     -2.651966000
H  -1.150227000      0.224520000     -3.395221000
H   0.510661000      2.416172000     -1.697721000

3  S=0  b3lyp-d3/6-311++G**  gas phase
Co   0.493315000      0.000016000      0.091454000
O  -1.559925000    -0.001677000     -1.692823000
O  -1.362044000      0.001031000      0.529392000
O  -0.107480000    -0.000872000     -1.669279000
N   2.241579000    -0.000629000     -0.627422000
N   0.742419000      2.026949000      0.129477000
N   0.741587000    -2.026602000      0.132332000
N   1.082612000      0.001551000      2.020820000
C  -2.102266000    -0.000141000     -0.498610000
C   4.770038000    -0.001899000     -1.649867000
C   4.112270000     -1.212190000     -1.425236000
C   4.111668000      2.088855000     -1.427152000
C   2.817939000      1.173977000     -0.926731000
C   1.119685000      2.389365000      1.541639000
C   1.870270000      2.332755000     -0.817934000
C  -0.458755000      2.804577000     -0.290836000

SS4
C  -0.459872000  -2.804493000  -0.286709000
C  1.869283000  -2.334113000  -0.814774000
C  2.817493000  -1.175917000  -0.924967000
C  1.884814000  1.249007000  2.194565000
C  1.884222000  -1.246034000  2.196419000
C  -0.060768000  0.002631000  2.986893000
C  1.118808000  -2.387148000  1.545048000
H  5.783926000  -0.002361000  -2.032262000
H  4.585744000  2.154479000  -1.638159000
H  1.702409000  3.313859000  1.554708000
H  2.855047000  1.102686000  1.721610000
H  2.364653000  3.267194000  -0.542212000
H  1.432411000  2.466876000  -1.809928000
H  -0.240126000  3.876088000  -0.283373000
H  -0.741066000  2.493078000  -1.294309000
H  -0.241680000  -3.876078000  -0.277202000
H  -0.742002000  -2.494840000  -1.290796000
H  1.701281000  -3.311781000  1.559355000
H  2.363158000  -3.268500000  -0.537928000
H  1.4313282000  -2.469023000  -1.806680000
H  4.585029000  -2.158259000  -1.654555000
H  0.196786000  2.587406000  2.083216000
H  2.059065000  1.457426000  3.254187000
H  2.058291000  -1.452985000  3.256353000
H  2.854571000  -1.100854000  1.723353000
H  0.328272000  0.003307000  4.008291000
H  -0.686517000  -0.869386000  2.829545000
H  -0.685933000  0.874843000  2.828237000
H  -1.276099000  -2.596748000  0.401626000
H  0.195860000  -2.584212000  2.086873000
H  -1.275018000  2.598436000  0.397937000
C  -3.553367000  -0.000180000  -0.439228000
C  -4.175636000  0.000577000  0.822296000
C  -4.326643000  -0.000944000  -1.615724000
C  -5.560843000  0.000558000  0.902675000
C  -5.710551000  -0.000961000  -1.520722000
C  -6.326572000  -0.000218000  -0.266490000
H  -3.572724000  0.001179000  1.720876000
H  -3.846163000  -0.001474000  -2.585786000
H  -6.047837000  0.001133000  1.869988000
H  -6.312373000  -0.001528000  -2.420977000
H  -7.408233000  -0.000233000  -0.199722000

2-acetaldehyde  S=0  b3lyp-d3/6-31+G*  gas phase
Co  0.378992000  0.083410000  -0.060320000
O  2.025684000  -0.520808000  -2.029744000
O  2.219038000  0.293202000  0.116360000
O  0.664353000  -0.039402000  -1.877844000
N  -1.483828000  -0.173333000  -0.432366000
N  0.331781000  -1.951303000  0.291746000
N  -0.133453000  2.093568000  -0.184968000
N  0.101592000  0.291743000  1.974356000
C  2.805516000  0.295747000  -1.152334000
C  -4.142120000  -0.569680000  -0.950607000
C  -3.618600000  0.726617000  -0.942681000
C  -3.296139000  -1.668929000  -0.764980000
C  -1.947122000  -1.429690000  -0.521928000
C  0.127619000  -2.139525000  1.769184000
C  -0.845757000  -2.453074000  -0.482060000
C  1.540590000  -2.717544000  -0.117866000
|   | X     | Y     | Z     |
|---|-------|-------|-------|
| C | 0.824365000 | 2.931245000 | -0.952538000 |
| C | -1.476582000 | 2.166785000 | -0.849435000 |
| C | -2.256592000 | 0.887953000 | -0.696327000 |
| C | -0.591948000 | -0.952563000 | 2.395389000 |
| C | -0.738873000 | 1.504960000 | 2.148692000 |
| C | 1.379934000 | 0.444322000 | 2.727123000 |
| C | -0.203069000 | 2.589088000 | 1.225773000 |
| H | 2.820564000 | 1.310651000 | -1.580688000 |
| H | -5.201332000 | -0.725369000 | -1.132585000 |
| H | -3.673666000 | -2.684718000 | -0.824651000 |
| H | -0.418754000 | -3.071158000 | 1.961856000 |
| H | -1.628613000 | -0.900355000 | 2.057647000 |
| H | -1.181235000 | -3.427729000 | -0.106796000 |
| H | -0.508589000 | -2.579571000 | -1.516257000 |
| H | 1.419817000 | -3.777658000 | 0.141913000 |
| H | 1.695536000 | -2.590897000 | -1.186804000 |
| H | 0.477855000 | 3.972390000 | -0.992588000 |
| H | 0.912719000 | 2.517325000 | -1.956728000 |
| H | -0.815634000 | 3.498007000 | 1.285858000 |
| H | -2.035105000 | 3.046206000 | -0.506242000 |
| H | -1.298731000 | 2.290483000 | -1.922627000 |
| H | -4.248658000 | 1.587692000 | -1.142181000 |
| H | 1.115747000 | -2.251012000 | 2.216660000 |
| H | -0.602768000 | -1.051158000 | 3.489708000 |
| H | -0.731654000 | 1.847789000 | 3.192056000 |
| H | -1.770282000 | 1.251854000 | 1.890897000 |
| H | 1.170878000 | 0.494852000 | 3.803939000 |
| H | 1.899369000 | 1.339993000 | 2.397357000 |
| H | 2.044268000 | -0.385904000 | 2.502677000 |
| H | 1.795400000 | 2.880077000 | -0.461034000 |
| H | 0.812195000 | 2.860666000 | 1.517260000 |
| H | 2.399252000 | -2.291754000 | 0.399427000 |
| C | 4.213079000 | -0.280619000 | -1.128943000 |
| H | 4.830676000 | 0.315822000 | -0.449883000 |
| H | 4.198992000 | -1.314530000 | -0.771781000 |
| H | 4.658547000 | -0.252472000 | -2.128510000 |

2-acetaldehyde  S=0  b3lyp-d3/6-31+G*  SMD-acetonitrile-solvation

| Co | 0.382649000 | 0.077010000 | -0.056838000 |
| O | 2.096726000 | -0.429700000 | -2.052980000 |
| O | 2.241548000 | 0.246645000 | 0.148964000 |
| O | 0.709324000 | 0.002151000 | -1.894202000 |
| N | -1.470989000 | -0.161917000 | -0.466766000 |
| N | 0.319281000 | -1.971421000 | 0.243997000 |
| N | -0.126349000 | 2.087764000 | -0.128425000 |
| N | 0.063651000 | 0.233586000 | 1.960673000 |
| C | 2.838819000 | 0.338468000 | -1.096480000 |
| C | -4.136527000 | -0.502149000 | -0.993682000 |
| C | -3.582438000 | 0.781359000 | -1.002509000 |
| C | -3.320055000 | -1.616699000 | -0.779684000 |
| C | -1.966330000 | -1.407041000 | -0.532554000 |
| C | 0.202883000 | -2.182600000 | 1.727929000 |
| C | -0.911407000 | -2.470591000 | -0.451880000 |
| C | 1.488049000 | -2.742909000 | -0.245508000 |
| C | 0.861811000 | 2.977570000 | -0.782034000 |
| C | -1.419471000 | 2.176249000 | -0.882842000 |
| C | -2.220557000 | 0.914655000 | -0.748237000 |
| C | -0.569950000 | -1.048295000 | 2.373415000 |
| C | -0.840855000 | 1.400696000 | 2.146304000 |
| C | 1.313673000 | 0.444229000 | 2.743853000 |
[(L)Co\((\text{OO})(\text{acetaldehyde})\)]^{+} S=1  b3lyp-d3/6-31+G*  SMD-acetonitrile-solvation

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| C    | -0.317661000 | 2.539605000 | 1.291432000 |
| H    | 2.852012000  | 1.380529000 | -1.461572000 |
| H    | -5.198747000 | -0.635456000 | -1.177887000 |
| H    | -3.717519000 | -2.625919000 | -0.814159000 |
| H    | -0.274061000 | -3.148100000 | 1.931218000 |
| H    | -1.610421000 | -1.043794000 | 2.045297000 |
| H    | -1.277976000 | -3.389790000 | 0.016926000 |
| H    | -0.628790000 | -2.711050000 | -1.481504000 |
| H    | 1.358696000  | -3.806551000 | 0.003904000 |
| H    | 1.582686000  | -4.014209000 | -0.773728000 |
| H    | 1.010053000  | 2.642892000  | -1.808248000 |
| H    | -0.995969000 | 3.399431000  | 1.322539000 |
| H    | -1.983242000 | 3.065497000  | -0.581804000 |
| C    | 4.256261000  | -0.222246000 | -1.089807000 |
| O    | 0.618302000  | 0.618302000  | -2.079549000 |
| O    | 0.213208000  | 0.213208000  | -2.163213000 |
| N    | -1.484967000 | -0.079318000 | -0.329501000 |
| N    | 0.055337000  | 2.270462000  | -0.203326000 |
| C    | 3.249843000  | -0.243807000 | -0.999062000 |
| C    | 1.434794000  | 0.334310000  | -0.370946000 |
| C    | 2.866266000  | 0.905452000  | 1.745935000  |
| C    | -0.262213000 | -0.212246000 | -0.789549000 |
| C    | 1.272342000  | -0.131238000 | -2.079347000 |

S57
TS to [(L)Co\textsuperscript{II}(OO)(acetaldehyde)]\textsuperscript{+}  S=1  b3lyp-d3/6-31+G*  SMD-acetonitrile-solvation

Co  -0.289324000  0.209860000  -0.261185000
O  -2.109900000  1.266094000  -1.719941000
O  -3.416730000  -0.488437000  0.614324000
O  -1.339484000  0.189186000  -1.813340000
N  1.654924000  -0.302214000  -0.669528000
N  0.668590000  2.210557000  -0.082650000
N  -0.337020000  -2.055283000  -0.026447000
N  -0.030310000  0.160192000  1.870490000
C  -4.103658000  0.266749000  -0.058093000
C  -4.343834000  -0.891500000  -0.730228000
C  3.403381000  -1.915357000  -0.606224000
C  3.916224000  0.438291000  -0.811481000
C  2.549269000  0.697321000  -0.773161000
C  0.950213000  2.018289000  1.372660000
C  1.939761000  2.079455000  -0.875608000
C  -0.125171000  3.331464000  -0.617899000
C  -1.475363000  -2.677820000  -0.779648000
C  0.937363000  -2.607137000  -0.498671000
C  2.048025000  -1.580082000  -0.577047000
C  1.114951000  1.076896000  2.124646000
C  0.297650000  -1.249110000  2.236247000
C  -1.239110000  0.623694000  2.600629000
C  -0.555945000  -2.226871000  1.434281000
H  -4.167574000  1.338165000  0.216718000
H  5.404939000  -1.124897000  -0.751712000
H  4.629302000  1.252930000  -0.892578000
H  1.842691000  3.023868000  1.531702000
H  2.028123000  0.573370000  1.801651000
H  2.670128000  2.852329000  -0.596556000
H  1.673972000  2.247557000  -1.925517000
H  4.049425000  4.288353000  -0.536910000
H  -0.377288000  3.131139000  -1.661671000
H  -1.482361000  -3.770534000  -0.651649000
H  -1.369160000  -2.429918000  -1.837306000

S58
TS addition from [(L)Co\((\text{OO})(\text{acetaldehyde})\)]\(^+\) S=1  b3lyp-d3/6-31+G* SMD-acetonitrile-solvation

Co  0.4940000  -0.047104000  -0.174176000
O   1.716301000  0.300859000  -2.675374000
O   2.370075000  -0.379849000  -0.044393000
O   0.576704000  -0.011352000  -2.071446000
N  -1.483681000  0.028838000  -0.470419000
N  -0.028915000  -2.275905000  -0.029719000
N   0.076469000  2.243962000  0.146560000
N  -0.183719000  -0.087163000  1.879758000
C   3.225188000  0.342628000  -0.573650000
C  -4.226431000  0.132276000  -0.762976000
C  -3.488192000  1.311683000  -0.698103000
C  -3.571659000  -1.097620000  -0.707733000
C  -2.183302000  -1.115870000  -0.561848000
C   0.012767000  -2.526723000  1.428020000
C  -1.390767000  -2.406156000  -0.584965000
C   0.916216000  -3.150225000  -0.742148000
C   1.064102000  3.217959000  -0.350499000
C  -1.200737000  2.438714000  -0.570113000
C  -2.098215000  1.223714000  -0.557349000
C  -0.545901000  -1.346048000  2.215548000
C  -0.624703000  1.106848000  2.263167000
C   1.479012000  -0.057139000  2.609241000
C  -0.078745000  2.376961000  1.615970000
H   2.972635000  1.365639000  -0.861475000
H  -5.307596000  0.172821000  -0.862571000
H  -4.120241000  -2.033122000  -0.756470000
H  -0.548627000  -3.437007000  1.690728000
H  -1.601189000  -1.194686000  1.978409000
H  -1.957372000  -3.203448000  -0.082425000
H  -1.300346000  -2.697984000  -1.637260000
H   0.655847000  -4.215541000  -0.633153000
H   0.917442000  -2.887247000  -1.803022000
H   0.721834000  4.256484000  -0.209414000
H   1.240366000  3.044089000  -1.415486000
H  -0.740509000  3.220165000  1.867426000
H  -1.744704000  3.315814000  -0.188842000
H  -0.958472000  2.639752000  -1.620035000
H  -3.958332000  2.285478000  -0.751053000
H   1.056597000  -2.697710000  1.701296000
H  -0.476275000  -1.548291000  3.292861000
[(L)CoII(dioxyl)]\(^+\) S=1 b3lyp-d3/6-31+G* SMD-acetonitrile-solvation

H: -0.625236000  1.226558000  3.355367000
H: -1.655656000  0.930337000  1.954987000
H:  1.298295000 -0.020932000  3.692089000
H:  2.056580000  0.816263000  2.307807000
H:  2.061490000 -0.944203000  2.368060000
H:  2.005440000  3.086454000  0.188288000
H:  0.906085000  2.606138000  2.028885000
H:  1.920577000 -2.983137000 -0.346767000
C:  4.628571000 -0.102755000 -0.768560000
H:  4.763005000 -1.149838000 -0.484538000
H:  4.909933000  0.047555000 -1.819290000
H:  5.290668000  0.540318000 -1.107934000

Co: -0.626976000  0.000084000 -0.574742000
O:  2.329986000  0.000326000 -1.098905000
O:  0.110833000  0.000038000  2.286261000
N:  1.253972000 -0.000273000 -0.133446000
N: -0.415099000  2.031645000 -0.363544000
N: -0.415921000 -2.031546000 -0.363576000
N:  1.230356000  0.000285000  1.398617000
C:  3.890494000 -0.000652000  0.565790000
C:  3.227747000 -1.214525000  0.354328000
C:  3.228243000  1.213409000  0.353793000
C:  1.888300000 -0.010275000 -0.021448000
C:  2.056580000  0.816263000  2.307807000
C:  1.153723000  2.799227000 -1.393716000
C: -0.923108000  2.384757000  1.006193000
C:  1.050722000  2.338178000 -0.472612000
C: -1.154302000 -2.798758000 -1.394211000
C:  1.049848000 -2.338804000 -0.471705000
C:  1.887807000 -1.175607000 -0.020945000
C: -0.664910000  1.247040000  1.982938000
C: -0.665821000 -1.247102000  1.982867000
C: -2.711122000  0.001047000  1.570624000
C: -0.925050000 -2.384380000 -1.021448000
C:  4.933065000 -0.000797000  0.870521000
H:  3.739096000  2.164472000  0.463618000
H: -0.452132000  3.310505000  1.354175000
H:  0.404061000  1.099880000  2.146936000
H:  1.292875000  3.264239000  0.058827000
H:  1.274592000  2.492647000 -1.532613000
H: -0.994656000  3.876076000 -1.252435000
H: -0.795851000  2.487437000 -2.375681000
H: -0.995966000 -3.875687000 -1.252802000
H: -0.795641000 -2.487184000 -2.375952000
H: -0.455288000 -3.310990000  1.353895000
H:  1.291335000 -3.264621000  0.060451000
H:  1.274232000 -2.494104000 -1.531481000
H:  3.738221000 -2.165746000  0.464560000
H: -1.992890000  2.574184000  0.915506000
H: -1.126894000  1.465637000  2.953462000
H: -1.128778000 -1.465503000  2.953168000
H:  0.402785000 -1.100901000  2.147312000
H: -2.951106000  0.001511000  2.641439000
H: -3.143656000 -0.877433000  1.096880000
H: -3.142881000  0.879561000  1.096233000
H: -2.213310000 -2.555467000 -1.312337000
H: -1.994984000 -2.572637000  0.914396000
H: -2.212811000  2.556520000 -1.311151000
| (L)Co^{III}(dioxyl)\(^+\) | S=2 | \(b3\text{lyp-d3/6-31+G}^*\) | SMD-acetonitrile-solvation |
|------------------------|------|--------------------------|----------------------------|
| Co                     | -0.742678000 | 0.000126000 | -0.750924000 |
| O                      | -2.374118000 | 0.000355000 | -1.037610000 |
| O                      | -0.197923000 | 0.000088000 | -2.348677000 |
| N                      | 1.225733000 | -0.000230000 | -0.190511000 |
| N                      | -0.385904000 | 2.177482000 | -0.307301000 |
| N                      | -0.386701000 | -2.177351000 | -0.307311000 |
| N                      | -1.180216000 | 0.000230000 | 1.422285000 |
| C                      | 3.882980000 | -0.000689000 | 0.518742000 |
| C                      | 3.211451000 | -1.208392000 | 0.317055000 |
| C                      | 3.211898000 | 1.207246000 | 0.316938000 |
| C                      | 1.869936000 | 1.170411000 | -0.055485000 |
| C                      | -0.861463000 | 2.423321000 | 1.081269000 |
| C                      | 1.075489000 | 2.392304000 | -0.436487000 |
| C                      | -1.121802000 | 3.022864000 | -1.271885000 |
| C                      | -1.122790000 | -3.022475000 | -1.271979000 |
| C                      | 1.074627000 | -2.392731000 | -0.436304000 |
| C                      | 1.869502000 | -1.170722000 | -0.055380000 |
| C                      | -0.579733000 | 1.235549000 | 1.993349000 |
| C                      | -0.580338000 | -1.235298000 | 1.993333000 |
| C                      | -2.644321000 | 0.000589000 | 1.674089000 |
| C                      | -0.862538000 | -2.422996000 | 1.081195000 |
| H                      | 4.926645000 | -0.000867000 | 0.819883000 |
| H                      | 3.713443000 | 2.161936000 | 0.440359000 |
| H                      | -0.387188000 | 3.325505000 | 1.489414000 |
| H                      | 0.492638000 | 1.077668000 | 2.113748000 |
| H                      | 1.396955000 | 3.270396000 | 0.138319000 |
| H                      | 1.290127000 | 2.593185000 | -1.491605000 |
| H                      | -0.940519000 | 4.089572000 | -1.076997000 |
| H                      | -0.796375000 | 2.774114000 | -2.283872000 |
| H                      | -0.941924000 | -4.089246000 | -1.077049000 |
| H                      | -0.797141000 | -2.773862000 | -2.283929000 |
| H                      | -0.388750000 | -3.253423000 | 1.489370000 |
| H                      | 1.394839000 | -3.270817000 | 0.138648000 |
| H                      | 1.289312000 | -2.593834000 | -1.491371000 |
| H                      | 3.712643000 | -2.163256000 | 0.440563000 |
| H                      | 1.935267000 | 2.610548000 | 1.030283000 |
| H                      | 1.995632000 | 1.433314000 | 2.990130000 |
| H                      | -0.996395000 | -1.433001000 | 2.990083000 |
| H                      | 0.492096000 | -1.077999000 | 2.113821000 |
| H                      | -2.825916000 | 0.000709000 | 2.757184000 |
| H                      | -3.103519000 | -0.876889000 | 1.223698000 |
| H                      | -3.103116000 | 0.878290000 | 1.223563000 |
| H                      | -2.189559000 | -2.810235000 | -1.185083000 |
| H                      | -1.936429000 | -2.609639000 | 1.030780000 |
| H                      | -2.189838000 | 2.811020000 | -1.184852000 |

**TS to [(L)Co^{III}(dioxyl)]^+ \(S=1\)**

\(b3\text{lyp-d3/6-31+G}^*\) | SMD-acetonitrile-solvation

| Co                     | -0.686803000 | -0.000909000 | -0.630314000 |
| O                      | -2.445928000 | -0.004029000 | -1.231413000 |
| O                      | -0.747573000 | -0.001153000 | -2.333814000 |
| N                      | 1.253601000 | 0.002295000 | -0.308181000 |
| N                      | -0.376909000 | 2.195391000 | -0.242878000 |
| N                      | -0.369577000 | -2.196388000 | -0.242646000 |
| N                      | -1.126005000 | -0.001983000 | 1.415402000 |
| C                      | 3.927282000 | 0.005982000 | 0.346245000 |
| C                      | 3.249191000 | -1.202300000 | 0.174615000 |
| C                      | 3.245302000 | 1.212324000 | 0.176780000 |
| C                      | 1.893618000 | 1.176814000 | -0.157670000 |
| C                      | -0.807761000 | 2.441589000 | 1.156536000 |

S61
TS to [(L)Co\textsuperscript{III}(dioxyl)]\textsuperscript{+} S=2 b3lyp-d3/6-31+G* SMD-acetonitrile-solvation
TS C-insertion S=2  b3lyp-d3/6-31+G*  SMAD-acetonitrile-solvation

Co  
   -0.451528000  
   -0.019841000  
   -0.222784000
O  
   -3.255914000  
   -0.892749000  
   -1.972164000
O  
   -2.112121000  
   -0.005385000  
   0.236611000
O  
   -0.664678000  
   -0.094322000  
   -1.856187000
N  
   1.532879000  
   0.008298000  
   -0.562360000
N  
   -0.012809000  
   2.180109000  
   -0.056216000
N  
   0.065249000  
   -2.169451000  
   0.137990000
N  
   0.042547000  
   0.084481000  
   1.925041000
C  
   -3.587103000  
   -0.503315000  
   -0.835713000
C  
   4.238184000  
   0.037140000  
   -1.034012000
C  
   3.567744000  
   -1.177958000  
   -0.878689000
C  
   3.522930000  
   1.235628000  
   -0.987493000
C  
   2.150057000  
   1.184510000  
   -0.752969000
C  
   0.148627000  
   2.489422000  
   1.390191000
C  
   1.245703000  
   2.388322000  
   -0.811714000
C  
   -1.110774000  
   2.976567000  
   -0.645020000
C  
   -1.000310000  
   -3.048961000  
   -0.390977000
C  
   1.334898000  
   -2.394285000  
   -0.595829000
C  
   2.193376000  
   -1.157397000  
   -0.653918000
C  
   0.814498000  
   1.340160000  
   2.134039000
C  
   0.849962000  
   -1.123905000  
   2.251970000
C  
   -1.174017000  
   0.107067000  
   2.779029000
C  
   0.227717000  
   2.353719000  
   1.605182000
H  
   -3.773079000  
   -1.262020000  
   -0.044571000
H  
   5.311435000  
   0.049533000  
   -1.201066000
H  
   4.012465000  
   2.194275000  
   -1.126901000
H  
   0.735268000  
   3.408515000  
   1.518604000
H  
   1.838454000  
   1.183191000  
   1.779466000
H  
   1.767901000  
   3.289935000  
   -0.468494000
H  
   0.981988000  
   2.541539000  
   -1.863693000
H  
   -0.884418000  
   4.051180000  
   -0.596350000
H  
   -1.249472000  
   2.677632000  
   -1.685745000
H  
   -0.723112000  
   -4.106688000  
   -0.277939000
H  
   -1.165674000  
   -2.812534000  
   -1.442539000
H  
   0.843496000  
   -3.238799000  
   1.812307000
H  
   1.889089000  
   -3.240296000  
   -0.171540000
H  
   1.079891000  
   -2.652883000  
   -1.629101000

S63
int C-insertion  S=2  b3lyp-d3/6-31+G*  SMD-acetonitrile-solvation

Co  0.414186000  0.045942000  -0.298306000
O  4.272429000  -0.875238000  -0.350647000
O  2.244753000  0.088575000  0.115426000
O  0.631363000  -1.914148000  -0.549005000
N  1.554617000  -0.034148000  -0.549005000
N  0.065866000  2.184859000  -0.061925000
N  0.124925000  2.215234000  0.075938000
N  0.049528000  -0.035751000  1.857800000
C  3.212677000  -0.209757000  -0.821214000
C  4.279740000  -0.146235000  -0.854454000
C  3.637624000  1.089043000  -0.748125000
C  3.528693000  -1.323329000  -0.835652000
C  2.146784000  -1.231856000  -0.689077000
C  0.031537000  -2.462737000  1.395075000
C  -1.219950000  -2.419701000  -0.759862000
C  1.136172000  -2.996060000  -0.670937000
C  -0.870149000  3.144161000  -0.494741000
C  -1.436140000  2.381993000  -0.594569000
C  -2.252035000  1.112562000  -0.605664000
C  -0.682408000  -1.304876000  2.137348000
C  -0.777595000  1.151466000  2.220181000
C  1.308285000  -0.011921000  2.650315000
C  -0.225137000  2.399122000  1.546912000
H  2.790046000  -0.830046000  -1.652296000
H  -3.360220000  -0.191425000  -0.956965000
H  -3.998201000  -2.297304000  -0.930556000
H  -0.598794000  -3.386544000  1.573861000
H  -1.720682000  -1.178746000  1.827934000
H  -1.717746000  -3.323134000  -0.384802000
H  -0.997386000  -2.584583000  -1.819832000
H  0.919769000  -4.073748000  -0.574522000
H  1.227014000  -2.742214000  -1.728364000
H  0.586872000  4.190986000  -0.310637000
H  0.944135000  2.971397000  -1.569873000
H  -0.858170000  3.264909000  1.785527000
H  -2.086590000  3.206398000  -0.150717000
H  -1.244437000  2.643703000  -1.640919000
H  -4.193446000  2.020977000  -0.773506000
H  0.982163000  -2.623085000  1.765819000
H  -0.683715000  -1.507698000  3.216111000
H  -0.783943000  1.286563000  3.309160000
H  -1.806878000  0.965083000  1.909549000
H  1.059393000  -0.050063000  3.719014000

S64
TS O-O bond formation

S=2  b3lyp-d3/6-31+G*  SMD-acetonitrile-solvation
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| O    | -1.242260000 | -0.274927000 | -0.000003000 |
| C    | -0.223636000 | 0.399736000 | 0.000007000 |
| H    | -0.298313000 | 1.506440000 | 0.000019000 |
| C    | 1.167284000  | -0.152333000 | 0.000001000 |
| H    | 1.703815000  | 0.227584000  | 0.880969000 |
| H    | 1.167068000  | -1.246267000 | 0.000232000 |
| H    | 1.703624000  | 0.227242000  | -0.881242000 |

**acetaldehyde**  S=0  b3lyp-d3/6-31+G*  SMD-acetonitrile-solvation
## Optimized Cartesian Coordinate

\[ [\text{Co}^{3+}(\text{Me}_2\text{TPADP})(\text{O}_2)]^+ \] (1)

| 1 | 1 |
|---|---|
| Co | 0.70464 | 1.19478 | 0.95561 |
| O | 0.49650 | -0.56450 | 1.42931 |
| O | -0.10818 | -0.24306 | 0.16195 |
| N | 0.43339 | 2.76715 | -0.28098 |
| N | -0.92096 | 1.88322 | 1.90917 |
| N | 2.54352 | 0.97218 | 0.08806 |
| N | 1.68541 | 2.10153 | 2.31153 |
| C | -1.43325 | 3.09435 | 1.25578 |
| C | -0.36151 | 2.36786 | -1.47670 |
| C | -0.30421 | 3.79054 | 0.50776 |
| C | 1.79232 | 3.21159 | -0.69462 |
| C | 1.01845 | 2.65900 | 3.33623 |
| C | -0.43458 | 2.26700 | 3.36045 |
| C | -2.02206 | 0.89263 | 2.13663 |
| C | 2.80394 | -0.38901 | -0.45519 |
| C | 3.57895 | 1.28076 | 1.13671 |
| C | 2.61349 | 1.97486 | -1.03111 |
| C | 0.30237 | 2.16386 | 2.22205 |
| C | 3.76230 | 2.89406 | 3.14813 |
| C | 1.69141 | 3.40547 | 4.29757 |
| C | 3.07841 | 3.53467 | 4.18428 |
| H | 2.03085 | -0.61605 | -1.19489 |
| H | -2.19852 | 2.75233 | 0.55783 |
| H | -2.36254 | 0.60454 | 1.14344 |
| H | 0.14951 | 1.57355 | -2.01785 |
| H | -1.33066 | 1.97930 | -1.16900 |
| H | -0.50443 | 3.23204 | -2.13989 |
| H | 0.39699 | 4.25781 | 1.20243 |
| H | -0.70497 | 4.57917 | -0.14080 |
| H | 1.74360 | 3.88653 | -1.55784 |
| H | 2.22215 | 1.48881 | -1.92539 |
| H | 1.14904 | 3.86516 | 5.11626 |
| H | -0.52094 | 3.78837 | 3.99528 |
| H | -1.07249 | 3.04172 | 3.79769 |
| H | -1.92112 | 3.78519 | 1.95145 |
| H | -1.62145 | 0.00886 | 2.63072 |
| H | -2.84870 | 1.32064 | 2.71552 |
| H | 2.71503 | -1.10525 | 0.36008 |
| H | 3.80153 | -0.43753 | -0.90688 |
| H | 3.86243 | 0.33178 | 1.60369 |
| H | 4.48207 | 1.69731 | 0.67912 |
| H | 2.24007 | 3.76671 | 1.13299 |
| H | 3.65457 | 2.24310 | -1.24071 |
| H | 4.82419 | 2.95308 | 3.06685 |
| H | 3.62832 | 1.11916 | 4.91474 |

\[ [\text{Co}^{2+}(\text{Me}_2\text{TPADP})(\text{O}_2)]^+ \] (2)

| 1 | 1 |
|---|---|
| Co | 0.966772 | 0.747683 | 1.314997 |
| O | 1.262997 | -0.351840 | 2.797516 |
| O | 0.250712 | -0.742901 | 0.488022 |
| O | 0.830666 | -1.899391 | 1.165666 |
| N | 0.668917 | 1.876399 | -0.367599 |
| N | -0.858667 | 1.518294 | 1.968968 |
| N | 2.933303 | 0.596145 | 0.662791 |
| N | 1.674206 | 2.207139 | 2.344517 |

[S67]
| C    | X    | Y    | Z    |
|------|------|------|------|
| H -2.13713 | -0.16678 | 2.49555 | H 0.36950 | 2.67933 | -2.51505 |
| H -2.26018 | 3.29092 | 0.91641 | H -0.66065 | 1.39156 | -1.83515 |
| H -1.71082 | 3.05903 | 3.08341 | H 1.02950 | 1.05495 | -2.18328 |
| H -1.31988 | 1.47028 | 3.73111 | H -2.49508 | 0.07488 | 0.77344 |
| H -0.02793 | 4.18002 | 4.62248 | H -2.02463 | 1.99682 | -0.25460 |
| H 3.04927 | 1.10876 | -1.38336 | H 3.02575 | -0.97381 | -0.62009 |
| H 2.25989 | 3.44891 | -1.30233 | H -0.55752 | 3.94774 | -0.73557 |
| H 0.18331 | 3.80858 | 0.85494 |     |     |     |
References

S1. Shin, B.; Sutherlin, K. D.; Ohta, T.; Ogura, T.; Solomon, E. I.; Cho, J. Reactivity of a Cobalt(III) – Hydroperoxo Complex in Electrophilic Reactions. *Inorg. Chem.* **2016**, *55*, 12391-12399.

S2. Sheldrick, G. M. *SHELXTL/PC*. Version 6.12 for Windows XP; Bruker AXS Inc.; Madison, WI, 2001.

S3. Jašík, J.; Žabka, J.; Roithová, J.; Gerlich, D. Infrared Spectroscopy of Trapped Molecular Dications Below 4 K. *Int. J. Mass Spectrom.* **2013**, *354*, 204-210.

S4. Jašík, J.; Gerlich, D.; Roithová, J. *J. Phys. Chem. A* **2015**, *119*, 2532-2542.

S5. Gerlich, D.; Jašík, J.; Andris, E.; Navrátil, R.; Roithová, J. Collisions of FeO$^+$ with H$_2$ and He in a Cryogenic Ion Trap. *ChemPhysChem* **2016**, *17*, 3723-3739.

S6. Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133-A1138.

S7. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O$^+$; ; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision D.01; Gaussian, Inc.; Wallingford, CT, 2009.

S8. Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648-5652.

S9. Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. J. Energies, Structures, and Electronic Properties of Molecules in Solution with the C-PCM Solvation Model. *J. Comput. Chem.*
S10. Fukuzumi, S.; Kondo, Y.; Mochizuki, S.; Tanaka, T. Complex Formation Between NADH Model Compounds and Metalloporphyrins. *J. Chem. Soc., Perkin Trans.* 1989, 2, 1753-1761.

S11. Furutachi, H.; Hashimoto, K.; Nagatomo, S.; Endo, T.; Fujinami, S.; Watanabe, Y.; Kitagawa, T.; Suzuki, M. Reversible O-O Bond Cleavage and Formation of a Peroxo Moiety of a Peroxocarbonate Ligand Mediated by an Iron(III) Complex. *J. Am. Chem. Soc.* 2005, 127, 4550-4551.

S12. Zhao, R.; Guo, J.; Zhang, C.; Lu, Y.; Dagnaw, W. M.; Wang, Z.-X. DFT Mechanistic Insight into the Dioxygenase-like Reactivity of a Co$^{III}$-peroxo Complex: O-O Bond Cleavage via a [1,3]-Sigmatropic Rearrangement-like Mechanism. *Inorg. Chem.* 2020, 59, 2051-2061.

S13. Cho, D.; Choi, S.; Cho, J.; Baik, M.-H. Peroxocobalt(III) Species Activates Nitriles via a Superoxocobalt(II) Diradical State. *Dalton Trans.*, 2020, 49, 2819-2826.