Supporting Information

Umpolung in a Pair of Cobalt(III) Terminal Imido/Imidyl Complexes
W. Mao, D. Fehn, F. W. Heinemann, A. Scheurer, M. van Gastel, S. A. V. Jannuzzi, S. DeBeer*, D. Munz*, K. Meyer*
Table of Contents
Experimental Procedures .................................................................................................................. S3
General Methods .......................................................................................................................... S3
Synthesis and Characterization .................................................................................................. S5
Reactivity Studies ......................................................................................................................... S23
Kinetic Experiments ................................................................................................................... S31
ENDOR Details ............................................................................................................................ S40
XAS Details .................................................................................................................................. S41
Crystallographic Details .............................................................................................................. S45
Computational Details ................................................................................................................ S53
References .................................................................................................................................... S92
Experimental Procedures

General Methods

If not stated otherwise, all complex syntheses were carried out inside an MBraun inert-gas glovebox containing an atmosphere of dinitrogen. The used solvents were purified using a two-column solid-state solvent purification system (JC Meyer Solvent System, Irvine, CA, www.jcmeyer-solventsystems.com), transferred to the glovebox without exposure to air and stored over activated molecular sieves.

Elemental analysis results were obtained using Euro EA 3000 (Euro Vector) and EA 1108 (Carlo-Erba) elemental analyzers in the Chair of Inorganic and General Chemistry at the Friedrich-Alexander-University Erlangen-Nürnberg (FAU). Commercial laboratories refuse samples that contain fluorine as it destroys the modern elemental analyzers. Besides this practical problem, fluorine often causes substantial variations from the expected masses.[1]

Infrared vibrational spectra were recorded on a Shimadzu IRAffinity-1 spectrometer in pressed KBr pellets under ambient conditions.

Electronic absorption spectra were recorded on a Shimadzu double beam UV-3600 UV/vis/NIR spectrophotometer in given solvents at room temperature or at −35 °C. Cuvettes of the type 117.100-QS from Hellma with 10 mm layer thickness were used.

Magnetism data of powdered samples (10.0–25.0 mg), loaded within polycarbonate gel capsules, were collected on a Quantum Design MPMS-3 SQUID magnetometer. DC susceptibility was recorded in the temperature range of 2–300 K with an applied DC field of 1 T, if not stated otherwise, or by means of field-dependent measurements in the temperature range of 2–150 K under DC magnetic fields of 1.0, 3.0, and 5.0 T, respectively. Values of the magnetic susceptibility were corrected for core diamagnetism of the sample using tabulated Pascal’s constants.[2] For simulation and analysis of the data, the program "JulX2", written by Dr. Eckhard Bill (MPI CEC, Mülheim/Ruhr) was used.[3]

NMR spectra were recorded on JEOL ECX 270, JEOL ECX 400, or JEOL ECZ 400S instruments, operating at respective frequencies of 269.71, 400.18, and 399.79 MHz (1H NMR), as well as 67.82, 100.62, and 100.53 MHz (13C NMR). 19F NMR spectra were recorded on a JEOL ECX 400 or JEOL ECX 400S instrument operating at 376.54 and 376.17 MHz, respectively. If not stated otherwise, the data were collected at room temperature. The solvent residual signals of incomplete deuterated solvent molecules were used as internal reference for the 1H NMR spectra and the solvent signals for 13C NMR spectral data.[4] The multiplicity of signals is abbreviated as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet, m = multiplet. Deuterated NMR solvents were stored over molecular sieves in thin layer chromatography plates and activated at 100 °C to +150 °C. At the indicated temperatures, the probe and the sample are thermally equilibrated at least for 5 minutes prior to shimming and recording of the spectral data.

EPR spectra were recorded on a JEOL continuous wave spectrometer JES-FA200, equipped with an X-band Gunn diode oscillator bridge, a cylindric mode cavity, and a helium cryostat. The samples were measured in the solid state under nitrogen atmosphere in quartz glass EPR tubes at 7 K. The spectra shown were measured using the following parameters: microwave frequency = 8.959 GHz, modulation width 0.8 and 0.01 mT, microwave power 1.0 mW, modulation frequency 100 kHz, time constant of 0.1 s. Data analysis and simulation of the data was performed using the software “review” and “eesim”, written by Dr. Eckhard Bill (MPI CEC, Mülheim/Ruhr).[5,6] on the basis of a spin-Hamiltonian description of the electronic ground state:

$$\hat{H} = D \left( S_x^2 - \frac{1}{3} S(S + 1) + \frac{E}{D} (S_x^2 - S_y^2) \right) + \mu_B g S \hat{S}$$

Here, \(S\) represents the total spin quantum number of the coupled system, \(D\) and \(E/D\) are the axial and rhombic zero-field parameters, respectively, and \(g\) is the g-matrix. Calculations are based on the \(S = 5/2\) routines developed by Gaffney and Silverstone.[7] EPR line widths, \(W\), are given in units of mT at full-width-half-maximum (FWHM).

Cyclic voltammograms measurements were carried out at room temperature under inert gas atmosphere with an Autolab Type-III potentiostat. The complex was measured in THF (0.1 m NBu4PF6) using a glassy carbon working electrode, and platinum wires as a counter and a quasi-reference electrode. For each measurement, ca. 20 mg of
material was dissolved in ca. 5 mL of electrolyte (ca. 4 mM). After the initial measurements, ferrocene was added as an internal standard and the measurements were repeated. The voltammograms were corrected by positioning the oxidation potential of ferrocene at 0 V. Corrected voltammograms without ferrocene are presented.

**Pulsed EPR and Davies ENDOR** measurements were performed at 10 K with an Elexys FT EPR spectrometer equipped with a SuperFT X-band bridge. The sample was positioned in a Bruker dielectric ring resonator (4118X-MD-4-W1) inside an Oxford helium cryostat CF 935. The Davies ENDOR experiments were measured using stochastic acquisition in order to suppress baseline artifacts due to heating. A BSA1025-400 RF Amplifier from Bonn Elektronik GmbH was used.

**Sample preparation for X-ray absorption spectroscopy**
To achieve 1.5-2.0% of cobalt mass fraction, 24-30 mg of pure crystalline material were ground with 49-59 mg of boron nitride with agate mortar and pestle at atmosphere and temperature conditions suitable to each compound. The finely ground powder was packed and sealed into an aluminum cell previously cleaned with pH 7 aqueous EDTA using 38-µm thick Kapton tape. All samples were kept at cryogenic temperatures and mounted on the cryostat holder under liquid nitrogen.

**X-ray absorption spectroscopy in high-energy resolution fluorescence-detected mode (Kα-HERFD)**
The data were collected at the European Synchrotron Radiation Facility (ESRF) beam line ID26 (6 GeV, 30 mA, 16-bunch mode) using a Si(311) liquid nitrogen cooled double crystal monochromator calibrated versus the first inflection point of metallic Co foil at 7709 eV. Silicon-coated mirrors were used to focus the beam to 200 x 100 µm (h x v), providing nominal flux of ~1x10^{13} photons/s. To avoid radiation-induced spectral changes, aluminum foils of 20 µm each were used to attenuate the incident flux. The measurements were conducted at 30 K in a liquid He cryostat, with the samples positioned at 45° relative to the incident beam. The emission spectrometer was equipped with five Si(531) spherically bent crystals (for Kα at 6931 eV, Bragg angle: 77°) with 100 mm diameter and 1 m curvature radius in Rowland geometry. The flight path between the sample and the detector was filled with helium to mitigate the attenuation of emitted photons. The detector was a silicon avalanche photodiode with 200 µm thickness and 10x10 mm² active area, behind a slit with 1 mm opening. The emission spectrometer was set to the maximum of Kα lines at 6931.5 eV and the absorption spectrum was collected in continuous scan mode from 7689 to 7809 eV with integration set to give 0.1 eV step size. Scans from 7629 to 8369 eV were collected for normalization.

In order to assess the radiation damage rate on each sample, quick near-edge XAS spectra were taken on the same spot until changes in consecutive spectra became noticeable. The changes overall are the K-edge shifting down in energy (denoting photoreduction) and modulations in the pre-edge region. Multiple consecutive spectra without changes were used to determine the maximum dwell time on each spot of each sample, which in the sequence was set as the scan time. The final data was composed by an average of scans on 30-70 spots.

[Cp₂Fe][PF₆] was obtained from Sigma-Aldrich and used as received. [(TIMMN^mes)Co(Cl)][PF₆] and MesN₃[9] were synthesized as described in literature. Carbon dioxide (99.8%, used as received) was purchased from Aldrich. Carbon monoxide (99.997%, used as received) was purchased from AIR LIQUIDE.
Synthesis and Characterization

\[ \text{[(TIMMN}^{\text{mes}}\text{)}\text{Co}^\text{II}\text{Cl}](PF_6)} \] (1): To a suspension of \([(\text{TIMMN}^{\text{mes}}\text{)}\text{Co}^\text{II}\text{Cl}](PF_6)} \) (510 mg, 0.60 mmol) in 20 mL of THF, sodium amalgam (0.9% w/w, 1867 mg, 0.74 mmol, 1.2 eq.) was added and the mixture was vigorously stirred for 1 h at room temperature. Afterwards, the mixture was filtered through celite® and the solution was evaporated to dryness. The residue was washed with benzene (6 × 10 mL) and dried \textit{in vacuo} to yield 280 mg (57%) of product as green solid. Single-crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of \textit{n}-pentane into a saturated toluene solution of \([(\text{TIMMN}^{\text{mes}}\text{)}\text{Co}^\text{II}\text{Cl}](PF_6)} \) at room temperature overnight.

\(^1\text{H NMR} \) (400 MHz, THF-\textit{d}_8) \( \delta \) [ppm]: 44.73 (bs, 6H), 21.96 (s, 3H), 18.65 (bs, 3H), 7.27 (s, 6H), 2.48 (s, 9H), 0.50 (bs, 18H).

\textbf{Elemental Analysis (\%):} Calculated for C\textsubscript{39}H\textsubscript{45}CoF\textsubscript{6}N\textsubscript{7}P\timesC\textsubscript{7}H\textsubscript{8}: C 60.86, H 5.88, N 10.80. Found: C 60.67, H 5.69, N 10.92.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure_s1.png}
\caption{\(^1\text{H NMR spectrum of } [(\text{TIMMN}^{\text{mes}}\text{)}\text{Co}^\text{II}](PF_6)} \) (1), recorded at 400 MHz at room temperature in THF-\textit{d}_8.}
\end{figure}
[(TIMMN\textsuperscript{mes})Co\textsuperscript{I}](PF\textsubscript{6}) (1) was further characterized by single-crystal X-ray diffraction analysis. In the crystal structure of 1, the asymmetric unit contained two independent molecules of the complex salt. For one of the complex cations, the molecular structure is shown in Figure S2. According to the crystallographic analysis, the cobalt center is in a distorted trigonal pyramidal, C\textsubscript{3}-symmetric coordination environment, with the cobalt atom located 0.349/0.322 Å above the plane of the three carbenes (d\textsubscript{oop}). The TIMMN\textsuperscript{mes} ligand coordinates in a tetradentate fashion with an average Co–C\textsubscript{carbene} bond distance of 1.9606(13)/1.9741(13) Å and a Co–N bond distance of 2.2504(11)/2.2364(11) Å.

Figure S2. Solid-state molecular structure of the cation [(TIMMN\textsuperscript{mes})Co\textsuperscript{I}]\textsuperscript{+} in crystals of [(TIMMN\textsuperscript{mes})Co\textsuperscript{I}](PF\textsubscript{6})\textcdotC\textsubscript{7}H\textsubscript{8} (1·C\textsubscript{7}H\textsubscript{8}). Hydrogen atoms, co-crystallized solvent molecules and counter anion are omitted for clarity. Thermal ellipsoids are displayed at 50\% probability. Selected bond lengths (Å) and angles: Co–C\textsubscript{2} 1.9542(13)/1.9880(13), Co–C\textsubscript{6} 1.9787(12)/1.9550(13), Co–C\textsubscript{10} 1.9490(13)/1.9793(13), Co–N\textsubscript{1} 2.2504(11)/2.2364(11), \(\angle\) (C\textsubscript{6}–Co–C\textsubscript{10}) 113.79(5)/113.24(5), \(\angle\) (C\textsubscript{6}–Co–C\textsubscript{2}) 124.16(5)/127.12(5), \(\angle\) (C\textsubscript{2}–Co–C\textsubscript{10}) 112.70(5)/111.73(5).
[(TIMMM\textsuperscript{mes})Co\textsuperscript{III}(NMes)](PF\textsubscript{6})\textsubscript{(2)}: One equivalent of MesN\textsubscript{3} (33 mg, 0.20 mmol, 1.0 eq.) was slowly added to a solution of [(TIMMM\textsuperscript{mes})Co\textsuperscript{(I)}](PF\textsubscript{6}) (166 mg, 0.20 mmol) in 3 mL of THF at −35 °C. The mixture was stirred at −35 °C for additional 0.5 h. The color of the solution changed from yellow to green gradually with concomitant N\textsubscript{2} gas evolution and formation of bubbles. Removal of the solvent under vacuum afforded a green residue, which was washed with n-pentane (4 × 4 mL) and dried in vacuo to yield 170 mg (89%) of product as green solid. Single-crystals suitable for X-ray diffraction analysis were obtained by diffusion of diethyl ether into a DCM solution of [(TIMMM\textsuperscript{mes})Co\textsuperscript{III}(NMes)](PF\textsubscript{6})\textsubscript{(2)} at −25 °C overnight.

\textbf{1H NMR} (400 MHz, CH\textsubscript{2}Cl\textsubscript{2}-d\textsubscript{2}) \(\delta\) [ppm]: 7.22 (d, \(J = 1.4\) Hz, 3H), 7.10 (d, \(J = 1.4\) Hz, 3H), 6.58 (s, 3H), 6.32 (s, 3H), 5.88 (s, 2H), 5.04 (d, \(J = 12.9\) Hz, 3H), 4.47 (d, \(J = 12.9\) Hz, 3H), 2.02 (s, 9H), 1.58 (s, 9H), 1.11 (s, 9H), 0.76 (s, 3H), 0.64 (s, 6H).

\textbf{13C NMR} (101 MHz, CH\textsubscript{2}Cl\textsubscript{2}-d\textsubscript{2}) \(\delta\) [ppm]: 138.07, 137.05, 135.52, 135.12, 133.28, 132.84, 129.40, 128.55, 127.13, 123.27, 121.24, 63.56, 24.25, 23.09, 20.62, 18.74, 17.56.

\textbf{Elemental Analysis} (%): Calculated for C\textsubscript{48}H\textsubscript{56}CoF\textsubscript{6}N\textsubscript{8}P: C 60.76, H 5.95, N 11.81. Found: C 60.49, H 5.72, N 11.62.

\textbf{IR} (in KBr pellet) \(\nu\) [cm\textsuperscript{−1}]: 2918, 1564, 1479, 1439, 1377, 1323, 1288, 1249, 1030, 845, 729, 557.

\textbf{UV-vis} \(\lambda\) (nm) / \(\varepsilon\) [\(10^{-3}\) M\(^{-1}\) cm\(^{-1}\)]: 302 / 28.63; 432 / 7.42; 616 / 2.33; 706 / 2.81.

\textbf{Figure S3.} \textsuperscript{1}H NMR spectrum of [(TIMMM\textsuperscript{mes})Co\textsuperscript{III}(NMes)](PF\textsubscript{6})\textsubscript{(2)}, recorded at 400 MHz at room temperature in CH\textsubscript{2}Cl\textsubscript{2}-d\textsubscript{2}.
Figure S4. $^{13}$C NMR spectra of [(TIMMN$^{\text{mes}}$)Co$^{\text{III}}$(NMes)](PF$_6$) (2), recorded at 101 MHz at room temperature in CH$_2$Cl$_2$-d$_2$. The carbene carbon resonance was not observed. This is similar to the Co(III) oxido and imido complexes [PhB($^{\text{Bu}}$)$_3$Co$^{\text{III}}$O]$^{10}$ and [(TIMMN$^{\text{mes}}$)Co$^{\text{III}}$(NAd)](BPh$_4$),$^{[8]}$ for which the carbene carbon resonances have not been observed as well.
Figure S5. IR vibrational spectrum of [(TIMMN\textsuperscript{mes})Co\textsuperscript{III}(NMes)](PF\textsubscript{6}) (2), measured as KBr pellet.

Figure S6. UV-vis electronic absorption spectrum of [(TIMMN\textsuperscript{mes})Co\textsuperscript{III}(NMes)](PF\textsubscript{6}) (2), recorded in THF at –35 °C.
An electrochemical analysis of [(TIMM\textsuperscript{mes})Co\textsuperscript{III}(NMes)](PF\textsubscript{6}) (2) was carried out using cyclic voltammetry (CV). The CV revealed a reversible oxidation \( E_{1/2} \) at \(-0.52\) V, which corresponds to the [(TIMM\textsuperscript{mes})Co(NMes)]\textsuperscript{2+/1} redox couple, and an irreversible reduction \( E_{p,c} \) at \(-2.35\) V (vs. Fc/Fc\textsuperscript{+}) (Figure S7). In order to prove the reversibility of the [(TIMM\textsuperscript{mes})Co(NMes)]\textsuperscript{2+/1} redox wave, a Randles-Ševčík analysis was carried out. The corresponding data are shown in Figure S8. The quality of the linear dependence between the peak potentials of the oxidation and reduction events on the applied scan rate appears to be satisfactory. Thus, we recognize the oxidation to [(TIMM\textsuperscript{mes})Co(NMes)]\textsuperscript{2+} to proceed cleanly and reversibly.

**Figure S7.** Cyclic voltammogram of [(TIMM\textsuperscript{mes})Co\textsuperscript{III}(NMes)](PF\textsubscript{6}) (2) in THF (0.1 M NBu\textsubscript{4}PF\textsubscript{6}), recorded at a scan rate of 200 mV s\textsuperscript{-1} and referenced versus the Fc/Fc\textsuperscript{+} couple. Dashed black lines indicate the position of the redox waves.

**Table S1.** Scan rate (\( \nu \)), anodic and cathodic current ratio (\( i_{pa}/i_{pc} \)), anodic (\( E_{pa} \)) and cathodic (\( E_{pc} \)) peak potentials, anodic and cathodic peak separation (\( E_{pa} - E_{pc} \)) data

| \( \nu \) (mV/s) | \( \Delta i_{pa} \) (\( \mu \text{A} \)) | \( \Delta i_{pc} \) (\( \mu \text{A} \)) | \( i_{pa}/i_{pc} \) | \( E_{pa} \) (mV) | \( E_{pc} \) (mV) | \( E_{pa} - E_{pc} \) (mV) | \( (E_{pa} + E_{pc})/2 \) (mV) |
|------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 50               | 18.58          | -17.17         | -1.08          | -452           | -599           | 147            | -525           |
| 100              | 26.04          | -24.80         | -1.05          | -432           | -615           | 183            | -524           |
| 200              | 36.19          | -34.76         | -1.04          | -406           | -636           | 230            | -521           |
| 300              | 43.38          | -42.88         | -1.01          | -388           | -648           | 260            | -518           |
| 400              | 49.59          | -48.63         | -1.02          | -373           | -660           | 287            | -517           |
| 500              | 54.72          | -52.91         | -1.03          | -361           | -670           | 309            | -516           |
Figure S8. Cyclic voltammograms of the oxidation of \([\text{TIMM}^{\text{mes}}]\text{Co}^{\text{III}}(\text{NMes})\)(PF_6) \((2)\) at different voltage scan rates (upper panel) and plots of the Randles-Ševčík analysis (lower panel) indicating its reversible character.
SUPPORTING INFORMATION

\[\text{[(TIMMN}^{\text{mes}})\text{Co(NMes)}](\text{PF}_6)_2 (3)\]: To a green solution of \[\text{[(TIMMN}^{\text{mes}})\text{Co}^{\text{III}}(\text{NMes})](\text{PF}_6)_2 (2) (190 mg, 0.20 mmol)\] in THF (8 mL) was added \[\text{[Cp}_2\text{Fe}(\text{PF}_6)_2 (72 mg, 0.22 mmol, 1.1 eq.) at } -35 ^\circ\text{C}\]. The reaction mixture was stirred at \(-35 ^\circ\text{C}\) for 30 min, and the color of the solution gradually changed from green to dark brown. The reaction mixture was filtered through filter paper, and the filtrate was taken to dryness in vacuo. The residue was washed with cold n-pentane (8 x 5 mL) and dried in vacuo to yield 195 mg (89%) of product as a brown solid. Single-crystals suitable for X-ray diffraction analysis were obtained by diffusion of n-pentane into a THF solution of \[\text{[(TIMMN}^{\text{mes}})\text{Co(NMes)}](\text{PF}_6)_2 (3)\] at \(-35 ^\circ\text{C}\) overnight.

\(^1\text{H NMR}\) (400 MHz, DCM-\(d_2\), \(-55 ^\circ\text{C}\)) \(\delta\) [ppm]: 17.63 (bs, 2H), 14.98 (bs, 3H), 13.94 (bs, 3H), 13.31 (bs, 3H), 12.38 (bs, 3H), 10.07 (bs, 9H), 6.77 (s, 9H), 5.95 (s, 6H), 2.03 (s, 18H).

**Elemental Analysis** (%): Calculated for C_{48}H_{56}CoF_{12}N_{8}P_{2}: C 52.70, H 5.16, N 10.24. Found: C 53.06, H 4.79, N 9.87.

**UV-Vis** \(\lambda\) (nm) / \(\varepsilon\) [10\(^{-3}\) M\(^{-1}\) cm\(^{-1}\)]: 264 / 18.69; 302 / 21.67; 346 / 16.37; 403 / 8.74; 515 / 2.86.

VT\(^{-1}\) H NMR spectra of \[\text{[(TIMMN}^{\text{mes}})\text{Co(NMes)}](\text{PF}_6)_2 (3)\] revealed that complex 3 starts to decompose at temperatures above \(-15 ^\circ\text{C}\) (Figure S10). Despite multiple attempts, and due to the pronounced thermal instability, a reproducible IR vibrational spectrum was not obtained for this complex.

![Figure S9. \(^1\text{H NMR spectrum of }\text{[(TIMMN}^{\text{mes}})\text{Co(NMes)}](\text{PF}_6)_2 (3), recorded at 400 MHz at } -55 ^\circ\text{C in DCM-}d_2\).](image-url)
Supporting Information

Figure S10. VT-^1^H NMR spectra of [(TIMMN^mes^)Co(NMes)](PF_6)_2 (3), recorded at 400 MHz in DCM-d_2.
Figure S11. UV-vis electronic absorption spectrum of [(TIMMN^{mes})Co(NMes)](PF_6)_2 (3), recorded at –35 °C in THF (upper panel); UV-vis electronic absorption spectra of [(TIMMN^{mes})Co^{III}(NMes)](PF_6) (2) (green) and [(TIMMN^{mes})Co(NMes)](PF_6)_2 (3) (brown), recorded at –35 °C in THF (lower panel).
Supporting Information

\[ ([\text{TIMNN}^{\text{mes}}]^+\text{Co}(\text{NMes})^+)(\text{PF}_6)^- (4)) \]: The THF solution (10 mL) of \([([\text{TIMNN}^{\text{mes}}]^+\text{Co}^{III}(\text{NMes})][\text{PF}_6]) (2) (150 mg, 0.16 mmol) was stirred at room temperature overnight, and the color of the solution changed from green to dark yellow. Removal of the solvent under vacuum afforded a yellow residue, which was extracted with benzene (20 mL). Filtration of the mixture and lyophilization of the benzene phase afforded the product as a yellow solid (130 mg, 87%). Single crystals suitable for X-ray diffraction analysis were obtained by diffusion of \(n\)-pentane into a solution of \([([\text{TIMNN}^{\text{mes}}]^+\text{Co}(\text{NMes})^+)(\text{PF}_6)) (4)\) in a solvent mixture of THF/Benzene at room temperature overnight.

\(^1\text{H NMR} (400 \text{ MHz, THF-}d_8) \delta \text{ [ppm]}: 77.60 \text{ (bs), 53.34 (bs), 22.70 (bs), 18.82 (s), 12.27 (s), 11.03 (s), 10.28 (s), 5.69 (s), 5.21 (s), 3.84 (bs), 1.27 (s), 1.09 (s) -2.57 (bs).} \] The \(^1\text{H NMR} \) spectrum of \([([\text{TIMNN}^{\text{mes}}]^+\text{Co}(\text{NMes})^+)(\text{PF}_6)) (4)\) is complicated due to the complex’s paramagnetic nature and the lack of symmetry.

Elemental Analysis (%): Calculated for C\(_{48}\)H\(_{56}\)CoF\(_6\)N\(_8\)P: C 63.15, H 6.09, N 10.91. Found: C 63.22, H 6.02, N 11.00.

\( \text{IR (in KBr pellet)} \nu [\text{cm}^{-1}]: 2918, 1610, 1580, 1562, 1489, 1462, 1441, 1398, 1387, 1323, 1258, 1232, 1153, 1003, 930, 847, 706, 685, 583, 557. \)

\( \text{UV-vis } \lambda \text{ (nm) / } \varepsilon [10^{-3} \text{ M}^{-1} \text{ cm}^{-1}]: 333 / 5.97; 423 / 4.97. \)

Figure S12. \(^1\text{H NMR} \) spectra of \([([\text{TIMNN}^{\text{mes}}]^+\text{Co}(\text{NMes})^+)(\text{PF}_6)) (4)\), recorded at 400 MHz at room temperature in THF-\(d_8\).
**Figure S13.** IR vibrational spectrum of [(TIMM{mes})\textsuperscript{I}Co\textsuperscript{(NMes)}\textsuperscript{-}](PF\textsubscript{6}) (4), measured as KBr pellet.

**Figure S14.** UV-vis electronic absorption spectrum of [(TIMM{mes})\textsuperscript{I}Co\textsuperscript{(NMes)}\textsuperscript{-}](PF\textsubscript{6}) (4), recorded in C\textsubscript{6}H\textsubscript{6}. 

Complex 4 was further characterized by SQUID magnetization measurement. According to the SQUID measurement, cobalt(I) complex 4 possesses a magnetic moment, $\mu_{\text{eff}}$, of 3.10 $\mu_B$ at 300 K; thus, supporting the high-spin $S = 1$, Co$^I$, $d^8$ electronic structure assignment (Figure S15). This value is higher than the calculated spin-only value of 2.83 $\mu_B$ for a high-spin $d^8$ ($S = 1$) system. This deviation is generally considered to be caused by a substantial orbital angular momentum contribution from the cobalt ion. VT-VF SQUID measurements were fitted with an average $g$-value of 2.24 and a zero-field splitting parameter, $D$, of 11.5 cm$^{-1}$.

**Figure S15.** VT SQUID magnetization data for a microcrystalline sample of [(TIMMN$^{\text{mes}}$)*Co'(NMes)'](PF$_6$) (4) (upper panel). The magnetic moment varied from 1.81 $\mu_B$ at 2 K to 3.10 $\mu_B$ at 300 K at 1 T. Experimental data are represented by black squares and the red line corresponds to the global fit for $S = 1$; VT-VF SQUID magnetization data for [(TIMMN$^{\text{mes}}$)*Co'(NMes)'](PF$_6$) (4) ($\mu_{\text{eff}}$ = 3.18 $\mu_B$ at 150 K) (lower panel). Simulation parameters: $S = 1.0$, $2zJ = 20.53$ cm$^{-1}$, $D = +11.5$ cm$^{-1}$, $E/D = 0.33$, $g_{\text{avg}} = 2.24$. 
[(TIMMNmes)*Co(NMes)](PF$_6$) (4) was further characterized by single-crystal X-ray diffraction analysis. Its molecular structure is represented in Figure S16. In the molecular structure of 4, the modified TIMMN* ligand coordinates to the Co ion through two of its remaining carbenoid carbons, the anchoring nitrogen and the newly formed imine N atom. In this ligand environment, the cobalt center is located 0.153 Å above the trigonal plane. The distance between the N-anchor and the metal ion is 2.2155(14) Å and, consequently, indicative for a bonding interaction.

Figure S16. Solid-state molecular structure of the cation [(TIMMNmes)*Co(NMes)]$^+$ in crystals of [(TIMMNmes)*Co(NMes)](PF$_6$)·C$_6$H$_6$ (4·C$_6$H$_6$). Hydrogen atoms, co-crystallized solvent molecules and counter anion are omitted for clarity. Thermal ellipsoids are displayed at 50% probability. Selected bond lengths (Å) and angles: Co–C$_2$ 1.9496(16), Co–C$_6$ 1.9305(16), Co–N$_{8}$ 2.0128(14), C$_{40}$–N$_{8}$ 1.423(2), C$_{10}$–N$_{8}$ 1.318(2), Co–N$_{1}$ 2.2155(14), $\angle$(C$_6$–Co–N$_8$) 107.48(6)$^\circ$, $\angle$(C$_6$–Co–C$_2$) 112.15(7)$^\circ$, $\angle$(C$_2$–Co–N$_8$) 138.45(6)$^\circ$, $\angle$(Co–N$_8$–C$_{40}$) 125.56(11)$^\circ$, $\angle$(Co–N$_8$–C$_{10}$) 114.04(11)$^\circ$, $\angle$(C$_{40}$–N$_8$–C$_{10}$) 118.62(14)$^\circ$, $d_{op}$ (N$_1$) = 0.417 Å.
[(TIMMNmes)*Co(NMes)’](PF6)2 (5): [(TIMMNmes)Co(NMes)](PF6)2 (3) (132 mg, 0.12 mmol) was dissolved in THF (8 mL) at -35 °C, and the mixture was further stirred at room temperature for additional 0.5 h. The color of the solution gradually changed from brown to yellow-green. Removal of the solvent under vacuum afforded a yellow-green residue, which was washed with n-pentane (3 x 3 mL) and dried in vacuo to yield 125 mg (95%) of product as yellow-green solid. Single-crystals suitable for X-ray diffraction analysis were obtained by diffusion of diethyl ether into a solution of [(TIMMNmes)*Co(NMes)’](PF6)2 (5) in a solvent mixture of DCM/Toluene at room temperature overnight.

1H NMR (270 MHz, DCM-d2) δ [ppm]: 131.06 (bs), 79.68 (bs), 70.94 (bs), 45.51 (s), 39.61 (bs), 37.42 (s), 22.89 (bs), 16.67 (bs), 13.61 (bs), 10.54 (s), 8.45 (bs), 6.16 (s), 2.72 (s), 0.35 (bs), -1.41 (s), -10.53 (bs), -14.03 (s). The 1H NMR spectrum of [(TIMMNmes)*Co(NMes)’](PF6)2 (5) is complicated due to the complex’s paramagnetic nature and the lack of symmetry.

Elemental Analysis (%): C48H56CoF12N8P2: C 52.70, H 5.16, N 10.24. Found: C 52.14, H 4.66, N 10.21.

IR (in KBr pellet) ν [cm⁻¹]: 2924, 1609, 1562, 1552, 1477, 1470, 1411, 1398, 1383, 1217, 843, 739, 687, 559.

UV-vis λ (nm) / ε [10⁻³ M⁻¹ cm⁻¹]: 251 / 13.33; 346 / 1.77; 418 / 1.01.

Figure S17. 1H NMR spectra of [(TIMMNmes)*Co(NMes)’](PF6)2 (5), recorded at 400 MHz at room temperature in DCM-d2.
**Figure S18.** IR vibrational spectrum of [(TIMMN$^{\text{mes}}$)$^{\text{II}}$(NMes)](PF$_6$)$_2$ (5), measured as KBr pellet.

**Figure S19.** UV-vis electronic absorption spectrum of [(TIMMN$^{\text{mes}}$)$^{\text{II}}$(NMes)](PF$_6$)$_2$ (5), recorded in THF.
[(TIMMNmes)*CoII(NMes)](PF6)2 (5) was further characterized by single-crystal X-ray diffraction analysis (Figure S20). Complex 5 features a similar coordination geometry as that of complex 4 but with two well-separated PF6− counter anions (Figure S20). In this ligand environment, the Co center is located 0.173 Å above the trigonal plane. Compared to 4, and as expected, dicationic 5 exhibits shorter Co–N(anch) (2.1947(18) Å in 5, 2.2155(14) Å in 4) and Co–N(imine) (1.9218(19) Å in 5, 2.0128(14) Å in 4) bonds. Interestingly, despite the smaller radius of the Co(II) ion, the average Co–C bond distance of 2.016(2) Å is significantly longer than that of Co(I) cation 4 (1.9400(16) Å); likely due to enhanced π-backbonding in the case of lower-valent 4.[11] The C(Mesityl)–N(imine) and C(carbene)=N(imine) bond lengths in 5 (1.436(3) and 1.337(3) Å) are similar to those in 4 (1.423 (2) and 1.318(2) Å).

Figure S20. Solid-state molecular structure of the cation [(TIMMNmes)*CoII(NMes)]2+ in crystals of [(TIMMNmes)*CoII(NMes)](PF6)2•CH2Cl2 (5·CH2Cl2). Hydrogen atoms, co-crystallized solvent molecules and counter anion are omitted for clarity. Thermal ellipsoids are displayed at 50% probability. Selected bond lengths (Å) and angles: Co–C2 2.015(2), Co–C6 2.016(2), Co–N8 1.9218(19), C40–N8 1.436(3), C10–N8 1.337(3), Co–N1 2.1947(18), C1–N1 1.464(3), C5–N1 1.474(3), C9–N1 1.479(3), ∡(C6–Co–N8) 114.92(9)°, ∡(C6–Co–C2) 123.27(9)°, ∡(C2–Co–N8) 119.54(9)°, ∡(Co–N8–C40) 121.56(15)°, ∡(Co–N8–C10) 120.69(15)°, ∡(C40–N8–C10) 117.73(19)°, dloop (N1) = 0.439 Å.

Figure S21. CW X-band EPR spectrum of [(TIMMNmes)*CoII(NMes)](PF6)2 (5) recorded as a 2 mM solution in THF at 9 K (black trace). Experimental conditions: microwave frequency ν = 8.959 GHz, modulation amplitude = 0.8 mT, microwave power = 1.0 mW, modulation frequency = 100 kHz, time constant = 0.1 s. Red trace: Simulation with effective spin Seff = ½ for the lowest Kramers doublet of an S = 3/2 spin-system. Simulation parameters (red trace): effective g-values g1 = 5.17, g2 = 3.49 and g3 = 1.99, linewidths WFWHM,1 = 18.0 mT, WFWHM,2 = 48.2 mT and WFWHM,3 = 40.2 mT, pseudo-Voigt lines used with ratios (Lorentz = 0, Gauss = 1) V1 = V2 = V3 = 1.00. Blue trace: For comparison, a simulation within the Spin Hamiltonian formalism for an S = 3/2 system is shown. Simulation...
parameters (blue trace): $D = 19.3 \text{ cm}^{-1}$ (fixed, taken from magnetic data), $E/D = 0.13$, real $g$-values: $g_1 = g_2 = 2.21$ and $g_3 = 2.11$; linewidths: $W_1 = W_2 = 22.0 \text{ mT}$, and $W_3 = 35.0 \text{ mT}$.

Complex 5 was further characterized by SQUID magnetization measurement. According to the SQUID measurement, cobalt(II) complex 5 possesses a magnetic moment, $\mu_{\text{eff}}$, of 4.35 $\mu_B$ at 300 K (Figure S22). This value is higher than the calculated spin-only value of 3.87 $\mu_B$ for a high-spin $d^7$ ($S = 3/2$) system. Such deviation is generally considered to be caused by a substantial orbital angular momentum contribution from the cobalt ion. VT-VF SQUID measurements were fitted with an average $g$-value of 2.24 and a zero-field splitting parameter, $D$, of 19.3 cm$^{-1}$.

Figure S22. VT SQUID magnetization data for a microcrystalline sample of $\left[\text{TIMMN}^{\text{mes}}\right]^{\text{+}}\text{Co}^{\text{II}}(\text{NMes})^\text{´}\right\left[\text{PF}_6\right]_2$ (5) (upper panel). The magnetic moment varied from 3.21 $\mu_B$ at 2 K to 4.35 $\mu_B$ at 300 K at 1 T. Experimental data are represented by black squares and the red line corresponds to the global fit for $S = 3/2$; VT-VF SQUID magnetization data for $\left[\text{TIMMN}^{\text{mes}}\right]^{\text{+}}\text{Co}^{\text{II}}(\text{NMes})^\text{´}\right\left[\text{PF}_6\right]_2$ (5) ($\mu_{\text{eff}} = 4.32 \mu_B$ at 150 K) (lower panel). Simulation parameters: $S = 3/2$, $D = +19.3 \text{ cm}^{-1}$, $E/D = 0.13$ (fixed, taken from EPR), $g_{\text{avg}} = 2.24$. Grey symbols are experimental data, solid red lines are numerical fits.
Reactivity Studies

Reactivity studies of 2 with styrene, cyclohexene, 1,4-cyclohexadiene, triphenylphosphine as well as CO2 and CO were carried out. However, these efforts turned out rather unproductive. For example, 2 reacted under 1 atm. of CO at room temperature overnight to give yellow, diamagnetic \( [\text{TIMMN}^{\text{mes}}]^{+}\text{Co}(\text{CO})_3(\text{NMes})]^{[\text{PF}_6]} \) (6) (Scheme S1) rather than the anticipated intermolecular imido transfer products mesityl isocyanate (MesNCO) and the corresponding cobalt(II) complex. Complex 6 was characterized by NMR as well as UV/Vis electronic absorption and IR vibrational spectroscopy, SC-XRD analysis (Figures S23–S27), and CHN elemental analysis. The formation of the cobalt dicarbonyl 6 can be rationalized by the sequential processes of intramolecular imido migratory insertion, followed by CO coordination to cobalt (Scheme S1). Indeed, reacting \( [\text{TIMMN}^{\text{mes}}]^{+}\text{Co}(\text{NMes})]^{[\text{PF}_6]} \) (4) with 1 atm. of CO cleanly produced 6 within 2 mins. These results suggest that the intramolecular imido insertion reaction in 2 is favored over the intermolecular imido transfer to CO. The bent imido linkage (157.97(13)°) observed for 2 closely resembles that of the previously reported uranium(V) mesityl imido complex, \( [\text{([ArO]}_2\text{tacn})\text{U(NMes)},{]^{[\text{PF}_6]}]}^{[\text{PF}_6]} \) which features a similarly bent imido ligand with a \( \text{U}–\text{N}–\text{C(Mes)} \) angle of 154.7(8)°. In this case, the bent imido fragment is reactive and undergoes multiple bond metathesis with CO2 to produce the corresponding U(V) oxo species and free mesityl isocyanate (MesNCO). Indeed, 2 behaves similarly, and, under 1 atm. of CO2, yields complicated mixtures of cobalt species and free MesNCO (15% NMR yield, Scheme S1), as revealed by 1H NMR and IR spectroscopy by comparison to an authentic sample of MesNCO (Figures S28, S29). The low yield may result from secondary reactivity of MesNCO with 2. The mechanism of formation is likely similar to that described for the above-mentioned U(V) imido complex; namely a retro-cycloaddition reaction of a four-membered metallacycle (via a cobalt(III) carbimate species) formed from the \([2\pi + 2\pi] \) cycloaddition of 2 with CO2, along with the cobalt(III) oxo species \( [(\text{TIMMN}^{\text{mes}})\text{Co}^{\text{III}}(\text{O})]^+ \) as another product. Attempts to isolate the proposed cobalt(III) carbimate intermediate and oxo complex proved futile. In any case, this imido/oxo exchange reaction further corroborates the nucleophilic character of the imido nitrogen of 2.

The reactivity of 3 was also probed in reactions with an excess of styrene, cyclohexene, 1,4-cyclohexadiene, triphenylphosphine, CO2, CS2 and phenyl isocyanate. However, either no reaction or no intermolecular imido transfer reactions were observed at −35 °C and room temperature during an extended period of time. These results prove the intramolecular insertion reaction in 3 to be much faster than the intermolecular imido transfer.

In a typical procedure, compound 2 (or 3, 4, 5) (15 mg) was dissolved in 0.4 mL of THF-d8 at −35 °C, and to this solution an excess of reagent A (see below) dissolved in 0.2 mL of cold THF-d8 was added. The reaction mixture was standing in the freezer (−35 °C) overnight. Afterwards, the reaction mixture was transferred to a J-Young NMR tube and was slowly warmed up to room temperature before being inserted into the probe of JEOL 400 MHz spectrometer. The reaction progress was followed by 1H and, if applicable, with 31P NMR spectroscopy.

Alternatively, compound 2 (or 3, 4, 5) (15 mg) was dissolved in 0.5 mL of THF-d8 in a J-Young NMR tube at −35 °C. The solution was degassed and exposed to 1 atm. of CO or CO2 at −35 °C. Afterwards, the reaction mixture was slowly warmed up to room temperature before being inserted into the probe of JEOL 400 MHz spectrometer. The reaction progress was followed by 1H NMR spectroscopy.

Reagents A:
Styrene, cyclohexene, 1,4-cyclohexadiene, triphenylphosphine, CS2 and phenyl isocyanate
Scheme S1. Reactivity of 2 and 3.
SUPPORTING INFORMATION

\[(\text{TIMMN}^{\text{mes}}\text{Co}^{\text{III}}(\text{NMes})(\text{PF}_6)_2 (6): A precooled (−35 °C) solution of [(TIMMN\text{mes})\text{Co}^{\text{III}}(\text{NMes})(\text{PF}_6)_2 (95 mg, 0.10 mmol) in 8 mL THF was exposed to 1 atm. of CO. The reaction solution was allowed to warm to room temperature and stood at room temperature overnight. The solution color changed from green to yellow gradually. Removal of the solvent under vacuum afforded a yellow residue, which was washed with n-pentane (4 × 2 mL) and dried in vacuo to yield 96 mg (96%) of product as yellow solid. Single-crystals suitable for X-ray diffraction analysis were obtained by diffusion of diethyl ether into a solution of [(TIMMN\text{mes})\text{Co}^{\text{III}}(\text{NMes})(\text{PF}_6)_2 (6) in a solvent mixture of THF/Benzene at room temperature overnight.

\[^1\text{H} \text{NMR} (400 \text{ MHz, THF-d}_8) \delta [\text{ppm}]: 7.57 (s, 2H), 7.01 (s, 2H), 6.94 (s, 2H), 6.89 (s, 2H), 6.73 (d, J = 2.7 Hz, 1H), 6.58 (s, 2H), 6.35 (s, 2H), 6.25 (d, J = 2.7 Hz, 1H), 6.05 (d, J = 10.9 Hz, 2H), 5.27 (d, J = 10.9 Hz, 2H), 4.80 (s, 2H), 2.25 (s, 6H), 2.13 (s, 3H), 2.04 (s, 6H), 2.01 (s, 9H), 1.99 (s, 6H), 1.93 (s, 6H).

\[^{13}\text{C} \text{NMR} (101 \text{ MHz, THF-d}_8) \delta [\text{ppm}]: 178.97, 147.76, 144.60, 139.91, 138.03, 137.13, 135.88, 135.76, 135.62, 134.02, 129.88, 129.64, 129.41, 128.91, 128.12, 125.45, 122.50, 117.12, 116.30, 114.93, 113.82, 112.41, 111.72, 109.91, 109.43, 107.91, 106.82, 105.73, 104.64, 103.55, 102.46, 101.37, 100.28, 99.19, 98.10, 97.01, 95.92, 94.83, 93.74, 92.65, 91.56, 90.47, 89.38, 88.30, 87.21, 86.12, 85.03, 83.94, 82.85, 81.76, 80.67, 79.58, 78.49, 77.40, 76.31, 75.22, 74.13, 73.04, 71.95, 70.86, 69.77, 68.68, 67.59, 66.50, 65.41, 64.32, 63.23, 62.14, 61.05, 60.96, 59.87, 58.78, 57.69, 56.60, 55.51, 54.42, 53.33, 52.24, 51.15, 50.06, 49.97, 48.88, 47.79, 46.70, 45.61, 44.52, 43.43, 42.34, 41.25, 40.16, 39.07, 38.98, 37.89, 36.80, 35.71, 34.62, 33.53, 32.44, 31.35, 30.26, 29.17, 28.08, 27.99, 26.90, 25.81, 24.72, 23.63, 22.54, 21.45, 20.36, 20.27, 19.18, 19.09, 18.00, 17.91, 16.82, 15.73, 14.64, 13.55, 12.46, 11.37, 10.28, 9.19, 8.10, 7.01, 5.92, 4.83, 3.74, 2.65, 1.56, 0.47.

Elemental Analysis (%): Calculated for C_{50}H_{56}CoF_{6}N_{8}O_{2}P: C 59.76, H 5.62, N 11.15. Found: C 60.33, H 5.50, N 10.79.

IR (in KBr pellet) ν [cm⁻¹]: 2922, 2002, 1938, 1661, 1605, 1481, 1408, 1354, 1279, 1250, 1223, 1182, 1030, 845, 700, 583, 557.

UV-vis λ (nm) / ε [10⁻³ m⁻¹ cm⁻¹]: 327 / 15.40.
Figure S23. $^1$H NMR spectra of [(TIMMN$^\text{mes}$)$^\ast$Co(CO)$_2$(NMes)](PF$_6$) (6), recorded at 400 MHz at room temperature in THF-$d_8$. 
Figure S24. $^{13}$C NMR spectra of $\left[\text{TIMM}^{\text{mes}}\right]^+\text{Co}(\text{CO})_2(\text{NMes})^-'\right](\text{PF}_6)$ (6), recorded at 101 MHz at room temperature in THF-$d_8$. 
**Figure S25.** IR vibrational spectrum of \([\text{TIMMN}^{\text{mes}}]^{\text{Co}^\text{I}(\text{CO})_2(\text{NMes})'][\text{PF}_6](6)\), measured as KBr pellet.

**Figure S26.** UV-vis electronic absorption spectrum of \([\text{TIMMN}^{\text{mes}}]^{\text{Co}^\text{I}(\text{CO})_2(\text{NMes})'][\text{PF}_6](6)\), recorded in THF.
Figure S27. Solid-state molecular structure of the cation [(TIMM^mes)Co(\text{CO})_2(NMes)]^+ in crystals of [(TIMM^mes)Co(\text{CO})_2(NMes)](PF_6) (6). Hydrogen atoms, co-crystallized solvent molecules and counter anion are omitted for clarity. Thermal ellipsoids are displayed at 50% probability. Selected bond lengths (Å) and angles:

- Co–C2 1.923(6), Co–C6 1.909(6), Co–C49 1.762(7), Co–C50 1.763(7), C49–O1 1.152(8), C50–O2 1.152(8), C40–N8 1.412(8), C10–N8 1.288(8), Co–N1 2.129(5), \( \angle \) (C6–Co–C50) 92.2(3)°, \( \angle \) (C6–Co–C49) 98.0(3)°, \( \angle \) (C6–Co–N1) 80.2(2)°, \( \angle \) (C2–Co–C50) 95.1(3)°, \( \angle \) (C2–Co–C49) 92.4(3)°, \( \angle \) (C2–Co–N1) 81.1(2)°, \( \angle \) (C6–Co–C2) 161.3(2)°, \( \angle \) (Co–C49–O1) 175.7(6)°, \( \angle \) (Co–C50–O2) 175.2(6)°, \( \angle \) (C50–Co–C49) 122.7(3)°, \( \angle \) (C40–N8–C10) 127.5(5)°.
Figure S28. \(^1\)H NMR spectral monitoring of the reaction of [(TIMMM\textsuperscript{mes})Co\textsuperscript{III}(NMes)](PF\textsubscript{6}) (2) with CO\textsubscript{2} at room temperature in THF-\textit{d\textsubscript{8}} (400 MHz).

Figure S29. IR vibrational spectra of mesityl isocyanate (MesNCO, black) and reaction mixture of (TIMMM\textsuperscript{mes})Co\textsuperscript{III}(NMes)](PF\textsubscript{6}) (2) with CO\textsubscript{2} (red), measured as KBr pellet. The volatiles of the reaction mixture were removed under vacuum before IR measurement.
Kinetic experiments

Scheme S2. Intramolecular migratory insertion reactions by complexes 2 and 3.

The conversion of 2 to 4 (3 to 5) was monitored by UV-Vis spectroscopy. The initial concentration of complex 2 or 3 was held constant (0.70 mM for 2, 0.58 mM for 3) for each run, the reaction temperature was varied. In a typical experiment, a J. Young absorption cell (pathlength of 1 cm) was charged with 0.70 mM of 2 (0.58 mM of 3) in THF in an N₂-filled glovebox. The cell was placed in a UV-Vis spectrometer, and the electronic absorption spectra were recorded in 1-minute-intervals at a certain temperature. The rate of conversion of 2 to 4 (3 to 5) at a certain temperature was determined by monitoring the disappearance of the band at 710 nm of 2 (515 nm of 3) over time. The linear plots of ln(Abs) vs. time show the reactions are first-order in [2] (or [3]). The slope represents the reaction rate constant at the measured temperature.

Figure S30. Monitoring of the intramolecular imido insertion of complex 2 by electronic absorption spectroscopy at 298.15 K. Selected spectra shown here were recorded in 30-minute-intervals.
35 °C
\[ y = -5.2787 \times 10^{-4}x - 0.17679 \]
\[ R^2 = 0.99836 \]

30 °C
\[ y = -3.3125 \times 10^{-4}x - 0.17623 \]
\[ R^2 = 0.9985 \]
25 °C
\[ y = -1.7498 \times 10^{-3} x - 0.18055 \]
\[ R^2 = 0.99701 \]

20 °C
\[ y = -1.1454 \times 10^{-5} x - 0.16207 \]
\[ R^2 = 0.99917 \]
Figure S31. Plots of the ln[Abs] versus reaction time [t] at various temperatures in THF.
Figure S32. Eyring plot for the conversion 2 to 4 in THF over the temperature range 283.15–308.15 K. Activation parameters derived from linear regression analysis: \( \Delta H^\ddagger = +77(2) \) kJ/mol, \( \Delta S^\ddagger = -57(6) \) J/mol K; \( \Delta G^\ddagger = +94 \) kJ/mol for 298.15 K.

Figure S33. Monitoring of the intramolecular imido insertion of complex 3 by electronic absorption spectroscopy at 298.15 K. Spectra were recorded in 1-minute-intervals.
0 °C
y = -3.403 \times 10^{-4}x - 0.20054
R^2 = 0.99764

-5 °C
y = -2.1006 \times 10^{-4}x - 0.19511
R^2 = 0.99854
Figure S34. Plots of the ln[Abs] versus reaction time [t] at various temperatures in THF.
Figure S35. Eyring plot for the conversion 3 to 5 in THF over the temperature range 248.15–273.15 K. Activation parameters derived from linear regression analysis: $\Delta H^\ddagger = +47(1)$ kJ/mol, $\Delta S^\ddagger = -139(4)$ J/mol·K; $\Delta G^\ddagger = +88$ kJ/mol for 298.15 K.
Figure S36. Davies ENDOR spectra recorded at 9.70 GHz on \([\text{TIMM}^{\text{mes}}\text{Co}^\text{IV}(\text{NAd})](\text{OTf})_2\) (black trace) and
\([\text{TIMM}^{\text{mes}}\text{Co}(\text{NMes})](\text{PF}_6)_2\) (3) (red trace). Experimental conditions (for black spectrum): $T = 10 \text{ K}$, $B = 335.0 \text{ mT}$, MW ($\pi/2$) = 100 ns, prep ($\pi$) = 200 ns, $\tau = 400 \text{ ns}$, RF pulse = 8 $\mu$s, repetition time = 1 ms, 2 h acquisition time. Experimental conditions (for red spectrum): $T = 10 \text{ K}$, $B = 348.2 \text{ mT}$, MW ($\pi/2$) = 100 ns, prep ($\pi$) = 200 ns, $\tau = 400 \text{ ns}$, RF pulse = 8 $\mu$s, repetition time = 1 ms, 2 h acquisition time.

Table S2. Observed bands in the ENDOR spectrum for \([\text{TIMM}^{\text{mes}}\text{Co}^\text{IV}(\text{NAd})](\text{OTf})_2\) (black trace) and Zeeman frequency for H$^+$ at 335.0 mT: 14.26 MHz.

| Frequency in MHz | A/2 in MHz | Assignment |
|------------------|------------|------------|
| 14.0 and 14.5    | 0.25       | Proton     |
| 13.7 and 14.9    | 0.60       | Proton     |
| 13.2 and 15.3    | 1.03       | Proton     |
| 12.0 and 16.5    | 2.22       | Proton     |
| 6.5 and 22.0     | 7.74       | Proton     |

Table S3. Observed bands in the ENDOR spectrum for \([\text{TIMM}^{\text{mes}}\text{Co}(\text{NMes})](\text{PF}_6)_2\) (3) (red trace) and Zeeman frequency for H$^+$ at 348.2 mT: 14.83 MHz.

| Frequency in MHz | A/2 in MHz | Assignment |
|------------------|------------|------------|
| 12.0 and 17.6    | 2.79       | Proton     |
| 8.6 and 21.1     | 6.28       | Proton     |
| 7.0 and 22.7     | 7.86       | Proton     |
| 25.0             | 10.20      |            |
| 31.7             | 16.84      |            |
| 34.5             | 19.86      |            |
Figure S37. Experimental Co HERFD XAS spectrum of [(TIMMN\textsuperscript{mes})Co\textsuperscript{II}(Cl)]\textsuperscript{(PF\textsubscript{6})} and the corresponding TDDFT calculated spectrum of [(TIMMN\textsuperscript{mes})Co\textsuperscript{II}(Cl)]\textsuperscript{2+}. Main excited states calculated by TDDFT/B3LYP are numbered and the respective acceptor natural transition orbitals are shown on the right. Transitions 1s to 3d: states 1(\(\beta\)), 2(\(\beta\)), and 3(\(\beta\)); MLCT: states 4(\(\alpha\)), 5(\(\alpha\)), 6(\(\beta\)) and 7(\(\beta\)).

Figure S38. Experimental Co HERFD XAS spectrum of [(TIMMN\textsuperscript{mes})Co\textsuperscript{III}(NAd)](BPh\textsubscript{4}) and the corresponding TDDFT calculated spectrum of [(TIMMN\textsuperscript{mes})Co\textsuperscript{III}(NAd)]\textsuperscript{2+}. Main excited states calculated by TDDFT/B3LYP are numbered and the respective acceptor natural transition orbitals are shown on the right. Transitions 1s to 3d: states 1(\(\alpha\)), 2(\(\beta\)), 3(\(\alpha\)), and 4(\(\beta\)); MLCT: states 5(\(\alpha\)), 6(\(\beta\)), 7(\(\alpha\)) and 8(\(\beta\)). The NTOs are pairwise coincidental because the species is closed shell (\(\alpha = \beta\)).
Figure S39. Experimental Co HERFD XAS spectrum of ([TIMMN mes]<sup>IV</sup>Co<sup>IV</sup>(Ad))(OTf)<sub>2</sub> and the corresponding TDDFT calculated spectrum of ([TIMMN mes]<sup>IV</sup>Co<sup>IV</sup>(Ad))<sup>2+</sup>. Main excited states calculated by TDDFT/B3LYP are numbered and the respective acceptor natural transition orbitals are shown on the right. Transitions 1s to 3d: states 1(β), 2(β), and 3(β); MLCT: states 6(α), 7(β), 8(α) and 9(β).

Figure S40. Experimental Co HERFD XAS spectrum of ([TIMMN mes]<sup>III</sup>Co<sup>II</sup>(NMes))(PF<sub>6</sub>)<sub>2</sub> and the corresponding TDDFT calculated spectrum of ([TIMMN mes]<sup>III</sup>Co<sup>II</sup>(NMes))<sup>+</sup>. Main excited states calculated by TDDFT/B3LYP are numbered and the respective acceptor natural transition orbitals are shown on the right. Transitions 1s to 3d: states 1(α), 2(β), 3(α), and 4(β); MLCT: states 5(α), 6(β), 7(α), 8(β), 9(α) and 10(β). The NTOs are pairwise coincidental because the species is closed shell (α = β).
Figure S41. Experimental Co HERFD XAS spectrum of [(TIMMN\textsuperscript{mes})Co\textsuperscript{III}(N\textbullet Mes)]\textsuperscript{2+} (3) and the corresponding TDDFT calculated spectrum of [(TIMMN\textsuperscript{mes})Co\textsuperscript{III}(N\textbullet Mes)]\textsuperscript{2+}. Main excited states calculated by TDDFT/B3LYP are numbered and the respective acceptor natural transition orbitals are shown on the right. Transitions 1s to 3d: states 1(α), 2(β), 3(α) and 4(β); MLCT: states 8(α), 9(β), 10(α) and 11(β).

In all cases, the first three to four excited states (depending on the number of b holes in the 3d shell) correspond to excitations from Co(1s) to molecular orbitals with large Co(3d) character. The main exception are states 1 and mainly state 2 of the calculated spectrum of the dication in 3, where the large N\textsuperscript{mes} character can be observed from the plots on Figure S41, right panel. The larger N\textsuperscript{mes} character in the acceptor NTO of state 2 is consistent with the excitation of a β electron to N radical bearing a spin-up electron.

While the experimental pre-edge peak of [(TIMMN\textsuperscript{mes})Co\textsuperscript{II}(Cl)](PF\textsubscript{6}) has clearly two features, the TDDFT calculation shows only one. This is due to the known multiplet structure of d\textsuperscript{7} systems, which the particle-hole approximation of TDDFT cannot capture.\textsuperscript{[13]}

In all cases, the first feature at the rising edge is attributed to transitions from Co(1s) to low-lying doubly degenerate π* orbitals located at the tricarbene ligand according to TDDFT. The acceptor NTOs in this region are composed of linear combinations of π* molecular orbitals located and N-C-N portion with antiphase combination of the 2p atomic orbitals perpendicular to the plane of the five-membered ring.

The energy shift of +93.2 eV was applied to all calculated spectra in order to match the position of the pre-edge peaks. To match the position of the rising edge features, a shift of +91.9 eV would have been appropriate, however the former was preferred because the TDDFT protocol can more reliably calculate pre-edge transitions. The 1.3 eV difference indicate a systematic error in the calculations of intra-metal transitions (characteristic of the pre-edge peak) and metal to ligand charge transfer (characteristic of the rising edge features in all tricarbene systems investigated). In fact, the relative position of the 1s to 3d transitions and MLCT transitions has been previously shown to be systematically dependant on the Hartree-Fock exchange content of the DFT functional,\textsuperscript{[14]} which is 20% for B3LYP. Tuning this fraction could potentially result in better reproduction of the experimental differences between pre-edge and rising edge features, but is outside the scope of the present work and provides no further insights into the electronic structure.
Table S4. Summary of important structural parameters for complexes 1–3 and [(TIMEN\textsuperscript{mes})Co(NAr\textsuperscript{OMe})\textsuperscript{+} (2\textsuperscript{*})\textsuperscript{15}] as well as copper nitrene [(EMind\textsubscript{L})Cu(N(C\textsubscript{6}H\textsubscript{4}t\textsubscript{Bu}))\textsuperscript{16}] in the solid state.

| parameter                        | 1\textsuperscript{10} | 2* | 2   | 3   | [(EMind\textsubscript{L})Cu(N(C\textsubscript{6}H\textsubscript{4}Bu))] |
|----------------------------------|------------------------|----|-----|-----|----------------------------------|
| \(d\) (Co=N8)                   | -                      | 1.675(2) Å | 1.6770(14) Å | 1.697(3) Å | -                               |
| \(d\) (Co=N1)                   | 2.2434(11) Å           | 4.010 Å     | 3.236 Å       | 2.058(3) Å | -                               |
| \(d\) (C–N8)                    | -                      | 1.386(4) Å | 1.369(2) Å    | 1.310(5) Å | 1.310(3) Å                      |
| \(d\) (N8–C\textsuperscript{13}t) | -                      | 2.982 Å     | 2.795(3) Å    | -            |
| \(d\) (Co=Co=Co)                | -                      | 0.399(4)/1.413(4) Å | 1.426(2)/1.425(2) Å | 1.441(5)/1.450(5) Å | 1.431(3)/1.437(3) Å |
| \(d\) (C\textsuperscript{10}t=Co) | -                      | 1.391(4)/1.376(4) Å | 1.390(2)/1.392(2) Å | 1.364(5)/1.365(6) Å | 1.377(3)/1.369(3) Å |
| \(d\) (C\textsuperscript{10}t=Co) | -                      | 1.386(4)/1.384(4) Å | 1.39(3)/1.391(3) Å | 1.415(6)/1.397(6) Å | 1.411(3)/1.402(3) Å |
| \(d\) (Co–C2)                   | 1.9711(13) Å           | 1.940(3) Å | 1.9585(17) Å | 1.968(3) Å | -                               |
| \(d\) (Co–C6)                   | 1.9669(13) Å           | 1.938(3) Å | 1.9132(17) Å | 1.954(4) Å | -                               |
| \(d\) (Co–C10)                  | 1.9642(13) Å           | 1.962(3) Å | 1.9563(17) Å | 1.939(3) Å | -                               |
| av. \(d\) (Co–C)                | 1.9674(13) Å           | 1.947(3) Å | 1.9427(17) Å | 1.954(3) Å | -                               |
| av. \(d\) (C–N1)                | 1.4626(16) Å           | 1.444(4) Å | 1.428(2) Å   | 1.487(4) Å | -                               |
| \(d_{\text{oop}}\) (Co)         | 0.336 Å                | 0.902 Å    | 0.882 Å      | 0.317 Å    | -                               |
| \(\angle\) (Co=N8–C)            | -                      | 168.6(2)°  | 157.97(13)°  | 174.1(2)°  |
| \(\angle\) (C6-Co=Co)           | 125.64(5)°             | 100.29(11)° | 113.42(7)°  | 98.68(14)° | -                               |
| \(\angle\) (C10-Co=C2)          | 112.22(5)°             | 104.08(11)° | 92.34(7)°   | 149.71(14)° | -                               |
| \(\angle\) (C10-Co=C6)          | 113.52(5)°             | 96.46(11)° | 95.33(7)°    | 101.58(14)° | -                               |
| av. \(\angle\) (C-Co=C)         | 117.13(5)°             | 100.3(1)°  | 100.36(7)°  | 116.66(14)° | -                               |
| \(\angle\) (N1-Co=N8)           | -                      | 173.2°     | 156.45°      | 142.66(13)° | -                               |
| av. \(\angle\) (C-N1-C)         | 113.59(10)°            | 118.2(3)°  | 119.91(15)°  | 110.8(3)°  | -                               |
| \(\Sigma\) N1                   | 340.77(10)°            | 354.6(3)°  | 359.74(15)°  | 332.5(3)°  | -                               |
| \(d_{\text{oop}}\) (N1)         | 0.377 Å                | 0.196 Å    | 0.042 Å      | 0.462 Å    | -                               |

[a] There are two crystallographically independent molecules in the unit cell of 1, the bond distances and angles reported here are the average of the two molecules.
Green prism-shaped crystals of [(TIMMN\textsuperscript{mes})Co\textsuperscript{II}(NMes)](PF\textsubscript{6}) \cdot C\textsubscript{2}H\textsubscript{4} were grown by slow diffusion of n-pentane into a saturated toluene solution at room temperature overnight. Green needle-shaped crystals of [(TIMMN\textsuperscript{mes})Co\textsuperscript{III}(NMes)](PF\textsubscript{6}) \cdot 2 CH\textsubscript{2}Cl\textsubscript{2} were grown by slow diffusion of diethyl ether into a DCM solution at −25 °C overnight. Brown plate-shaped crystals of [(TIMMN\textsuperscript{mes})Co(NMes)](PF\textsubscript{6}) \cdot 5 C\textsubscript{6}H\textsubscript{6}O \cdot 0.5 C\textsubscript{2}H\textsubscript{5}H\textsubscript{2} were grown by slow diffusion of n-pentane into a saturated THF solution at −35 °C overnight. Orange plate-shaped crystals of [(TIMMN\textsuperscript{mes})Co\textsuperscript{II}(NMes)](PF\textsubscript{6}) \cdot C\textsubscript{6}H\textsubscript{6} were obtained at room temperature by slow diffusion of n-pentane into a THF/benzene mixture overnight. Green plate-shaped crystals of [(TIMMN\textsuperscript{mes})Co\textsuperscript{III}(NMes)](PF\textsubscript{6}) \cdot CH\textsubscript{2}Cl\textsubscript{2} were obtained at room temperature by slow diffusion of diethyl ether into a DCM/toluene mixture overnight. Yellow plate-shaped crystals of [(TIMMN\textsuperscript{mes})Co\textsuperscript{II}(CO)\textsubscript{2}(NMes)](PF\textsubscript{6}) (6) were obtained by diffusion of diethyl ether into a tetrahydrofuran/benzene mixture at room temperature overnight.

Suitable single crystals were embedded in protective perfluoropolyalkylether oil and transferred to the cold nitrogen gas stream of the diffractometer. Intensity data of all investigated crystals of the (TIMMN\textsuperscript{mes})-ligand system were collected at 100 K using MoK\textsubscript{α} radiation (\(\lambda = 0.71073\) Å) either on a Bruker Kappa PHOTON 2 \(\mu\)S Duo diffractometer equipped with QUAZAR focusing Montel optics (for 1, 3, 4, and 5) or on a Bruker Smart APEX 2 diffractometer using a Triangular curved graphite monochromator (for 2 and 6). Data were corrected for Lorentz and polarization effects, and, in addition, semi-empirical absorption corrections were performed on the basis of multiple scans using SADABS.\textsuperscript{[17]} The structures were solved by direct methods (SHELX XT 2014/5)\textsuperscript{[18]} and refined by full-matrix least-squares procedures on \(F^2\) using SHELXL 2018/3.\textsuperscript{[19]} All non-hydrogen atoms were refined with anisotropic displacement parameters. All other hydrogen atoms were placed in positions of optimized geometry. The isotropic displacement parameters of all H atoms were tied to those of the corresponding carrier atoms by a factor of either 1.2 or 1.5.

In the crystal structure of 1, the asymmetric unit contained two independent molecules of the complex salt. One of the PF\textsubscript{6}\textsuperscript{−} anions was disordered. Two alternative orientations were refined and resulted in site occupancies of 58(2) and 42(2) % for the atoms P1 – F16 and P1A – F16A, respectively. The compound crystallized with a total of two molecules of toluene in its asymmetric unit. While one of the toluene molecules was located on a general position the other was situated on two different crystallographic inversion centers and was accordingly disordered. Similarity restraints and pseudo-isotropic restraints were applied in the refinement of the anisotropic displacement parameters of the atoms of toluene C301 – C307. In the crystal structure of 2, the PF\textsubscript{6}\textsuperscript{−} anion was disordered. Two alternative orientations were refined and resulted in site occupancies of 56.6(5) and 43.4(5) % for the atoms F11 – F16 and F11A – F16A, respectively. Similarly restraints were applied to the anisotropic displacement parameters of the disordered fluorine atoms. The compound crystallized with two molecules of CH\textsubscript{2}Cl\textsubscript{2} per formula unit. One of these solvent molecules was disordered. Two alternative orientations were refined and resulted in site occupancies of 43(2) and 57(2) % for the atoms C100 – C112 and C110 – C114, respectively. The crystals of 3 suffered from an extremely rapid loss of included solvent and had to be handled at low temperatures all the time. One of the PF\textsubscript{6}\textsuperscript{−} anions was disordered. Two alternative orientations were refined and resulted in site occupancies of 57(2) and 43(2) % for the atoms P2 – F26 and P2A – F26A, respectively. The compound crystallized with five molecules of THF and half a molecule of n-pentane per formula unit. The n-pentane molecule was situated on a crystallographic inversion center and, correspondingly, was disordered. Three out of the five THF molecules were disordered. Two alternative orientations each were refined and resulted in the following site occupancies for the affected atoms: 54.4(19) and 45.6(19) % for O100 – C104 and O110 – C114; 44.7(19) and 55.3(19) % for O400, C401, C402, C404 and O410, C411, C412, C414; 61.1(9) and 38.9(9) % for O500 – C504 and O510 – C514, respectively. Similarity restraints were applied to the anisotropic displacement parameters of the disordered atoms. For the n-pentane additional pseudo-isotropic restraints were applied. Compound 4 crystallized with one molecule of benzene per formula unit. The PF\textsubscript{6}\textsuperscript{−} anion was disordered. Two alternative orientations were refined and resulted in site occupancies of 74.8(5) and 25.2(5) % for the atoms F11 – F16 and F11A – F16A, respectively. Similarity restraints were applied to the anisotropic displacement parameters of the disordered atoms. Compound 5 crystallized with one molecule of CH\textsubscript{2}Cl\textsubscript{2} per formula unit. One of the PF\textsubscript{6}\textsuperscript{−} anions was disordered. Two alternative orientations were refined and resulted in site occupancies of 53.0(5) and 47.0(5) % for the atoms F23 – F26 and F23A – F26A, respectively. All examined crystals of compound 6 proved to be multiply twinned. For the present
crystal a twin rotation about the reciprocal 0 0 1 axis of 180° was detected as the major twin element. The refinement resulted in twin individual mass fractions of 0.954(1) and 0.046(1).

Crystallographic data, data collection, and structure refinement details for the crystal structure determinations are given in Tables S5 and S6. Representations of the molecular structures are shown in Figures S42–S47.
SUPPORTING INFORMATION

Table S5. Crystallographic data, data collection and refinement details.

|                     | [(TIMMN\textsubscript{mes})Co\textsuperscript{I}]PF\textsubscript{6}·C\textsubscript{7}H\textsubscript{8} (1) | [(TIMMN\textsubscript{mes})Co\textsuperscript{II}(NMes)]PF\textsubscript{6}·2CH\textsubscript{2}Cl\textsubscript{2} (2) | [(TIMMN\textsubscript{mes})Co(NMes)]PF\textsubscript{6}·2(PF\textsubscript{6})·5(C\textsubscript{4}H\textsubscript{8}O)·0.5(C\textsubscript{5}H\textsubscript{12}) (3) |
|---------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|
| empirical formula    | C\textsubscript{39}H\textsubscript{45}CoN\textsubscript{7}·PF\textsubscript{6}·C\textsubscript{7}H\textsubscript{8} | C\textsubscript{48}H\textsubscript{56}CoN\textsubscript{8}·PF\textsubscript{6}·2(CH\textsubscript{2}Cl\textsubscript{2}) | C\textsubscript{48}H\textsubscript{56}CoN\textsubscript{8}·2(PF\textsubscript{6})·5(C\textsubscript{4}H\textsubscript{8}O)·0.5(C\textsubscript{5}H\textsubscript{12}) |
| \(M \text{ [g mol}^{-1}\)] | 907.85                                                          | 1118.76                                                          | 1490.46                                                          |
| crystal size [mm]    | 0.30 x 0.28 x 0.11                                               | 0.35 x 0.12 x 0.08                                               | 0.32 x 0.17 x 0.07                                               |
| temperature [K]      | 100                                                             | 100                                                             | 100                                                             |
| crystal system       | triclinic                                                       | triclinic                                                       | triclinic                                                       |
| space group (no. Int. Tables) | \(P\overline{1} (2)\)                                           | \(P\overline{1} (2)\)                                           | \(P\overline{1} (2)\)                                           |
| \(a \text{ [Å]}\)    | 10.9424(8)                                                      | 10.5847(4)                                                      | 10.9566(12)                                                     |
| \(b \text{ [Å]}\)    | 20.6497(15)                                                     | 15.5674(6)                                                      | 15.9933(17)                                                     |
| \(c \text{ [Å]}\)    | 20.8666(16)                                                     | 17.7324(7)                                                      | 22.234(2)                                                       |
| \(\alpha \text{ [°]}\) | 91.615(3)                                                   | 74.777(2)                                                      | 101.673(3)                                                     |
| \(\beta \text{ [°]}\) | 103.508(3)                                                      | 73.005(2)                                                      | 91.146(3)                                                       |
| \(\gamma \text{ [°]}\) | 102.181(2)                                                      | 70.890(2)                                                      | 106.587(3)                                                     |
| \(V \text{ [Å}^3\)] | 4466.4(6)                                                       | 2594.88(18)                                                    | 3644.2(7)                                                       |
| \(Z\)                | 4                                                              | 2                                                              | 2                                                              |
| \(\mu \text{ [mm}^{-1}\)] | 0.486                                                        | 0.633                                                          | 0.365                                                          |
| \(F(000)\)           | 1896                                                           | 1160                                                           | 1572                                                           |
| abs. corr.           | SADABS                                                         | SADABS                                                         | SADABS                                                         |
| \(T_{\text{min}}; T_{\text{max}}\) | 0.709; 0.746                                                      | 0.702; 0.746                                                   | 0.656; 0.746                                                   |
| 2\(\theta\)-range [°] | 3.9 ≤ 2\(\theta\) ≤ 59.1                                     | 4.0 ≤ 2\(\theta\) ≤ 59.2                                     | 3.6 ≤ 2\(\theta\) ≤ 54.2                                     |
| coll. refl.          | 162252                                                         | 109595                                                         | 147561                                                         |
| indep. refl.         | 25046                                                          | 14412                                                          | 16070                                                          |
| obs. refl.           | 22008                                                          | 10952                                                          | 13474                                                          |
| \(F_0 \geq 4.0\sigma(F)\) | 1235                                                         | 726                                                            | 1112                                                           |
| no. ref. param.      | 0.0931                                                         | 0.1016                                                         | 0.1968                                                         |
| \(R_1 \text{ [F}_0 \geq 4.0\sigma(F)\) | 0.0351                                                        | 0.0422                                                         | 0.0784                                                         |
| \(GooF F^2\)         | 1.051                                                          | 1.022                                                          | 1.125                                                          |
| \(\Delta \rho_{\text{max/min}} \text{ [eÅ}^{-3}\)] | 1.059; -0.666                                                 | 0.972; -0.860                                                  | 1.305; -0.665                                                  |
Table S6. Crystallographic data, data collection and refinement details.

|                | \([\text{TMMN}^\text{mes}]^\text{Co}^\text{II}(\text{Nmes})^\text{'}](\text{PF}_6)^2\) | \([\text{TMMN}^\text{mes}]^\text{Co}^\text{I}(\text{CO})_2(\text{Nmes})^\text{'}](\text{PF}_6)\) |
|----------------|---------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|
| empirical formula | \(\text{C}_{48}\text{H}_{56}\text{CoN}_8 \cdot \text{PF}_6 \cdot (\text{C}_6\text{H}_6)\) | \(\text{C}_{50}\text{H}_{56}\text{CoN}_8\text{O}_2 \cdot \text{PF}_6\) |
| \(M\) [g mol\(^{-1}\)] | 1027.01 | 1178.80 | 1004.92 |
| crystal size [mm] | 0.17x0.11x0.03 | 0.21x0.20x0.11 | 0.16x0.14x0.04 |
| temperature [K] | 100 | 100 | 100 |
| crystal system | triclinic | monoclinic | triclinic |
| space group (no. Int. Tables) | \(P\overline{1} (2)\) | \(P2_1/c (14)\) | \(P\overline{1} (2)\) |
| \(a\) [Å] | 11.8376(6) | 11.663(2) | 11.5104(6) |
| \(b\) [Å] | 14.0753(8) | 31.311(6) | 14.7839(8) |
| \(c\) [Å] | 16.9674(9) | 15.555(3) | 16.1844(9) |
| \(\alpha\) [°] | 99.978(2) | 90 | 67.129(4) |
| \(\beta\) [°] | 109.326(2) | 110.137(7) | 77.243(4) |
| \(\gamma\) [°] | 101.492(2) | 90 | 75.081(3) |
| \(V\) [Å\(^3\)] | 2525.3(2) | 5333(2) | 2429.4(2) |
| \(Z\) | 2 | 4 | 2 |
| \(\mu\) [mm\(^{-1}\)] | 0.439 | 0.567 | 0.458 |
| \(F(000)\) | 1076 | 2428 | 1048 |
| abs. corr. | SADABS | SADABS | SADABS |
| \(T_{\text{min}}; T_{\text{max}}\) | 0.706; 0.746 | 0.715; 0.746 | 0.686, 0.746 |
| 2\(\theta\)-range [°] | 3.7 ≤ 2\(\theta\) ≤ 61.1 | 3.7 ≤ 2\(\theta\) ≤ 57.4 | 3.6 ≤ 2\(\theta\) ≤ 52.0 |
| coll. refl. | 118283 | 245863 | 103498 |
| indep. refl. | 15450 | 13787 | 9527 |
| obs. refl. \(F_0 ≥ 4.0\sigma(F)\) | 11228 | 11819 | 6654 |
| no. ref. param. | 698 | 716 | 626 |
| \(wR_2\) | 0.0993 | 0.1410 | 0.2264 |
| \(R_1 (F_0 ≥ 4.0\sigma(F))\) | 0.0459 | 0.0526 | 0.0791 |
| \(GooF F^2\) | 1.026 | 1.075 | 1.080 |
| \(\Delta f_{\text{max},\text{min}}\) [eÅ\(^{-3}\)] | 0.487; -0.602 | 1.543; -0.950 | 1.536; -0.475 |
Figure S42. Thermal ellipsoid representations and the applied numbering scheme of the two crystallographically independent complex salt molecules of [(TIMMN<sub>mes</sub>)Co]<sub>I</sub>[PF<sub>6</sub>] in crystals of [(TIMMN<sub>mes</sub>)Co]<sub>I</sub>[PF<sub>6</sub>] • C<sub>7</sub>H<sub>8</sub>. (50 % probability ellipsoids, solvent molecules and hydrogen atoms omitted for clarity).
Figure S43. Thermal ellipsoid representations and the applied numbering scheme of the complex salt of [(TIMM\textsuperscript{mes})\textsuperscript{Co\textsuperscript{III}}(NMes)]\textsuperscript{+}([PF\textsubscript{6}]\textsuperscript{-}) in crystals of [(TIMM\textsuperscript{mes})\textsuperscript{Co\textsuperscript{III}}(NMes)]\textsuperscript{+}([PF\textsubscript{6}]\textsuperscript{-}) \cdot 2 CH\textsubscript{2}Cl\textsubscript{2} (50 % probability ellipsoids, solvent molecules and hydrogen atoms omitted for clarity).

Figure S44. Thermal ellipsoid representation and the applied numbering scheme of the complex salt of [(TIMM\textsuperscript{mes})\textsuperscript{Co(NMes)}\textsuperscript{2+}([PF\textsubscript{6}]\textsuperscript{-}) in crystals of [(TIMM\textsuperscript{mes})\textsuperscript{Co(NMes)}\textsuperscript{2+}([PF\textsubscript{6}]\textsuperscript{-}) \cdot 5 C\textsubscript{4}H\textsubscript{8}O \cdot 0.5 C\textsubscript{6}H\textsubscript{12} (50 % probability ellipsoids, hydrogen atoms omitted for clarity).
Figure S45. Thermal ellipsoid representations and the applied numbering scheme of the complex salt of [(TIMMN mes)*Co'(NMes')]([PF_6]) in crystals of [(TIMMN mes)*Co'(NMes')][PF_6] ∙ C_6H_6 (50 % probability ellipsoids, solvent molecules and hydrogen atoms omitted for clarity).

Figure S46. Thermal ellipsoid representation and the applied numbering scheme of the complex salt of [(TIMMN mes)*Co''(NMes')]_2([PF_6])_2 in crystals of [(TIMMN mes)*Co''(NMes')]_2[PF_6]_2 ∙ CH_2Cl_2 (50 % probability ellipsoids, hydrogen atoms omitted for clarity).
Figure S47. Thermal ellipsoid representation and the applied numbering scheme of the complex salt of [(TIMMN$^{\text{mes}}$)$^{\text{+}}$Co$(\text{CO})_2$(NMes)$^{\text{-}}$](PF$_6$) in crystals of [(TIMMN$^{\text{mes}}$)$^{\text{+}}$Co$(\text{CO})_2$(NMes)$^{\text{-}}$](PF$_6$) (50 % probability ellipsoids, hydrogen atoms omitted for clarity).
SUPPORTING INFORMATION

Computational Details

All calculations were performed with ORCA v. 5.0.1, 5.0.2 and 5.0.3. Only the cations are used for calculations.

1.) CASSCF calculations: The positions of all hydrogen atoms were optimized (“optimizeshydrogens true”) with constrained coordinates of all other atoms using the geometric parameters as obtained by the solid-state structures. CASSCF calculations were performed at the triple-ζ (ZORA-def2-TZVPP on all atoms)\(^{[21]}\) level using CAS(10,7) for 2 and CAS(11,8) for 3 according to Figures 6, 7 (Figures S56, S57 and S58, respectively). The difference between the two active spaces relates to inclusion of the ligand-centered, σ-donor orbital which combines with the d(x^2-y^2) d-orbital. Despite of repeated attempts, adding the imido ligand’s σ- (p(z), respectively) orbital in 2 top the active space led to poor convergence (undesired rotation, respectively), likely due to strong s-character, low energy and mixing with the aryl substituent. Scalar relativistic effects were modeled within the “Zeroth Order Regular Approximation” (ZORA).\(^{[22]}\) The RIJCOSX approximation with the related auxiliary basis set SARC/J (autoaux for /C) was used to speed up the calculations.\(^{[23]}\) Tighter-than-default scf (“tightscf”) criteria were chosen. In the manuscript, the results for calculations without state-averaging are given. For the calculation of the absorption spectra, state-averaged calculations (2, 50 singlet, 45 triplet and 5 quintet roots; 3, 75 doublet, 24 quartet, 1 sextet root) were performed and energies were corrected using the 2\(^{nd}\) order perturbation theory NEVPT2 with frozen core electrons (Figures S59, S60).\(^{[24]}\) Spin-orbit coupling was considered by quasi-degenerate perturbation theory (ODPT; soc true), yet does not have a strong effect on the absorption spectra and is not included in Figures S59 and S60.

2.) DFT calculations: The geometric parameters of all isolated compounds were optimized at the ZORA-DFT-D3BJ/def2-SVP level of theory using the PBE, TPSS, PBE0 and TPSSh functionals.\(^{[25]}\) The transition states were modeled using only the PBE (results given below) and TPSSh functionals. For cobalt, the ZORA-def2-TZVP basis set was used. The RI approximation (RIJCOSX, respectively) with the related auxiliary basis set SARC/J was used to speed up the calculations.\(^{[23]}\) Tighter-than-default scf (“tightscf”) and optimization criteria (“tighttopf”) were chosen. All calculated structures were verified as true minima by the absence (N\(^{\text{mag}} = 0\) of negative eigenvalues in the harmonic vibrational frequency analysis. The PBE, TPSS, and TPSSh functional gave reasonable agreement with the structural parameters in the solid state, whereas PBE0 proved less accurate (Table S7). Spin contamination with PBE and TPSSh was moderate (Deviation from ideal S(S+1) was between 0.01 a.u. and 0.03 a.u.). The energies of all compounds were corrected by single-point calculations at the triple-ζ level of theory using the TPSSh functional and SMD solvation model for THF.\(^{[26]}\) Intrinsic bond orbitals were calculated according to Knizia.\(^{[27]}\) For the reaction of 2 on the singlet potential energy surface, unrestricted (and broken symmetry) calculations were performed with the PBE functional, which however repeatedly converged to the closed-shell wavefunction. Generally, switching from PBE to TPSSh (and even more so PBE0) systemically favors the high-spin- versus the low-spin states in line with increasing admixture of exact exchange. The values obtained at the TPSSh/PBE level of theory gave the best fit with the experimentally determined barriers and are thus shown in the manuscript. See below Figures S61, S62 for the results obtained with the PBE/PBE level of theory, which are consistent (yet with “later” spin-crossover for the transformation from 2 to 4). Further, single-point calculations at the ZORA-DLPNO-CCSD(T)/def2-TZVPP level of theory were conducted [default pro settings (normalpro), including correction for solvation in THF (SMD)]. However, high T1 values up to 0.03 were obtained (Table S8), and we thus judge these values rather unreliable.

3.) EPR calculations: The EPR spectrum of 3 was modeled with the TPSSh functional at the triple-ζ level of theory using the structural parameters from the solid-state (vide supra). For the calculation of the HFC tensor, 2\(^{nd}\) order contributions from spin-orbit-coupling (“aorb”) were included for the cobalt ion.

4.) K-edge X-ray absorption calculations: The K-edge XAS spectra were calculated with time-dependent density functional theory (TDDFT) within Tamm-Dancoff approximation, as previously described,\(^{[28]}\) using B3LYP\(^{[29]}\) exchange-correlation functional on structures derived from crystallography where only the H atoms were optimized. Scalar-relativistic effects were included by Douglas-Kroll-Hess formalism.\(^{[30]}\) The DKH all-electron adapted version of Aldrich’s triple-zeta basis function DKH-def2-TZVP(f)\(^{[21]}\) were used together with the SARC/J general-purpose auxiliary basis set for Coulomb fitting.\(^{[31]}\) The SCF convergence criteria were set with “TightSCF” keyword. The oscillator strength was taken as the sum of electric dipole, electric quadrupole and magnetic dipole contributions. The transitions were assigned based on the natural transition orbitals.\(^{[32]}\) The natural transition orbital plots were produced with VMD.\(^{[33]}\)
Table S7. Benchmark of functional regarding the structural parameters in the solid state. Bond lengths are given in [Å], angles in [°].

|      | Co=N | Co-N | Co=N-C |
|------|------|------|--------|
| PBE  | 1.666| 3.242| 153.9  |
| TPSS | 1.663| 3.232| 153.6  |
| PBE0 | 1.639| 3.202| 153.8  |
| TPSSh| 1.652| 3.216| 153.7  |
| Exp  | 1.677| 3.236| 158.0  |

Table S7. Benchmark of functional regarding the structural parameters in the solid state. Bond lengths are given in [Å], angles in [°].

Figure S48. Pertinent intrinsic bond orbitals (IBOs) for 2 (S = 0).

Figure S49. Pertinent intrinsic bond orbitals (IBOs) for 2 (S = 1).
Figure S50. Pertinent intrinsic bond orbitals (IBOs) for 4 (S = 1).
Figure S51. Pertinent intrinsic bond orbitals (IBOs) for 3 (S = 1/2).

Figure S52. Pertinent intrinsic bond orbitals (IBOs) for 5 (S = 3/2).
Figure S53. Changes of the IBOs (TPSSh//PBE) associated with one of the two imido-cobalt π-bonds (top, bottom) and the NHC–Co σ-bond (middle) along the reaction coordinate (NHC–NMes distance given) from 2 to 4 ($S = 0$).

Figure S54. Changes of the IBOs (TPSSh//PBE) associated with one of the two imido-cobalt π-bonds (top, bottom) and the NHC–Co σ-bond (middle) along the reaction coordinate (NHC–NMes distance given) from 2 to 4 ($S = 1$).
Figure S55. Changes of the IBOs (TPSSH//PBE) associated with one of the two imido-cobalt π-bonds (top, bottom) and the NHC–Co σ-bond (middle) along the reaction coordinate (NHC–NMes distance given) from 3 to 5 ($S = 1/2$).

ROOT 0: $E = -3685.8897633367$ Eh
0.82076 [160]: 2222200
0.05701 [151]: 2221111
0.05504 [157]: 2222020
0.01802 [145]: 2220202
0.00906 [149]: 2221021
0.00480 [143]: 2220112
0.00444 [159]: 2222110
0.00440 [153]: 2221201
0.00381 [123]: 2202202

Figure S56. Configurations for ground state of 2 [CASSCF(10,7)].

ROOT 0: $E = -3685.6424459891$ Eh
0.84016 [503]: 22222100
0.07658 [492]: 22220120
0.02011 [478]: 22211111
0.01222 [446]: 22121210
0.00871 [499]: 22221110
0.00736 [432]: 22112201
0.00518 [283]: 20222102
0.00438 [471]: 22210121
0.00387 [420]: 22110221
0.00299 [464]: 22202102
0.00270 [72]: 02222102

Figure S57. Configurations for ground state of 3 [CASSCF(11,8)].
Figure S58. Entire active space for the dication in 3 according to the configurations in Fig. S57.
Figure S59. Absorption spectra of [(TIMMM$_{\text{mes}}$)Co$^{III}$NMes](PF$_6$)$_2$ (2), recorded at $-35$ °C in THF (green) and as obtained by calculations (black) at the CASSCF/NEVPT2 level of theory.

Figure S60. Absorption spectra of [(TIMMM$_{\text{mes}}$)Co(NMes)](PF$_6$)$_2$ (3), recorded at $-35$ °C in THF (brown) and as obtained by calculations (black) at the CASSCF/NEVPT2 level of theory.
**Figure S61.** Mechanism for the conversion of 2 to 4 as obtained at the ZORA-PBE(SMD=THF)/def2-TZVPP//ZORA-PBE/def2-SVP level of theory.

**Figure S62.** Mechanism for the conversion of 3 to 5 as obtained at the ZORA-PBE(SMD=THF)/def2-TZVPP//ZORA-PBE/def2-SVP level of theory.
### XYZ Coordinates

113

|   | S  | \(E\text{(PBE)}\) | \(G\text{(PBE)}\) | \(E\text{ (SP, PBE, SMD)}\) | \(E\text{ (SP, TPSSH, SMD)}\) | \(E\text{ (SP, CCSD(T))}\) | T1 |
|---|-----|-----------------|---------------|---------------------|---------------------|-----------------|---|
| 2s | 0   | -3697.19125     | -3696.34213   | -3699.55154         | -3699.63701         | -3702.96432     | 0.02058905 |
| \(\text{ts}[2-4s]\) | 0   | -3697.14802     | -3696.29997   | -3699.50745         | -3699.59331         | -3702.91807     | 0.01841242 |
| 4s | 0   | -3697.18504     | -3696.33684   | -3699.54265         | -3699.62966         | -3702.95549     | 0.0149314  |
| 2t | 1   | -3697.17334     | -3696.32693   | -3699.53382         | -3699.62511         | -3702.96108     | 0.01743221 |
| \(\text{ts}[2-4t]\) | 1   | -3697.14053     | -3696.2965    | -3699.49993         | -3699.58986         | -3702.92282     | 0.0170283 |
| 4t | 1   | -3697.20235     | -3696.35731   | -3699.5612           | -3699.65391         | -3703.00111     | 0.0202279 |
| 3d | 0.5 | -3696.9056      | -3696.06157   | -3699.26842         | -3699.47339         | -3702.8049      | 0.02878635 |
| \(\text{ts}[3-5d]\) | 0.5 | -3696.87809     | -3696.03133   | -3699.23641         | -3699.44443         | -3702.77524     | 0.01652248 |
| 5d | 0.5 | -3696.94001     | -3696.09105   | -3699.29534         | -3699.50899         | -3702.85431     | 0.01358472 |
| 3q | 1.5 | -3696.88306     | -3696.03611   | -3699.24288         | -3699.45767         | -3702.80043     | 0.01835016 |
| \(\text{ts}[3-5q]\) | 1.5 | -3696.85495     | -3696.00956   | -3699.21275         | -3699.42236         | -3702.76518     | 0.01826898 |
| 5q | 1.5 | -3696.93742     | -3696.0889    | -3699.29444         | -3699.50822         | -3702.86579     | 0.01250231 |

Table S8. Energies for geometry-optimized structures. Energies are given in [Eh].

**XYZ Coordinates**

113

2s_\text{PBE}

Co 10.92410295935775
N 10.15297613717679
N 12.52359567178927
N 13.65595016952075
N 9.07905882746422
N 8.22276880965449
N 9.68288429430726
N 10.79699103587216
N 11.21268726455360
C 11.46803648807048
C 11.46471968325727
C 11.79496541782010
C 12.37464965847119
C 13.83082142950620
C 14.13692494444675
C 14.54289511248454
H 15.59285161994768
C 9.89682774105393
H 10.86821126386117
H 9.35625504812557
C 9.33915669299411
C 7.85679314519341
H   7.48233924438812  8.14731154587601  5.76438650504648
C   7.32195347417365  10.36778178034585  5.99838808901164
H   6.38295378892811  10.61643725492281  6.49227778807658
C   9.17881329309244  9.54494879556211  2.22148291582551
H   8.26399728567579  9.6645800585692  2.8275196891492
H   8.88617076327834  9.01636402130847  1.29083033842495
C   10.47902792684214 11.68387483318179  2.56110955423505
C   9.48672440904646  11.35098973520358  0.5071659983311
H   8.87035247002741  10.84045185607751 -0.23353316835389
C   10.18438217309865 12.52262100154640  0.43779760442794
C   10.34171399591694 13.23714448735348  0.37498416118388
C   14.05735429929912 11.29512830653646  5.83036459919137
C   14.34519700997260 12.67342647246346  5.72098019857014
C   14.72309629939006 13.36034378126048  8.8449049802582
H   14.9280336730032  14.43671623011796  6.81203790902762
C   14.85166245297300 12.71499002899708  8.1266529867422
C   14.62563671383697 13.32964075608333  8.17818626014432
H   14.74571489280395 10.80078913330649  9.13278128962123
C   14.24029733409242 10.59215719345579  7.04331604198069
C   14.27095313012049 13.3770872863763  4.3978892060464
H   14.85243619587489 12.84640714182824  3.62547642680051
C   14.66143874414485 14.40398573311849  4.47437377799204
H   13.22910398352993 13.4319716779358  4.04089730710111
C   15.22389072145773 13.49838083264241  9.3606407853103
C   14.5656630339553 14.26477721899169  5.97407234187338
H   16.18459114407874 14.0277152958857  9.2258636880807
C   15.31493183877586 12.84859250016227 10.24673137255693
C   14.08316854993314  9.09339269691232  7.13684463745374
H   15.00106827794140  8.57481024695399  6.80183870551858
C   13.25569008170813  8.71499384724232  6.51330125471623
H   13.89726331620625  8.78270879427502  8.17805160824830
C   7.90486379080255  12.75770276705968  5.71212642509016
C   7.9474369390622  13.38886223469842  6.97721175056544
C   7.66082034670553  14.76549463929860  7.03371358080788
H   7.7223955170054  15.2690431910208  8.00740842020860
C   7.28087764266478  15.50308490978342  5.89943679232314
C   7.1399631835034  14.81031104806645  4.68342627636349
H   6.7813445077728  15.3489989545920  3.79637504926527
C   7.44004597482405  13.4427275527584  4.56390691011873
C   8.19295178757661  12.64285980761653  8.26220204480229
| Atom | x       | y       | z       |
|------|---------|---------|---------|
| H    | 8.8903760530567 | 13.193860638791 | 8.9138695893638 |
| H    | 8.60260894625216 | 11.6371110207741 | 8.09929089100365 |
| H    | 7.24235048270437 | 12.5306245893974 | 8.8173301584380 |
| C    | 7.02839796656220 | 16.9872202158175 | 5.98568543794055 |
| H    | 6.53968426368304 | 17.2663517191043 | 6.9470134478341 |
| H    | 6.37324541985062 | 17.3378999984786 | 5.1706446786107 |
| C    | 7.24558814598659 | 12.7443763318925 | 3.2441723683061 |
| H    | 6.52778194907971 | 12.7507491783074 | 2.6155236515134 |
| H    | 6.86448558368156 | 11.7162116063559 | 3.37485708805265 |
| C    | 11.77178792582041 | 13.7453123935072 | 1.86653461909422 |
| C    | 11.39366022084855 | 14.9502351656949 | 2.47793364838474 |
| C    | 12.35677815864114 | 15.98097579951540 | 2.55525497304008 |
| C    | 12.07878360944492 | 16.92975028141622 | 3.03035147516891 |
| C    | 13.6490570193072 | 15.83169026708159 | 2.01526985412325 |
| C    | 13.97810665331741 | 14.6076082754829 | 1.40298751545815 |
| C    | 14.984300622859513 | 14.4664408299000 | 0.98591859742105 |
| C    | 13.02678535943311 | 13.5441779290841 | 1.32669130740368 |
| C    | 10.9957467697993 | 15.1412093016078 | 3.03207419429815 |
| H    | 9.23668888777112 | 14.9518749520043 | 2.2654236021952 |
| H    | 9.864351715063344 | 16.1620826243211 | 3.41933585362853 |
| C    | 9.82378163365741 | 14.4328512407669 | 3.85928372311078 |
| C    | 14.66859916687832 | 16.93679722776515 | 2.12998801878064 |
| H    | 15.25576829013749 | 16.83152820441764 | 3.06281212858290 |
| C    | 14.19093163883972 | 17.93072089508384 | 2.1561309375370 |
| H    | 15.38477843703501 | 16.91846978208822 | 1.29117446644614 |
| C    | 13.46403684937394 | 12.21378946504596 | 0.74125962267157 |
| C    | 14.49130632344043 | 12.25173226063939 | 0.34493232905332 |
| H    | 12.7948550783526 | 11.89527812986242 | -0.07859492099220 |
| C    | 13.42657155233196 | 11.42306645853862 | 1.51446269203404 |
| C    | 11.30388336091239 | 12.85576413383572 | 7.06951532627377 |
| C    | 11.4345362067941 | 14.2317809773597 | 7.47744708248205 |
| C    | 11.56729889104292 | 14.53353024651105 | 8.83637954216312 |
| C    | 11.65584885782506 | 15.58692736994892 | 9.13654732424165 |
| C    | 11.46792504644794 | 12.19063033846038 | 9.41930401508213 |
| C    | 11.47567131893268 | 11.39848267202819 | 10.1809353069199 |
| C    | 11.30680287652226 | 11.82557938055375 | 8.07662549812375 |
| C    | 11.39112460545267 | 15.3203886526795 | 6.44250047120795 |
| Element | X-Coordinate | Y-Coordinate | Z-Coordinate |
|---------|--------------|--------------|--------------|
| H       | 9.30091866925008 | 8.87844647037464 | 1.1856803588692 |
| C       | 10.57071005308200 | 11.68431501687192 | 0.24229024993398 |
| C       | 9.59122695385304 | 11.38687906267382 | 0.35780343009380 |
| H       | 9.00500908484929 | 10.87700805671321 | -0.4073979997849 |
| C       | 10.22182637968272 | 12.59915746643190 | 0.34682200638532 |
| H       | 10.30832036985914 | 12.35700722871962 | -0.4318345247584 |
| C       | 14.16868744818933 | 11.37478994543923 | 5.93247392899414 |
| C       | 14.59609931644440 | 12.69207128712887 | 5.51681551224372 |
| C       | 14.88379510730367 | 13.61296770239766 | 6.48695720906901 |
| H       | 15.10274355509308 | 14.64179824669753 | 6.17153694021473 |
| C       | 15.03769032150135 | 13.25746295186068 | 7.83965195656639 |
| C       | 14.77973949279468 | 11.92644827436588 | 8.2025033834811 |
| H       | 14.90016751890133 | 11.62252644924430 | 9.25051743667096 |
| C       | 14.34929621949938 | 10.96190659485046 | 7.27276045231319 |
| C       | 14.31011778355460 | 13.09892284066603 | 4.08229413231740 |
| H       | 14.81311686367009 | 12.39183838148406 | 3.9786112653643 |
| C       | 14.72512567655321 | 14.10265420095520 | 3.90725773889812 |
| C       | 13.24463954398288 | 13.11757174652904 | 3.7954695702761 |
| C       | 15.42859897399454 | 14.28117778252881 | 8.8731932370445 |
| H       | 14.52197074467279 | 14.73919812131580 | 9.31349681667164 |
| C       | 16.03211858507448 | 15.09502840646545 | 8.43659896157228 |
| H       | 16.00248810875427 | 13.8294871789880 | 9.70025736576125 |
| C       | 14.13310728722900 | 9.54404261711944 | 7.74349427413104 |
| C       | 15.08968358439393 | 8.98951451533028 | 7.78710024362800 |
| C       | 13.45320043505937 | 8.97394518903077 | 7.09261248414828 |
| C       | 13.71077483789289 | 9.54387482796652 | 8.76224932987407 |
| C       | 7.78282157037654 | 12.90432427120359 | 5.64218137936518 |
| C       | 7.89043182345026 | 13.54213444598970 | 6.89645792393134 |
| C       | 7.63050783853242 | 14.92622462160772 | 6.94474196668452 |
| C       | 7.73737318766597 | 15.44213851440242 | 7.90859399946062 |
| C       | 7.22693680756069 | 15.65620602307146 | 5.8149635379397 |
| C       | 7.05649565683734 | 14.95992645099329 | 4.60144048299080 |
| C       | 6.70167273151567 | 15.50221209005712 | 3.71493319990336 |
| C       | 7.32948935035785 | 13.58834470592883 | 4.4885532949698 |
| C       | 8.19977516453140 | 12.79466666706797 | 8.1692999199694 |
| C       | 8.92435915885033 | 13.3553054627895 | 8.78707563103339 |
| C       | 8.62150530811938 | 11.80081165699252 | 7.98578101148086 |
| C       | 7.27906209894396 | 12.67413301636400 | 8.77067940540312 |
| C       | 6.99067622320315 | 17.14383568232718 | 5.88832037098514 |
| C       | 6.81323196489933 | 17.47810197485793 | 6.92402203505274 |
| Atom | X          | Y            | Z            |
|------|------------|--------------|--------------|
| H    | 6.12589459188794 | 17.4483063207170 | 5.27390473894543 |
| H    | 7.87006244904816  | 17.69880427845115 | 5.50872409690941 |
| C    | 7.14031658203234  | 12.86659027982536 | 3.17876848410770 |
| H    | 8.11334600095225  | 12.58347153951471 | 2.73983145844138 |
| H    | 6.6085325622761   | 13.50229678467718 | 2.4526306919753  |
| H    | 6.55799930547807  | 11.93591055702104 | 3.3091188046200  |
| C    | 7.14031658203234  | 12.86659027982536 | 3.17876848410770 |
| H    | 8.11334600095225  | 12.58347153951471 | 2.73983145844138 |
| H    | 6.6085325622761   | 13.50229678467718 | 2.4526306919753  |
| H    | 6.55799930547807  | 11.93591055702104 | 3.3091188046200  |
| C    | 11.7608808890336  | 13.83405670153963 | 1.82113878667445 |
| C    | 11.38732051252409 | 14.94183974882842 | 2.60848877598847 |
| C    | 12.31308934771936 | 15.99299812839105 | 2.7385968198593  |
| H    | 12.03829772461700 | 16.85885155206444 | 3.5529414031206  |
| C    | 13.56121709735126 | 15.9757297758853  | 2.0897840078383  |
| C    | 13.88748908883344 | 14.85178668465153 | 1.30731211874251 |
| H    | 14.86597401327840 | 14.81058155308039 | 0.8082107252551  |
| C    | 13.01420474014018 | 13.76147028387883 | 1.1689303381956  |
| C    | 10.0428336368347  | 14.99086203893953 | 3.27350058182438 |
| H    | 9.22754600616414  | 14.93088357343922 | 2.53025690317765  |
| C    | 9.91106551241057  | 15.92132020653192 | 3.84706894131042  |
| H    | 9.91451714197007  | 14.1410688431646 | 3.96702170482889  |
| C    | 14.54568073730943 | 17.10414980603460 | 2.26756187296629  |
| C    | 15.25477590440345 | 16.87777272450253 | 3.0872810363316  |
| C    | 14.04006306779428 | 18.05005794113422 | 2.52418911999474 |
| C    | 15.14548127237829 | 17.26786804616181 | 1.35610772072533 |
| C    | 13.42399746545593 | 12.53016988144253 | 0.39975666398157 |
| C    | 14.48023173197388 | 12.59310295114599 | 0.09294325772680 |
| H    | 12.81756029072194 | 12.37983627780731 | -0.51198129050014 |
| C    | 13.30001033784963 | 11.62377071699378 | 1.02173850991836 |
| C    | 11.30381675846794 | 12.40581028046492 | 7.09536904677021 |
| C    | 11.55494299108119 | 13.75213228784322 | 7.57481721277049 |
| C    | 11.74644362192362 | 13.96494509421589 | 8.94012350792214 |
| C    | 11.93456966225482 | 14.99126180380084 | 9.28719300826889 |
| C    | 11.71294306714784 | 12.91728934691888 | 8.89895696924826 |
| C    | 11.42628652358086 | 11.61847149907002 | 9.41907110548915 |
| H    | 11.36153842540819 | 10.79444617510607 | 10.14416766912042 |
| C    | 11.21031166754214 | 11.33406467620544 | 8.06749513665486 |
| C    | 11.56533557187559 | 14.88862356716316 | 6.59269800556357 |
| C    | 10.54420663825028 | 15.07971839417704 | 6.21188503770831 |
| C    | 12.19104720162952 | 14.65687409920553 | 5.71288879916989 |
| C    | 11.93656043161328 | 15.81590736140963 | 7.06045058950446 |
| C    | 12.0550547844922  | 13.17951967756669 | 11.34391118269341 |
| H    | 13.09753326055388 | 13.22091642002768 | 11.52886633962012 |
## SUPPORTING INFORMATION

|  |  |  |  |
|---|---|---|---|
| H | 11.59494155462560 | 12.38775522191995 | 11.99361435289824 |
| H | 11.58936183423057 | 14.14701594603506 | 11.67664754652363 |
| C | 10.82648134131426 | 9.4777688632366 | 7.63119794077421 |
| H | 11.08277561636361 | 9.20128157997533 | 8.0091303417370 |
| H | 11.3249546222807 | 9.67962452579926 | 6.68368276773917 |
| H | 9.73609389257930 | 9.87149139886454 | 7.44690039938722 |

### 3d_PBE

|  |  |  |  |
|---|---|---|---|
| Co | 1.31137877458080 | 2.30522917368106 | 15.87812961637711 |
| N | 2.11269318622430 | 4.86381091356833 | 16.36266203651144 |
| N | 3.49242874944938 | 3.28704819576422 | 17.43830395055043 |
| N | 4.17083810339453 | 1.40677485994038 | 16.60524673369484 |
| N | 2.46213322788172 | 4.36682162484261 | 14.08689457648961 |
| N | 1.32731761463638 | 2.9668024630869 | 12.90200344356020 |
| N | -0.27871820833685 | 4.66477990687888 | 16.57729735825876 |
| N | -1.49791486124749 | 2.8995651285921 | 16.87420983451455 |
| N | 0.96268894763652 | 0.78117556693303 | 16.45497179081973 |
| C | 2.68630698947025 | 4.48795032561247 | 17.6375054237051 |
| H | 3.34516668346051 | 5.26051949525663 | 18.08739413510991 |
| H | 1.85745618516919 | 4.28842716217343 | 18.34209526903244 |
| C | 3.12026705984096 | 2.28234534931314 | 16.57525987908848 |
| C | 4.74446576623006 | 3.0466201767726 | 17.99566252734721 |
| H | 5.22891818036566 | 3.73088484173929 | 18.6982767904302 |
| C | 5.1692149364872 | 1.8566281195777 | 17.47145996273223 |
| H | 6.09556900813418 | 1.29991680023938 | 17.61477071457557 |
| C | 3.00752089184370 | 5.06493932655178 | 15.24736114683087 |
| H | 3.13814060154993 | 6.13137654374988 | 14.9718574404183 |
| C | 4.00291097173134 | 4.66219092361336 | 15.50436996131328 |
| C | 1.65596341245219 | 3.26060423693031 | 14.20212834478396 |
| C | 2.66559026405126 | 4.73643172910215 | 12.7635877341778 |
| H | 3.28565366382483 | 5.58475137778179 | 12.47086621782104 |
| C | 1.95143797350446 | 3.84375241568697 | 12.01408519951990 |
| H | 1.80825673409744 | 3.76212555653136 | 10.93618377852294 |
| C | 0.85312883082306 | 5.56071113168038 | 16.31149563071909 |
| H | 0.78387981584352 | 6.39391509312664 | 17.0409574290870 |
| C | 0.74413902142735 | 5.99517714733441 | 15.30148289422088 |
| C | -0.25415973753681 | 3.29856099353523 | 16.43837742081397 |
| C | -1.5109681598250 | 5.11510220651621 | 17.0376124667684 |
| H | -1.73179617092893 | 6.17035071784353 | 17.2035039873733 |
| C | -2.82143074489081 | 3.99993129241396 | 17.21327364457456 |
H  -3.30704792020698  3.88706631872587  17.56474920511619
C  4.35587143230735  0.24101464138809  15.77053245674261
C  4.25272933573426 -1.04684048513685  16.34009627598382
C  4.45327046698288 -2.15219046198504  15.49082672546205
H  4.35777376945676 -3.16094566005003  13.63775050637199
C  4.81011024506929 -2.00633244065649  14.13843938863566
C  4.98043152085382 -0.70020644981904  13.63775050637199
H  5.30210217933883 -0.56373937186923  12.59698042410852
C  4.76276937253651  0.43907208037172  12.81284710494448
C  4.03152331638739 -1.27372213131218  11.81284710494448
H  4.98929482641659 -1.52764705793162  18.30551545160351
H  3.34918949732624 -2.12195126643503  17.98612893843838
H  3.62232733154590 -0.3927512466046  18.32769471049448
C  5.06494874717045 -3.20667098764928  13.26411687505398
H  4.58348749079734 -4.11417665277490  13.66385796777318
H  6.14980046601986 -3.41278635291090  13.1956107603228
H  4.70422019152876 -3.04476263621882  12.2381454160351
C  4.96975106747186  1.81659919650366  13.85279948800806
H  5.60723602506537  1.76906681907291  12.95546073492138
H  5.4555342605754  2.49866591767161  14.57307751795378
H  4.01017264414435  2.27348394447083  13.5527767815431
C  0.3174634631856  2.05143010088770  12.4213968174275
C  0.64319260378193  0.70116442037718  12.1838153214313
C  -0.3504895054242 -0.11744149704926  11.6154799614210
H  -0.1157630669776 -1.17299745226609  11.42587185816282
C  -1.61456461776028  0.38239546910073  11.2501096868041
C  -1.89040051525382  1.74184298962228  11.5016408821598
H  -2.87621390044702  2.14725785072375  11.23877305234252
H  -0.94665584444679  2.59678251018875  12.09282780615289
C  2.01049227007386  0.1671165335733  12.50512491565747
H  2.08143446388522 -0.90958447954876  12.2848155934169
H  2.26533514276263  0.31260315874082  13.5684536005464
H  2.7916094603018  0.67988137732427  11.91434714308886
C  -2.64228509108354 -0.50032180312969  10.59081668550485
H  -2.40826808084976 -1.56976176332810  10.71935660200421
H  -2.68512287228386 -0.29996661425698  9.50371026208420
H  -3.65469183644292 -0.31385818234557  10.98952747467965
C  -1.28657888720940  4.03124169860865  12.4114202170811
H  -2.33053584673864  4.25690794858062  12.14268918649787
H  -0.64180584952828  4.74655079992084  11.86888600195679
| Atom | X          | Y          | Z          | H          | X          | Y          | Z          |
|------|------------|------------|------------|------------|------------|------------|------------|
| H    | -1.16078062599094 | 4.2356345135021 | 13.49215290084091 |
| C    | -1.92266234187201     | 1.55255391937223     | 17.17622453629500   |
| C    | -2.26247089554042     | 0.67307575718071     | 16.1230583655878    |
| C    | -2.65261557511611     | -0.63126483085231     | 16.45777233086216    |
| H    | -2.92206343782338     | -1.32206230561747     | 15.64800432331169    |
| C    | -2.73034514543644     | -1.07022801853168     | 17.79454516080119    |
| C    | -2.43194630680476     | -0.14515929198966     | 18.81026976200451    |
| H    | -2.51796627205450     | -0.45721401414752     | 19.85929204534565    |
| C    | -2.04139081265576     | 1.17848133572765     | 18.53432076060344    |
| C    | -2.22304696693360     | 1.12640502988225     | 14.69472654924255    |
| H    | -1.18771435844549     | 1.29955747084199     | 14.35417001829272    |
| H    | -2.76891175967264     | 2.07622386598289     | 14.55331112022313    |
| C    | -2.67110496380163     | 0.37479617736561     | 14.02775571804815    |
| C    | -3.13946988408978     | -2.48314226826145     | 18.11632216200035    |
| H    | -4.10303686965426     | -2.73824927143426     | 17.64020579086528    |
| H    | -3.24598597083992     | -2.64252329116483     | 19.20180982623642    |
| H    | -2.3933915691103      | -3.20516054573528     | 17.73493629988428    |
| C    | -1.82632471157716     | 2.13749372535901     | 19.6804593455644     |
| H    | -1.12049996846888     | 2.95028198702893     | 19.44458241528773    |
| H    | -1.45304889721406     | 1.60516047619228     | 20.57077278431551    |
| H    | -2.78036507182882     | 2.61459140027988     | 19.97439043584984    |
| C    | 0.86905458349482      | -0.27376704270087     | 17.25713563603186    |
| C    | 0.60827017485182      | -1.57851289585426     | 16.67413144498152    |
| C    | 0.46590785323558      | -2.67062770945738     | 17.52956159852778    |
| H    | 0.27457511730230      | -3.66084427746096     | 17.09576053482113    |
| C    | 0.55171842027340      | -2.54513774974375     | 18.93611372055403    |
| C    | 0.82651517114788      | -1.27109371937344     | 19.49119853792950    |
| H    | 0.91468805097426      | -1.17583025869632     | 20.58134711458027    |
| C    | 0.99929445097064      | -0.13926769425554     | 18.69968967577980    |
| C    | 0.55241382431594      | -1.73847894563060     | 15.18713912606843    |
| H    | 1.58251515351508      | -1.77837460998383     | 14.78172500671362    |
| H    | 0.05130200118353      | -0.88607394347499     | 14.70051192516263    |
| H    | 0.04344346361618      | -2.67355802473098     | 14.90382657227549    |
| C    | 0.32848836187152      | -3.72965945024941     | 19.82654943711371    |
| H    | 0.51989424152949      | -4.68237833875518     | 19.30631964779117    |
| H    | -0.72736127999360     | -3.74956789836684     | 20.16405195420502    |
| H    | 0.95055531979609      | -3.68481466343184     | 20.7366322739379    |
| C    | 1.36724329680832      | 1.18068899052627      | 19.30418252424453    |
| H    | 1.15340554931772      | 1.20138729763394      | 20.38409487768527    |
| H    | 0.83666192561631      | 2.00798017071247      | 18.80559750316738    |

**S70**
|         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|
| **H**   | 2.45001 | 1.37467 | 350929010 | 19.17501 | 1254978368 | **SUPPORTING INFORMATION** |
| **113** | **3q_PBE** |         |         |         |         |

Co 1.44621769106577 2.54968288761603 16.06312449381625
N 2.10287568491377 4.65601120716496 16.39172167434329
N 3.73401578183331 3.31582724279205 17.40509773612341
N 4.32389402520090 1.39769739982789 16.59346026727007
N 2.31226902102830 4.41176450228323 14.05169728922692
N 1.19772821202290 3.00825101546841 12.86111540875899
N -0.244500854484448 4.63642768595485 16.86885717401117
N -1.47451714866640 2.86896357561585 17.10288634488210
N 1.06835510218123 0.86610188070279 16.3130507262402
C 2.90743196506357 4.49498381223484 17.61562139378589
H 2.21553120102611 4.35331851756999 18.46684841959193
C 3.31405226993623 2.31297329763548 16.55204593490109
C 4.96419189454077 3.02544094308567 17.97833734901059
H 5.46879619537528 3.68407860520968 18.68671456172262
H 5.33489296093880 1.81079100703837 17.4591793267144
H 6.23532482853416 1.21476505936949 17.61207730940905
C 2.9222351937565 5.01406711534710 15.21898797740607
C 2.99233828246859 6.1109643870420 15.076608263433
C 3.9409356674589 4.615714254785 15.36936668198255
C 1.5631242100935 2.6533182431505 14.15321151600197
C 2.44709124750354 4.84746852298479 12.73899457059628
H 3.0183852226553 5.73232479559758 12.45517900192601
C 1.74302131499576 3.94956713694279 11.9860120922964
C 1.567761781181905 3.89805027659102 10.91097456671740
C 0.88413872373911 5.47639136450981 16.5031662014937
C 0.99110401032187 6.28857324836899 17.2482530642614
H 0.69917504044296 5.93803639973345 15.51671362424091
C -0.25829648775097 3.27937700139335 16.62105165370772
C -1.42796475313054 5.07137319572984 17.44652065547763
C -1.62320132402713 6.11269128400144 17.70648723059748
C -2.20473917217606 3.9506059966136 17.58560787692223
C -3.20687336715757 3.82519818669912 17.99635302859826
C 4.44659794599594 0.2184227969080 15.76542324410767
C 4.29304940061871 -1.0597728470579 16.34239395472700
C 4.4356562959501 -2.17236574501784 15.49148658913455
C 4.30836426548072 -3.17550211593475 15.91671190431096
| Atom  | X    | Y    | Z    |
|-------|------|------|------|
| C     | 2.88 | 2.97 | 1.72 |
| C     | 2.54 | 2.18 | 1.62 |
| H     | -2.65 | -1.26 | 2.98 |
| C     | 2.09 | 1.12 | 1.85 |
| C     | 2.20 | 1.38 | 1.47 |
| H     | 2.65 | 2.39 | 1.44 |
| H     | 2.70 | 0.75 | 1.39 |
| C     | 3.33 | -2.56 | 1.77 |
| H     | 4.09 | 2.82 | 1.90 |
| H     | 3.72 | 1.51 | 2.05 |
| C     | 0.91 | -0.12 | 1.72 |
| C     | 0.58 | 1.44 | 1.62 |
| C     | 0.38 | 2.48 | 1.52 |
| H     | 0.14 | 3.47 | 1.71 |
| H     | 1.24 | 1.47 | 2.06 |
| H     | 1.00 | 2.23 | 1.23 |
| H     | 1.06 | 0.07 | 1.87 |
| C     | 1.68 | 0.92 | 1.95 |
| C     | 1.05 | 1.47 | 1.91 |
| H     | 1.51 | 1.47 | 1.87 |
| H     | 0.69 | 0.97 | 2.05 |
| C     | 1.92 | 1.39 | 1.95 |
| H     | 1.24 | 1.46 | 2.02 |
| H     | 1.00 | 1.23 | 1.87 |
| H     | 2.58 | 1.52 | 2.07 |

4s_PBE
Co 3.1753075768427 2.9911964589130 3.93185595906261
N 3.44878629078178 0.93915440856345 6.01218848739235
| Atoms | x       | y       | z       |
|-------|---------|---------|---------|
| N     | 1.2852  | 0.1820  | 4.0530  |
|       | 3.4545  | 5.0004  | 4.9411  |
|       | 4.7365  | 2.3651  | 1.8808  |
| C     | 2.3651  | 1.4793  | -0.0621 |
| H     | 1.8808  | 2.7572  | -0.4098 |
| C     | 3.1566  | 3.9050  | 4.2671  |
| C     | 3.5226  | 3.5226  | 4.6712  |
| H     | 3.7447  | 2.0879  | 4.5075  |
| C     | 3.8406  | 5.0755  | 3.2332  |
| C     | 4.2671  | 4.6712  | 4.5075  |
| C     | 4.1549  | 3.8973  | 4.2671  |
| H     | 4.8430  | 5.4075  | 5.2903  |
| C     | 5.1245  | 4.3273  | 5.2118  |
| C     | 5.1245  | 5.1245  | 5.2118  |
| C     | 5.1245  | 5.1245  | 5.2118  |
| C     | 5.1245  | 5.1245  | 5.2118  |
| C     | 5.1245  | 5.1245  | 5.2118  |
| C     | 5.1245  | 5.1245  | 5.2118  |
| C     | 5.1245  | 5.1245  | 5.2118  |
| C     | 5.1245  | 5.1245  | 5.2118  |
| C     | 5.1245  | 5.1245  | 5.2118  |
| C     | 5.1245  | 5.1245  | 5.2118  |

SUPPORTING INFORMATION
|   |   |   |   |
|---|---|---|---|
| H | -0.89191557927156 | 5.23914136097816 | 4.27149633903952 |
| H | -0.56489524702079 | 6.41095350800916 | 2.96339798788116 |
| H | 0.77036410756294 | 5.48859697521993 | 3.70591077878406 |
| C | -1.61044302926467 | 3.97498358173921 | -1.30578712253305 |
| H | -0.74528782427088 | 4.06483161380519 | -1.99072350543949 |
| H | -2.14977471021131 | 4.9366076285978 | -1.33191164346819 |
| H | -2.27221673647579 | 3.1956072478139 | -1.72046060502582 |
| C | -0.13626290578017 | 0.51430045604955 | 2.09499416851854 |
| C | -0.43225258546218 | -0.16947947502575 | 1.28351482796252 |
| H | -0.65800237555577 | 0.19855945002449 | 3.01672557487684 |
| C | 0.94695741459022 | 0.38213552140716 | 2.27729305557482 |
| H | 4.61279027069668 | 2.23183274582819 | 1.07675066581055 |
| C | 3.80001201426351 | 2.93293278418375 | 0.15991809898486 |
| C | 4.41203547599922 | 3.8956961467218 | -0.6594579212369 |
| C | 3.78741682909323 | 4.44573320327858 | -1.37623305956954 |
| C | 5.79307189585706 | 4.16304032638405 | -0.60005728530798 |
| C | 6.56952293075793 | 3.44390599951476 | 0.31609851882592 |
| H | 7.64662202860066 | 3.63171585598647 | 0.38675678764706 |
| C | 6.00442511312559 | 2.4653535998481 | 1.16312410945459 |
| C | 2.32605301122413 | 2.66346344825721 | 0.07507389949304 |
| H | 2.11124702254302 | 1.58622577121910 | -0.04012251391736 |
| H | 1.86746363284529 | 3.1989437130100 | -0.7711541699997 |
| H | 1.81618644294382 | 2.98819185063314 | 0.99879973535487 |
| C | 6.41017079955135 | 5.21326968198952 | -1.48795952070875 |
| H | 7.51161309667324 | 5.18254704918353 | -1.45021143929001 |
| C | 6.09364980963669 | 6.22550813880427 | -1.1746021255035 |
| H | 6.09901577604403 | 5.08644088825033 | -2.5401174811008 |
| C | 6.68287272744390 | 1.69090255448553 | 2.12785652193972 |
| H | 6.39725283437024 | 1.65958655734565 | 3.12892457500497 |
| H | 7.85788091151344 | 2.15287904952121 | 2.22495914884869 |
| H | 7.0049577948089 | 0.64285037276483 | 1.80518992291097 |
| C | 4.53853701477130 | 6.29295843567411 | 6.15824099653439 |
| C | 5.48891231993434 | 7.32313764088289 | 5.99406495180883 |
| C | 5.01896051474264 | 8.57808792864409 | 5.56249839932936 |
| H | 5.74787357176797 | 9.38659338385338 | 5.41886348442711 |
| C | 3.65940157358316 | 8.82698634024903 | 5.3104376587019 |
| C | 2.73691259823175 | 7.79363333354752 | 5.55965256577969 |
| C | 1.66333487122684 | 7.98261639660172 | 5.42567909256824 |
| C | 3.14964257381881 | 6.5255936730175 | 5.9971702515919 |
| C | 6.95956229198689 | 7.13103918020243 | 6.25877925482278 |
### SUPPORTING INFORMATION

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| H    | 7.50581390781246  | 6.98928781693563  | 5.30901912155777  |
| H    | 7.16548802120235  | 6.25771128615735  | 6.89752047164744  |
| H    | 7.38033104895041  | 8.02242867366070  | 6.75432663687460  |
| C    | 3.19989936320896  | 10.16603574849907 | 4.78710297849032  |
| H    | 3.20881794284727  | 10.17162007067476 | 3.68032398339140  |
| H    | 3.85981485140961  | 10.98390851235357 | 5.1221593541152  |
| H    | 2.17017421062034  | 10.39776764932327 | 5.1079290663588  |
| C    | 2.14579739617288  | 5.44912673797369  | 6.31352015883333  |
| H    | 2.21017156221014  | 4.60229595542464  | 5.59741015713541  |
| H    | 1.11694821122598  | 5.83991982703561  | 6.27181368142949  |
| H    | 2.31008964096469  | 5.02707594312322  | 7.32219008380342  |
| C    | 5.49125703288377  | 4.83615219683548  | 3.58158993085506  |
| C    | 6.90603251640508  | 4.89260660932839  | 3.70512592951638  |
| C    | 7.61173916957812  | 5.79380679445438  | 2.88853657437366  |
| H    | 8.70709875724516  | 5.82922455981950  | 2.97369196661354  |
| C    | 6.96744694069022  | 6.64057563417546  | 1.96627173908166  |
| C    | 5.56906438928976  | 6.54114417461841  | 1.85427399179762  |
| H    | 5.04168849953656  | 7.17959825496778  | 1.13260197786601  |
| C    | 4.81910941963863  | 5.64473394339641  | 2.63136211159016  |
| C    | 7.65489736698185  | 4.00716830694927  | 4.67151280906225  |
| H    | 8.73096048894170  | 3.99028237391495  | 4.43105374477586  |
| H    | 7.28552818088117  | 2.96817789784983  | 4.64274103045567  |
| H    | 7.56213103246576  | 4.35091988505071  | 5.71840454110841  |
| C    | 7.76198018565782  | 5.95679804011409  | 1.11108966467482  |
| H    | 8.40635013122767  | 7.05487161502544  | 0.39352785784360  |
| H    | 8.42873717467500  | 8.23041382922242  | 1.72367819263136  |
| C    | 7.10402725178059  | 8.26408235398605  | 0.52950214117521  |
| C    | 3.32900414672470  | 5.55079538849344  | 2.49071755407706  |
| H    | 2.82845359639492  | 6.03943625065394  | 3.34754128135522  |
| H    | 2.99263820365018  | 4.47769074400030  | 2.47850440749797  |
| H    | 2.96914101820488  | 6.02494369273653  | 1.56299965398067  |

**4t_PBE**

| Co     | 3.08637367164593 | 2.74106880529625 | 4.05653919015139 |
| N      | 3.32796388914319 | 1.22146758071407 | 5.72571274280863 |
| N      | 1.03274326328326 | 1.79076873857397 | 5.70773243714701 |
| N      | -0.03725045362058 | 2.58544877546006 | 4.0090737080013 |
| N      | 3.94993417768251 | 0.11517877157597 | 3.70302940363753 |
| N      | 4.56339775317320 | 1.11489901326164 | 1.88596006244678 |
| N      | 4.74235117038395 | 2.85426810429646 | 6.80280491400901 |

---

**S76**
SUPPORTING INFORMATION

N  4.94281620715979  5.05877613293855  6.7211157574207
N  4.63891697197882  3.84108704242842  4.61326957437971
C  2.15229381016555  1.44636932333435  6.56757246375194
H  1.87298194018485  0.56340227960822  7.18279684410665
C  2.38798410278291  2.28174340931598  7.25296457617352
C  1.24843864964428  2.4380228901415  4.9290314601116
C  -0.31303830769847  1.55761890059382  5.96145596171848
H  -0.67720594575153  1.07193171587625  6.8675892645793
C  -0.99117492765799  2.06245262383961  4.88470509170941
H  -2.05793525970393  2.09014522672372  4.66125346898563
C  3.29183855714789  -0.05131775939136  4.98367715700837
C  3.77925958958677  -0.8829441650048  5.53532926496527
H  2.22612759318264  -0.30844700186634  4.85172612971312
C  3.83522553618586  1.32388166861172  3.03809661453427
C  4.69948660887777  -0.820974112940  2.98246404380542
H  4.6815077359727  -1.8403266509987  3.32644048784564
C  5.07485847868484  -0.18572456323604  1.83265873584737
C  5.66409918555656  -0.54199043398687  0.98781436742464
H  4.62753672445645  1.48595987004741  6.36751103753879
C  4.81227141138437  0.83575803451817  7.24870868291165
H  5.39678197669547  1.27016670904535  5.6008976159380
C  4.78543645903589  3.93170554169639  5.92541648961799
H  4.85999206980376  3.31483638259909  8.12111268864773
C  4.8763802149536  2.63194442854030  8.9708253676124
C  4.98830890267729  4.67202450128329  8.06666098131010
H  5.09931260452690  5.40743016216090  8.86307588080285
C  -0.36880760743194  3.06083705346665  2.69398134308287
C  -0.55758102004821  4.44185406163494  2.47546641150906
C  -0.90452138877208  4.85712617376299  1.17713324066570
H  -1.05355475872292  5.92874022540602  0.98919005778200
C  -1.08909086328329  3.94131779056642  0.12409512038658
C  -0.91509520750573  2.57064763410179  0.39447846516467
H  -1.05889097865361  1.84043248943019  -0.41300354513981
C  -0.54570610966005  2.10569781506605  1.66785614534367
C  -0.41355079628511  5.43154757885491  3.60206670834076
H  -1.08804085627294  5.188473876567  4.44351417097869
H  -0.64523214843650  6.45392271566970  3.26243068349325
H  0.61253545679722  5.4269065326093  4.00637422511719
C  -1.43758803031662  4.41522982076344  -1.26489171740854
H  -0.52450153091574  4.53509412297962  -1.87933008432338
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| H    | -1.949524| 5.391987  | 0.518827  |
| H    | -2.088445| 3.694279  | 0.518827  |
| C    | -0.307270| 0.640567  | 0.518827  |
| H    | -0.455835| 0.044259  | 0.518827  |
| C    | -0.985150| 0.245168  | 0.518827  |
| H    | 0.726815  | 0.475351  | 0.518827  |
| H    | 1.389554  | 0.088470  | 0.518827  |
| C    | 4.260097  | 3.745272  | 0.518827  |
| H    | 3.482471  | 4.186142  | 0.518827  |
| C    | 5.584207  | 4.209743  | 0.518827  |
| H    | 6.558107  | 3.620058  | 0.518827  |
| C    | 7.595010  | 3.976106  | 0.518827  |
| H    | 8.245556  | 2.598711  | 0.518827  |
| C    | 9.474049  | 2.238031  | 0.518827  |
| H    | 10.207928 | 1.139223  | 0.518827  |
| C    | 1.852286  | 2.696654  | 0.518827  |
| H    | 2.027928  | 2.494105  | 0.518827  |
| C    | 5.933983  | 5.332822  | 0.518827  |
| H    | 7.015014  | 5.362482  | 0.518827  |
| H    | 5.657845  | 6.311956  | 0.518827  |
| C    | 5.394054  | 5.240758  | 0.518827  |
| C    | 7.322811  | 2.010970  | 0.518827  |
| H    | 6.937067  | 1.754653  | 0.518827  |
| H    | 8.150329  | 2.727972  | 0.518827  |
| C    | 7.747031  | 1.085047  | 0.518827  |
| C    | 4.603765  | 6.378499  | 0.518827  |
| C    | 5.599474  | 7.350082  | 0.518827  |
| C    | 5.188399  | 8.584312  | 0.518827  |
| H    | 5.951207  | 9.349955  | 0.518827  |
| C    | 3.843667  | 8.865520  | 0.518827  |
| C    | 2.875702  | 7.889390  | 0.518827  |
| H    | 1.813746  | 8.108045  | 0.518827  |
| C    | 3.227877  | 6.644301  | 0.518827  |
| H    | 7.057157  | 7.108869  | 0.518827  |
| C    | 7.586893  | 6.808296  | 0.518827  |
| H    | 7.212374  | 6.315849  | 0.518827  |
| C    | 7.534605  | 8.030668  | 0.518827  |
| C    | 3.448451  | 10.173370  | 0.518827  |
| H    | 3.474747  | 10.088668  | 0.518827  |
## SUPPORTING INFORMATION

| Atoms | Coordinates (Å) | Energy (eV) |
|-------|-----------------|-------------|
| C     | 2.17630967512727, 5.62740750118342 | 6.40399759196090 |
| H     | 2.17553388717225, 4.76154576458009 | 5.70744515528605 |
| H     | 1.17093566879620, 6.07690828290703 | 6.37658110833594 |
| C     | 5.36094739791960, 4.70797254070776 | 3.75103368008704 |
| C     | 6.77896957050575, 4.76702193207550 | 3.8343295061939 |
| C     | 7.47009873740875, 5.61536907587913 | 2.9509209660871 |
| H     | 8.56680061699752, 5.65780657849595 | 3.01539553105638 |
| C     | 6.8093368417691, 6.39481391291769 | 1.9840914353761 |
| C     | 5.41163900430781, 6.2685875183480 | 1.88901361902640 |
| C     | 4.87119620824460, 6.83849506873966 | 1.12243978575737 |
| C     | 7.5412868210636, 3.90807083183831 | 4.81334540521137 |
| C     | 6.8152984826551, 3.8894652316377 | 4.5642059500102 |
| C     | 7.17107454650582, 2.86639836853441 | 4.7956511033967 |
| C     | 7.45560305729141, 4.26146164007845 | 5.8578407727039 |
| C     | 7.58339500345895, 7.27957518577284 | 1.03843211964470 |
| C     | 8.01350159077688, 6.69179600289912 | 0.2046435013541 |
| C     | 8.42443411939642, 7.7834639735531 | 1.54610448589513 |
| C     | 6.94013607100435, 8.05661539317883 | 0.59146557923757 |
| C     | 3.18731618240238, 5.2959255651645 | 2.59656969518180 |
| C     | 2.6479300932179, 5.74411129141102 | 3.45928542561718 |
| C     | 2.86594945579054, 4.2664505369255 | 2.53273964860810 |
| C     | 2.82075198698109, 5.78327945183329 | 1.6780577919751 |

113

**5d_PBE**

Co 3.15452899174533, 2.85749507235324, 4.16026776771145

N 3.35956427219442, 1.27185300345141, 5.77414290392650

N 1.10210708721604, 1.90391324268311, 5.72954417919878

N 0.07737065863655, 2.56601601773437, 3.94209704714997

N 3.71389332493688, 0.19546702926239, 3.67588798236825

N 4.25874782544913, 1.26371616603045, 1.86889779936982

N 4.91503397012661, 2.79499623950114, 6.80169090590292

N 5.05295917385236, 4.9950936791151, 6.71849625375387

N 4.72598848630711, 3.80695995626977, 4.60329988323026

C 2.20431094475203, 1.568969831702, 6.62309613953282

H 1.89701045058988, 0.72178640885499, 7.27106513601598

H 2.46013994665552, 2.42677089261620, 7.2720762149264
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| H    | 0.83167303863438 | 0.32558476301749 | 2.25572018295434 |
| C    | 4.70379368986966 | 2.31589301959042 | 0.97932209228020 |
| C    | 3.79514898810489 | 2.91002359777770 | 0.07903799269492 |
| C    | 4.29087241145063 | 2.91009023597770 | -0.7850590041576 |
| H    | 3.59834163026600 | 4.36817500908112 | -1.4977676019918 |
| C    | 5.64532970610110 | 4.28634974437047 | -0.7868046378796 |
| C    | 6.51691837248020 | 3.65204575039732 | 0.11684999062347 |
| H    | 7.57790985558912 | 3.93183297318183 | 0.12777091126824 |
| C    | 6.07420154892700 | 2.66267895702602 | 1.01105560462905 |
| C    | 2.34950700510864 | 2.50340918527279 | 0.04559933133661 |
| H    | 2.22821267152133 | 1.40584501341572 | 0.02589599452175 |
| H    | 1.84025566287783 | 2.91842722601649 | -0.83778449828337 |
| C    | 1.28520300422159 | 2.86712676489207 | 0.93663697167643 |
| C    | 6.13767150336396 | 5.35849398340340 | -1.72388791435406 |
| H    | 7.23332447468567 | 5.32699912349175 | -1.84181743637564 |
| C    | 5.87300407357628 | 6.36339505907162 | -1.3438814468335 |
| H    | 5.68191313164321 | 5.26235703245749 | -2.72422091755460 |
| C    | 7.04181225254182 | 1.97724700950089 | 1.94097096134524 |
| H    | 6.61381431343638 | 1.84827564885060 | 2.95046687407121 |
| H    | 7.9706212010828 | 2.56095852030175 | 2.0358521405357 |
| H    | 7.3190366464004 | 0.97199925474852 | 1.57260957118723 |
| C    | 4.70626066841032 | 6.31877363814742 | 6.25269065220755 |
| C    | 5.69132288495701 | 7.30735469645378 | 6.05751294444689 |
| C    | 5.26568902451818 | 8.54259446593843 | 5.53050018048681 |
| H    | 6.01811955220136 | 9.32482558730808 | 5.3657844702819 |
| C    | 3.92161291962059 | 8.81140734421646 | 5.22014407014166 |
| C    | 2.96322805411425 | 7.81572380973375 | 5.50415277700336 |
| H    | 1.89969549257399 | 8.02937966618152 | 5.33382424613454 |
| C    | 3.32764800225639 | 6.56890183085209 | 6.03325073803401 |
| C    | 7.14461229901707 | 7.10641163820633 | 6.40035855972939 |
| H    | 7.74800055078551 | 6.97985370973099 | 5.48385230537042 |
| H    | 7.31718043492675 | 6.22872266951114 | 7.04276337592526 |
| H    | 7.53803868518166 | 7.99128249566177 | 6.92910310218499 |
| C    | 3.51384108923544 | 10.12617514997427 | 4.60926817114599 |
| H    | 3.54486990849360 | 10.06391895610271 | 3.50466840133701 |
| H    | 4.19226456297676 | 10.94239170354575 | 4.90790197741269 |
| H    | 2.48630833257153 | 10.40908120822838 | 4.8930274148523 |
| H    | 2.27840860324796 | 5.55181135858934 | 6.40932428682379 |
| C    | 2.29339958146679 | 4.66075452478380 | 5.74302606316326 |
| H    | 1.26857225398473 | 5.98620357954511 | 6.33918983314768 |
| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| H    | 2.41462773874651 | 5.18765296439111 | 7.44446493290050 |
| C    | 5.42625805770267 | 4.70632223245494 | 3.75261088186291 |
| C    | 6.83838117281502 | 4.83609349656839 | 3.83989012212373 |
| C    | 7.46619839617911 | 5.75255886206205 | 2.98023440689170 |
| C    | 8.55856383853190 | 5.8574037492380 | 3.03381349506635 |
| C    | 6.75079941531543 | 4.70632223245494 | 3.83989012212373 |
| C    | 7.46619839617911 | 5.75255886206205 | 2.98023440689170 |
| C    | 6.75079941531543 | 4.70632223245494 | 3.83989012212373 |
| C    | 7.46619839617911 | 5.75255886206205 | 2.98023440689170 |
| C    | 6.75079941531543 | 4.70632223245494 | 3.83989012212373 |
| H    | 4.86768118385213 | 4.01628181875644 | 4.50753184047798 |
| C    | 3.20839979993669 | 5.1925546487550 | 2.6610825844158 |
| C    | 2.64750730783624 | 5.56421809308445 | 3.5551054643147 |
| H    | 2.9661534865530 | 4.10581971950354 | 2.52470618300561 |
| H    | 2.77574508857432 | 5.6904744729535 | 1.77799953739397 |

5q_PBE

| Atom | X           | Y           | Z           |
|------|-------------|-------------|-------------|
| Co   | 3.14720437670786 | 2.66678075560358 | 3.85904047233816 |
| N    | 3.39051604972213 | 1.14017141996311 | 5.67696882699869 |
| N    | 1.11227616898830 | 1.83383255601613 | 5.72696632488051 |
| N    | 0.05029841417124 | 2.80767809151221 | 4.11899127137977 |
| N    | 0.40358249224219 | -0.03460961247155 | 3.68811997225248 |
| C    | 4.6938327975376 | 0.8907312248651 | 1.8482975793758 |
| N    | 4.75607148056392 | 2.80947178898951 | 6.76411902314539 |
| N    | 4.86346348118064 | 5.01366593016493 | 6.71323958803447 |
| N    | 5.450380239003568 | 3.82880413545634 | 4.60246891821242 |
| C    | 2.23101879108044 | 1.36736811695795 | 6.54092132543494 |
| H    | 1.91152948467997 | 0.46108511674733 | 7.09438707098232 |
| H    | 2.49880703589481 | 2.14185450149686 | 7.28092354430931 |
| C    | 1.31453342013473 | 2.52192992198595 | 4.55482902818019 |
| C    | -0.23576167709844 | 1.70797151929758 | 6.02792044373387 |
| H    | -0.06729032370046 | 1.20635928753586 | 6.92288142786894 |
| C    | -0.90900786465798 | 2.32214875781318 | 5.00045952998482 |
| H    | -1.97765502478466 | 2.43991257323377 | 4.81593158043626 |
| At   | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 3.36674250399983 | 0.15511607192376 | 4.98004762272274 |
| H    | 3.86077340476681  | 0.96293877644747  | 5.55793931018380 |
| H    | 2.30880422680094  | 0.43645746656638  | 4.82926547255341 |
| C    | 3.96670365886965  | 1.13380812888625  | 2.97560894623824 |
| C    | 4.76676425866640  | 1.00245773424613  | 3.01318288585255 |
| H    | 4.2506966875635   | 2.01258002595324  | 3.39418482859492 |
| C    | 5.18576841619744  | 4.9250696687563   | 1.84524515100694 |
| H    | 5.79036736423754  | 0.80023434341066  | 1.02600534421554 |
| C    | 4.69440632844236  | 1.44244406813739  | 6.30360757342924 |
| H    | 4.91142057255628  | 0.78501239445779  | 7.16983779207394 |
| C    | 5.4671799230703   | 1.27154342246998  | 5.53027392858333 |
| C    | 4.71733774382807  | 3.8991180130255   | 5.91956079276292 |
| C    | 4.93924985776265  | 3.24821576964145  | 8.08325040840436 |
| H    | 5.02816715417001  | 2.5595203211436   | 8.91934548192491 |
| C    | 5.00965383314555  | 4.61252867243657  | 8.04426383632494 |
| H    | 5.13554918413262  | 5.3407373104773   | 8.84587396903440 |
| C    | -0.2570221737937  | 3.36772545369669  | 2.82272614066004 |
| C    | -0.50832252997464 | 4.7485284839915   | 2.80143041368009 |
| C    | -0.79296759826243 | 5.22619472773683  | 1.39000617222136 |
| H    | -0.99202535823256 | 6.29841455364169  | 1.25939648697526 |
| C    | -0.85526564178599 | 4.37699978458563  | 0.27067607462533 |
| C    | -0.63037389847156 | 2.99884908853099  | 0.46856733214043 |
| H    | -0.69941753443662 | 2.31547430146500  | -0.38788775611332 |
| C    | -0.33507584251734 | 2.46649887663236  | 1.73349068342961 |
| C    | -0.48515519144569 | 5.70266814792622  | 3.85167757838499 |
| H    | -0.62529421632818 | 5.1929347773470   | 4.81806350848152 |
| H    | -1.28198262235810 | 6.45826734897414  | 3.74844530545253 |
| H    | 0.47339098164303  | 6.25313698950831  | 3.90164655738640 |
| C    | -1.20546480129833 | 4.91114395805138  | -1.09373559762226 |
| H    | -0.67606709488878 | 4.36541483069742  | -1.89320625773350 |
| H    | -0.96998790330490 | 5.98406915451464  | -1.18738737562285 |
| H    | -2.28877312568008 | 4.79533346446074  | -1.28694011337399 |
| C    | -0.13232385623454 | 0.98409029825037  | 1.93170233155644 |
| H    | -0.18734809763770 | 0.44869498237881  | 0.97088162130797 |
| H    | -0.90521259968027 | 0.55472424951110  | 2.59586762762070 |
| H    | 0.85083291284260  | 0.76320198552612  | 2.38875103954940 |
| C    | 5.02639636921030  | 1.91348914156755  | 0.88061659968084 |
| C    | 4.06422117753582  | 2.29930449256601  | -0.07795696314546 |
| H    | 4.41854925208460  | 3.32136612449830  | -0.97514038145270 |
| H    | 3.68825200368691  | 3.62768085074317  | -1.73567935591836 |
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | 5.681342   | 3.943980   | -0.942104  |
| C       | 6.612759   | 3.943980   | -0.942104  |
| H       | 7.067460   | 3.943980   | -0.942104  |
| C       | 6.314974   | 3.943980   | -0.942104  |
| C       | 2.706220   | 1.652289   | -0.142822  |
| C       | 6.017199   | 5.052735   | -1.905298  |
| H       | 7.103757   | 5.228127   | -1.964737  |
| C       | 5.534562   | 6.001969   | -1.590539  |
| C       | 4.516032   | 6.341031   | -2.921793  |
| C       | 5.009976   | 7.326386   | 6.038033   |
| C       | 5.069568   | 8.554915   | 5.502918   |
| C       | 5.820282   | 9.334773   | 5.319432   |
| C       | 3.720078   | 8.823371   | 5.213588   |
| C       | 2.765074   | 7.834743   | 5.527727   |
| C       | 1.698839   | 8.053447   | 5.382941   |
| C       | 3.135322   | 6.591049   | 6.060711   |
| C       | 6.958781   | 7.134294   | 6.367920   |
| C       | 7.556151   | 7.003073   | 5.447949   |
| C       | 7.142475   | 6.265060   | 7.018778   |
| C       | 7.352032   | 8.026369   | 6.884651   |
| C       | 3.307763   | 10.135982  | 4.599857   |
| C       | 3.453755   | 10.111916  | 3.503129   |
| C       | 3.912246   | 10.973020  | 4.987419   |
| C       | 2.244994   | 10.360807  | 4.787712   |
| C       | 2.095981   | 5.573308   | 6.461496   |
| C       | 2.064411   | 4.713135   | 5.764445   |
| C       | 1.093178   | 6.027461   | 6.474524   |
| C       | 2.290932   | 5.173016   | 7.473486   |
| C       | 5.186288   | 4.707834   | 3.714723   |
| C       | 6.596344   | 4.873806   | 3.798390   |
| C       | 7.209283   | 5.758964   | 2.896004   |
| C       | 8.297552   | 5.897976   | 2.958574   |
### SUPPORTING INFORMATION

|    |    |    |    |
|----|----|----|----|
| C  | 6.48866530865488 | 6.45344906116651 | 1.90306339084961 |
| C  | 5.1099803024731  | 6.19280490572334 | 1.79305858005547 |
| H  | 4.53184250406962  | 6.7737937070763  | 0.99571364567372 |
| C  | 4.45137640705100  | 5.31826708143851 | 2.66800147790704 |
| C  | 7.4313040533658   | 4.0874020130105  | 4.77971316430872 |
| H  | 8.49866079820329  | 4.13639722484589 | 4.50907917418224 |
| H  | 7.13821352387077  | 3.02315461735862 | 4.7885926369947 |
| H  | 7.34811748455482  | 4.4577336175278  | 5.8167605425430 |
| C  | 7.18977920012762  | 7.39391610908257 | 0.95773980338565 |
| H  | 7.86044251123667  | 6.84331986725909 | 0.27142485392727 |
| H  | 7.81979092617397  | 8.11875481242357 | 1.50304571846899 |
| H  | 6.47441954743093  | 7.96089833234439 | 0.33997591890595 |
| C  | 2.99800336093409  | 4.98365802835700 | 2.49712282114593 |
| H  | 2.40594065656093  | 5.1981295396866  | 3.40327099414504 |
| H  | 2.85600695037542  | 3.89870766657560 | 2.22707271200012 |
| C  | 2.5353708879223   | 5.52256081128369 | 1.65408193177074 |

### ts[2-4]s_PBE

|    |    |    |    |
|----|----|----|----|
| Co | 1.13000904245427 | 2.15388819187021 | 15.59188299061648 |
| N  | 2.09231420828302  | 4.99483214928833 | 16.444965669798 |
| N  | 2.96864639025366  | 3.03950073169236 | 17.57891827147761 |
| N  | 3.89225780803485  | 1.2837657054121  | 16.6516174205303 |
| N  | 2.52142633966993  | 4.28748074401044 | 14.17911496967773 |
| N  | 1.28429764114063  | 3.1476350945439  | 12.8140598331212 |
| N  | -0.30859360089411 | 4.69858966386909 | 16.15085045261148 |
| N  | -1.49450422060415 | 2.91122864718814 | 16.51271979533254 |
| N  | 1.30147429259867  | 0.75994767229998 | 16.5727821340213 |
| C  | 2.18315915807595  | 4.25288638781803 | 17.69820203295437 |
| C  | 2.65813413452499  | 4.84758234698052 | 18.5051581086781 |
| C  | 1.16064582365369  | 3.99703370845367 | 18.02902964967092 |
| C  | 2.67748314777291  | 1.97885599027297 | 16.7126580268053 |
| C  | 4.82701891343309  | 2.97781499474720 | 18.0360998061820 |
| H  | 4.69866837725315  | 3.71939258081184 | 18.72129312942522 |
| C  | 4.85481702075081  | 1.88034651244067 | 17.4611905738419 |
| H  | 5.85521167963670  | 1.45875306588795 | 17.55649109820085 |
| C  | 3.07990095111463  | 4.85573687911188 | 15.41187286326858 |
| H  | 3.52212728223273  | 5.83007981473873 | 15.11921060119229 |
| C  | 3.90521390533262  | 4.22711663212585 | 15.78772468337162 |
| C  | 1.63296667132692  | 3.22608310036162 | 14.15280042571199 |
| C  | 2.73987507789081  | 4.81873753732951 | 12.91075614040300 |
| Atom | X-coordinates | Y-coordinates | Z-coordinates |
|------|---------------|---------------|---------------|
| C    | 3.42777711331978 | 5.64519107954535 | 12.72847971390853 |
| C    | 1.96180040976740 | 4.09648155145499 | 12.04966938059306 |
| H    | 1.8235763848623  | 4.17136782102951 | 10.97101657257822 |
| C    | 0.85442681730052 | 5.62173501668480 | 16.11418357359464 |
| H    | 0.59441441767461 | 6.43853160518639 | 16.81919012198935 |
| C    | 0.54189537183891 | 6.07109196891419 | 15.10840011295922 |
| H    | -0.22697526309946 | -0.32272334531053 | 16.11899460992070 |
| C    | -1.58459119130565 | 5.12663949896966 | 16.50598617997808 |
| H    | -1.84923514142152 | 6.18421643628413 | 16.57843606262758 |
| C    | -2.33218699102419 | 4.00401013605234 | 16.71607333064591 |
| H    | -3.37491762903925 | 3.88174145067066 | 17.00845362465773 |
| C    | 4.18523232343523 | 0.08541641853068 | 15.90697529939553 |
| C    | 4.29907536220070 | -1.15209477808416 | 16.58159302685110 |
| C    | 4.56743562580158 | -2.29638204370378 | 15.80440815268078 |
| H    | 4.63240782484119 | -3.26682638263963 | 16.3140471611244 |
| C    | 4.76328221350609 | -2.23597753983501 | 14.41537704789275 |
| C    | 4.75389616026783 | -0.96677043402065 | 14.3029339092455 |
| H    | 4.98060345382051 | -0.88302570641345 | 12.73176712848481 |
| C    | 4.49085782583306 | 0.20550528999790 | 14.52824979737041 |
| C    | 4.2149904791860 | -1.29456877182939 | 18.07926723826221 |
| H    | 5.18975395383802 | -1.63130276122467 | 18.47860254612861 |
| C    | 3.46304719458972 | 2.05177783523178 | 18.3599645365128 |
| H    | 3.94785169930820 | -0.35762827229949 | 18.58762770159643 |
| C    | 4.98542212799332 | -3.48648527724243 | 13.60332576467998 |
| H    | 5.43003936303055 | -4.29314914929843 | 14.21034106945102 |
| C    | 5.64604379296361 | -3.2996287864562 | 12.73921317862775 |
| H    | 4.02586963406060 | -3.86700284302303 | 13.20456104737898 |
| C    | 4.60476221926431 | 1.55759076774448 | 13.87717242588159 |
| H    | 4.05845921820266 | 1.46665845671155 | 12.8379738105932 |
| H    | 6.31953710661240 | 0.22003185986091 | 14.42375141714553 |
| H    | 3.63659075922999 | 2.08281390474996 | 13.86967363751743 |
| C    | 0.23487305238106 | 2.33025943251705 | 12.26534427780322 |
| H    | 0.49273046566552 | 0.98718667217777 | 11.9177991753705 |
| C    | -0.55376069646505 | 0.2496095892735 | 11.33510839461654 |
| H    | -0.36894670348523 | -0.79764903820799 | 11.06207532925007 |
| C    | -1.81871997133653 | 0.81289194431207 | 11.08690351038120 |
| H    | -2.03055958531416 | 2.15801264471625 | 11.44609804189722 |
| H    | -3.01339385504644 | 2.61407132631735 | 11.26707166310715 |
| C    | -1.02407030309374 | 2.93561348015368 | 12.04209846832890 |
| C    | 1.83386343422072 | 0.36120798479196 | 12.1830179862331 |
SUPPORTING INFORMATION

H   1.87624897100104  -0.66964637808054  11.79734899161172
H   2.04008553069102  0.32478921524650  13.26796780413180
H   2.65200096038752  0.93978209949367  11.71903300300592
C   -2.93390634399933  -0.09571585490480  10.49214214888812
H   -2.54893951698452  -0.89870245128398  9.9657754703726
H   -3.53785631746908  0.5788729944266  9.7800108298366
H   -3.62187378099536  -0.36465793845218  11.28339019841344
C   -1.28859278858931  4.35827029842632  12.46780099731023
H   -2.34153558112034  4.63214216162662  12.29409618563781
H   -0.65718819284262  5.08101905873543  11.91918065031919
H   -1.07044314824284  4.49420103820255  13.54295510246484
C   -1.83347083670640  1.58494874636046  16.97234064632900
C   -2.0761968981245  0.55117544549908  16.04404120985309
C   -2.35339951045708  -0.73033775231648  16.54602762730579
H   -2.5272189926932  -1.54675635189080  15.83264949117131
C   -2.40955814924692  -0.9981459201639  17.92677202919334
C   -2.19624004024214  0.0686417342480  18.81537653544216
H   -2.2351243394726  -0.11808117176493  19.89638505367878
C   -1.91168691246444  1.37116236675453  18.3673522751303
C   -2.04045689900184  0.82109258798155  14.56822466154600
H   -1.03160238150320  1.13176702098886  14.23762402686661
H   -2.72611321376726  1.64007121342480  18.24753610909749
H   -2.3200670260187  -0.07380145015477  13.99071574817300
C   -2.71240918148673  -2.3853371206931  18.43194326805109
H   -3.79465864246039  -2.60495721070686  18.36307027676829
H   -2.4144964102925  -2.50434186653161  19.48629692821919
H   -2.18229290016909  -3.14882310379438  17.83677315274575
C   -1.71972710015180  2.48769327609036  19.36517928984227
H   -0.92078484528028  3.18687628632250  19.06336650853875
H   -1.46325303419402  2.0836726840266  20.3577082122770
H   -2.64037418095568  3.08902721539492  19.48336046572379
C   1.21927122906679  -0.3335209628973  17.38563733921328
C   1.02312842005595  -1.60989916597227  16.74786215177835
C   0.84582444935515  -2.74799509388668  17.54237900254177
H   0.70826431231723  -3.71834561186156  17.04511285535542
C   0.81940556155191  -2.68957008982417  18.95264529961653
C   0.93325647298638  -1.43169724629251  19.55833017521243
C   0.96938285190805  -1.35973712531546  20.65460545405564
C   1.21233946441144  -0.26205231447760  18.8153245536238
C   1.01294860618589  -1.70500364294996  15.24951052902004
SUPPORTING INFORMATION

H 1.99674496668231 -1.43009969767132 14.82918383187932
H 0.28030680819544 -1.00084452292024 14.81675452057859
H 0.76921863555827 -2.72776927252782 14.91771742372041
C 0.58736905182102 -3.93269557433104 19.77243531567793
H 1.21046117452668 -4.77044959712732 19.42476873762448
H -0.46362270927915 -4.27172111167305 19.69348863481848
H 0.8018233010547 -3.76337405747483 20.84087356405793
C 1.43795083619666 1.04395037301384 19.52368069244858
H 1.03713888132469 1.01239267286892 20.55045052510785
H 0.9600179859260 1.8745724245302 18.98192132719429
H 2.51698094936965 1.28285712136888 19.59883963565871
113
ts[2-4]t
Co 1.26531417328467 2.39687147914171 15.72582196137975
N 2.01017532979160 4.76388570244833 16.31084307047576
N 3.28300058303988 3.11746006873974 17.4832961813341
N 4.09736406686122 1.28680349040218 16.58330834506635
N 2.43014789354820 4.39038438318389 14.01754176055105
N 1.30061638049755 3.07147146563460 12.73401327875588
N -0.37608110363580 4.59300103414195 16.5360996296534
N -1.55013353186586 2.80110872169218 16.83341896000622
N 1.44735028406235 1.06196279468842 16.81083258631929
C 2.48261487108723 4.31895827466796 17.61409641217008
H 3.10509481094411 5.07109596018403 18.44538127113110
H 1.58206797009708 4.12800338912202 18.2296144938132
C 2.93345939385311 2.06258199434744 16.62013862410078
C 4.57652072926265 2.95916607243085 17.981834070577
H 5.02266216062234 3.65518001261540 18.69289693337960
C 5.07534273066992 1.81575850316180 17.4244630169785
H 6.03930881411501 1.32571657159326 17.54798977703123
C 2.9640335350908 4.97236192670773 15.24848810483305
H 3.19195795811792 6.04028054268582 15.04534427226101
H 3.90649238376863 4.46786548909477 15.53067401388062
C 1.61509572730940 3.27749413994631 14.45762159773574
C 2.64405613909829 4.84414192854466 12.72194197905116
C 3.27486207906797 5.70237539807178 12.48714709251753
C 1.93334237622228 4.00414051651563 11.90870329227485
H 1.80968578197332 3.98951859188175 10.82579943695946
C 0.75378185047314 5.47213945496666 16.2240140698514
H 0.68766290539615 6.34195902469217 16.91199486995593
SUPPORTING INFORMATION

H  0.65681086597478  5.85459805194891  15.19132155006963
C  -0.36165094502175  3.23482930220820  16.29316237526963
C  -1.54635678220953  4.99804450804482  17.17124395985999
H  -1.75078593164577  6.03626400031055  17.4375330297236
C  -2.29148625756187  3.86537335853448  17.34795823452093
H  -3.27269902602054  3.71678540278349  17.79791292406062
C  4.32730709272057  0.12191046617404  15.77512830775818
C  4.33204253489938  -1.16268850526075  16.3640921320162
C  4.55322394358291  -2.26678727037227  15.51601687249227
H  4.53819228582724  -3.27249815891401  15.95690342236729
C  5.08754350715037  -0.67969400341336  12.5571976559222
C  4.65837458904801  0.31453475370442  14.410296845233
C  4.16458231017587  -1.40161746050719  13.84327419343536
H  5.05340373582724  -1.92406012659145  18.2418695305920
C  3.2824558497047  -2.04245866258399  18.0429326967645
C  4.02916435377905  -0.47439597974475  18.41764522187322
C  4.99560037050483  -3.32743089014474  13.25342238441559
H  5.2894187077097  -4.21956510612742  13.83113746728054
H  5.76352384896385  -3.14664120720328  12.48149690293662
C  4.05487905405571  -3.57300076145245  12.72435884323231
C  4.80690881235813  1.70372866452027  13.84536112242110
C  5.08929832055488  1.67051851893162  12.78093433747408
C  5.58841592364809  2.27034493904802  14.38574485624152
C  3.86666248628013  2.27176572439639  13.9401396379036
C  0.29753149744109  2.16987762296522  12.22690578882409
C  0.59584202453934  0.80253416165212  12.05895612851327
C  -0.39991860043806  -0.02089245585868  11.50203719213954
H  -0.18442043871561  -1.08981686439985  11.37420871533998
C  -1.64877488760054  0.48455981963347  11.09806577107993
C  -1.90842545108689  1.85443772554287  11.29873070120396
H  -2.88968198759624  2.26239537559344  11.02206280461876
C  -0.9589566670198  2.71536815748868  11.8730422179591
C  1.92910386910488  0.25196493171640  12.47665167369710
C  1.9832099741188  -0.83652654483953  12.31893166176551
H  2.11876415002867  0.45027446464824  13.54613086791380
H  2.75501481836579  0.72120163232575  11.91208377165124
C  -2.68437612390886  -0.41044512848332  10.46496123230963
H  -2.48695260807110  -1.47467595829648  10.67574113657651
### SUPPORTING INFORMATION

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| C    | 1.23496247526212 | 0.02016844135099 | 17.65382311618312 |
| C    | 0.81866330504952 | -1.22780724336882 | 17.06038655933264 |
| C    | 0.52503742273510 | -2.31291527480718 | 17.89233688737653 |
| C    | 0.52093430807158 | -3.25709680728267 | 17.42672634555196 |
| C    | 0.16183631758859 | -2.24001767793422 | 19.29860100619419 |
| C    | 1.05961921482083 | -1.02551133903917 | 19.85948292206450 |
| H    | 1.15998627432805 | -0.94894189957700 | 20.95144219213640 |
| C    | 1.38063512756706 | 0.09471223034324 | 19.08010005535773 |
| C    | 0.73284509905905 | -1.35737179310349 | 15.5662032321083 |
| C    | 1.74320261567895 | -1.33078637200300 | 15.11642468814855 |
| H    | 0.16809063513067 | -0.52076680803730 | 15.1208771137209 |
| C    | 0.25115340381115 | -2.30633346559925 | 15.2779225102885 |
| H    | 0.22419572202835 | -3.40921079194590 | 20.16367979649907 |
| C    | 0.52665747784701 | -4.37078705892387 | 19.71253240170905 |
|   |   |   |   |
|---|---|---|---|
| H | -0.87511202440469 | -3.45008341397371 | 20.29671608515704 |
| H | 0.67332829848210  | -3.34548460850347 | 21.16932440116395 |
| C | 1.89540568679851   | 1.34467474047403  | 19.73792762157572 |
| H | 1.66568646477671   | 1.35049816247746  | 20.81643460093201 |
| H | 1.45299586464613   | 2.24708739956800  | 19.28210224088997 |
| H | 2.99424840693794   | 1.43910698064995  | 19.63393097984192 |
References

[1] A. Marcó, R. Compañó, R. Rubio, I. Casals, Microchim. Acta 2003, 142, 13-19.
[2] G. A. Bain, J. F. Berry, J. Chem. Educ. 2008, 85, 532-536.
[3] E. Bill, SQUID Program JuX2, 2019.
[4] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, Organometallics 2010, 29, 2176-2179.
[5] E. Bill, EPR Program Eview, 2019.
[6] E. Bill, EPR Program Esem, 2019.
[7] B. J. Gaffney, H. J. Silverstone, Plenum Press, New York 1993.
[8] W. Mao, D. Fehn, F. W. Heinemann, A. Scheurer, D. Munz, K. Meyer, Angew. Chem. Int. Ed. 2021, 60, 16480-16486.
[9] D. G. Brown, N. Sanguantrakun, B. Schulze, U. S. Schubert, C. P. Berlinguette, J. Am. Chem. Soc. 2012, 134, 12354-12357.
[10] M. K. Goetz, E. A. Hill, A. S. Filatov, J. S. Anderson, J. Am. Chem. Soc. 2018, 140, 13176-13180.
[11] a) X. Hu, Y. Tang, P. Gantzel, K. Meyer, Organometallics 2003, 22, 612-614; b) X. Hu, I. Castro-Rodríguez, K. Olsen, K. Meyer, Organometallics 2004, 23, 755-764.
[12] S. C. Bari, C. Anthon, F. W. Heinemann, E. Bill, N. M. Edelstein, K. Meyer, J. Am. Chem. Soc. 2008, 130, 12536-12546.
[13] J. F. Berry, S. DeBeer George, F. Neese, Phys. Chem. Chem. Phys. 2008, 10, 4361-4374.
[14] M. Roemelt, M. A. Beckwith, C. Duboc, M. N. Collomb, F. Neese, S. DeBeer, Inorg. Chem. 2012, 51, 660-667.
[15] X. Hu, K. Meyer, J. Am. Chem. Soc. 2004, 126, 16322-16323.
[16] K. M. Barsch, I. M. DiMuco, D. A. Iovan, A. Li, S. Zheng, C. J. Titus, S. J. Lee, K. D. Irwin, D. Nordlund, K. M. Lancaster, T. A. Betley, Science 2019, 365, 1135-1143.
[17] I. Bruker AXS, SADABS 2014/5, Bruker AXS area detector scaling and absorption correction, 2014.
[18] G. M. Sheldrick, Acta. Crystallogr. A 2008, 64, 112-122.
[19] G. M. Sheldrick, Acta. Crystallogr. C Struct. Chem. 2015, 71, 3-8.
[20] a) F. Neese, F. Wenmohs, U. Becker, C. Riplinger, J. Chem. Phys. 2020, 152, 224108; b) F. Neese, WIREs Comput. Mol. Sci. 2022, e1606.
[21] F. Weigend, R. Ahrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297-3305.
[22] a) E. van Lenthe, E. J. Baerends, J. G. Snijders, J. Chem. Phys. 1994, 101, 9783-9792; b) C. v. Wüllen, J. Chem. Phys. 1998, 109, 392-399; c) E. van Lenthe, A. Ehlers, E.-J. Baerends, J. Chem. Phys. 1999, 110, 8943-8953.
[23] F. Weigend, Phys. Chem. Chem. Phys. 2006, 8, 1057-1065.
[24] C. Angeli, R. Ciriminagara, S. Evangelisti, T. Leininger, J. P. Malrieu, J. Chem. Phys. 2001, 114, 10252-10264.
[25] a) J. P. Perdew, M. Emzerhof, K. Burke, J. Chem. Phys. 1996, 105, 9982-9985; b) C. Adamo, V. Barone, J. Chem. Phys. 1999, 110, 6158-6170; c) J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, Phys. Rev. Lett. 2003, 91, 146401; d) V. N. Staroverov, G. E. Scuseria, J. Tao, J. P. Perdew, J. Chem. Phys. 2003, 119, 12129-12137.
[26] A. V. Marenich, C. J. Cramer, D. G. Truhlar, J. Phys. Chem. B 2009, 113, 6378-6396.
[27] G. Knizia, J. Chem. Theory Comput. 2013, 9, 4834-4843.
[28] S. DeBeer George, T. Petrenko, F. Neese, J. Phys. Chem. A 2008, 112, 12936-12943.
[29] a) P. A. M. Dirac, Proc. R. Soc. Lond. A 1929, 123, 714-733; b) J. C. Slater, Phys. Rev. 1951, 81, 385-390; c) S. H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 1980, 58, 1200-1211; d) A. D. Becke, Phys. Rev. A 1988, 38, 3098-3100; e) A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652.
[30] M. Reither, A. Wolf, J. Chem. Phys. 2004, 121, 10945-10956.
[31] F. Weigend, Phys. Chem. Chem. Phys. 2006, 8, 1057-1085.
[32] F. Plasser, M. Wormit, A. Dreuw, J. Chem. Phys. 2014, 141, 024106.
[33] W. Humphrey, A. Dalke, K. Schulten, J. Mol. Graphics. 1996, 14, 33-38.