Supporting Information

Nitrogen Oxyanion Reduction by Co(II) Augmented by a Proton Responsive Ligand: Recruiting Multiple Metals

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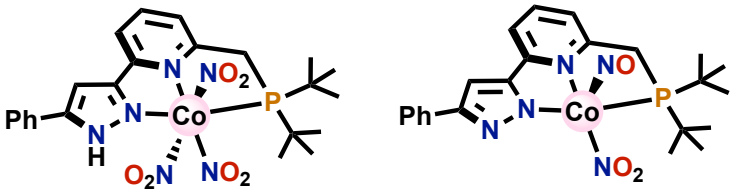
Experimental.

General. All manipulations were carried out under an atmosphere of ultra-high purity nitrogen using standard Schlenk techniques or in a glovebox under N_2. Solvents were purchased from commercial sources, purified using Innovative Technology SPS-400 PureSolv solvent system or by distilling from conventional drying agents and degassed by the freeze-pump-thaw method thrice prior to use. Glassware was oven-dried at 150 C overnight and flame dried prior to use. NMR spectra were recorded in various deuterated solvents at 25°C on a Varian Inova-400 or 500 spectrometer (^{1}H: 400.11 MHz, 500.11 MHz, respectively). Proton chemical shifts are reported in ppm versus solvent protic impurity and referenced to $SiMe_4$. Mass spectrometry analyses were performed in an Agilent 6130 MSD (Agilent Technologies, Santa Clara, CA) quadrupole mass spectrometer equipped with a Multimode (ESI and APCI) source. All starting materials have been obtained from commercial sources and used without further purification.

Synthesis of $(PNNH)Co(NO_2)_3$ and $(PNN)Co(NO_2)(NO)$.

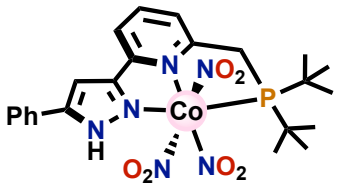


Excess sodium nitrite (0.0950 g, 1.38 mmol, 5 equivalents) were added to a solution of $(PNNH)CoCl_2$ (0.2805 g, 0.55 mmol, 2 equivalents) in 10 mL of DCM. Catalytic amounts of 18-Crown-6 ether (5 mol %) were added to help solubilize the nitrite salt. After stirring for 4h at RT, the violet solution turned brown. A white precipitate was filtered away on a plug of Celite and all volatiles were removed. The crude material (0.275 g) was characterized by ^{1}H NMR, ^{31}P NMR, and IR spectroscopy (Figs S1-2) and was shown to contain two products. Single crystals suitable for X-ray diffraction were grown by slow diffusion of cyclohexane vapor into a concentrated DCM solution. Two distinct crystal types (one red and one orange) were present in the crystallization vial, and both were characterized by single crystal X-ray diffraction. Characterization of each product is shown below under their respective independent synthesis.

To confirm the basicity of the solution at the end of the reaction, the pH was measured. All DCM solvent was removed and the crude mixture was dissolved in water. pH measurements were performed at 22.0 ºC on a Schott Instruments Lab 860 pH meter with an Orion ROSS Ultra Glass Triode pH electrode and showed that this solution had a pH of 8.35.

The ideal stoichiometry of 5 $NaNO_2$: 2 $(PNNH)CoCl_2$ was determined by multiple experiments, varying the equivalents of $NaNO_2$. Our criteria for this ideal stoichiometry was based on observing the formation of only $(PNNH)Co(NO_2)_3$ and $(PNN)Co(NO_2)(NO)$ as the cobalt-containing products, along with complete consumption of $NaNO_2$. When fewer equivalents are used, minor diamagnetic impurities are present in addition to the desired products, which we attribute to insufficient amounts of NO_2^- present to displace all Cl^- and OH^-, thus giving rise to a small quantity of compounds with varied X type ligands. Any ratio of $NaNO_2$ larger than 5 $NaNO_2$: 2 $(PNNH)CoCl_2$ gives only the desired products.

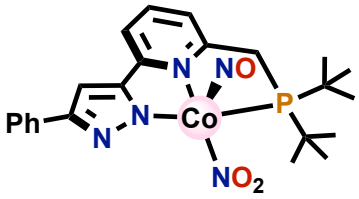
Independent synthesis of (PNNH)Co(NO$_2$)$_3$.



A solution of PNNH (0.359 g, 1 mmol) was dissolved in THF (10 mL) and added to a slurry of $Na_3[Co(NO_2)_6]$ (0.404 g, 1 mmol). This reaction stirred for 12 h, yielding a yellow solution, upon which all volatiles were removed under reduced pressure. The crude yellow solid was redissolved in DCM and filtered through a plug of celite to remove byproduct $NaNO_2$. All volatiles were removed. This gave rise to a yellow-orange powder in 91.5% yield (0.459 g of recovered material), which was characterized by ^{1}H NMR, ^{31}P NMR, ^{13}C NMR, and mass spectrometry to confirm independent synthesis of (PNNH)Co(NO$_2$)$_3$. The ^{13}C NMR spectrum of this compound is fully consistent with the structure, including chemically equivalent *t*-Bu quaternary carbon and methyl carbon via only one chemical shift.

^{1}H NMR of (PNNH)Co(NO$_2$)$_3$ (Fig S3): (400 MHz, CD_2Cl_2, 298K): δ(ppm) 7.85 (d, $J_{H,H}$ = 8 Hz, 2H), 7.67 (t, $J_{H,H}$ = 7.8 Hz, 1H), 7.50 (d, $J_{H,H}$ = 7.7 Hz, 1H), 7.44 (t, $J_{H,H}$ = 7.9 Hz, 2H), 7.35 (d, $J_{H,H}$ = 7.7 Hz, 2H), 7.03 (s, 1H), 3.09 (d, $J_{H,P}$ = 3.3 Hz, 2H) 1.19 (d, $J_{H,P}$ = 12 Hz, 18H).
^{31}P NMR of (PNNH)Co(NO$_2$)$_3$ (Fig S3): (162 MHz, CD_2Cl_2 213K): δ(ppm) 78.69
^{13}C NMR of (PNNH)Co(NO$_2$)$_3$ (Fig S4): (126 MHz, d^8-THF, 298K): δ(ppm) 163.63 (d, $J_{C,P}$ = 16.6 Hz), 137.94 (s), 129.98 (s), 128.84 (s), 126.89 (s), 124.10 (d, $J_{C,P}$ = 8.5 Hz), 123.17 (s), 117.82 (s), 101.61 (s), 35.21 (s), 33.49 (s), 33.31 (d, $J_{C,P}$ = 5.2 Hz), 33.14 (s), 30.88 (d, $J_{C,P}$ = 13.9 Hz), 27.94 (s).
IR (Fig S2): ν_{NO} = 1298, 1415 cm^{-1}
APCI-MS(+): 530.14: [(PNNH)Co(NO$_2$)]$^+$, [M-(NO$_2$)]$^+$

Independent synthesis of (PNN)Co(NO$_2$)(NO).

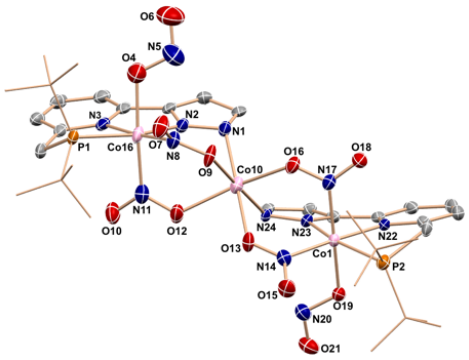


A solution of (PNNH)Co(NO$_2$)$_3$ (0.0981 g, 0.170 mmol) was dissolved in THF (5 mL) and cooled to -78 °C. A solution of 2,3,4,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (0.0483 g, 0.171 mmol) was dissolved in THF and also cooled to -78 °C. The 2,3,4,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene was added dropwise to (PNNH)Co(NO$_2$)$_3$ at -78 °C and allowed to slowly warm to room temperature over the course of 12 h upon which the color changed from yellow to red. All volatiles were removed under reduced pressure and 82.6 mg of a crude red powder was isolated (87.0% yield). ^{1}H NMR, ^{31}P NMR, ^{13}C NMR, mass spectrometry, and unit cell determination from a single crystal confirm independent synthesis of (PNN)Co(NO$_2$)(NO). The ^{13}C NMR spectrum of this compound is fully consistent with the structure, including two chemical shifts proving chemically inequivalent *t*-Bu quaternary carbons and methyl carbons.

^{1}H NMR of (PNN)Co(NO$_2$)(NO) (Fig S5): (400 MHz, d^8-THF, 298K): δ(ppm) 7.85 (t, $J_{H,H}$ = 8 Hz, 1H), 7.70 (d, $J_{H,H}$ = 7.9 Hz, 2H), 7.48 (d, $J_{H,H}$ = 7.7 Hz, 1H), 7.25 (d, $J_{H,H}$ = 7.9 Hz, 1H), 7.11 (t, $J_{H,H}$

= 7.8 Hz, 2H), 6.97 (t, $J_{H,H}$ = 7.7 Hz, 1H) 6.82 (s, 1H), 3.29 (d, $J_{H,P}$ = 3.3 Hz, 1H), 3.26 (d, $J_{H,P}$ = 3.3 Hz, 1H), 1.18 (d, $J_{H,P}$ = 11.2 Hz, 9H), 1.08 (d, $J_{H,P}$ = 11.2 Hz, 9H).
^{31}P NMR of (PNN)Co(NO_2)(NO) (Fig S5): (162 MHz, d^8-THF 213K): δ(ppm) 73.68
^{13}C NMR of (PNN)Co(NO_2)(NO) (Fig S6): (126 MHz, CD_2Cl_2 298K): δ(ppm) 151.9 (s), 140.54 (s), 134.50 (s), 129.35 (d, $J_{C,P}$ = 8.7 Hz), 128.30 (s), 126.75 (s), 125.14 (s), 117.23 (d, $J_{C,P}$ = 13.5 Hz), 101.62 (s), 37.13 (d, $J_{C,P}$ = 11.5 Hz), 35.38 (d, $J_{C,P}$ = 13.9 Hz), 32.23 (d, $J_{C,P}$ = 20.2 Hz), 29.78 (s), 29.19 (s), 28.38 (d, $J_{C,P}$ = 8.5 Hz), 26.40 (s), 25.57 (s).
IR (Fig S2): ν_{NO} = 1670 cm^{-1}
APCI-MS(+): 514.14: $[(PNNH)Co(NO_2)(NO)]^+$, $[M+H]^+$

Synthesis of $(PNN)_2Co_3(NO_2)_6$.



A solution of (PNNH)$CoCl_2$ (0.0784 g, 0.154 mmol) was dissolved in acetonitrile (7 mL) and cooled to -45 °C. A slurry of excess $NaNO_2$ (5 equivalents) in acetonitrile was likewise cooled to -45 °C, and then added to the solution of (PNNH)$CoCl_2$ with several washes with acetonitrile. In this execution, acetonitrile was used in place of DCM to maximize solubility of $NaNO_2$ at the lowered temperature. The reaction was stirred at -45 °C for 30 minutes, upon which a red crystal was detected and analyzed by single crystal X-ray diffraction studies.

Spectral data.

NMR details: for diamagnetic complexes, specific assignments have been made. For paramagnetic complexes specific assignments are not made.
IR details: All IR spectra were obtained by using a KBr press.

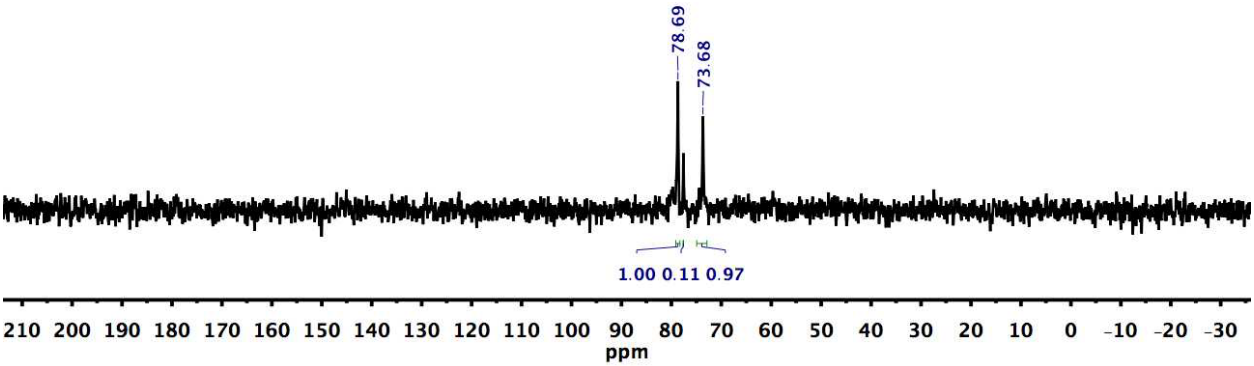


Figure S1. ^{31}P NMR of (PNN)Co(NO_2)(NO) and (PNNH)Co$(NO_2)_3$ mixture (162 MHz, d_8-THF, 213K).

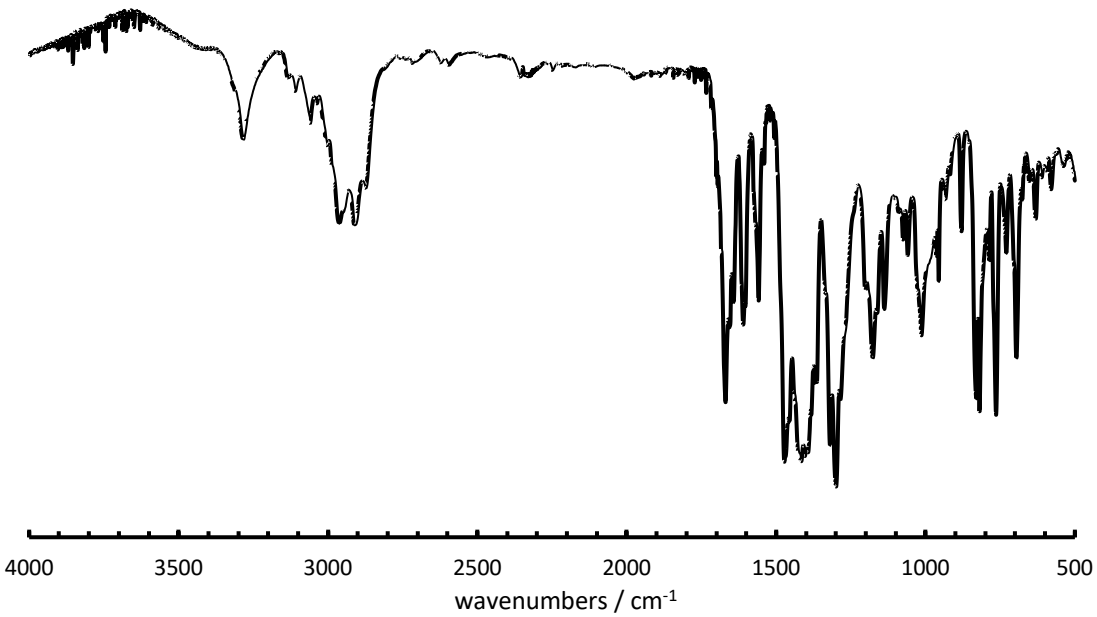


Figure S2. FT-IR spectrum of $(PNNH)Co(NO_2)_3$ and $(PNN)Co(NO_2)(NO)$

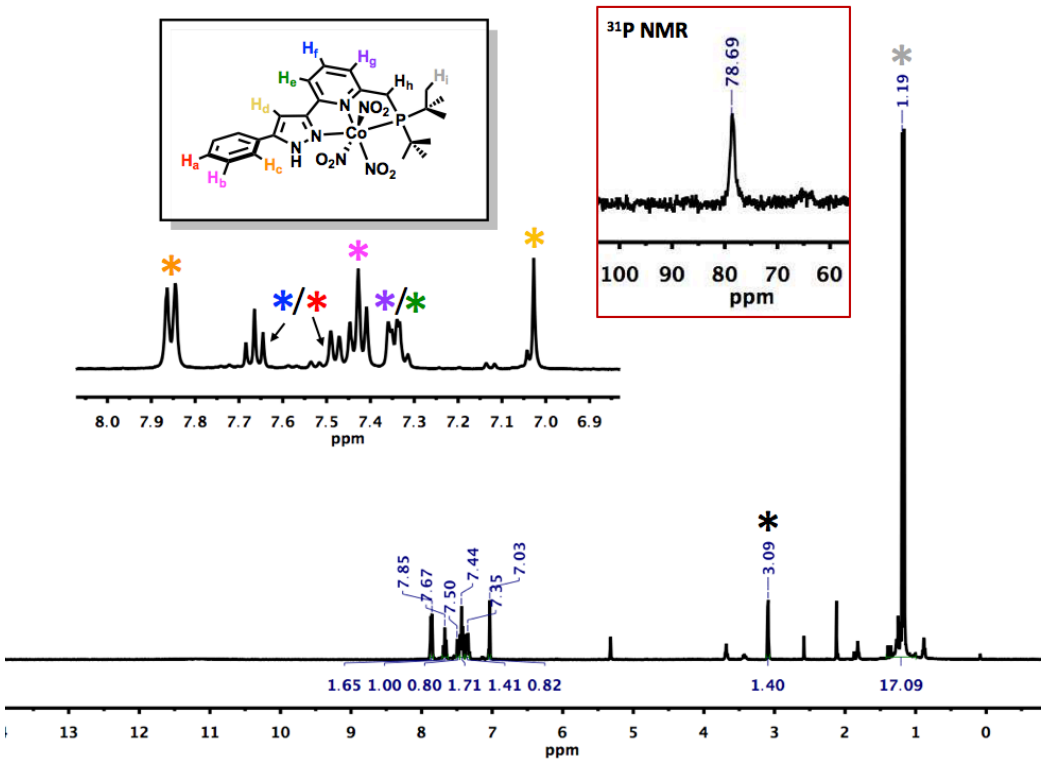


Figure S3. ^{1}H NMR (400 MHz, CD_2Cl_2, 298K) and ^{31}P NMR (inset, 162 MHz, CD_2Cl_2, 213K) of $(PNNH)Co(NO_2)_3$

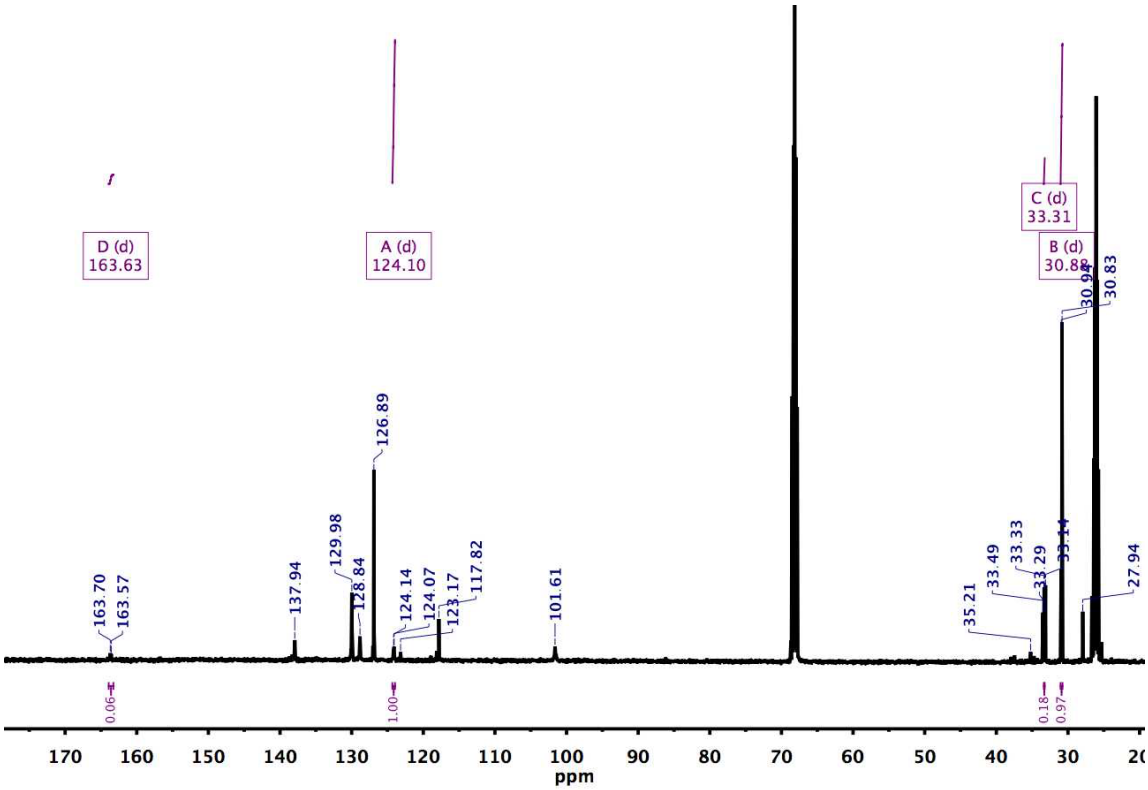


Figure S4. ^{13}C NMR (126 MHz, d^8-THF, 298K) of $(PNNH)Co(NO_2)_3$.

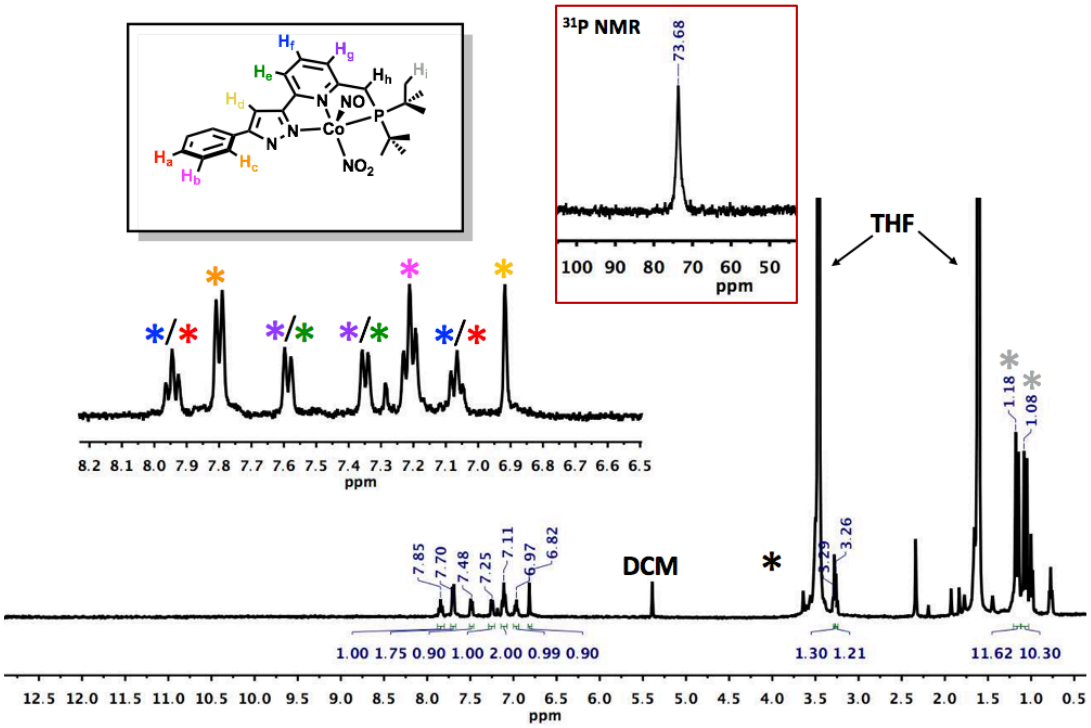


Figure S5. ^1H NMR (400 MHz, d^8-THF, 298K) and ^{31}P NMR (inset, 162 MHz, d^8-THF, 213K) of $(PNN)Co(NO_2)(NO)$

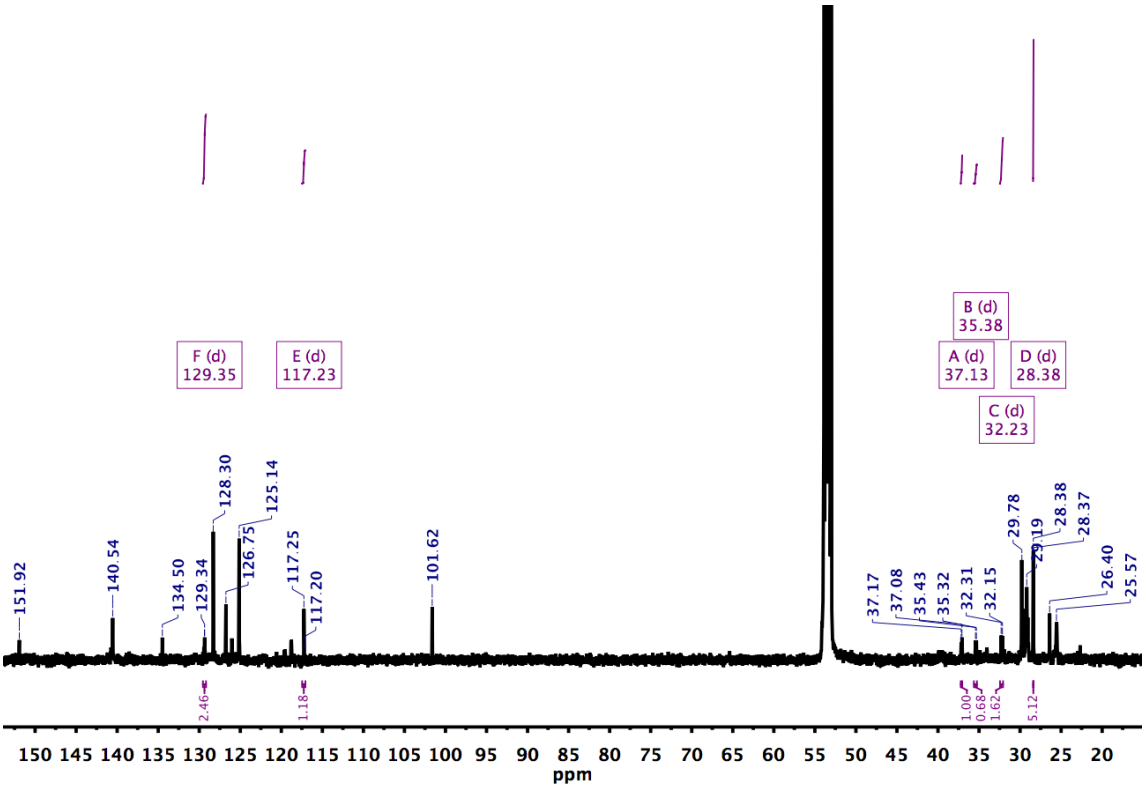


Figure S6. ^{13}C NMR (126 MHz, CD_2Cl_2, 298K) of (PNN)Co(NO_2)(NO).

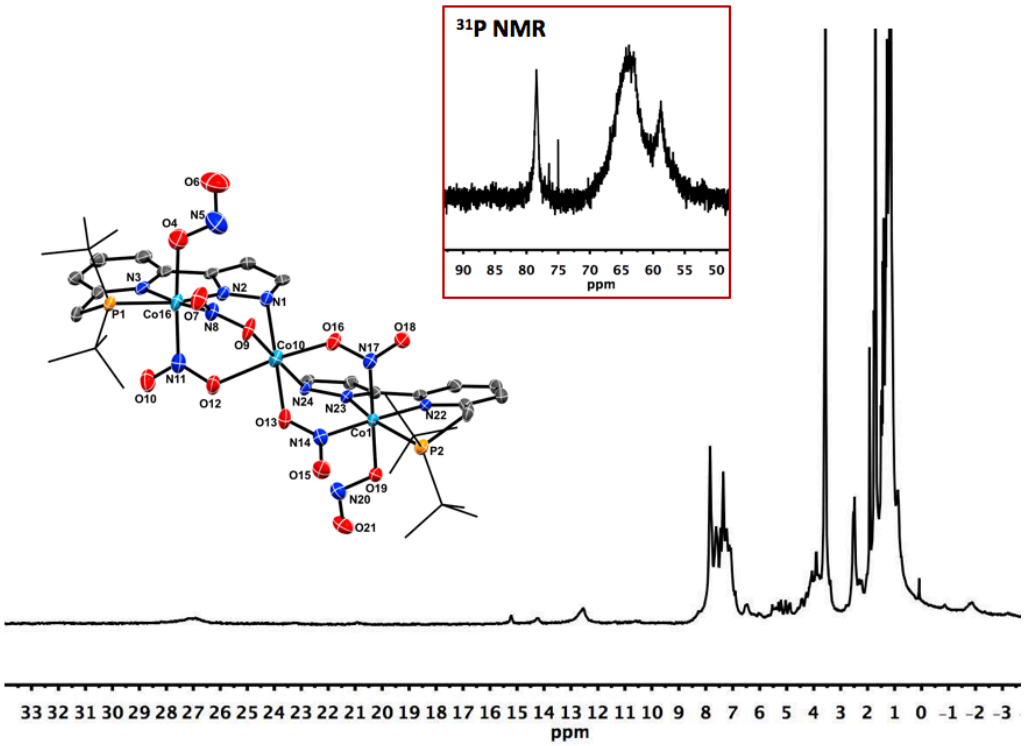


Figure S7. ^{1}H NMR (400 MHz, d^8-THF, 298K) and ^{31}P NMR (inset, 162 MHz, d^8-THF, 213K) of crystalline batch of $(PNN)_2Co_3(NO_2)_6$

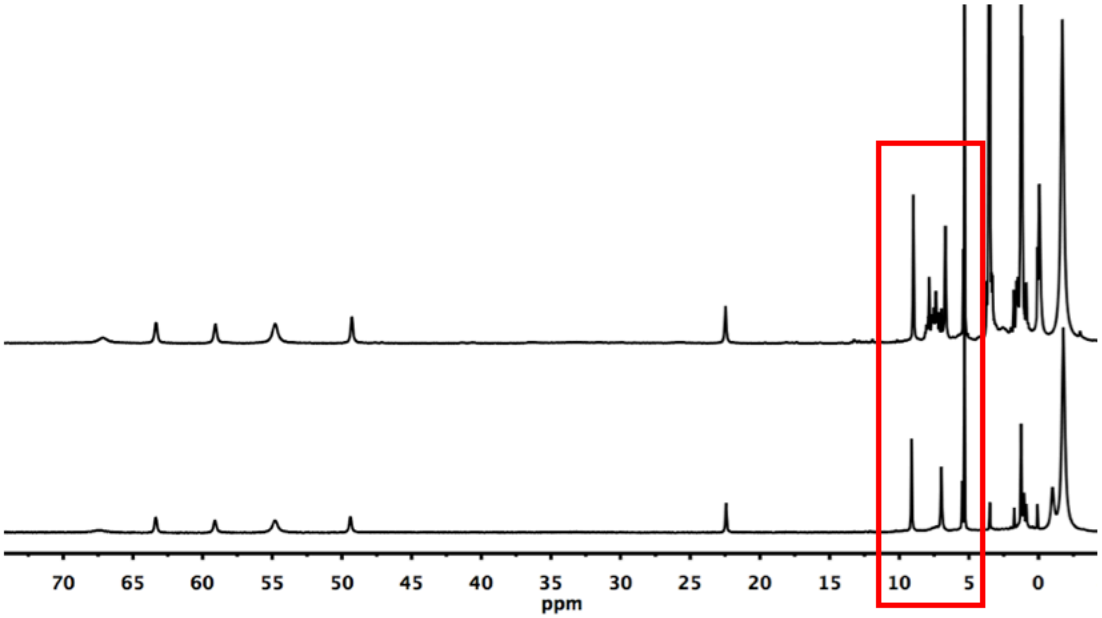


Figure S8. ^{1}H NMR (400 MHz, CD_2Cl_2, 298K) of reaction progress of $(PNNH)CoCl_2$ and $NaNO_2$ showing an intermediate time point where the reaction is not complete. Bottom spectrum is before addition of 18-C-6 (no reaction) and top is 30 minutes after addition of 18-C-6. The reaction does not proceed at room temperature without the addition of 18-C-6 to solubilize the $NaNO_2$. The 0-10 ppm region shows formation of $(PNNH)Co(NO_2)_3$ and $(PNN)Co(NO_2)(NO)$ (see aromatic region boxed in red) with the only other compound present being $(PNNH)CoCl_2$ starting material, suggesting no detectable intermediates in the reaction progress.

Crystallographic data.

Data for $(PNNH)Co(NO_2)_3$ (MSC#17129) (CCDC: 1954957)

General details

Single crystals suitable for X-ray diffraction were grown by vapor diffusion of cyclohexane vapors into a concentrated DCM solution. A orange crystal (approximate dimensions 0.200 x 0.200 x 0.050 mm^3) was placed onto the tip of MiTeGen and mounted on an Apex Kappa Duo diffractometer and measured at 173 K.

Data collection

A preliminary set of cell constants was calculated from reflections harvested from three sets of 12 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 118 reflections. The data collection was carried out using Mo Kα radiation (graphite monochromator) with a frame time of 180 seconds and a detector distance of 5.0 cm. A randomly oriented region of reciprocal space was surveyed to achieve complete data with a redundancy of 4. Sections of frames were collected with 0.50º steps in ω and ϕ scans. Data to a resolution of 0.84 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 1679 strong reflections from the actual data collection after integration (SAINT)[1]. The intensity data were corrected for absorption (SADABS)[2]. Please refer to Table S1 for additional crystal and refinement information.

Structure solution and refinement

The space group P 1 21/c 1 was determined based on intensity statistics and systematic absences. The structure was solved using the SHELX suite of programs [3] and refined using full-matrix least-squares on F^2 within the OLEX2 suite.[4] An intrinsic phasing solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.1040 and wR2 = 0.3087 (F^2, all data). The goodness-of-fit was 1.027. On the basis of the final model, the calculated density was 1.481 g/cm^3 and F(000), 1372 e$^-$.

1 SAINT, V8.30A, Bruker Analytical X-Ray Systems, Madison, WI, 2012.
2 SADABS, 2.03, Bruker Analytical X-Ray Systems, Madison, WI, 2016.
3 G. M. Sheldrick, Acta Cryst. A64, 112 - 122 (2008). Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
4 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr., 2009, 42, 339–341.

Table S1: Crystal data and structure refinement for (PNNH)Co(NO_2)$_3$

Empirical formula	C24 H32 Cl2 Co1 N6 O6 P1	
Formula weight	662.36	
Crystal color, shape, size	orange plate, 0.200 x 0.200 x 0.050 mm^3	
Temperature	173.0 K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, P 1 21/c 1	
Unit cell dimensions	a = 17.203(4) Å	α= 90°.
	b = 13.355(4) Å	β = 90.797(8)°.
	c = 12.931(3) Å	γ = 90°.
Volume	2970.5(13) Å^3	
Z	4	
Density (calculated)	1.481 Mg/m^3	
Absorption coefficient	0.860 mm^{-1}	
F(000)	1372	
Data collection		
Diffractometer	Bruker Apex Kappa Duo, Bruker	
Theta range for data collection	1.931 to 25.072°.	
Index ranges	-12<=h<=19, -15<=k<=15, -15<=l<=15	
Reflections collected	17205	
Independent reflections	4789 [R(int) = 0.1028]	
Observed Reflections	2469	
Completeness to theta = 25.078°	91.0 %	
Solution and Refinement		
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.96	
Solution	Direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting scheme	$w = [\sigma^2 Fo^2 + AP^2 + BP]^{-1}$, with	
	$P = (Fo^2 + 2\,Fc^2)/3$, A = 0.121, B = 20.860	
Data / restraints / parameters	4789 / 365 / 368	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2σ (I)]	R1 = 0.1040, wR2 = 0.2580	
R indices (all data)	R1 = 0.1925, wR2 = 0.3087	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.238 and -0.829 e.Å^{-3}	

Data for (PNN)Co(NO_2)(NO) (MSC#19074) (CCDC: 1954952)

General details

Single crystals suitable for X-ray diffraction were grown by vapor diffusion of ether vapors into a concentrated acetonitrile solution. A dark red crystal (approximate dimensions 0.09 × 0.08 × 0.02 mm^3) was placed onto the tip of a MiTeGen pin and mounted on a Bruker Kappa Duo diffractometer equipped with a ApexII CCD detector at 173 K.

Data collection

The data collection was carried out using Mo Kα radiation (λ = 0.71073 Å, graphite monochromator) with a frame time of 180 seconds and a detector distance of 40 mm. A collection strategy was calculated and complete data to a resolution of 0.84 Å with a redundancy of 3.66 were collected. Four major sections of frames were collected with 0.50º ω and ϕ scans. The total exposure time was 16.40 hours. The frames were integrated with the Bruker SAINT[1] software package using a narrow-frame algorithm. The integration of the data using a tetragonal unit cell yielded a total of 15185 reflections to a maximum θ angle of 25.07° (0.84 Å resolution), of which 4437 were independent (average redundancy 3.422, completeness = 99.8%, Rint = 11.95%, Rsig = 15.22%) and 2753 (62.05%) were greater than 2σ(F2). The final cell constants of a = 17.002(4) Å, b = 17.002(4) Å, c = 17.320(4) Å, volume = 5007.(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 1460 reflections above 20 σ(I) with 4.703° < 2θ < 38.68°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[2] The ratio of minimum to maximum apparent transmission was 0.654. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9330 and 0.9840. Please refer to Table S2 for additional crystal and refinement information.

Structure solution and refinement

The space group P-42_1c was determined based on intensity statistics and systematic absences. The structure was solved using the SHELX suite of programs [3] and refined using full-matrix least-squares on F^2 within the OLEX2 suite.[4] An intrinsic phasing solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0756 and wR2 = 0.1762 (F^2, all data). The goodness-of-fit was 1.058. On the basis of the final model, the calculated density was 1.390 g/cm^3 and F(000), 2188 e^- .

Disorder was modelled by splitting the molecule into two parts with occupancies 0.88 and 0.12. Disordered acetonitrile molecules, oriented along the c direction on a rotoinversion axis are present in the packing. The crystal was twinned by merohedry with twin law -1 0 0, 0 -1 0, 0 0 -1. The domain ratio between the two-component inversion twin is 84 :16.

1 SAINT, Bruker Analytical X-Ray Systems, Madison, WI, current version.
2 SADABS, Bruker Analytical X-Ray Systems, Madison, WI, current version.
3 G. M. Sheldrick, Acta Cryst. A64, 112 - 122 (2008). Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
4 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr., 2009, 42, 339–341.

Table S2: Crystal data and structure refinement for (PNN)Co(NO_2)(NO)

Empirical formula	C23.50 H29.75 Co N5.25 O3 P	
Formula weight	523.67	
Crystal color, shape, size	dark red plate, 0.09 × 0.08 × 0.02 mm^3	
Temperature	173.0 K	
Wavelength	0.71073 Å	
Crystal system, space group	Tetragonal, P-42_1c	
Unit cell dimensions	a = 17.002(4) Å	α = 90°.
	b = 17.002(4) Å	β = 90°.
	c = 17.320(4) Å	γ = 90°.
Volume	5006(3) $Å^3$	
Z	8	
Density (calculated)	1.390 g/cm^3	
Absorption coefficient	0.784 mm^{-1}	
F(000)	2188	

Data collection

Diffractometer	Kappa Apex II Duo, Bruker
Theta range for data collection	1.678 to 25.065°.
Index ranges	-20<=h<=12, -16<=k<=16, -14<=l<=20
Reflections collected	15185
Independent reflections	4437 [Rint = 0.1195]
Observed Reflections	2753
Completeness to theta = 25.065°	99.8 %

Solution and Refinement

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.4877
Solution	Intrinsic methods
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = [\sigma^2 Fo^2 + AP^2 + BP]^{-1}$, with
	$P = (Fo^2 + 2\,Fc^2)/3$, A = , B =
Data / restraints / parameters	4437 / 240 / 352
Goodness-of-fit on F^2	1.058
Final R indices [I>2σ (I)]	R1 = 0.0751, wR2 = 0.1523
R indices (all data)	R1 = 0.1378, wR2 = 0.1757
Absolute structure parameter	0.16(6)
Extinction coefficient	n/a
Largest diff. peak and hole	0.462 and -0.378 e.$Å^{-3}$

Twin Details

Type, twin law	by merohedry, -1 0 0, 0 -1 0, 0 0 -1
Twin element, domain ratio	2-component inversion twin, 84 : 16

Data for $(PNN)_2Co_3(NO_2)_6$ (MSC#19053) (CCDC: 1954955)

General details

Single crystals suitable for X-ray diffraction were grown from a concentrated acetonitrile solution. An orange crystal (approximate dimensions 0.17 × 0.13 × 0.07 mm^3) was placed onto the tip of a MiTeGen pin and mounted on a Bruker Kappa Duo diffractometer equipped with a ApexII CCD detector at 153 K.

Data collection

The data collection was carried out using Mo Kα radiation (λ = 0.71073 Å, graphite monochromator) with a frame time of 120 seconds and a detector distance of 40 mm. A collection strategy was calculated and complete data to a resolution of 0.84 Å with a redundancy of 4 were collected. Three major sections of frames were collected with 0.50º ω and ϕ scans. The total exposure time was 26.20 hours. The frames were integrated with the Bruker SAINT[1] software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 39846 reflections to a maximum θ angle of 25.12° (0.84 Å resolution). The final cell constants of a = 16.5137(8) Å, b = 21.4257(12) Å, c = 17.0816(9) Å, β = 104.073(3)°, volume = 5862.3(8) $Å^3$, are based upon the refinement of the XYZ-centroids of 6890 reflections above 20 σ(I) with 4.527° < 2θ < 48.83°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[2] The ratio of minimum to maximum apparent transmission was 0.905. Please refer to Table S3 for additional crystal and refinement information.

Structure solution and refinement

The space group $P2_1/c$ was determined based on intensity statistics and systematic absences. The structure was solved using SUPERFLIP[3] and refined using full-matrix least-squares on F^2 within the CRYSTALS suite.[4] A charge-flipping solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were initially refined with restraints on bond lengths and angles, after which the positions were used as the basis for a riding model.[5] The final full matrix least squares refinement converged to R1 = 0.0490 and wR2 = 0.1633 (F^2, all data). The goodness-of-fit was 0.8051. On the basis of the final model, the calculated density was 1.417 g/cm^3 and F(000), 2588 e^-. It was necessary to use PLATON/SQUEEZE[6] due to some residual electron density that was not possible to successfully modelled and was probably due to the presence of disordered acetonitrile molecules.

1 SAINT, Bruker Analytical X-Ray Systems, Madison, WI, current version.
2 SADABS, Bruker Analytical X-Ray Systems, Madison, WI, current version.
3 Palatinus, Lukas; Chapuis, G,. *J. Appl. Crystallogr.* **2007**, *40*, 786–790.
4 Betteridge, P. W.; Carruthers, J. R.; Richard, I.; Prout, K.; Watkin, D. J. *J. Appl. Crystallogr*. **2003**, *36*, 1487.
5 Cooper, R. I.; Thompson, A. L.; Watkin, D. J. *J. Appl. Crystallogr.* **2010**, *43*, 1100–1107.
6 Spek, A. L. PLATON SQUEEZE : A Tool for the Calculation of the Disordered Solvent Contribution to the Calculated Structure Factors. Acta Crystallogr. **2015**, *C71*, 9–18.

Table S3: Crystal data and structure refinement for $(PNN)_2Co_3(NO_2)_6$

Empirical formula	C48 H61 Co3 N13 O12 P2
Formula weight	1250.84
Crystal color, shape, size	orange plate, 0.17 × 0.13 × 0.07 mm^3

Temperature	153 K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, $P2_1/c$	
Unit cell dimensions	a = 17.08160(3) Å	α = 90°.
	b = 21.42570(3) Å	β = 104.073(3)°.
	c = 16.51370(3) Å	γ = 90°.
Volume	5862.37(8) $Å^3$	
Z	4	
Density (calculated)	1.417 g/cm^3	
Absorption coefficient	0.961 mm^{-1}	
F(000)	2588	

Data collection

Diffractometer	Kappa Apex II Duo, Bruker
Theta range for data collection	1.808 to 25.027°.
Index ranges	-20<=h<=12, -24<=k<=25, -18<=l<=19
Reflections collected	38630
Independent reflections	10309 [Rint = 0.057]
Observed Reflections	7195
Completeness to theta = 25.027°	99.5 %

Solution and Refinement

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00 and 0.90
Solution	Intrinsic methods
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = [\sigma^2 Fo^2 + AP^2 + BP]^{-1}$, with
	$P = (Fo^2 + 2\,Fc^2)/3$, A = , B =
Data / restraints / parameters	10300 / 30 / 730
Goodness-of-fit on F^2	0.8051
Final R indices [$I>2\sigma(I)$]	R1 = 0.0490, wR2 = 0.1322
R indices (all data)	R1 = 0.0808, wR2 = 0.1633
Largest diff. peak and hole	1.21 and -1.08 $e.Å^{-3}$

Computational details.

General details. DFT[1] calculations were carried out using Gaussian 09.[2] Geometry optimizations were performed at the B3LYP/6-31G(d) level of theory.[3] Reoptimization of each species, with the 6-311G(d) basis set did not show significant differences in bond length data or thermodynamic data, and therefore analysis was focused on the 6-31G(d) calculations. All optimized structures were confirmed to be minima by analyzing the harmonic frequencies.[4,5] Cartesian coordinates are shown in Tables S4-S8. We were focused on the final, separated products, hence focused on the singlet state, because we know the experimental products are LS Co(III). In addition, optimization

of other spin states were significantly higher in energy (>20 kcal/mol) and therefore not relevant to this discussion.

1. Parr, R.G.; Yang, W. Density-functional theory of atoms and molecules; Oxford University Press: New York, 1989.
2. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
3. (a) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200. (b) Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B* **1988**, *37*, 785. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (d) Stephens, P.J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M.J. *J. Phys. Chem.* **1994**, *98*, 11623.
4. (a) Schlegel, H. B.; McDouall, J. J. in Computational Advances in Organic Chemistry; Oeretir, C; Csizmadia, I. G., Eds.; Kluwer Academic: Amsterdam, The Netherlands, 1991. (b) Bauernschmitt, R.; Ahlrichs, R. *J. Chem. Phys.* **1996**, *104*, 9047.
5. Schlegel, H. B. *WIREs Comput. Mol. Sci.* **2011**, *1*, 790.

Discussion of 1 and 2

Figure S9 reveals that for the nitrite, there is no major bond lengthening within the NO_2 unit to suggest that it is on its way to the NO product. The singlet optimizes to a square pyramidal structure with apical chloride. The nitrito links CoONOCo in a W shape, which minimizes end to end repulsions between the pincer ligands. *One* chloride hydrogen bonds to an NH proton on the opposite metal (N….Cl = 3.32 Å), which lengthens that CoN distance by up to 0.07 Å and lengthens the CoCl distance by 0.04 Å. Co-Cl distances in the Cambridge Database to both di- and trivalent cobalt range from only 2.18 – 2.23 A, so the distances here, 2.30 – 2.34 A, are long, consistent with the CoCl lying along a singly occupied σ^*_{CoCl} orbital.

These results are to be compared to experimental data from the Cambridge Crystallographic Database. A wide range of Co(III) nitro compounds show NO distances in the narrow range 1.21 – 1.24 (KENFOY, JOBXED, MOCSUS, CIHHEJ). In (PNNH)Co$(NO_2)_3$ the range is 1.23 – 1.27. An example where NO_2 bridges via N and one O, Mg and Co shows terminal NO 1.24 and bridging NO 1.31 A (XURZER). An NO single bond lies in the range 1.46 – 1.49 A.(AZAPOG, DEKBUQ, GINSOO) Five coordinate cobalt nitrosyls have Co/N distances of 1.72 – 1.81 A, but NO distances short, at 1.11 – 1.18 A, thus still far from this calculated species. (BORBER, CNCOPP11, DADWOV and MEGKAM)

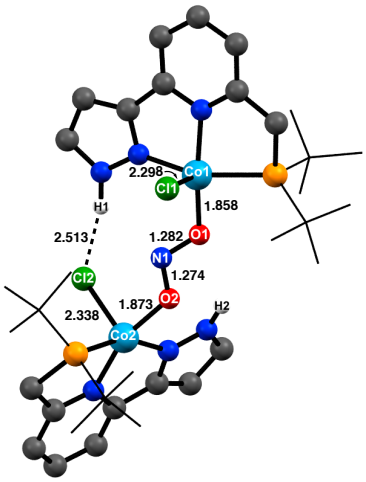


Figure S9. Bond lengths for the optimized structure of $[(PNNH)ClCoONOCoCl(PNNH)]^+$ (**1**), S = 0. O1-N1-O2 angle is 110.8

The singlet of species **2** starting with only one Co/O bond, optimizes to one with both nitro oxygens bonded to Co2 (Figure S10) giving a six-coordinate Co center. Optimization shows that steric conflicts are not excessive, and even beneficial. There is one NH…Cl hydrogen bond between different Co centers, which lengthens that CoCl distance by only 0.02 Å, as well as hydrogen bonding from one pyrazole NH to a terminal nitro oxygen; thus both pincer NH participate in hydrogen bonding. While there is no evidence of N/O dissociation during the geometry optimization, both N/O bonds are unusually long, ~1.35 Å, and the Co1N1 distance is unusually short, 1.76, all seeming to presage N1O2 scission to leave behind a nitrosyl. In summary, this shows that, in spite of bringing two reducing metals to bear on a single NO_2^{-1}, N/O bond scission is not barrierless.

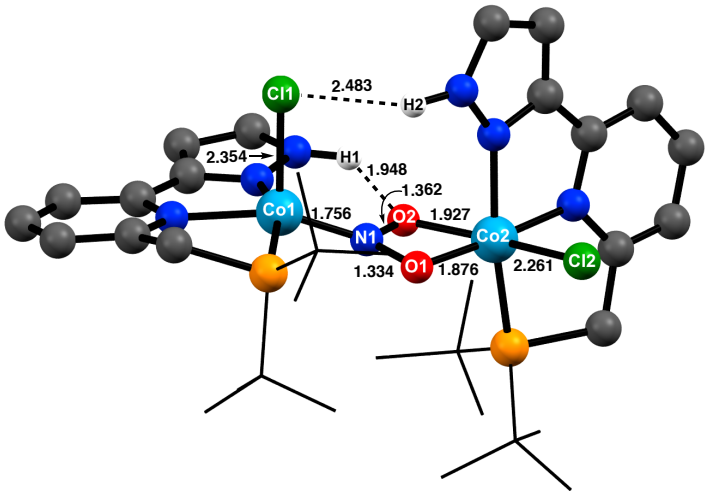


Figure S10. Optimized structure of $[(PNNH)ClCoNO_2CoCl(PNNH)]^+$ (**2**), S = 0 with selected bond lengths. Phenyl groups have been omitted for clarity along with all protons except those labelled. O1-N1-O2 angle is unusual, at 104.0°

Table S4. Cartesian coordinates of **1**

N	-2.190504	-1.713035	-1.035095
N	-1.048210	-2.191874	-1.567211
N	-4.520335	-1.146114	-0.149452
C	-1.274582	-3.284969	-2.351791
C	-2.646561	-3.526816	-2.303240
H	-3.175212	-4.306010	-2.830578
C	-3.172870	-2.529342	-1.475087
C	-4.504947	-2.211207	-0.996513
C	-5.672427	-2.893771	-1.333040
H	-5.629613	-3.737601	-2.012635
C	-6.876762	-2.470121	-0.780370
H	-7.802424	-2.980890	-1.026804
C	-6.883353	-1.386017	0.098076
H	-7.806839	-1.041030	0.550981
C	-5.684324	-0.745370	0.407144

Table S5. Cartesian coordinates of **2**

N	-1.392250	-1.473040	1.463305
N	-0.376495	-2.277046	1.817799
N	-3.593173	-0.216307	0.993357
C	-0.804119	-3.550860	2.073310
C	-2.182634	-3.544218	1.872206
H	-2.848816	-4.386034	1.980669
C	-2.498033	-2.234366	1.489183
C	-3.743673	-1.551612	1.187931
C	-4.998417	-2.156954	1.154247
H	-5.086928	-3.227379	1.301321
C	-6.119710	-1.358176	0.950746
H	-7.109721	-1.802321	0.914800
C	-5.962964	0.021070	0.833883
H	-6.822503	0.674518	0.729804
C	-4.680745	0.571559	0.884179

C	-5.598951	0.393256	1.391440	C	-4.444815	2.054956	0.938918
P	-4.018469	1.337393	1.111471	P	-2.716740	2.480873	0.395287
H	-6.501762	1.011501	1.365643	H	-5.216153	2.607384	0.395960
H	-5.520632	-0.030830	2.400452	H	-4.507328	2.349020	1.994225
C	-4.411517	2.611916	-0.268150	C	-2.872880	2.624997	-1.517940
C	-5.099081	1.863430	-1.432038	C	-3.488132	1.308898	-2.045984
H	-6.079319	1.462517	-1.156505	H	-4.518809	1.160719	-1.709450
H	-5.257805	2.570993	-2.254878	H	-3.512334	1.356644	-3.141387
H	-4.485831	1.042706	-1.817193	H	-2.899106	0.433336	-1.765941
C	-5.336309	3.759131	0.179382	C	-3.797193	3.783295	-1.948917
H	-4.861818	4.420180	0.908693	H	-3.372291	4.765816	-1.731909
H	-5.591940	4.371375	-0.694827	H	-3.935477	3.725749	-3.035756
H	-6.277704	3.394565	0.604672	H	-4.793143	3.728659	-1.497072
C	-3.082906	3.187952	-0.806021	C	-1.490985	2.811451	-2.181482
H	-2.416804	2.392210	-1.155722	H	-0.813370	1.996517	-1.927696
H	-3.300954	3.846482	-1.656273	H	-1.630579	2.812541	-3.269996
H	-2.545224	3.778781	-0.061259	H	-1.019799	3.759393	-1.917656
C	-3.656696	2.180179	2.782569	C	-2.386015	4.193828	1.198974
C	-3.096660	1.104309	3.736486	C	-1.910357	3.984541	2.650405
H	-2.917486	1.573941	4.712070	H	-1.716255	4.972520	3.086660
H	-3.783876	0.268200	3.888481	H	-2.655271	3.481487	3.269116
H	-2.157003	0.683806	3.374267	H	-0.993210	3.395425	2.706491
C	-4.918104	2.791915	3.428097	C	-3.662606	5.064196	1.236270
H	-4.635185	3.233176	4.391909	H	-3.400361	6.029805	1.685733
H	-5.373093	3.582681	2.828971	H	-4.082299	5.268466	0.249459
H	-5.681503	2.035225	3.636799	H	-4.444933	4.626273	1.863239
C	-2.573842	3.263488	2.600725	C	-1.280199	4.944072	0.430184
H	-1.687771	2.866153	2.094799	H	-0.379201	4.338228	0.304239
H	-2.936336	4.135353	2.048655	H	-1.609228	5.291973	-0.551938
H	-2.261526	3.616161	3.591220	H	-1.000326	5.831945	1.009621
H	-0.153441	-1.734743	-1.367335	H	0.587213	-1.979333	1.647520
Co	-2.796606	-0.407123	0.305734	Co	-1.748086	0.472389	1.137520
O	-1.207765	0.533813	0.513179	C	0.057277	-4.656473	2.515197
N	-0.101298	-0.114176	0.513656	C	-0.492304	-5.635174	3.362562
O	0.881619	0.667774	0.725715	C	1.397158	-4.772805	2.113579
C	-0.239761	-4.016667	-3.095423	C	0.281469	-6.707791	3.796611
C	-0.369318	-5.408119	-3.246714	H	-1.519667	-5.540148	3.702050
C	0.846655	-3.361105	-3.694913	C	2.166626	-5.848004	2.555527
C	0.570447	-6.128093	-3.980112	H	1.832544	-4.041551	1.440683
H	-1.197939	-5.925478	-2.771422	C	1.614658	-6.817196	3.394410

C	1.786506	-4.087865	-4.423724	H	-0.153816	-7.452881	4.456207
H	0.957904	-2.286822	-3.598245	H	3.200521	-5.929846	2.232939
C	1.651708	-5.469587	-4.570311	H	2.219029	-7.653253	3.734576
H	0.461458	-7.203651	-4.085841	Co	1.962136	0.145678	-0.575965
H	2.622700	-3.568028	-4.881953	C	3.498131	0.038659	-3.006832
H	2.385100	-6.031564	-5.141661	C	4.830440	0.694296	-1.201695
Co	2.667731	0.240084	0.360482	C	4.565794	0.152642	-3.895476
C	5.059516	1.506058	-0.456800	C	5.933696	0.845419	-2.043554
C	5.476885	-0.563855	0.568370	C	5.796360	0.580670	-3.405952
C	6.418261	1.716696	-0.677920	H	4.428897	-0.090250	-4.943589
C	6.849756	-0.393238	0.389453	H	6.889128	1.147004	-1.627266
C	7.325509	0.754740	-0.244699	H	6.644742	0.690144	-4.074474
H	6.750197	2.623614	-1.171534	N	3.622704	0.339308	-1.685338
H	7.532451	-1.161266	0.737278	C	2.162511	-0.421902	-3.340510
H	8.390939	0.896921	-0.396290	C	1.535344	-0.950908	-4.483026
N	4.593922	0.376703	0.162847	H	1.965601	-1.120426	-5.458365
C	3.991374	2.422456	-0.808809	C	0.242903	-1.278951	-4.078729
C	3.868833	3.642198	-1.499488	H	-0.628422	-0.897738	-2.123987
H	4.646018	4.218113	-1.978550	N	1.303941	-0.413998	-2.305500
C	2.505355	3.933784	-1.502855	N	0.163957	-0.946137	-2.759084
H	0.929692	2.797479	-0.561904	C	-0.882559	-1.868172	-4.810624
N	2.782013	2.005098	-0.395371	C	-1.837807	-2.660346	-4.151299
N	1.897558	2.907427	-0.836613	C	-1.013281	-1.652027	-6.192128
C	1.758192	5.057681	-2.073105	C	-2.902262	-3.215173	-4.858922
C	0.437251	4.893267	-2.524029	H	-1.726638	-2.874236	-3.091275
C	2.363879	6.320232	-2.182709	C	-2.074759	-2.215091	-6.896593
C	-0.261183	5.970739	-3.064684	H	-0.290043	-1.027746	-6.708890
H	-0.032196	3.913347	-2.487139	C	-3.024087	-2.995224	-6.232451
C	1.663742	7.392406	-2.730140	H	-3.628588	-3.834055	-4.339848
H	3.377485	6.463013	-1.819603	H	-2.164174	-2.039714	-7.964713
C	0.348863	7.222389	-3.169676	H	-3.850774	-3.433853	-6.783575
H	-1.278181	5.828998	-3.419056	C	4.913956	0.814697	0.292315
H	2.142809	8.364025	-2.806980	H	5.145233	-0.184197	0.678338
H	-0.195548	8.059971	-3.595734	H	5.721126	1.480866	0.605828
C	4.885804	-1.804857	1.177131	P	3.248819	1.258895	1.011959
H	4.771136	-2.546264	0.379295	C	3.156562	3.171543	0.803044
H	5.554514	-2.240566	1.924575	C	2.667935	3.471130	-0.632145
P	3.161434	-1.460234	1.809835	H	1.684394	3.036042	-0.827501
C	3.408933	-0.744866	3.576408	H	2.595929	4.559136	-0.758997
C	3.842430	0.732210	3.430398	H	3.359066	3.099259	-1.394710

H	3.090419	1.331918	2.906908	C	4.514267	3.879848	0.990200
H	3.970277	1.160447	4.432677	H	4.973829	3.688367	1.961505
H	4.796197	0.840143	2.905005	H	5.230593	3.607167	0.208434
C	4.487423	-1.472080	4.403676	H	4.356367	4.962990	0.911874
H	4.279050	-2.533251	4.547871	C	2.125658	3.755510	1.788645
H	5.483100	-1.373323	3.958426	H	1.952640	4.810064	1.539059
H	4.537588	-1.010497	5.397968	H	1.170995	3.227217	1.728063
C	2.061311	-0.769310	4.326200	H	2.469782	3.723178	2.825085
H	2.162215	-0.196959	5.256729	C	3.455379	0.773897	2.863444
H	1.257161	-0.310324	3.740910	C	2.083568	0.775190	3.568230
H	1.752582	-1.781202	4.599912	H	1.599845	1.753226	3.568630
C	2.338545	-3.186283	1.841769	H	1.387102	0.071599	3.109613
C	0.816460	-3.017144	2.020113	H	2.230381	0.476960	4.613598
H	0.539536	-2.548233	2.966061	C	4.426387	1.699666	3.625619
H	0.371402	-2.425501	1.219479	H	4.049082	2.718167	3.742344
H	0.347499	-4.008383	2.003706	H	4.567841	1.291727	4.634341
C	2.889868	-4.110412	2.945117	H	5.415544	1.745468	3.157249
H	2.617498	-3.777011	3.950010	C	4.027701	-0.660810	2.941482
H	2.454264	-5.108232	2.808846	H	5.090857	-0.699351	2.682150
H	3.978700	-4.223584	2.896809	H	3.944986	-1.001328	3.980803
C	2.590878	-3.862393	0.473676	H	3.491262	-1.366213	2.304544
H	3.613647	-4.243236	0.380014	Cl	-2.231030	0.779662	3.325009
H	1.924421	-4.729706	0.395363	Cl	2.500462	-2.054628	0.066019
H	2.384262	-3.200075	-0.370857	N	0.366197	0.584577	0.010984
Cl	-2.719923	-1.824931	2.112592	O	0.037844	1.041116	1.221186
Cl	2.202844	-0.899164	-1.627638	O	-0.825280	0.210471	-0.533667

Discussion of 3b and 3c

Likewise to **3a** (discussed in detail in manuscript), Species **3b** and **3c** were geometry optimized, and resulted in N/O bond scission (Figures S11 and S12). Species **3b** lacks any hydrogen bonding and is in progress of dissociating into independent species.

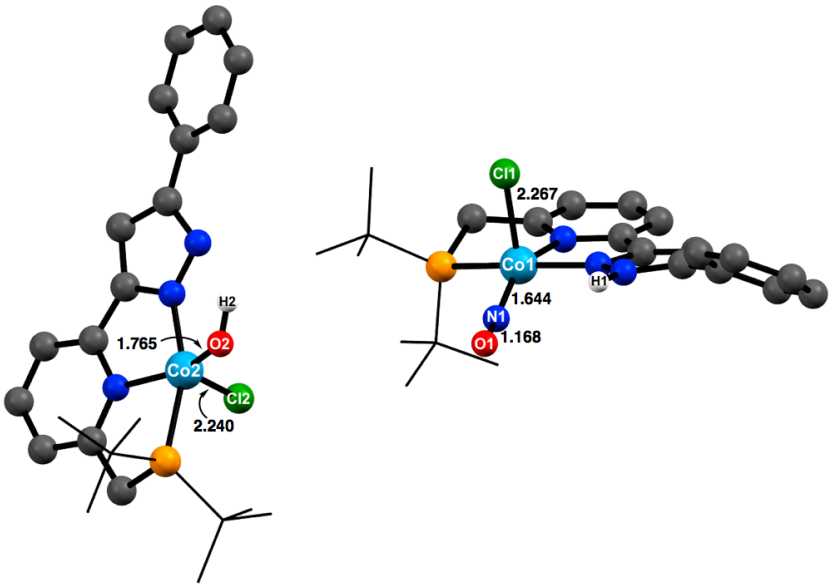


Figure S11. Optimized structure of **3b.** Co1-N1-O1 angle is 158.7°.

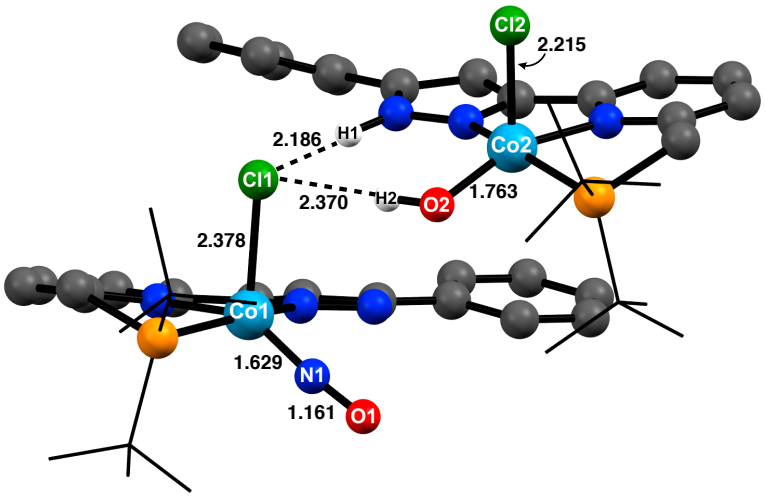


Figure S12. Optimized structure of **3c**. Co1-N1-O1 angle is 171.8°.

Table S6. Cartesian coordinates of **3a**

N	1.370003	2.418727	-0.658615
N	0.277582	2.619874	-1.420825
N	3.489275	2.417745	0.776850
C	0.158117	3.920670	-1.803570
C	1.250489	4.594356	-1.247293
H	1.495109	5.637378	-1.377595
C	1.967652	3.623060	-0.543040
C	3.160302	3.644181	0.291051
C	3.901918	4.776639	0.612083
H	3.624587	5.742545	0.205342
C	4.993963	4.638641	1.467427
H	5.588649	5.505389	1.738315
C	5.313595	3.381461	1.974947
H	6.153385	3.249070	2.648595
C	4.537971	2.278053	1.612680
C	4.798819	0.890495	2.132130
P	4.069492	-0.363408	0.965361
H	5.864410	0.730717	2.320009
H	4.277045	0.768655	3.089636
C	5.334977	-0.546264	-0.465892
C	5.677037	0.855842	-1.019450
H	6.183135	1.494061	-0.289678
H	6.362859	0.727415	-1.864539
H	4.797930	1.387827	-1.398951
C	6.644615	-1.218254	-0.007692
H	6.503267	-2.263423	0.276030
H	7.352372	-1.204036	-0.845281
H	7.122427	-0.692003	0.825405
C	4.697128	-1.359388	-1.610770
H	3.758137	-0.913966	-1.951416
H	5.395435	-1.371408	-2.456281
H	4.498824	-2.395732	-1.336091
C	3.885792	-1.947446	2.013060
C	2.629872	-1.797253	2.893981
H	2.551054	-2.689451	3.526646
H	2.671997	-0.926276	3.552755
H	1.719053	-1.716638	2.298553
C	5.107365	-2.152894	2.937363
H	4.949973	-3.077245	3.505786

Table S7. Cartesian coordinates of **3b**

N	3.985342	-1.185588	0.737515
N	3.120451	-1.821598	1.514677
N	5.765478	-0.047360	-0.662438
C	3.525354	-3.121531	1.569233
C	4.689278	-3.299854	0.794211
H	5.265804	-4.203732	0.660793
C	4.952565	-2.030084	0.280054
C	5.962067	-1.392446	-0.532639
C	7.061606	-2.006688	-1.141239
H	7.212552	-3.074100	-1.025175
C	7.941995	-1.227169	-1.881262
H	8.802560	-1.684758	-2.360452
C	7.720100	0.146444	-2.008979
H	8.393069	0.771163	-2.586445
C	6.608910	0.713428	-1.386497
C	6.265324	2.180236	-1.500389
P	5.170656	2.701842	-0.077462
H	7.169587	2.787993	-1.603347
H	5.670471	2.326288	-2.410806
C	6.364996	3.104514	1.366182
C	7.292110	1.882710	1.565074
H	7.946188	1.699951	0.706892
H	7.937677	2.079656	2.429339
H	6.736055	0.964494	1.778608
C	7.246298	4.341908	1.111064
H	6.667068	5.268651	1.092908
H	7.972587	4.431862	1.928687
H	7.816778	4.271050	0.178057
C	5.555242	3.296676	2.668478
H	4.867226	2.465798	2.843860
H	6.257426	3.354291	3.509654
H	4.974978	4.221513	2.666516
C	4.256935	4.249759	-0.714909
C	3.127147	3.777425	-1.653146
H	2.615743	4.665561	-2.046309
H	3.495242	3.198213	-2.504114
H	2.395729	3.158137	-1.129992
C	5.178417	5.202670	-1.505245
H	4.583328	6.059304	-1.846275

H	6.049067	-2.261376	2.396607	H	6.004836	5.596048	-0.910335
H	5.216572	-1.346132	3.668535	H	5.594610	4.726493	-2.399282
C	3.703452	-3.181166	1.107721	C	3.610042	4.998236	0.468121
H	2.891808	-3.052739	0.385630	H	3.017163	4.327893	1.099009
H	4.613057	-3.443266	0.562075	H	4.347212	5.507304	1.094675
H	3.450061	-4.039129	1.741194	H	2.936759	5.767531	0.070157
Co	2.317544	0.937358	0.236714	Co	4.186758	0.634553	0.265964
C	-0.930644	4.411899	-2.651597	C	2.783695	-4.113597	2.362780
C	-1.297328	5.767614	-2.589949	C	2.982612	-5.490580	2.167318
C	-1.603291	3.557839	-3.543026	C	1.857921	-3.704353	3.339335
C	-2.315419	6.257795	-3.403377	C	2.283054	-6.428210	2.925099
H	-0.795657	6.434195	-1.894400	H	3.682014	-5.830979	1.408602
C	-2.623172	4.054151	-4.351697	C	1.154291	-4.643777	4.090997
H	-1.317210	2.513461	-3.625004	H	1.710583	-2.643089	3.511209
C	-2.980541	5.402816	-4.285782	C	1.363935	-6.010230	3.889431
H	-2.590350	7.306704	-3.348211	H	2.454039	-7.488495	2.758531
H	-3.129111	3.389100	-5.045017	H	0.447689	-4.307082	4.845129
H	-3.770265	5.788126	-4.923770	H	0.819432	-6.741380	4.480465
Co	-2.358913	-0.991617	0.388475	Co	-3.855331	-0.211787	-0.360754
C	-3.585031	-3.255585	-0.805398	C	-6.352350	-1.023831	-1.536849
C	-5.165911	-1.588617	-0.318146	C	-4.612851	-2.477334	-2.137318
C	-4.579359	-4.130035	-1.236462	C	-7.273464	-1.736254	-2.299524
C	-6.202886	-2.420101	-0.742868	C	-5.488418	-3.229091	-2.925460
C	-5.905859	-3.706708	-1.191703	C	-6.825600	-2.846541	-3.013563
H	-4.314862	-5.114648	-1.605402	H	-8.313839	-1.431760	-2.325892
H	-7.224863	-2.057136	-0.727914	H	-5.124395	-4.107052	-3.448319
H	-6.701682	-4.368302	-1.519065	H	-7.518642	-3.419754	-3.621498
N	-3.886477	-2.018678	-0.324327	N	-5.041342	-1.377882	-1.489366
C	-2.151421	-3.489618	-0.885691	C	-6.654436	0.111493	-0.673819
C	-1.338596	-4.466898	-1.473409	C	-7.824568	0.771780	-0.263462
H	-1.637954	-5.384205	-1.957141	H	-8.839456	0.582440	-0.577907
C	-0.040168	-3.964175	-1.398137	C	-7.418976	1.691695	0.702514
N	-1.394112	-2.468616	-0.446654	N	-5.592623	0.606445	-0.015721
N	-0.120213	-2.761370	-0.757463	N	-6.066400	1.550009	0.808684
C	1.200616	-4.534779	-1.938624	C	-8.175656	2.651955	1.510515
C	2.114789	-3.737901	-2.646285	C	-7.761991	2.983316	2.811974
C	1.434784	-5.914668	-1.818602	C	-9.333737	3.247389	0.984801
C	3.242224	-4.318350	-3.226529	C	-8.489345	3.900971	3.566524
H	1.923293	-2.675944	-2.771573	H	-6.895347	2.496681	3.252846
C	2.566891	-6.486590	-2.394659	C	-10.060422	4.159196	1.746244

H	0.734618	-6.533933	-1.265197	H	-9.650089	3.010796	-0.027004
C	3.470989	-5.690525	-3.101863	C	-9.638696	4.490572	3.036012
H	3.932217	-3.701914	-3.795109	H	-8.165643	4.144902	4.573851
H	2.741249	-7.553597	-2.294975	H	-10.952375	4.617399	1.329615
H	4.345697	-6.140041	-3.562340	H	-10.206230	5.202907	3.627350
C	-5.367824	-0.160067	0.106844	C	-3.180970	-2.872066	-1.889814
H	-5.256630	0.477810	-0.777363	H	-3.169873	-3.593226	-1.064890
H	-6.369127	0.011618	0.509152	H	-2.740869	-3.370267	-2.757973
P	-4.018043	0.319432	1.295118	P	-2.179998	-1.403634	-1.323699
C	-4.598406	-0.336592	3.004041	C	-1.629003	-0.527306	-2.937420
C	-4.536784	-1.882124	3.013029	C	-2.883940	0.021758	-3.655036
H	-3.525327	-2.273529	2.883800	H	-3.436733	0.740345	-3.043923
H	-4.895459	-2.227618	3.989409	H	-2.557047	0.543645	-4.562209
H	-5.185099	-2.333226	2.256406	H	-3.570310	-0.771322	-3.968169
C	-6.060063	0.065109	3.306930	C	-0.913514	-1.485090	-3.915955
H	-6.225683	1.142108	3.315733	H	0.032733	-1.862263	-3.530788
H	-6.769352	-0.391969	2.610069	H	-1.538802	-2.335922	-4.206410
H	-6.313720	-0.310460	4.305098	H	-0.693427	-0.926192	-4.833518
C	-3.669340	0.202110	4.113339	C	-0.696803	0.653811	-2.597792
H	-3.948184	-0.272134	5.061252	H	-0.448348	1.175987	-3.529745
H	-2.616226	-0.030282	3.934764	H	-1.177629	1.384687	-1.940848
H	-3.761204	1.281118	4.254217	H	0.247107	0.345452	-2.142380
C	-3.827745	2.221196	1.238971	C	-0.738481	-2.039229	-0.245391
C	-2.390898	2.547001	1.700609	C	-0.351147	-0.891948	0.713788
H	-2.196390	2.229445	2.729081	H	-0.071263	0.022342	0.181036
H	-1.636976	2.086427	1.057366	H	-1.162660	-0.669353	1.412871
H	-2.249155	3.633506	1.663717	H	0.530005	-1.205489	1.283692
C	-4.844622	2.973544	2.122708	C	0.489608	-2.472955	-1.071208
H	-4.723576	2.778691	3.189947	H	0.989196	-1.643914	-1.576009
H	-4.682737	4.047575	1.972385	H	1.220075	-2.890653	-0.370382
H	-5.880562	2.764173	1.838858	H	0.245206	-3.255383	-1.797842
C	-4.031672	2.705315	-0.213537	C	-1.215089	-3.259121	0.572958
H	-5.083306	2.655777	-0.515025	H	-1.327421	-4.150870	-0.054349
H	-3.738874	3.760713	-0.260097	H	-0.437024	-3.486396	1.310485
H	-3.425605	2.159225	-0.937460	H	-2.144492	-3.071567	1.113082
Cl	1.249601	1.177206	2.140573	Cl	3.097620	0.421340	-1.680150
Cl	-1.875556	0.254179	-1.572237	Cl	-4.061699	-1.446081	1.529816
N	-1.486437	-1.117420	1.768147	N	-3.011457	1.187533	-0.183005
O	1.507226	-0.401393	-0.674704	O	3.277610	1.170365	1.681280
O	-0.878495	-1.530318	2.664125	O	-2.578650	2.137911	0.340448

H	0.739541	-0.059523	-1.169882	H	2.866387	0.385088	2.092462
H	0.612966	-2.045435	-0.606831	H	-5.434355	2.056888	1.413628
H	-0.423655	1.874116	-1.518122				

Table S8. Cartesian coordinates of **3c**

N	1.905371	-1.172540	-1.082662
N	0.787640	-1.759988	-1.523157
N	4.246358	-0.375371	-0.440247
C	0.906525	-3.116284	-1.564830
C	2.206858	-3.403625	-1.141114
H	2.659297	-4.377725	-1.044606
C	2.787137	-2.163345	-0.853685
C	4.114490	-1.726971	-0.452061
C	5.188421	-2.559542	-0.143816
H	5.057566	-3.635620	-0.140901
C	6.417559	-1.978210	0.153375
H	7.272029	-2.602862	0.395084
C	6.550263	-0.590410	0.125735
H	7.504927	-0.118077	0.331788
C	5.440187	0.196849	-0.183793
C	5.506971	1.699366	-0.298595
P	3.804543	2.425845	-0.077016
H	6.256383	2.115681	0.381447
H	5.817037	1.950256	-1.321241
C	3.567399	2.580876	1.819524
C	3.882215	1.204184	2.450163
H	4.927837	0.906903	2.323629
H	3.694679	1.273899	3.528344
H	3.242962	0.405096	2.061170
C	4.502197	3.628939	2.455853
H	4.240365	4.650089	2.167297
H	4.402924	3.567282	3.546823
H	5.558160	3.460788	2.217712
C	2.099046	2.922506	2.151584
H	1.404894	2.214961	1.694380
H	1.974100	2.882844	3.240574
H	1.818161	3.925741	1.825661
C	3.855404	4.116539	-0.959682
C	3.759296	3.884665	-2.481556
H	3.825945	4.862999	-2.973973
H	4.568897	3.261251	-2.869086

H	2.817130	3.415652	-2.770101
C	5.168329	4.876572	-0.670495
H	5.139038	5.829565	-1.213101
H	5.315117	5.107726	0.385897
H	6.047803	4.332899	-1.031098
C	2.639790	4.962755	-0.529291
H	1.702846	4.408242	-0.642284
H	2.720466	5.318102	0.501411
H	2.588623	5.848310	-1.174335
Co	2.637221	0.643619	-0.879891
C	-0.169604	-4.013229	-2.001874
C	0.062572	-5.398677	-2.050869
C	-1.430233	-3.524416	-2.386575
C	-0.936679	-6.271963	-2.471176
H	1.030467	-5.797999	-1.763894
C	-2.426111	-4.403395	-2.808171
H	-1.643755	-2.459997	-2.364876
C	-2.186208	-5.777850	-2.852213
H	-0.736762	-7.339076	-2.506450
H	-3.392061	-4.007789	-3.109402
H	-2.963757	-6.459178	-3.185846
Co	-2.634716	0.525224	0.509493
C	-3.874447	-2.028738	0.569905
C	-5.262292	-0.430695	-0.470144
C	-4.855486	-3.016491	0.415235
C	-6.271960	-1.374512	-0.641767
C	-6.062067	-2.678804	-0.182239
H	-4.659528	-4.025048	0.761747
H	-7.196756	-1.096359	-1.135649
H	-6.837941	-3.428943	-0.304764
N	-4.107777	-0.749620	0.150455
C	-2.559169	-2.200853	1.127544
C	-1.788803	-3.236963	1.656902
H	-2.083411	-4.262670	1.825198
C	-0.549502	-2.632847	1.939529
N	-1.783864	-1.075329	1.109315
N	-0.578319	-1.312757	1.604275
C	0.664154	-3.236099	2.513002
C	1.674298	-2.426969	3.062453
C	0.844121	-4.629308	2.523781

C	2.826433	-2.995960	3.602296
H	1.533820	-1.350821	3.070522
C	1.994260	-5.197117	3.070647
H	0.082228	-5.273110	2.092314
C	2.992703	-4.383605	3.611093
H	3.591848	-2.354669	4.033038
H	2.110818	-6.277898	3.074759
H	3.886124	-4.827043	4.042540
C	-5.348695	0.972282	-1.019126
H	-4.977424	0.956200	-2.049592
H	-6.380620	1.332312	-1.050963
P	-4.210078	2.088839	-0.055658
C	-5.237326	2.631615	1.471210
C	-5.477864	1.390079	2.360766
H	-4.547729	0.921096	2.691032
H	-6.025657	1.709254	3.255720
H	-6.087409	0.631730	1.860151
C	-6.619292	3.206997	1.092796
H	-6.561442	4.131816	0.518622
H	-7.230623	2.490040	0.535208
H	-7.161802	3.431786	2.019250
C	-4.447277	3.673656	2.291017
H	-5.023167	3.922916	3.190363
H	-3.480200	3.290134	2.626114
H	-4.277926	4.606446	1.747204
C	-3.702977	3.552186	-1.181942
C	-2.311260	4.020434	-0.698125
H	-2.321291	4.351383	0.346077
H	-1.559852	3.232790	-0.807311
H	-1.995146	4.874228	-1.309810
C	-4.687855	4.738343	-1.169470
H	-4.773984	5.220398	-0.192904
H	-4.313302	5.494619	-1.870215
H	-5.687646	4.452223	-1.510719
C	-3.591712	3.056325	-2.640196
H	-4.576190	2.860846	-3.079671
H	-3.130210	3.854417	-3.234477
H	-2.967492	2.166490	-2.738275
Cl	3.375041	0.644933	-2.973981
Cl	-1.746917	0.215420	-1.671194

N	-1.902655	1.382766	1.684725
O	1.121356	1.478457	-0.528809
O	-1.272828	1.804501	2.563409
H	0.312760	0.973232	-0.741304
H	-0.053219	-1.186292	-1.660732