C–H Amination Mediated by Cobalt Organoazide Adducts and the Corresponding Cobalt Nitrenoid Intermediates

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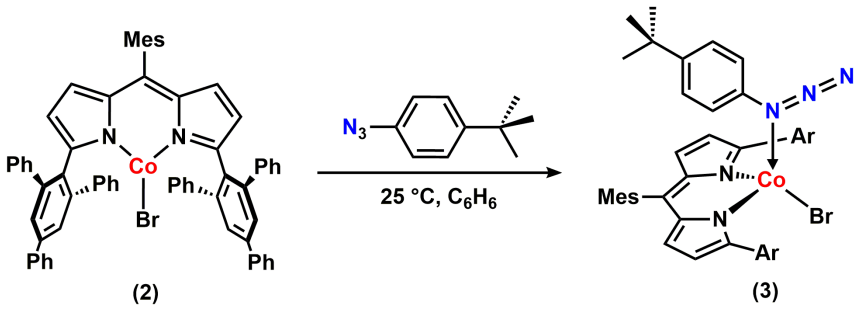
General Considerations.

All manipulations of metal complexes were carried out in the absence of water and dioxygen using standard Schlenk techniques, or in an MBraun inert atmosphere drybox under a dinitrogen atmosphere. Ligand and ligand precursors were synthesized as previously reported.[1] (^{Ar}L)CoCl(py) (**1**)[2] and (^{Ar}L)CoBr (**2**)[3] were prepared as previously reported. All glassware was oven dried for a minimum of 1 hour and cooled in an evacuated antechamber prior to use in the drybox. Benzene, diethyl ether, *n*-hexane, toluene, pentane, dichloromethane, and tetrahydrofuran were dried over 4 Å molecular sieves (Strem) prior to use. Chloroform-*d* was purchased from Cambridge Isotope Labs and used as received. Benzene-d_6 was purchased from Cambridge Isotope Labs, degassed, and stored over 4 Å molecular sieves prior to use. 4-(*tert*-butyl)aniline, 2,4,6-trifluoroaniline, 2,3,4,5,6-pentafluoroaniline, sodium azide, sodium nitrite, *tert*-butyl nitrite, 1,4-cyclohexadiene, styrene, and trifluoroacetic acid were purchased from Aldrich. All C–H substrates were dried over calcium hydride and distilled under nitrogen or vacuum. 1-Azido-4-(*tert*-butyl)benzene was synthesized following published literature procedures.[4] 1-Azido-2,3,4,5,6-pentafluorobenzene and 2-azido-1,3,5-trifluorobenzene were synthesized following published literature procedure.[5] (Azidomethyl)benzene was purchased from Alfa Aesar and used as received. 1-Azidobutane, 1-azido-4-methylpentane, (4-azidobutyl)benzene, and 6-azidohex-1-ene were prepared as previously reported.[6] Anhydrous cobalt(II) bromide was purchased from Aldrich and used as received. Celite® 545 (J. T. Baker) was dried in a Schlenk flask for 24 h under dynamic vacuum while heating to at least 150 °C prior to use in a drybox. Silica gel 32-63 μ (AIC, Framingham, MA) was used as received.

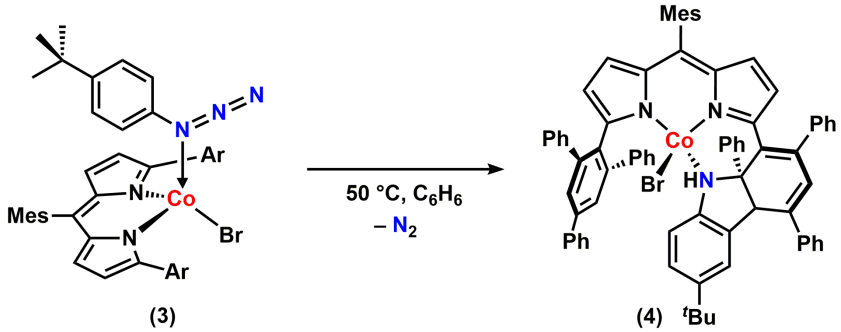
Characterization and Physical Measurements.

^{1}H NMR spectra were recorded on Varian Unity/Inova 500 MHz- or Agilent DD2 600 MHz spectrometers. ^{1}H NMR chemical shifts are reported relative to $SiMe_4$ using the chemical shift of residual solvent peaks as reference. Gas chromatography/mass spectrometry (GC/MS) was performed on an Agilent GC/MS 5975 Turbo system. EPR spectra were obtained on a Bruker EleXsys E-500 CW-EPR spectrometer. Spectra were measured as frozen toluene glasses at liquid He temperatures at a microwave power of 0.6325–2 mW. Spectral simulations incorporating spin state, rhombicity, and zero field splitting were performed using EasySpin.[7] UV/Visible spectra were recorded on a Varian Cary 50 UV/Visible spectrometer using a 0.1 cm quartz cuvette and a scan rate of 600 nm/ min. Elemental analyses were carried out on a Perkin Elmer 2400 Series II CHNS/O analyzer. IR spectra were obtained on a Varian Scimitar 1000 FT-IR spectrometer using a KBr liquid IR-cell with a path length of 0.1 mm.

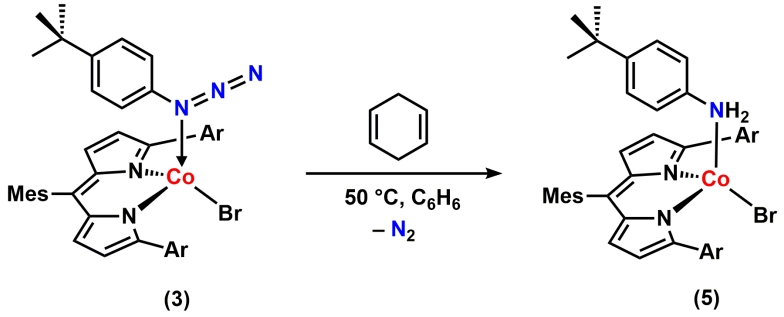
Metal Complexes Syntheses.



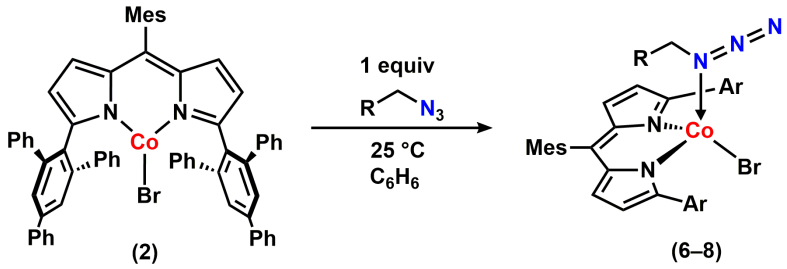
(^{Ar}L)CoBr(N_3(C_6H_4-*p*-^{t}Bu)), (3): In an oven-dried 20 mL vial, a solution of **(^{Ar}L)CoBr** (**2**) (50 mg, 0.05 mmol, 1.0 equiv) in benzene was added to a benzene solution of 1-azido-4-(*tert*-butyl)benzene (1.0 equiv) to observe an immediate color change from purple to reddish purple. The solution was lyophilized to afford **3** as a purple powder (53 mg, 90%). **^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 77.54 (s), 24.12 (s), 21.05 (s), 14.62 (s), 11.81 (s), 11.20 (s), 10.78 (s), −0.71 (s), −16.64 (s), −28.07 (s). Anal. Calc. for $C_{76}H_{62}BrCoN_5$: C 77.08, H 5.28, N 5.91; Found: C 77.10, H 5.39, N 5.87. Crystals suitable for X-ray diffraction were grown from a *n*-pentane:toluene solution at –35 °C.



(^{Ar}L)CoBr([3+2]annulation) (4): A benzene solution of **3** (50 mg, 0.042 mmol) was heated to 50 °C in a J. Young NMR tube for 20 hours to yield a blue-purple solution. Alternatively, a solution of **3** in benzene was stirred at room temperature for 3 days to afford **4** quantitatively. The solution was lyophilized to afford **4** as a purple powder (45 mg, 93%). **^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 68.00 (s), 55.54 (s), 29.68 (s), 26.35 (s), 20.67 (s), 14.11 (s), 13.12 (s), 10.89 (s), 10.18 (s), 9.32 (s), 8.56 (s), 5.76 (s), 5.00 (s), 4.28 (s), −5.40 (s), −5.92 (s), −9.28 (s), −10.88 (s). Anal. Calc. for $C_{76}H_{62}BrCoN_3$: C 78.95, H 5.41, N 3.63; Found: C 79.05, H 5.35, N 3.70. Crystals suitable for X-ray diffraction were grown from a *n*-hexane:benzene solution at –35 °C.



(^{Ar}L)CoBr(NH$_2$(C$_6$H$_4$-*p*-^{t}Bu)), (5): In an oven-dried 20 mL vial, a benzene solution of **3** (50 mg, 0.042 mmol, 1.0 equiv) was added to an excess amount of 1,4-cyclohexadiene (5.0 equiv) and the mixture was transferred to a J. Young NMR tube and heated to 50 °C for 12 hours. The solution was lyophilized to yield **5** as a reddish-purple powder (43 mg, 87%). **^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 56.99 (s), 40.57 (s), 20.61 (s), 13.86 (s), 10.92 (s), 9.64 (s), −1.37 (s), −6.50 (s), −34.39 (s). Anal. Calc. for $C_{76}H_{64}BrCoN_3$: C 78.81, H 5.57, N 3.63; Found: C 78.52, H 5.99, N 3.69. Crystals suitable for X-ray diffraction were grown from a *n*-hexane:benzene solution at room temperature.



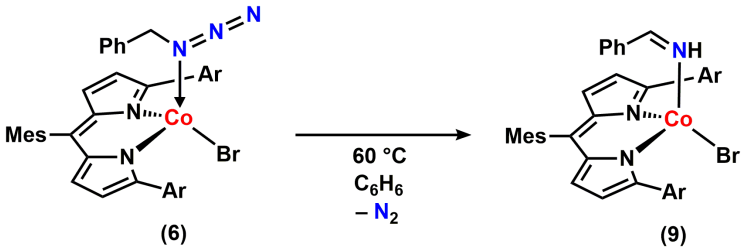
General procedure: In an oven-dried 20 mL vial, a diluted solution of alkyl azide (1.0 equiv) in benzene was added to a stirring solution of (^{Ar}L)CoBr (**2**) (50 mg, 0.05 mmol 1.0 equiv) to observe an immediate color change from purple to reddish purple. The solution was lyophilized to afford the corresponding azide adduct as a purple powder.

(^{Ar}L)CoBr(N$_3$CH$_2$R), R = Ph (6): 51 mg, 91%. **^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 66.33 (s), 64.75 (s), 16.19 (s), 8.69 (s), −0.38 (s), −2.04 (s). Anal. Calc. for $C_{73}H_{56}BrCoN_5$: C 76.77, H 4.94, N 6.13; Found: C 76.25, H 5.10, N 6.45.

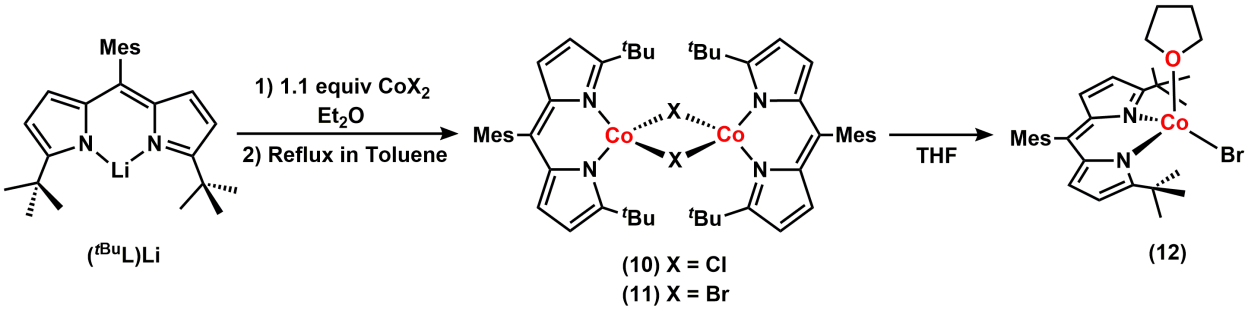
(^{Ar}L)CoBr(N$_3$CH$_2$R), R = (CH$_2$)$_3$(C$_6$H$_5$) (7): 53 mg, 90%. **^{1}H NMR** (500 MHz, C_6D_6): δ/ppm 65.48 (s), 29.40 (s), 17.48 (s), 9.27 (s), 8.79 (s), 6.30 (s), 4.95 (s), −2.00 (s), −24.71 (s). Anal.

Calc. for $C_{76}H_{62}BrCoN_5$: C 77.08, H 5.28, N 5.91; Found: C 77.00, H 5.35, N 5.60. Crystals suitable for X-ray diffraction were grown from a *n*-hexane:benzene solution at room temperature.

(^{Ar}L)CoBr(N_3CH_2R), R = $(CH_2)_2CH(CH_3)_2$ (8): 53 mg, 95 %. **^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 65.01 (s), 62.36 (s), 30.92 (s), 16.85 (s), 8.62 (s), 8.29 (s), 2.24 (s), −1.85 (s), −22.72 (s). Anal. Calc. for $C_{72}H_{62}BrCoN_5$: C 76.12, H 5.50, N 6.16; Found: C 75.80, H 5.19, N 5.46. Crystals suitable for X-ray diffraction were grown from a *n*-hexane:benzene solution at room temperature.



(^{Ar}L)CoBr($NHCHC_6H_5$) (9): A benzene solution of **6** (50 mg, 0.044 mmol) was heated to 60 °C for 24 hours in a J. Young NMR tube. The solution was lyophilized to afford **9** as a purple powder (42 mg, 87%). **^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 55.98 (s), 33.15 (s), 11.19 (s), 10.55 (s), 4.72 (s), 4.53 (s), 0.65 (s), −2.94 (s). Anal. Calc. for $C_{73}H_{56}BrCoN_3$: C 78.70, H 5.07, N 3.77; Found: C 79.05, H 4.89, N 4.02. Crystals suitable for X-ray diffraction were grown from a *n*-pentane:toluene solution at room temperature.



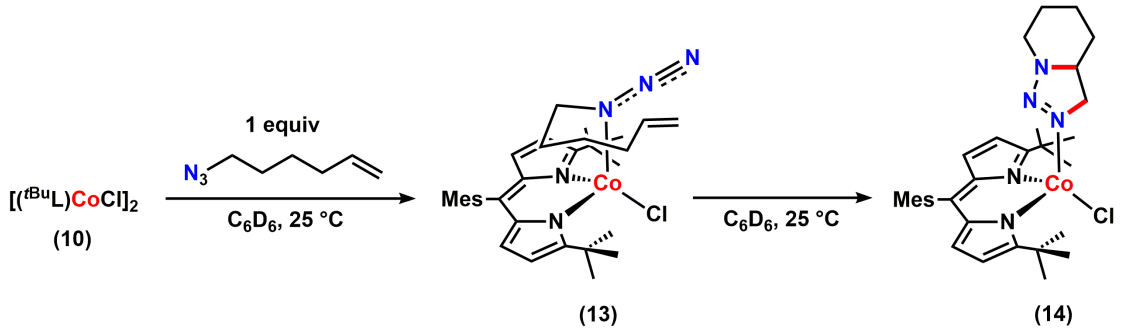
General procedure: In an oven-dried 20 mL vial, anhydrous CoX_2 (X = Cl or Br, 1.1 equiv) was dissolved in 3 mL of diethyl ether. The vial was placed in a liquid nitrogen-cooled cold well until frozen. In a separate vial, ($^{t\text{Bu}}$L)Li (0.2 g, 0.53 mmol, 1.0 equiv) was dissolved in 6 mL of diethyl ether and added to the thawing slurry of CoX_2. The reaction mixture was stirred for 4 hours at room temperature. The dark brown mixture was filtered through a coarse glass frit with Celite to remove lithium salts and excess cobalt halide, followed by washing with diethyl ether. The filtrate was concentrated *in vacuo*, redissolved in benzene, and filtered through a medium porosity glass frit with Celite. The Celite was washed with an additional 20 mL benzene and the filtrate was lyophilized. The dried powder was refluxed in toluene for 30 min to yield a bright red solution. The solvent was then removed *in vacuo* while heating. The dried material was dissolved in benzene and the solution was lyophilized to yield the corresponding dimeric species as a red powder.

[($^{t\text{Bu}}$L)CoCl]$_2$ (10): 210 mg, 85%. **^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 80.63 (s), 35.77 (s), 1.25 (s), −15.60 (s). Anal. Calc. for $C_{52}H_{66}Cl_2Co_2N_4$: C 66.74, H 7.11, N 5.99; Found: C 66.95, H 6.75, N 5.85.

[($^{t\text{Bu}}$L)CoBr]$_2$, (11): 245 mg, 91%. **^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 79.85 (s), 33.09 (s), −13.93. Anal. Calc. for $C_{52}H_{66}Br_2Co_2N_4$: C 60.95, H 6.49, N 5.47; Found: C 70.10, H 6.90, N 5.60. Crystals suitable for X-ray diffraction were grown from a *n*-hexane/benzene mixture at room temperature.

($^{t\text{Bu}}$L)CoBr(thf), (12): In an oven-dried 20 mL vial, **11** (20 mg, 0.02 mmol) was dissolved in 3 mL of THF to afford a dark brown solution. The THF was removed *in vacuo* and the dried material was redissolved in benzene and lyophilized to yield **12** as a green powder (22 mg, 97%). **^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 64.17 (s), 41.27 (s), 11.08 (s), 9.40 (s), 4.93 (s), 3.52 (s), 2.19 (s), 1.35 (s). Anal. Calc. for $C_{30}H_{41}BrCoN_2O$: C 61.65, H 7.07, N 4.79; Found: C 61.30, H 6.95, N 4.55.

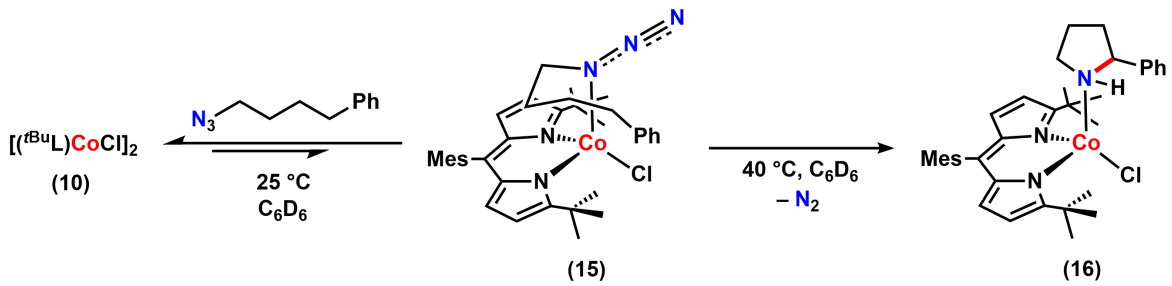
Crystals suitable for X-ray diffraction were grown from a *n*-hexane/THF mixture at room temperature.



(*t*^{Bu}L)CoX(N$_3$R), R = (CH$_2$)$_4$(C$_2$H$_3$): In an oven-dried 20 mL vial, a benzene solution of 6-azidohex-1-ene (1.0 equiv per Co center) was added to a stirring solution of **10** or **11** (0.02 mmol) in benzene at room temperature to observe an immediate color change from red to brown. Owing to the rapid conversion to the corresponding triazole bound species, the azide bound complex **13** could not be isolated. **X = Br: ^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 70.40 (s), 41.74 (s), 18.86 (s), 10.78 (s), 4.34 (s), 1.37 (s), −0.17 (s), −3.07 (s), −5.14 (s), −30.57 (s).

(*t*^{Bu}L)CoCl(1,2,3-dihydrotriazole) (14): A benzene solution of **13** (prepared *in situ* following the procedure described above using **10** (20 mg)) was stirred at room temperature for 1 hour. The solution was lyophilized to afford **14** as a brown powder (17 mg, 87%). **^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 61.44 (s), 32.52 (s), 27.04 (s), 19.98 (s), 9.30 (s), 3.79 (s), 1.34 (s), −2.83 (s). Anal. Calc. for $C_{32}H_{44}ClCoN_5$: C 64.80, H 7.48, N 11.81; Found: C 65.05, H 7.75, N 12.02.

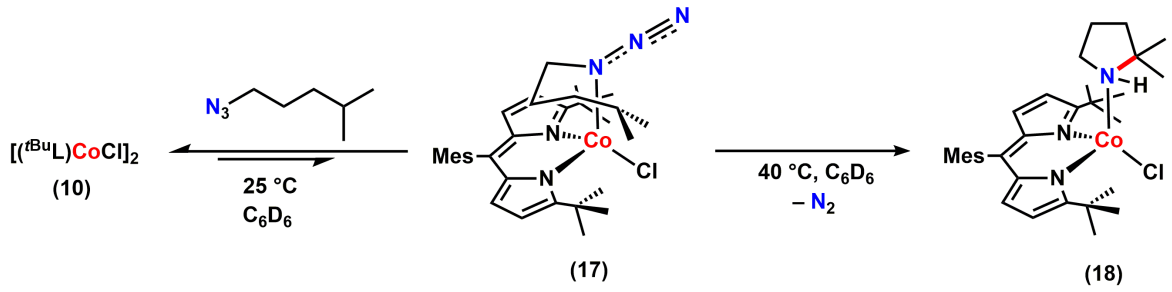
(*t*^{Bu}L)CoBr(1,2,3-dihydrotriazole): 24 mg, 95%. **^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 62.91 (s), 60.45 (s), 60.28 (s), 31.00 (s), 28.95 (s), 24.86 (s), 9.73 (s), 9.00 (s), 5.92 (s), 3.84 (s), 1.34 (s), −3.69 (s). Anal. Calc. for $C_{32}H_{44}BrCoN_5$: C 60.28, H 6.96, N 10.98; Found: C 60.45, H 7.05, N 11.10. Crystals suitable for X-ray diffraction were grown from a *n*-hexane:benzene solution at room temperature.



($^{t\text{Bu}}$L)CoX(N_3R), R = $(CH_2)_4(C_6H_5)$: In an oven-dried 20 mL vial, a benzene solution of (4-azidobutyl)benzene (1.0 equiv per Co center) was added to a stirring solution of **10** or **11** (0.02 mmol) in benzene at room temperature to observe an immediate color change from red to brown. Owing to a greater driving force to regenerate the dimeric species (**10** or **11**) during crystallization, the azide adduct complex was not isolable in the solid state. **X = Cl (15)**: **^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 66.39 (s), 47.19 (s), 8.92 (s), 8.30 (s), 6.95 (s), 6.50 (s), 4.48 (s), 2.14 (s), 1.40 (s), 1.31 (s), −0.88 (s), −0.54 (s), −1.70 (s), −15.98 (s), −32.26 (s). **X = Br**: **^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 76.33 (s), 35.62 (s), 5.188 (s), 3.86 (s), 1.74 (s), 1.35 (s), 0.88 (s), −1.78 (s), −2.83 (s).

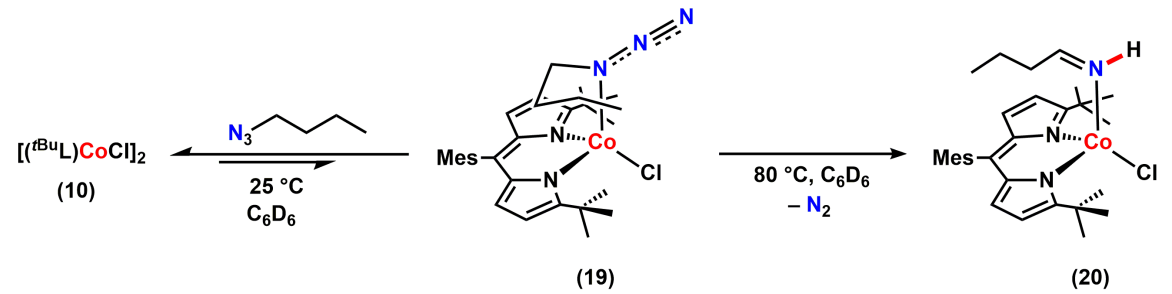
($^{t\text{Bu}}$L)CoCl(2-phenylpyrrolidine) (16): A benzene solution of **15** (prepared following the procedure described above using **10** (20 mg)) was heated to 40 °C for 24 hours in a J. Young NMR tube. The solution was lyophilized to afford **16** as a brown powder (23 mg, 89%). **^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 62.91 (s), 60.45 (s), 60.28 (s), 31.00 (s), 28.95 (s), 24.86 (s), 9.73 (s), 9.00 (s), 5.92 (s), 3.84 (s), 1.34 (s), −3.69 (s).

($^{t\text{Bu}}$L)CoBr(2-phenylpyrrolidine): 21 mg, 84%. **^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 62.91 (s), 60.45 (s), 60.28 (s), 31.00 (s), 28.95 (s), 24.86 (s), 9.73 (s), 9.00 (s), 5.92 (s), 3.84 (s), 1.34 (s), −3.69 (s). Anal. Calc. for $C_{36}H_{46}BrCoN_3$: C 65.55, H 7.03, N 6.37; Found: C 65.27, H 7.22, N 5.98. Crystals suitable for X-ray diffraction were grown from a *n*-hexane:benzene solution at room temperature.



(^{tBu}L)CoX(N$_3$R), R = (CH$_2$)$_3$CH(CH$_3$)$_2$ (17): In an oven-dried 20 mL vial, a benzene solution of 1-azido-4-methylpentane (1.0 equiv per Co center) was added to a stirring solution of **10** or **11** (0.02 mmol) in benzene at room temperature to observe an immediate color change from red to brown. Owing to a greater driving force to regenerate the dimeric species (**10** or **11**) during crystallization, the azide-bound complex was not isolable in the solid state. **X = Cl (17): ^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 67.00 (s), 46.95 (s), 9.68 (s), 8.28 (s), 4.68 (s), 2.14 (s), 1.31 (s), −0.11 (s), −1.21 (s), −1.91 (s), −32.15 (s). **X = Br: ^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 75.68 (s), 36.26 (s), 9.96 (s), 3.86 (s), 1.74 (s), 1.35 (s), 0.89 (s), −0.45 (s), −2.66 (s), −4.11 (s), −11.14 (s).

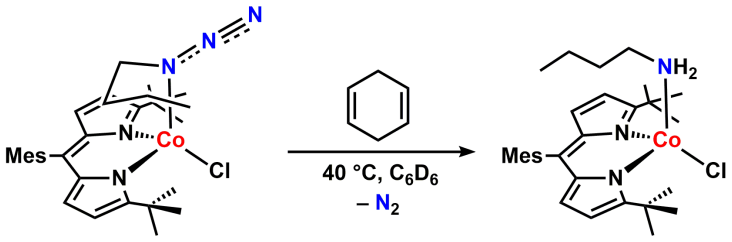
(^{Ar}L)CoCl(2,2-dimethylpyrrolidine) (18): A benzene solution of **17** (prepared following the procedure described above using **10** (20 mg)) was heated to 40 °C for 24 hours in a J. Young NMR tube. The solution was lyophilized to afford **18** as a brown powder (21 mg, 86%). **^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 62.91 (s), 60.45 (s), 60.28 (s), 31.00 (s), 28.95 (s), 24.86 (s), 9.73 (s), 9.00 (s), 5.92 (s), 3.84 (s), 1.34 (s), −3.69 (s). Anal. Calc. for $C_{34}H_{46}ClCoN_3$: C 67.77, H 8.18, N 7.41; Found: C 67.53, H 8.35, N 7.78. Crystals suitable for X-ray diffraction were grown from a *n*-hexane:benzene solution at room temperature.



(^{tBu}L)CoX(N$_3$R), R = (CH$_2$)$_3$CH$_3$ (19): In an oven-dried 20 mL vial, a benzene solution of 1-azidobutane (1.0 equiv per Co center) was added to a stirring solution of **10** or **11** (0.02 mmol) in benzene at room temperature to observe an immediate color change from red to brown. Owing to

a greater driving force to regenerate the dimeric species (**10** or **11**) during crystallization, the azide-bound complex was not isolable in the solid state. **X = Cl (19): ^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 66.87 (s), 46.77 (s), 10.93 (s), 8.94 (s), 4.60 (s), 2.14 (s), 1.31 (s), −0.19 (s), −0.76 (s), −1.66 (s), −31.94 (s). **X = Br: ^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 76.10 (s), 35.62 (s), 9.58 (s), 7.86 (s), 5.18 (s), 3.77 (s), 1.71 (s), −0.74 (s), −2.04 (s), −3.71 (s), −11.13 (s).

($^{t\text{Bu}}$L)CoCl(NHR), R = (CH)(CH$_2$)$_2$CH$_3$ (20): A benzene solution of **19** (prepared following the procedure described above using **10** (20 mg)) was heated to 80 °C for 24 hours in a J. Young NMR tube. The solution was lyophilized to afford **20** as a brown powder (21 mg, 91%). **^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 190.00 (s), 152.71 (s), 61.69 (s), 60.60 (s), 31.52 (s), 30.13 (s), 27.05 (s), 16.66 (s), 3.88 (s), 1.37 (s), −2.38 (s), −9.58 (s). Anal. Calc. for $C_{30}H_{42}ClCoN_3$: C 66.84, H 7.85, N 7.80; Found: C 66.50, H 9.01, N 8.15.



(19) (21)

($^{t\text{Bu}}$L)CoCl(NH$_2$R), R = (CH$_2$)$_3$CH$_3$ (21): In an oven-dried 20 mL vial, a benzene solution of 1-azidobutane (1.0 equiv per Co center) was added to a stirring solution of **10** (20 mg). To the stirring mixture, excess amount of 1,4-cyclohexadiene (10 equiv) was added. The mixture was transferred to a J. Young NMR tube and heated to 40 °C for 24 hours to observe a new paramagnetic species (**21**) by ^{1}H NMR spectroscopy. The authentic **21** can be prepared from **10** and a stoichiometric amount of butan-1-amine in benzene at room temperature. The dark brown mixture was lyophilized to afford **21** as a brown powder in quantitative yield (Figure S-9). **^{1}H NMR** (600 MHz, C_6D_6): δ/ppm 61.83 (s), 31.67 (s), 29.77 (s), 8.96 (s), 5.65 (s), 3.59 (s), 0.39 (s), -0.30 (s). Anal. Calc. for $C_{30}H_{44}ClCoN_3$: C 66.59, H 8.20, N 7.77; Found: C 66.90, H 7.92, N 7.45. Crystals suitable for X-ray diffraction were grown from a *n*-hexane:benzene solution at room temperature.

Non-Covalent Interaction Analysis.[8-9]

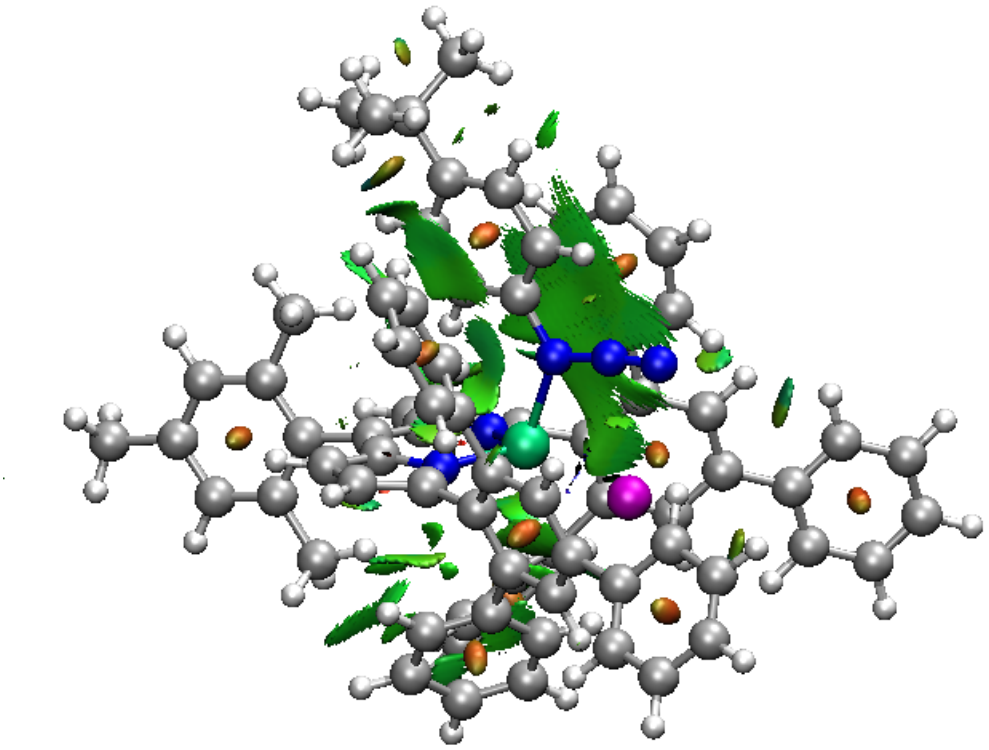
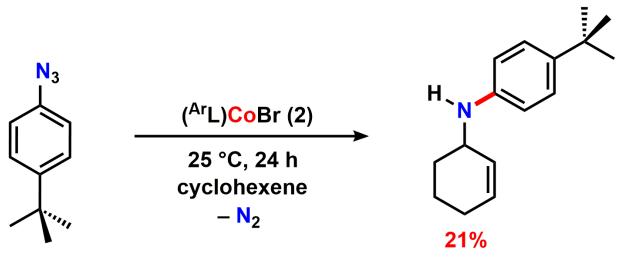


Figure S-1. Non-covalent interaction plot for **3**.

Stoichiometric Reactions.

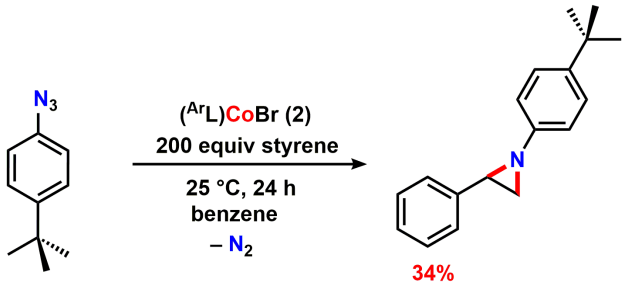
Reaction with cyclohexene.

To a stirring solution of **2** (20 mg, 0.02 mmol) in 0.7 mL of cyclohexene, a solution of 1-azido-4-(*tert*-butyl)benzene (1.0 equiv, 0.02 mmol) diluted in 0.3 mL of cyclohexene was added and allowed to stir at room temperature for 24 hours under an inert N_2 atmosphere. The reaction was removed from the glove box, concentrated *in vacuo*, and ran through a neutral alumina gel eluting with a 10:1 mixture of dichloromethane and methanol to remove paramagnetic materials. ^{1}H NMR and GC-MS revealed formation of 4-(*tert*-butyl)-*N*-(cyclohex-2-en-1-yl)aniline.[10] The yield was determined via ^{1}H NMR integration using 1,3,5-trimethoxybezene as an internal standard.



Reaction with styrene.

To a stirring solution of **2** (20 mg, 0.02 mmol) in benzene, a solution of 1-azido-4-(*tert*-butyl)benzene (1.0 equiv, 0.02 mmol) diluted in benzene was added followed by styrene (200 equiv, 4 mmol). The reaction mixture was allowed to stir at room temperature for 24 hour. The reaction was removed from the glove box, concentrated *in vacuo*, and ran through a neutral alumina gel eluting with a 10:1 mixture of dichloromethane and methanol to remove paramagnetic materials. ^{1}H NMR and GC-MS revealed formation of 1-(4-(*tert*-butyl)phenyl)-2-phenylaziridine.[11] The yield was determined via ^{1}H NMR integration using 1,3,5-trimethoxybezene as an internal standard.



Spectroscopic Characterization.

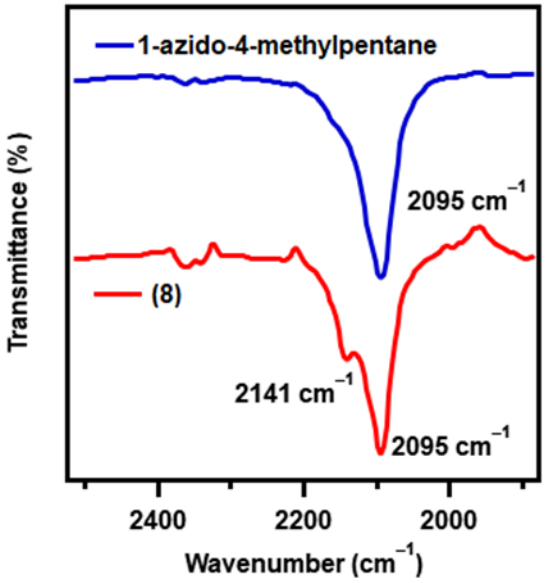


Figure S-2. Solution IR spectra of 1-azido-4-methylpentane and **8** in benzene in the presence of a slight excess amount of 1-azido-4-methylpentane.

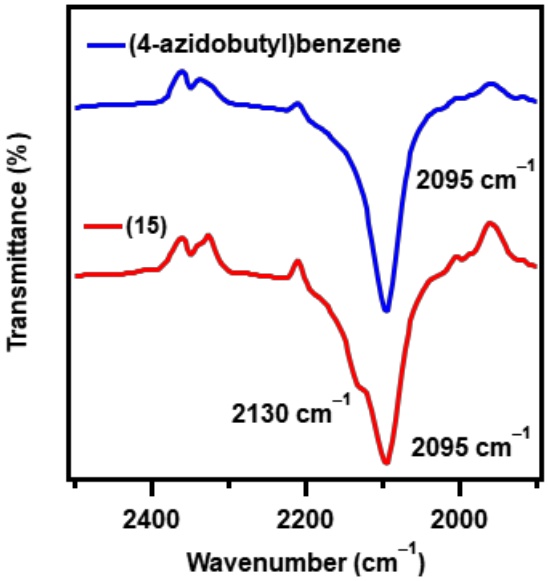


Figure S-3. Solution IR spectra of (4-azidobutyl)benzene and **15** in benzene in the presence of a slight excess amount of (4-azidobutyl)benzene.

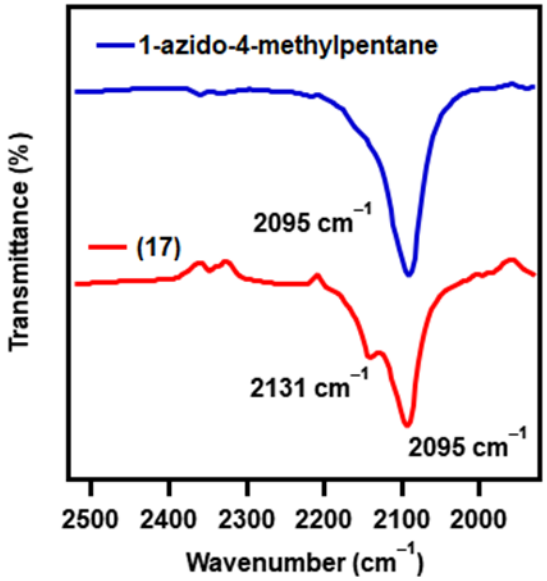


Figure S-4. Solution IR spectra of 1-azido-4-methylpentane and **17** in benzene in the presence of a slight excess amount of 1-azido-4-methylpentane.

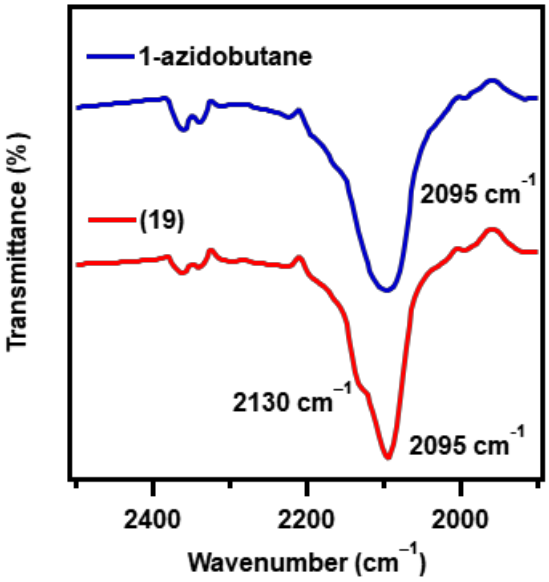


Figure S-5. Solution IR spectra of 1-azidobutane and **19** in benzene in the presence of a slight excess amount of 1-azidobutane.

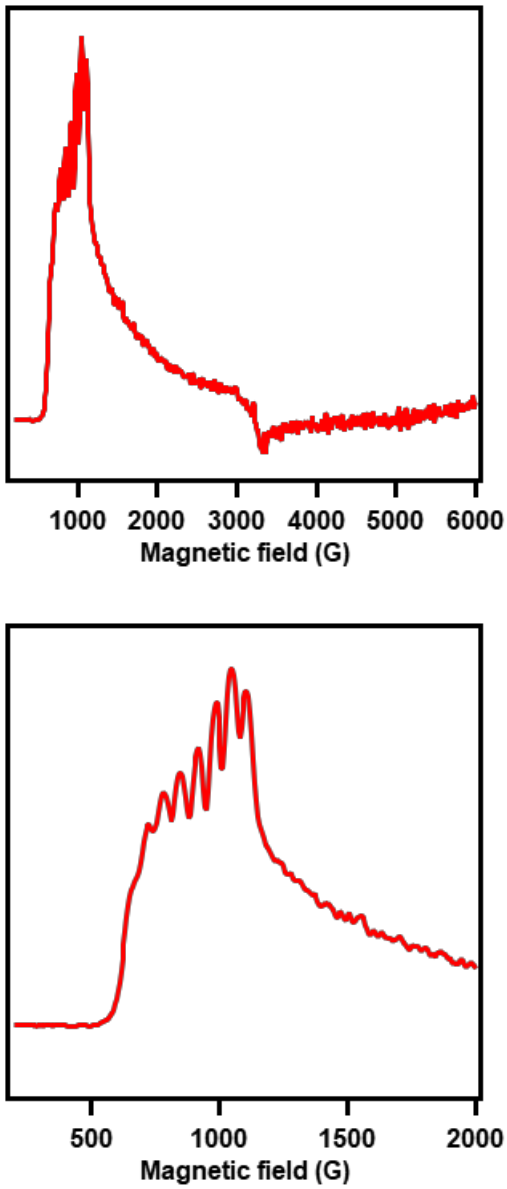


Figure S-6. Frozen toluene EPR spectrum of **8** at 4 K.

Reactivity Studies on 8.

(^{Ar}L)CoBr(N_3R) (**8**) (15 mg, 0.013 mmol) was dissolved in 0.7 mL of benzene-d_6 and the solution was transferred to a J. Young NMR tube. The reaction mixture was heated to 60 °C and its progression was monitored by ^{1}H NMR spectroscopy. ^{1}H NMR chemical shifts corresponding to the proposed nitrene intermediate are colored in red and the ones for the final imine adduct are colored in blue. The final imine adduct can be crystallized at room temperature from *n*-hexane/benzene mixture, however, the obtained X-ray structure cannot be modeled owing to the intrinsic disorder of the whole molecule. Instead, upon quenching the crude reaction mixture, the bound imine readily hydrolyzes to the corresponding 4-methylpentanal as confirmed by ^{1}H NMR spectroscopy supporting the identity of the bound imine moiety.[12]

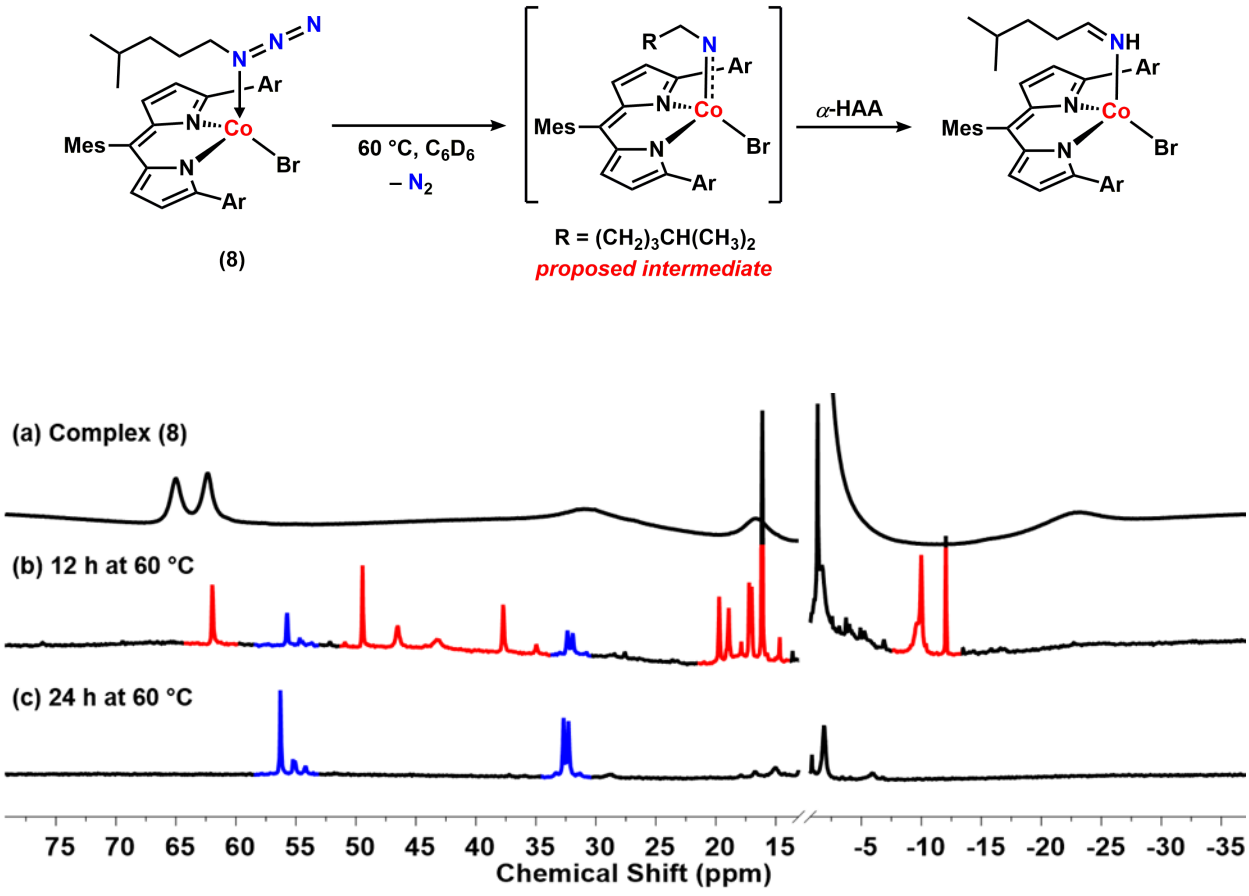


Figure S-7. Reaction progression for the conversion of **8** to the corresponding imine complex.

Binding equilibrium between 11 and alkyl azides.

Since **11** is more soluble than **10** in benzene, we used **11** to study binding dynamics between dimeric complexes and the monomeric organoazide bound species. A solution of **11** (5 mg, 4.8 μmol as a dimeric form) in benzene-d_6 was added to a solution of 1-azido-4-(*tert*-butyl)benzene (1.0 – 20 equiv) in benzene-d_6. Each reaction mixture was transferred to a J. Young NMR tube and the chemical shifts were tracked by ^{1}H NMR spectroscopy.

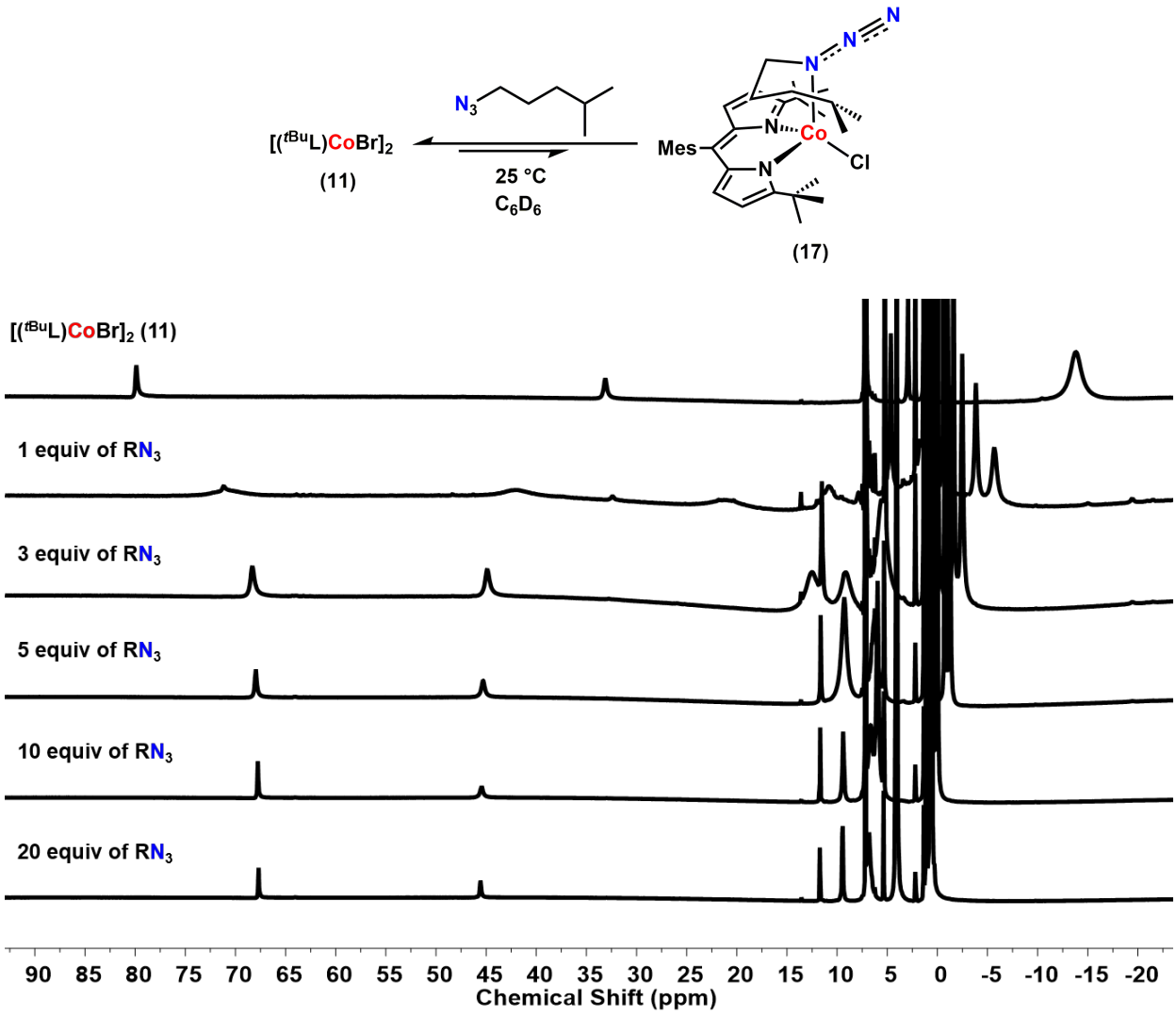


Figure S-8. 600 MHz ^{1}H NMR spectra of **17** at varying concentrations of 1-azido-4-methylpentane in benzene-d_6 at 25 °C.

Job plot analysis.[13]

Solutions of **11** and 1-azido-4-methylpentane (RN_3) were prepared in benzene-d_6 and the total concentration of the mixture was maintained constant throughout the analysis. The chemical shifts corresponding to **11** as a function of the concentration of alkyl azides were measured at 25 °C.

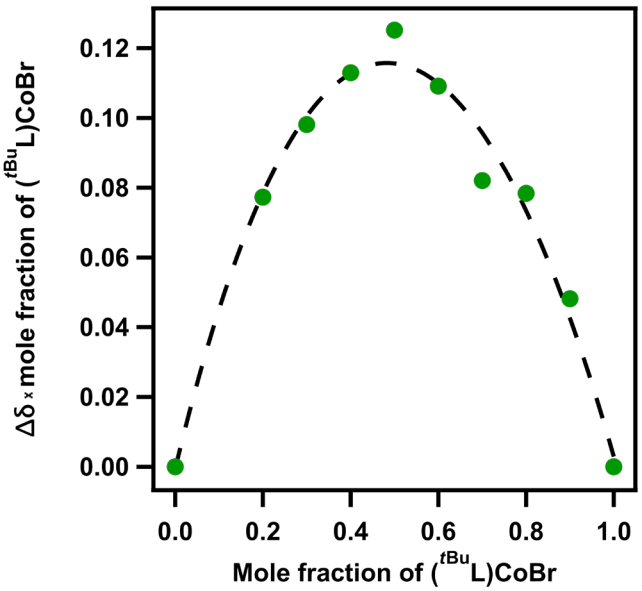


Figure S-9. Job plot obtained at 25 °C in benzene-d_6 with [**Co**] + [RN_3] = 8.85 mM**.**

Table S-1. Chemical shifts (ppm) of **11** as a function of [RN_3] at 25 °C in benzene-d_6.

Entry	2[11] (mM)	[RN_3] (mM)	Chemical shift (ppm)
1	8.85	0	80.69
2	7.97	0.88	80.63
3	7.08	1.77	80.59
4	6.20	2.66	80.57
5	5.31	3.54	80.50
6	4.43	4.43	80.44
7	3.54	5.31	80.40
8	2.66	6.20	80.36
9	1.77	7.08	80.30
10	0.88	7.97	73.71

^{1}H NMR titration.[14]

A solution of **11** was prepared in benzene-d_6 and its concentration (1.1 mM) was maintained constant throughout the titration with various alkyl azides. The chemical shifts corresponding to **11** as a function of the concentration of alkyl azide were measured at 25 °C to reveal almost identical binding affinities towards the cobalt center among three different alkyl azide substrates.

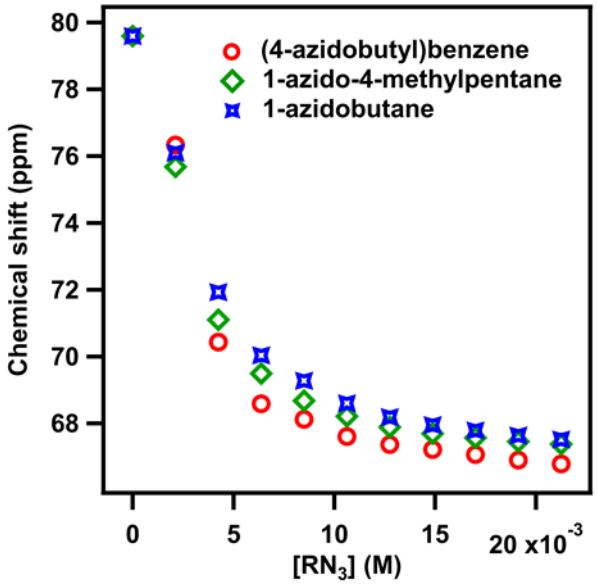
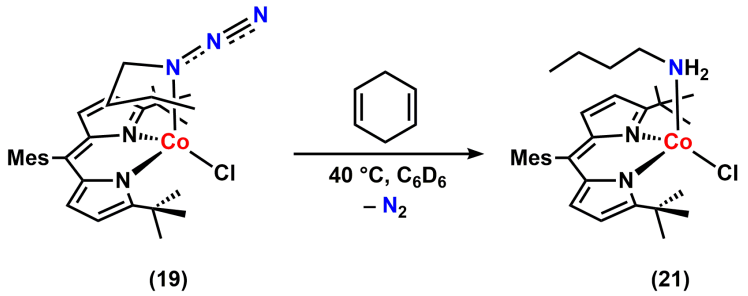


Figure S-10. 600 MHz ^{1}H NMR titration curves of **11** with organoazides. Chemical shifts (ppm) for **11** as a function of concentration of each azide at 25 °C in benzene-d_6.

Reactivity studies on 19 with cyclohexene.

A solution of **19** was prepared by adding 1.0 equivalent of 1-azidobutane to **10** in benzene-d_6. To the stirring solution, 10 equivalents of 1,4-cyclohexadiene was added. The reaction mixture was transferred to a J. Young NMR tube and heated to 40 °C for 24 h to observe formation of **21**.



(19) (21)

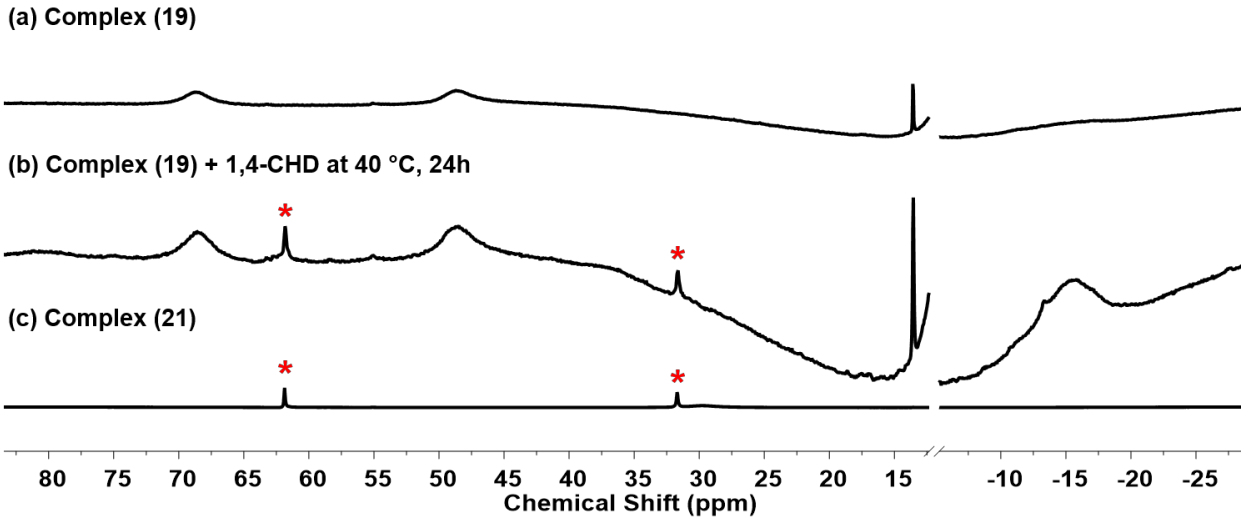


Figure S-11. Reaction progression for the conversion of **19** to **21** in benzene-d_6 at 40 °C.

^{1}H NMR Spectra of Metal Compounds.

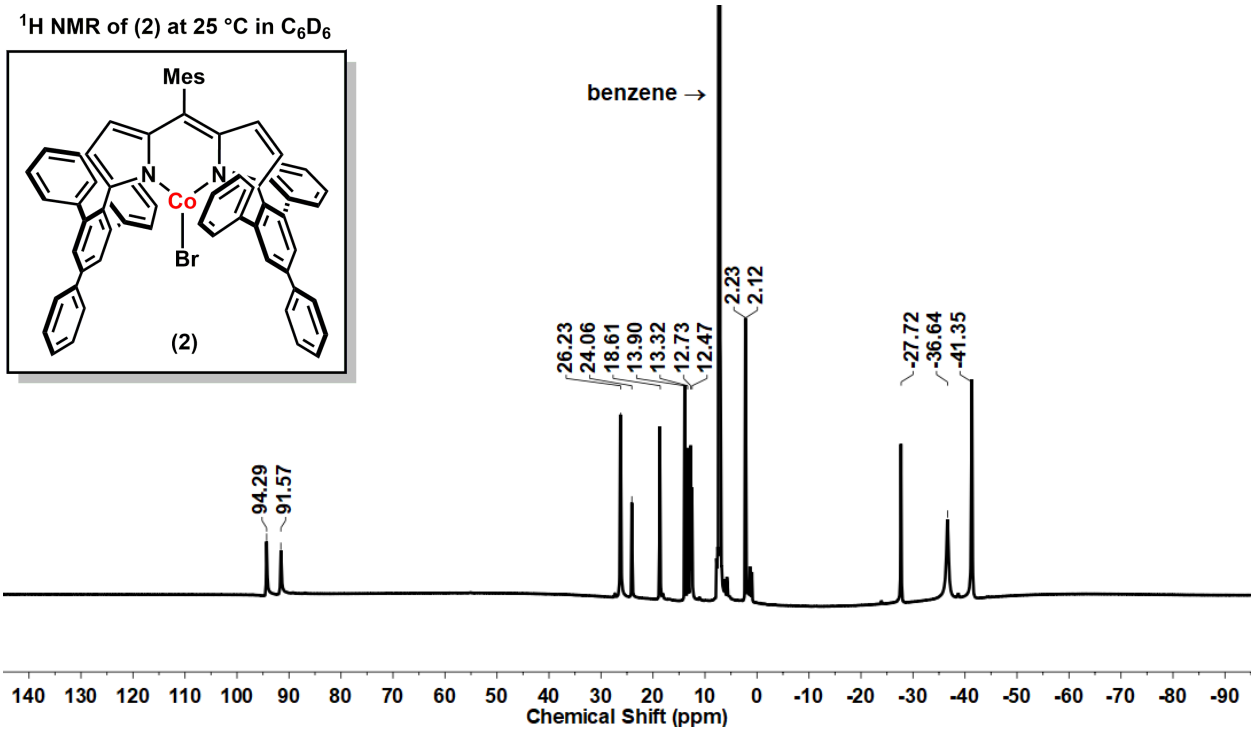


Figure S-12. 500 MHz ^{1}H NMR spectrum of (^{Ar}L)CoBr (**2**) in benzene-d_6.

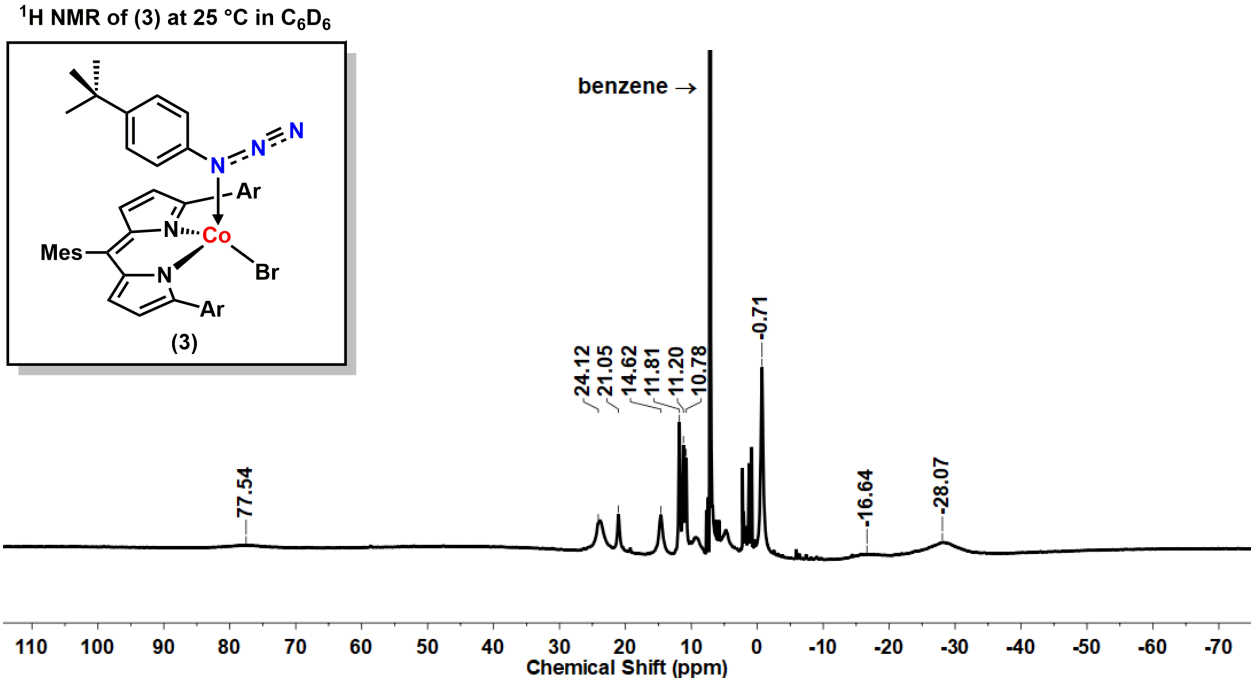


Figure S-13. 500 MHz ^{1}H NMR spectrum of (^{Ar}L)CoBr(N_3(C_6H_4-*p*-^{t}Bu)) (**3**) in benzene-d_6.

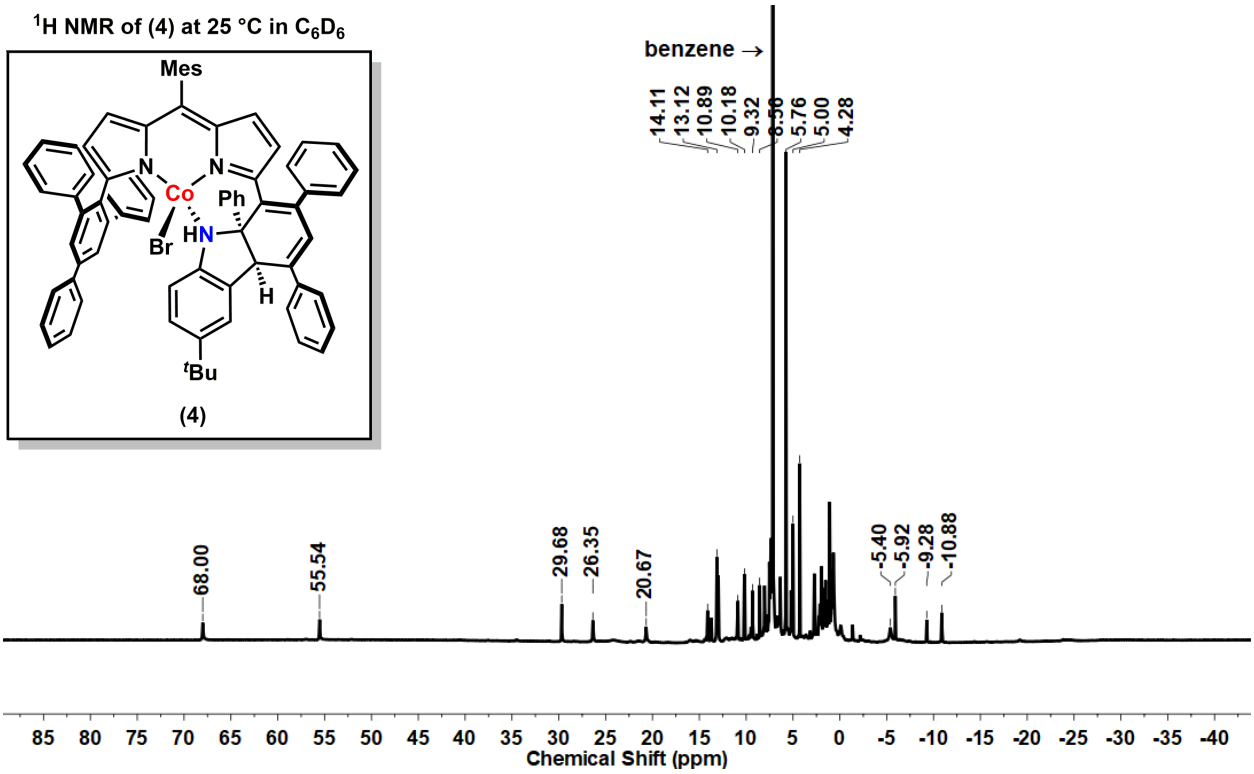


Figure S-14. 500 MHz ^{1}H NMR spectrum of (^{Ar}L)CoBr([3+2]annulation) (**4**) in benzene-d_6.

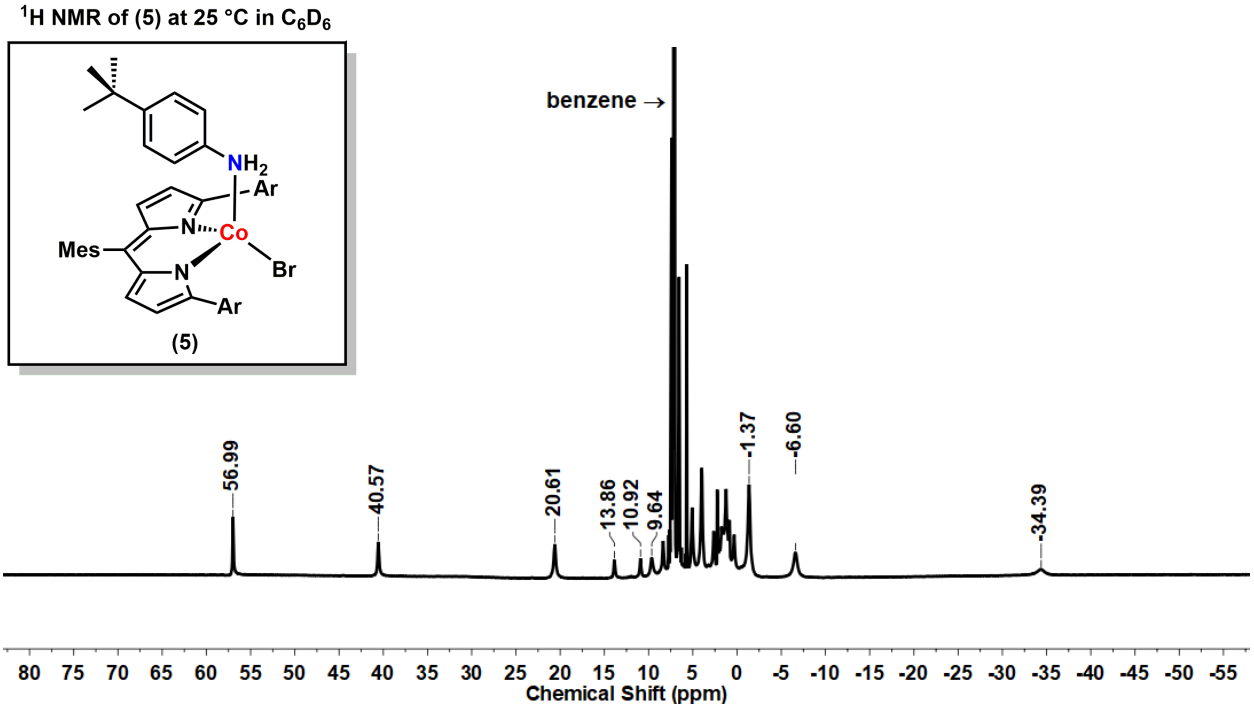


Figure S-15. 500 MHz ^{1}H NMR spectrum of (^{Ar}L)CoBr(NH$_2$(C_6H_4-*p*-^{t}Bu)) (**5**) in benzene-d_6.

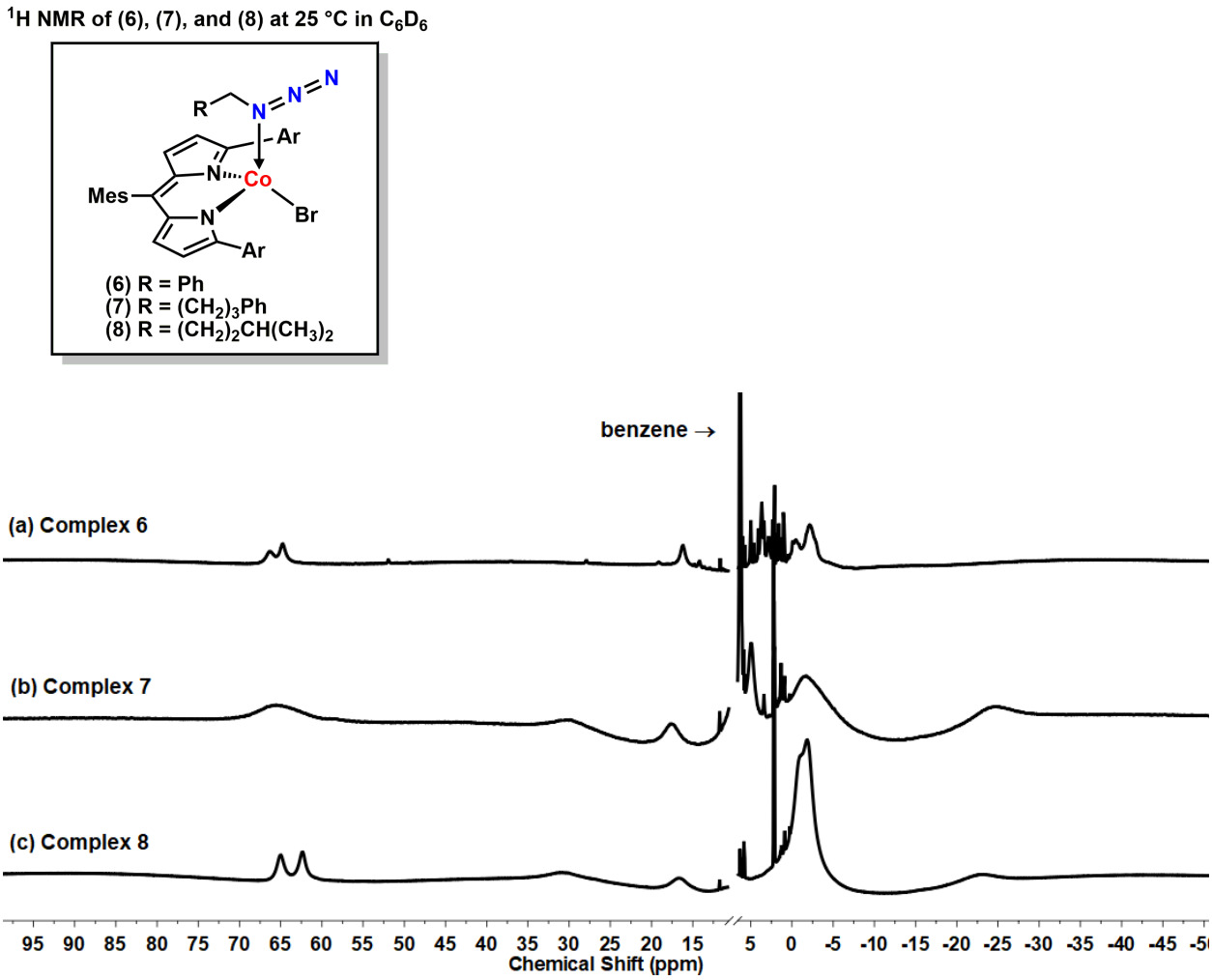


Figure S-16. 500 MHz ^{1}H NMR spectra of (^{Ar}L)CoBr(N_3CH_2R) (**6**, **7**, and **8**) in benzene-d_6.

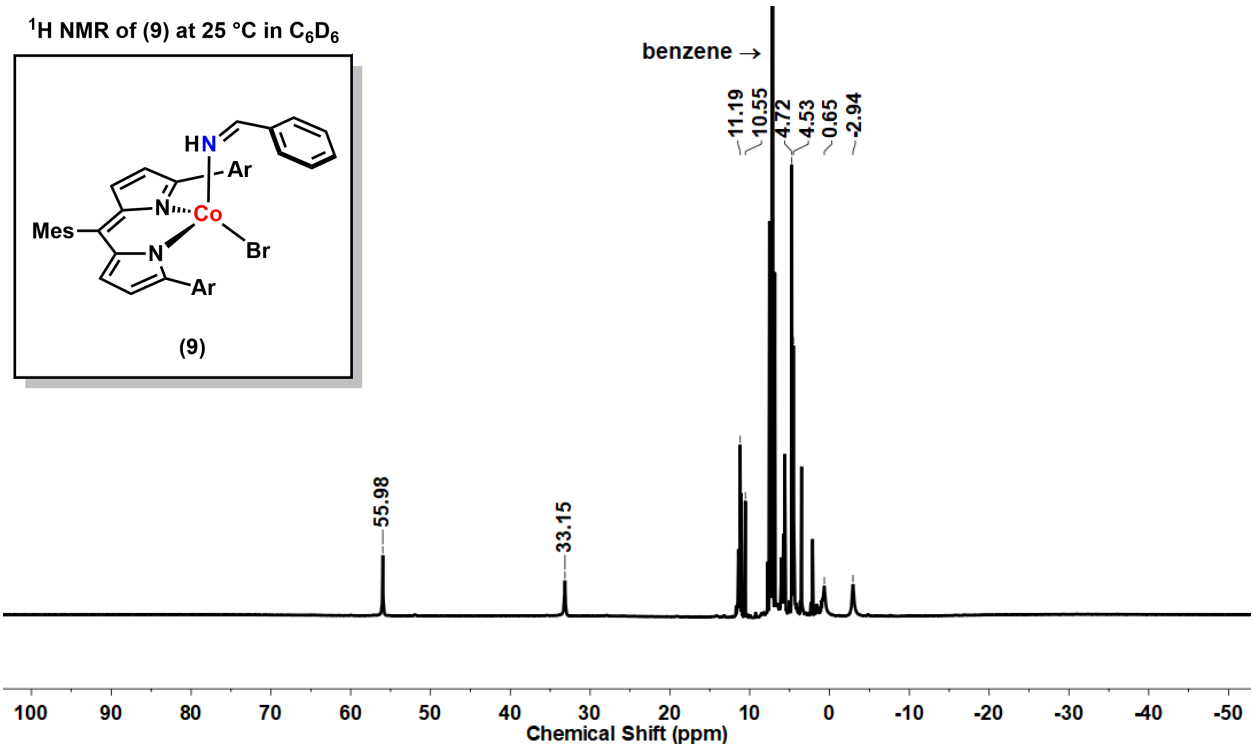


Figure S-17. 500 MHz ^{1}H NMR spectrum of (^{Ar}L)CoBr(NHCHC$_6$H$_5$) (**9**) in benzene-d_6.

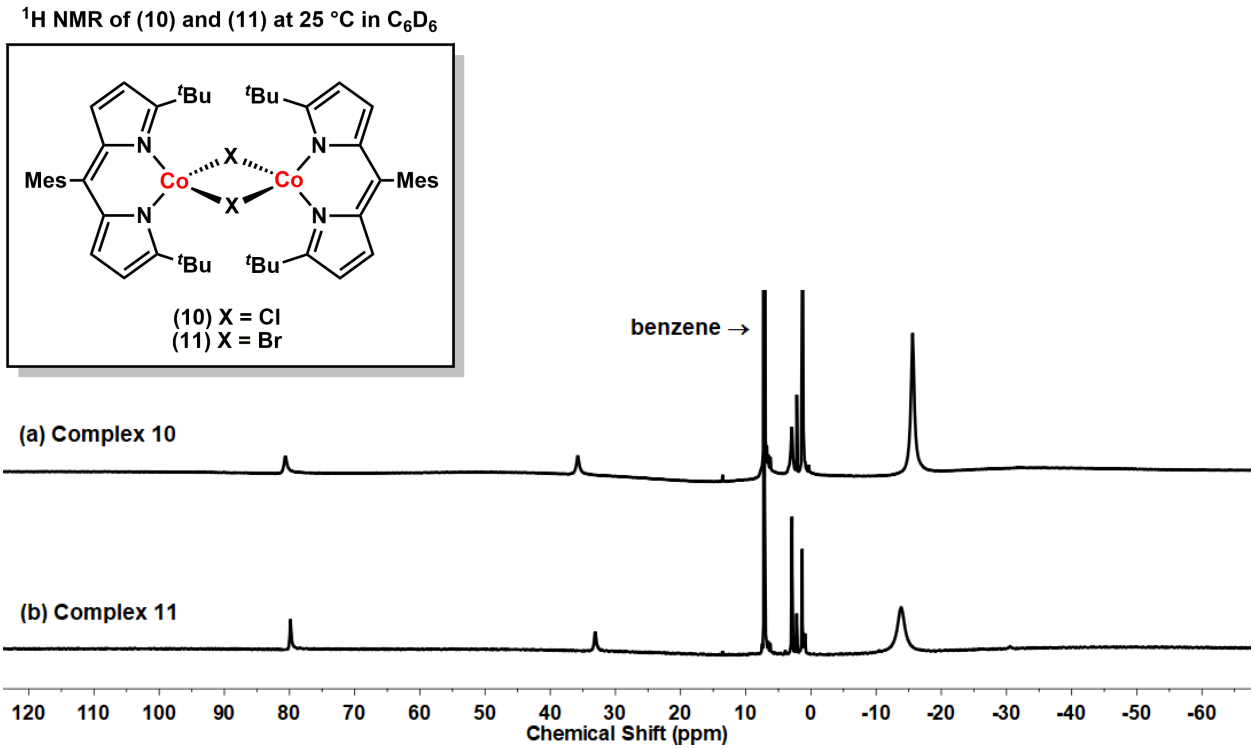


Figure S-18. 500 MHz ^{1}H NMR spectra of (a) [(^{tBu}L)CoCl]$_2$ (**10**) and (b) [(^{tBu}L)CoBr]$_2$ (**11**) in benzene-d_6.

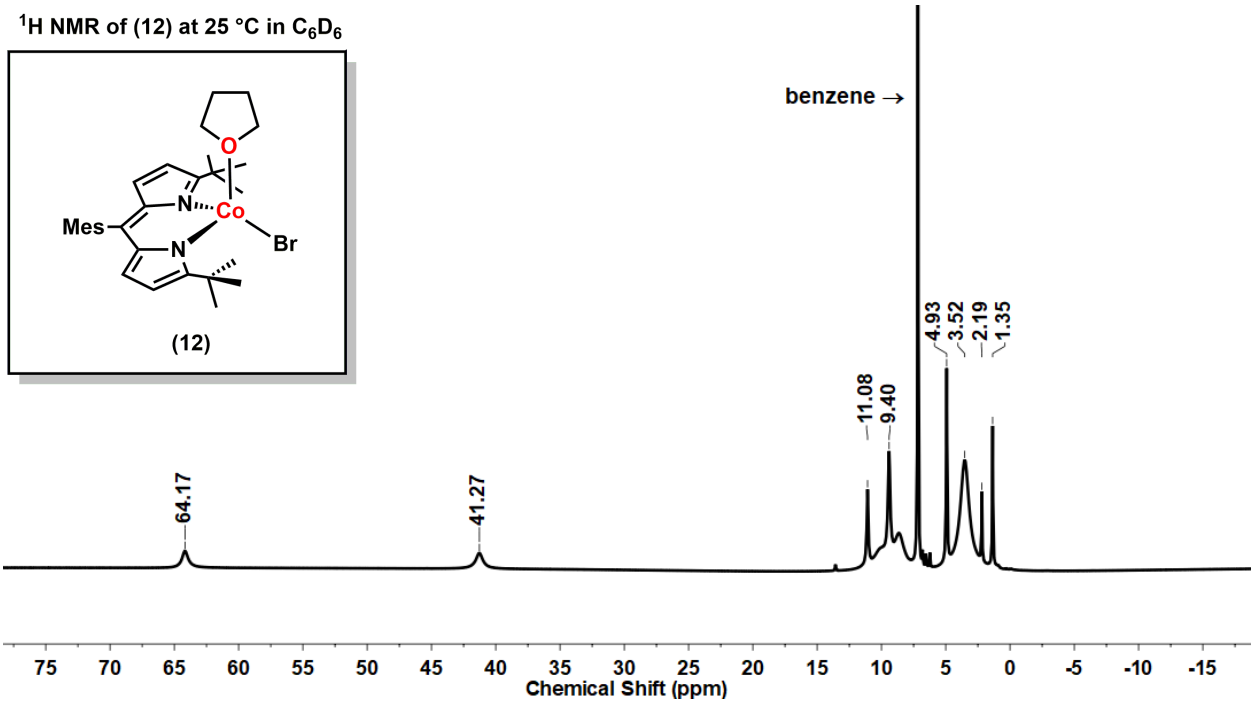


Figure S-19. 500 MHz ^{1}H NMR spectrum of ($^{t\text{Bu}}$L)CoBr(thf) (**12**) in benzene-d_6.

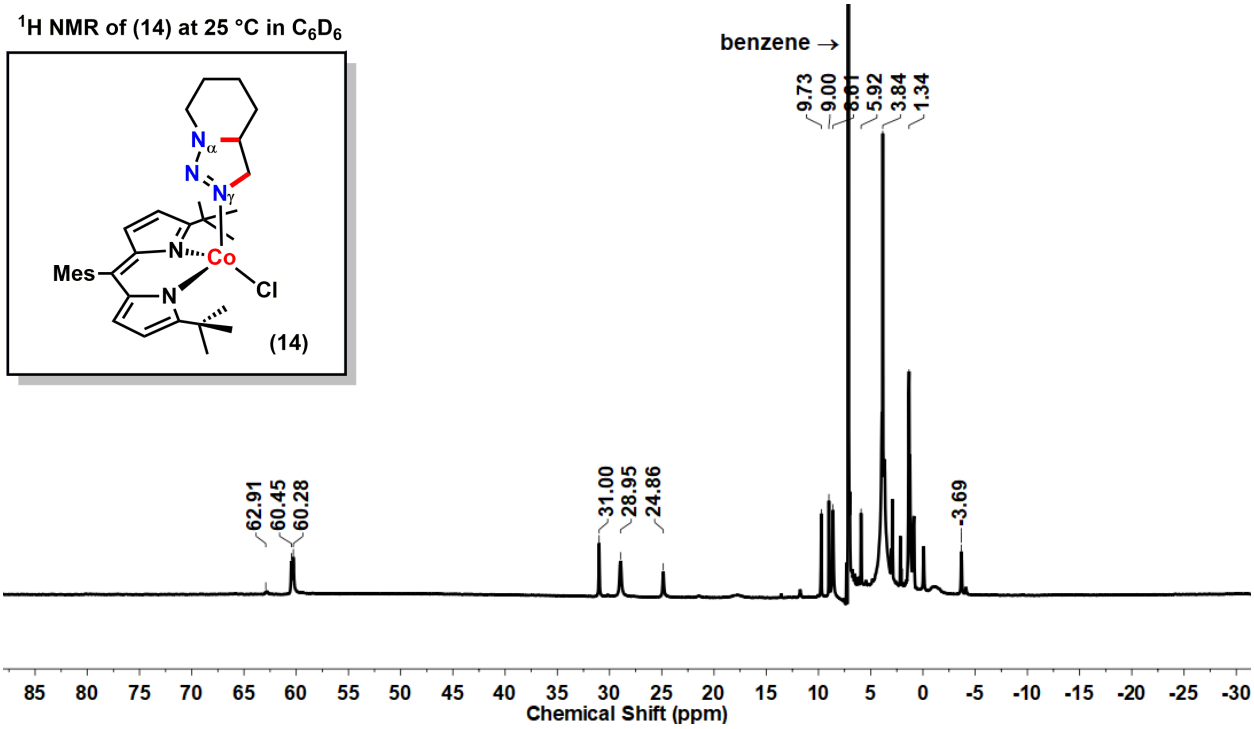


Figure S-20. 500 MHz ^{1}H NMR spectrum of ($^{t\text{Bu}}$L)CoCl(1,2,3-dihydrotriazole) (**14**) in benzene-d_6.

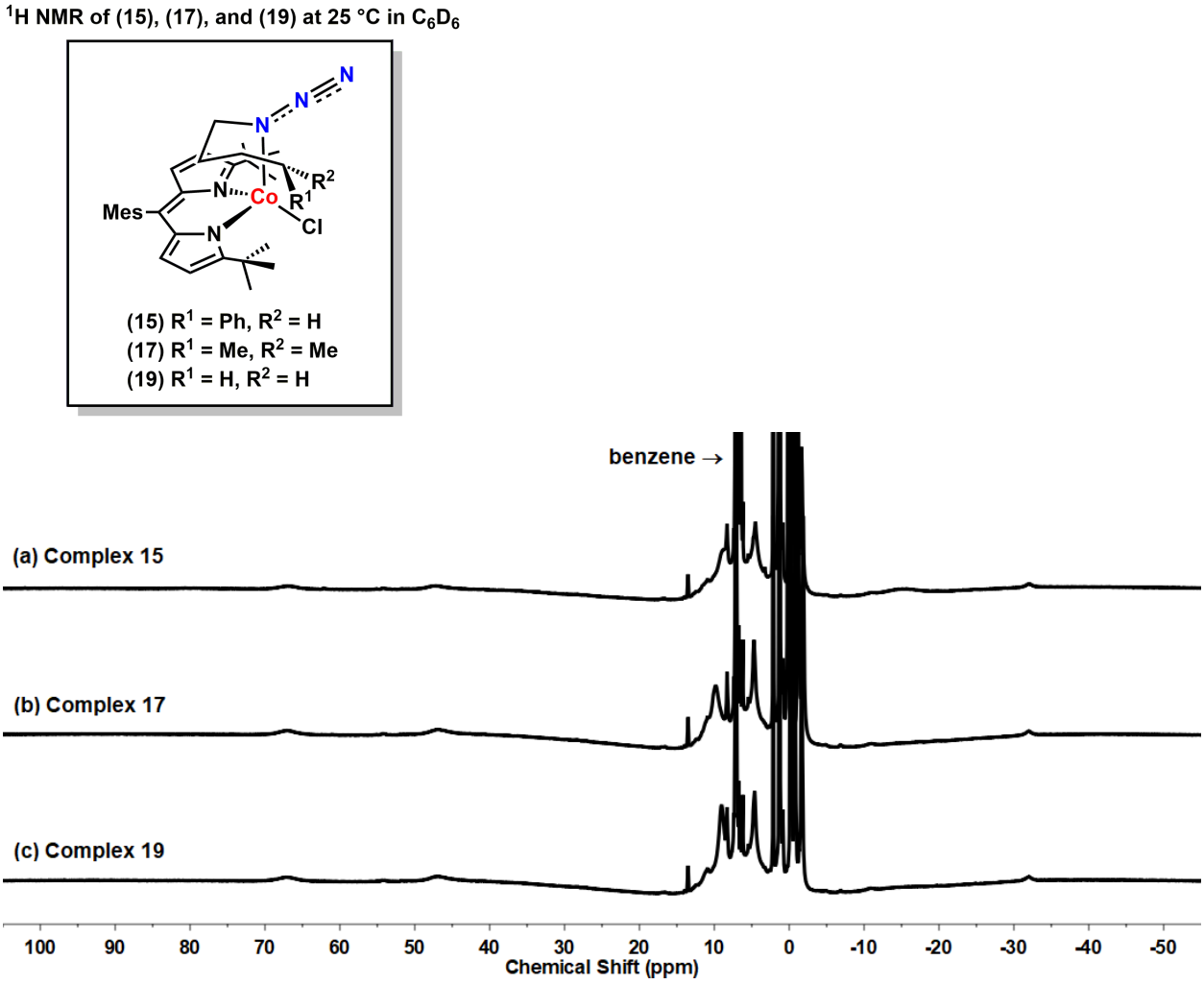


Figure S-21. 500 MHz ^{1}H NMR spectra of ($^{t\text{Bu}}$L)CoCl(N_3R) (**15**, **17**, and **19**) in benzene-d_6.

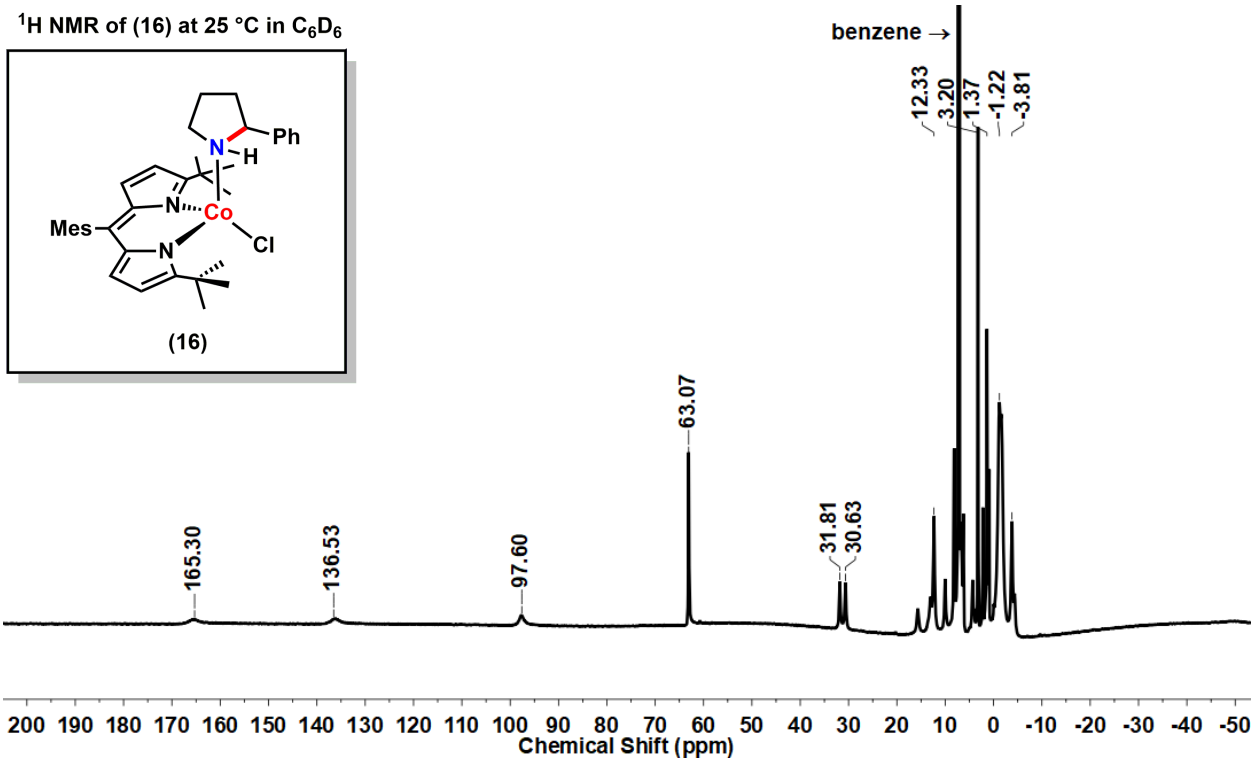


Figure S-22. 500 MHz ^{1}H NMR spectrum of ($^{t\text{Bu}}$L)CoCl(2-phenylpyrrolidine) (**16**) in benzene-d_6.

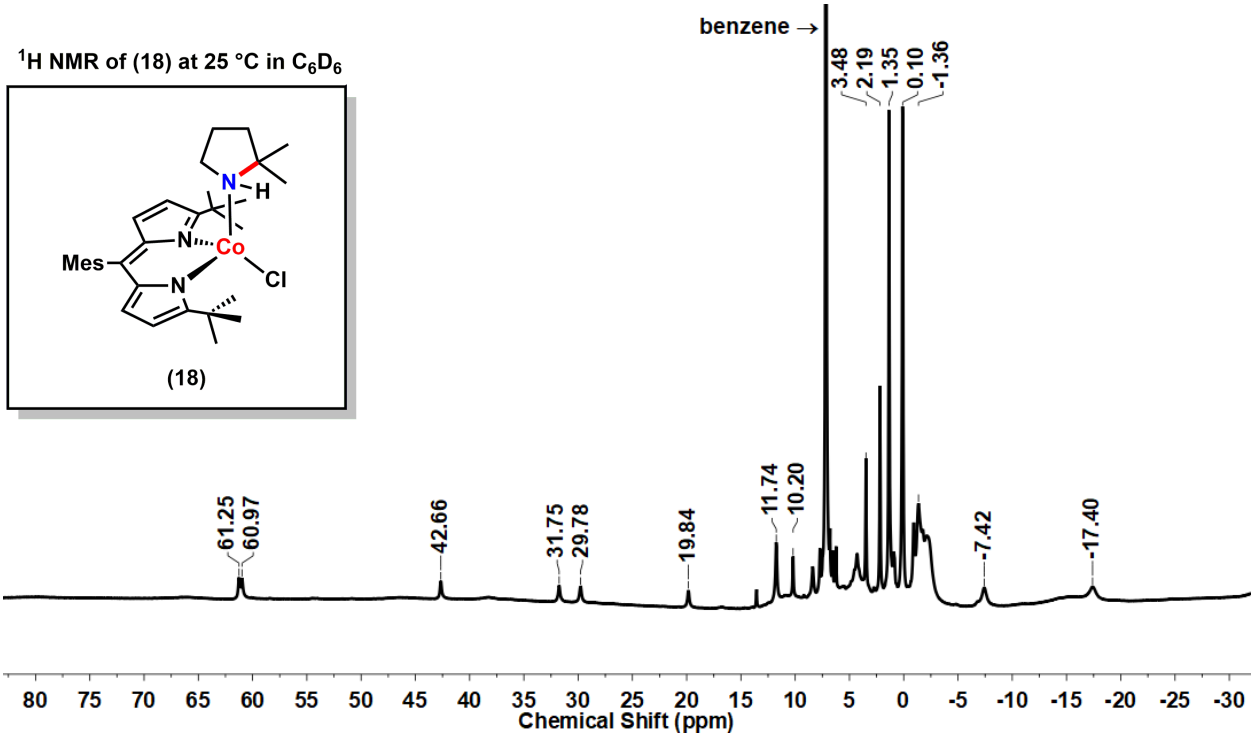


Figure S-23. 500 MHz ^{1}H NMR spectrum of ($^{t\text{Bu}}$L)CoCl(2,2-dimethylpyrrolidine) (**18**) in benzene-d_6.

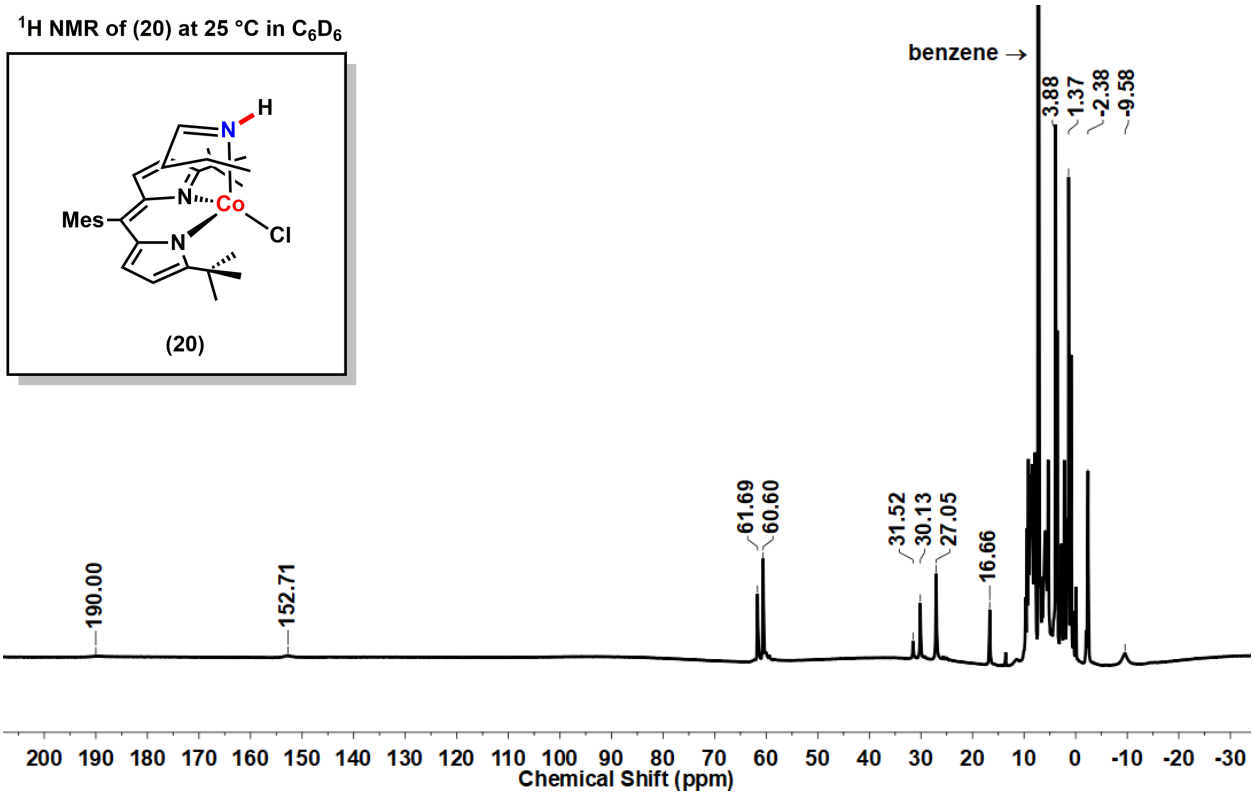


Figure S-24. 500 MHz ^{1}H NMR spectrum of ($^{t\text{Bu}}$L)CoCl(butan-1-imine) (**20**) in benzene-d_6.

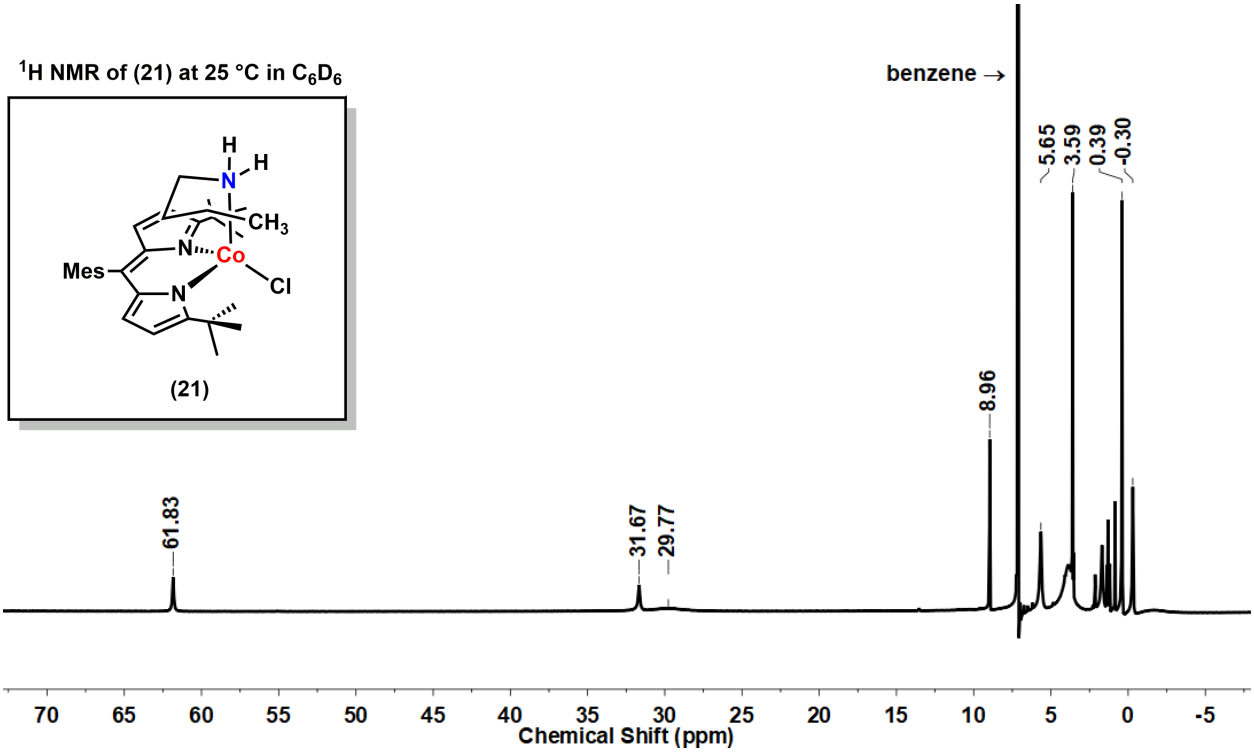


Figure S-25. 500 MHz ^{1}H NMR spectrum of ($^{t\text{Bu}}$L)CoCl(*n*-BuNH$_2$) (**21**) in benzene-d_6.

X-Ray Diffraction Techniques.

General. All structures were collected on a Bruker three-circle platform goniometer equipped with an Apex II CCD and an Oxford cryostream cooling device. Radiation was from a graphite fine focus sealed tube Mo Kα (0.71073 Å) source. Crystals were mounted on a cryoloop or glass fiber pin using Paratone N oil. Structures were collected at 100 K. Data was collected as a series of φ and/or ω scans. Data was integrated using SAINT[15] and scaled with either a numerical or multi-scan absorption correction using SADABS.[15] The structures were solved by intrinsic methods or Patterson maps using SHELXL-2018[16] and refined against F^2 on all data by full matrix least squares with SHELXL-2018.[16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the atoms they are linked to (1.5 times for methyl groups). Further details on particular structures are noted below. Please refer to cif files for detail of disorder refinement.

For section 2.5.1. Initial 100 K structure was solved and refined as described above. For data sets obtained following heating at 345 K, non-H atoms of the product were located in difference Fourier maps, calculated with coefficients F_0(heated) – F_0(initial_100 K), and then refined with constraints on the product molecule's atomic displacement parameters to the corresponding values of the reactant molecule (EADP instructions of SHELXL-2018, for the azide adduct and iminyl units).[16] The percentage of the reactant in the crystal was treated as a variable in the refinements.

More specifically, for the reactive fragment, all non-H atoms of the product were located in the reaction- difference maps, calculated with coefficients F_o(heat)-F_o(initial), and then refined with restraints on the reacted fragment's bond lengths and constraints of the atomic displacement parameters to the corresponding values of the un-reacted fragment (SADI and EADP instructions of SHELXL2018). The restraints of the atomic displacement parameters (SIMU/RIGU instructions of SHELXL-2018) if necessary, have been applied for such disorder refinement. For the non-reactive fragment, the restraints on bond lengths (SADI/SAME instructions of SHELXL-2018), as well as the restraints of the atomic displacement parameters, if necessary, have been applied for the disorder refinement. In order to get a reasonable bond length for the severely

disordered hexane and avoid a non-positive definite of atomic displacement parameters, the restraints of DFIX and ISOR were applied.

For section 2.5.2. The X-ray crystal structures of **7–N_2** and **8–N_2** were obtained from **7** and **8** respectively, using synchrotron radiation (0.41328 Å) at ChemMatCARS located at the Advanced Photon Source housed at Argonne National Lab. The data was collected at 100 K (Cryojet N_2 cold stream) using a vertically mounted Bruker D8 three-circle platform goniometer equipped with a PILATUS3 X CdTe 1M detector. Data was collected as a series of φ and/or ω scans. Data were integrated using SAINT and scaled with a multi-scan absorption correction using SADABS.[15] Structures were solved by intrinsic phasing using SHELXT (Apex2 program suite v2014.1) and refined against F^2 on all data by full matrix least squares with SHELXL-2014. All non-hydrogen atoms were refined anisotropically. H atoms were placed at idealized positions and refined using a riding model. For the refinement of **8–N_2** specifically, a disordered hexanes molecule (1/2 occupied) was identified in the final stages of refinement. The disorder of the solvent was dealt with by application of the program Squeeze (Spek, A. L. *Acta Cryst*. **2015**, C*71*, 9-18) as implemented in Platon (Spek, A. L. *Acta Cryst*. **2009**, D*65*, 148-155) which allows for the mathematical compensation of the electron contribution of disordered solvent contained in the voids to the calculated diffraction intensities.

Interpretation of single-crystal transformation results.

(1) Both **7** and **8** are stable at room temperature as supported by clean ^{1}H NMR spectra (Figure S-16), proving that there is no loss of N_2 and subsequent decomposition to amide, imine, or other unknown spices at room temperature. If **7** or **8** co-crystallized with either Co^{III} amide or Co^{II} imine at room temperature, we should see a second set of distinct chemical shifts by ^{1}H NMR spectroscopy. However, those features have not been detected in the ^{1}H NMR of the crystalline material (Figure S-16). Specifically, the corresponding imine complex of **8** can be generated only upon heating (above 60 °C, 24 h) and displays distinct ^{1}H NMR chemical shifts with respect to the azide adduct precursor **8** (Figure S-7).

(2) The chemical composition and purity of **7** and **8** have also been supported by CHN elemental analysis (SI 8-9).

(3) Formation of the authentic Co^{III} alkyl amide complex (^{Ar}L)CoBr(NHR) via decomposition of **7** or **8** has proven unsuccessful. Specifically, treatment of **7** or **8** with excess amount of external H–atom donors (e.g., 1,4-cyclohexadiene) shows no reactivity at room temperature. This lack of intermolecular H–atom abstraction (HAA) reactivity has been clearly stated in section 2.4 and the conclusion section to highlight the differences in reactivity between the alkyl azide adducts (**7** and **8**) and the analogous aryl azide adduct **3**. We note that independent synthesis of the authentic amide complexes from (^{Ar}L)CoBr (**2**) via salt-metathesis or stepwise deprotonation/oxidation has not been successful either, suggesting that formation of a Co^{III} amide complex is highly unlikely.

(4) In addition to the absence of intermolecular HAA reactivity, intramolecular HAA pathways to generate a Co^{III} amide complex directly from the azide adduct precursor (e.g., **7** or **8**) can be ruled out by considering the mechanism of an intramolecular 1,2-hydrogen shift observed for **8** (for literature supporting that an α–H atom participates in formation of imine products from metal-nitrene precursors: *J. Am. Chem. Soc*., **2019**, *141* (19), 7797-7806). Given that the imine adduct is the exclusive product upon thermal decomposition of **8** via the intramolecular 1,2-hydrogen shift (Figure S-7), the corresponding Co^{III} amide complex cannot even exist as an intermediate, unless the H–atom shift is stepwise, which accompanies formation of a highly unstable secondary carboradical on the C1 (or Cα) position. To the best of our knowledge, there is no literature precedent supporting the presence of such an unstable intermediate. Therefore, it is impractical that such a synthetically inaccessible molecule can be naturally generated and even co-crystallized with **7** or **8** within the same crystalline lattice at room temperature.

Table S-2. Changes in occupancy of nitrogen atoms for **8**. The initial occupancy values for N_β and $N\gamma$ atoms of **8** (dark structure, before heating) were set to 1 for the purpose of comparing the relative changes in the occupancies before and after heating. As such, the noted occupancy values indicate relative conversions.

	N_α	N_β	N_γ
Initial_100 K	1.000	1.000	1.000
1st heating	0.839(4), 0.161(4)	0.839(4)	0.839(4)
2nd heating	0.829(4), 0.171(4)	0.829(4)	0.829(4)
3rd heating	0.810(4), 0.190(4)	0.810(4)	0.810(4)
4th heating	0.797(4), 0.203(4)	0.797(4)	0.797(4)

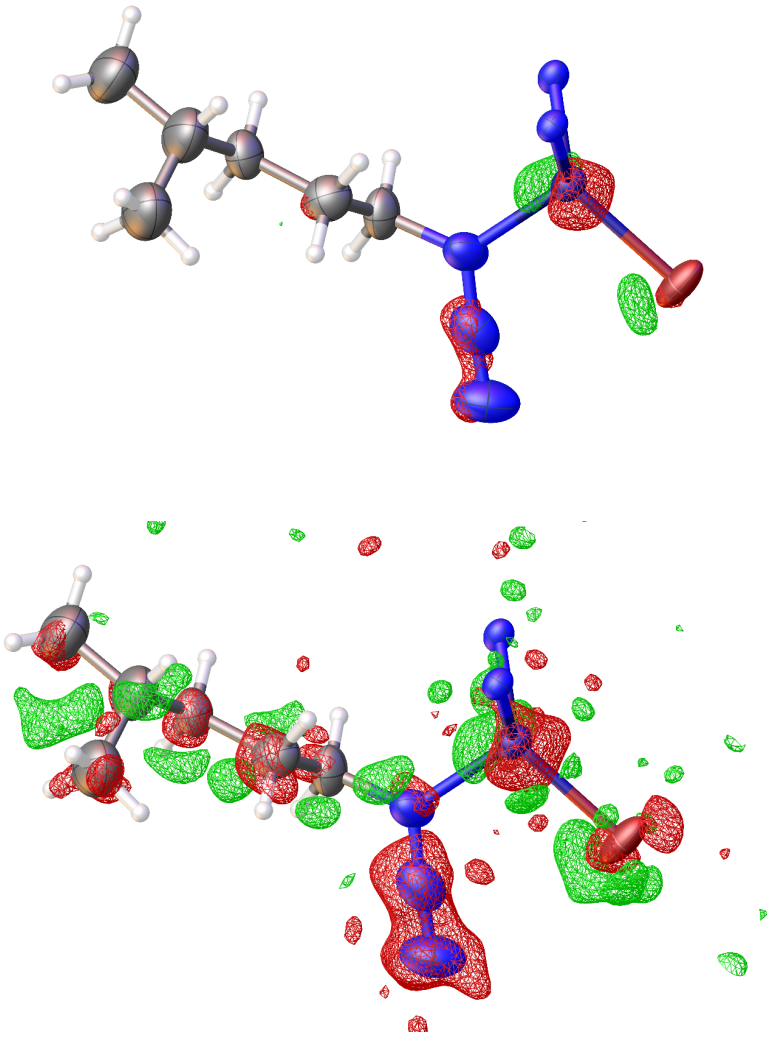


Figure S-26. Reaction-difference map obtained for complex **8** at 100 K following four iterations of heating to 345 K (8-heat4) (top: at 1.2 electron density level, bottom: at 0.6 electron density level). Green and red colors represent positive- and negative electron densities, respectively.

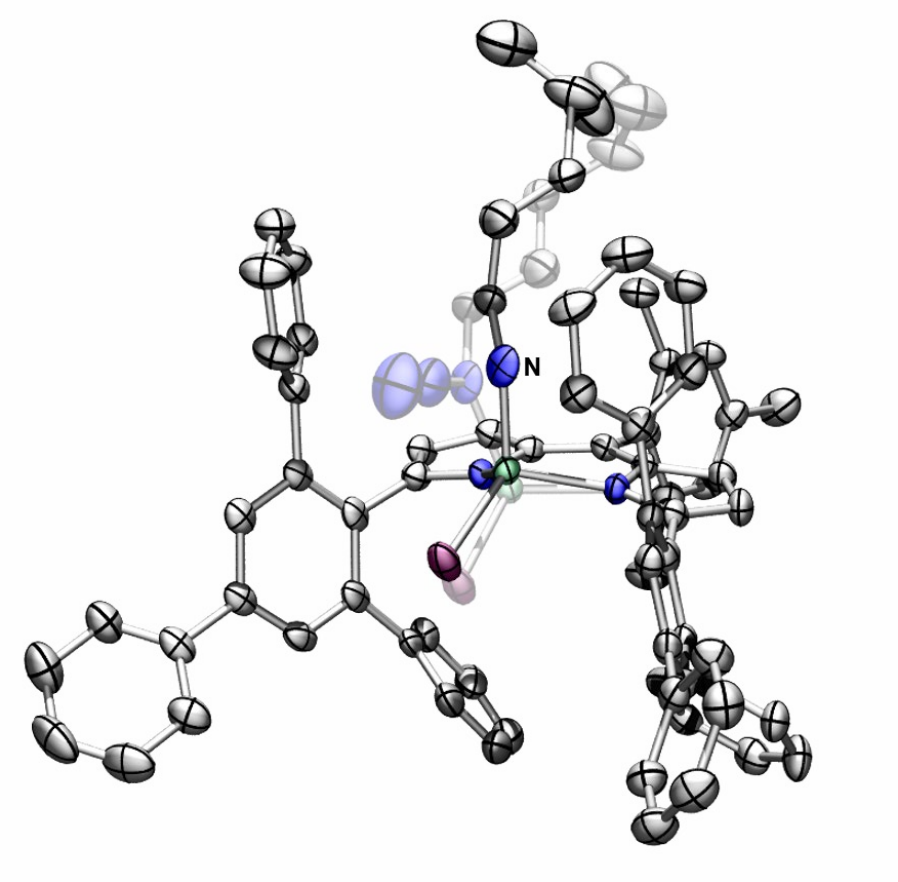


Figure S-27. Solid-state molecular structure for **8–N_2 (8-heat4)**. Thermal ellipsoid plot showing the dark structure (faded) and the heated structure (bold) generated from complex **8**.

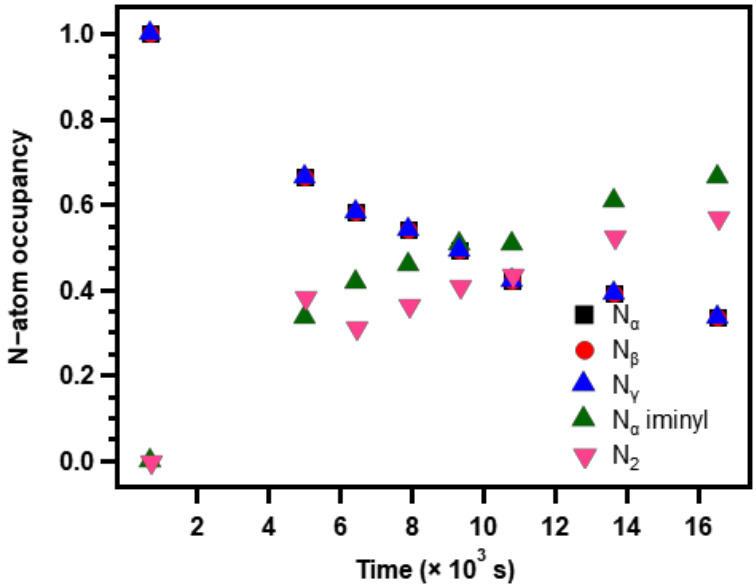


Figure S-28. Changes in occupancy of the organoazide N-atoms in **7** during synchrotron irradiation (λ = 0.41328 Å).

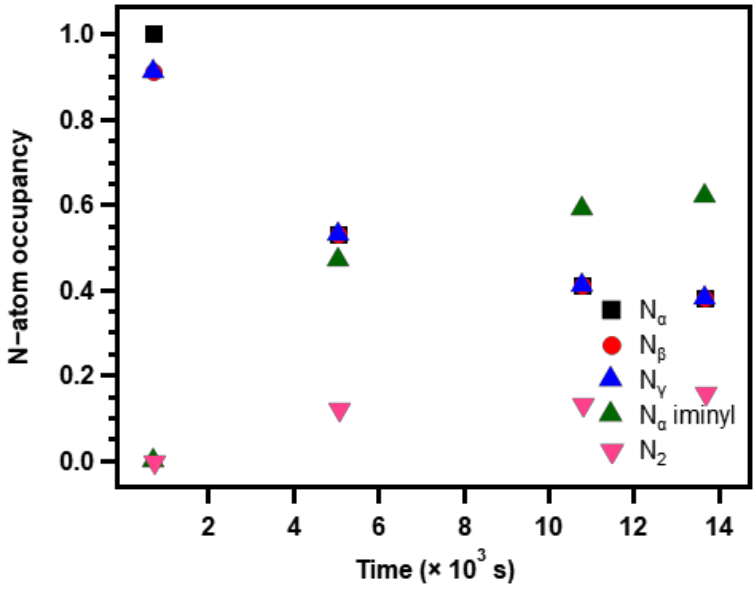


Figure S-29. Changes in occupancy of the organoazide N-atoms in **8** during synchrotron irradiation (λ = 0.41328 Å).

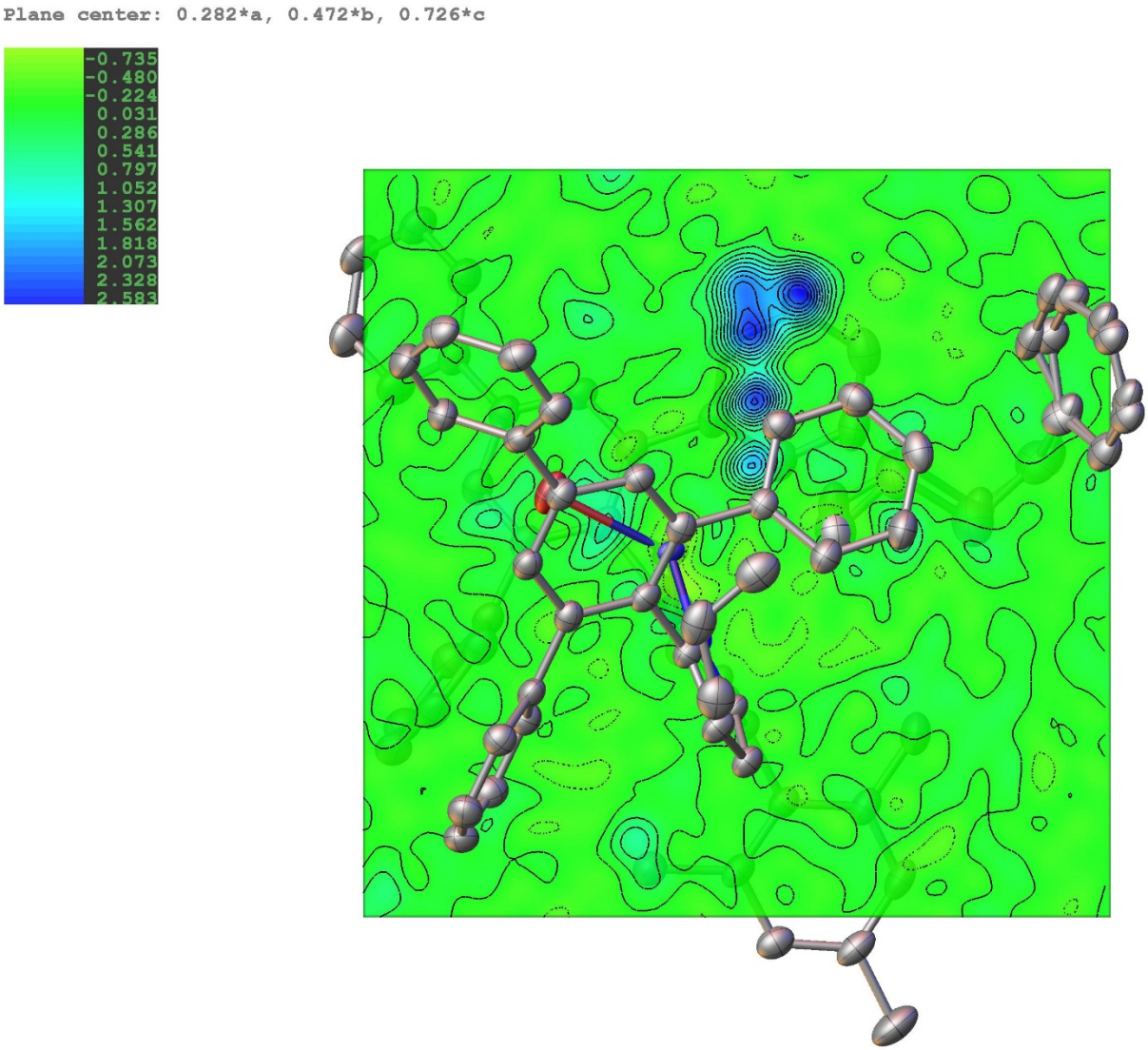


Figure S-30. Electron density map for **7**−N_2, which illustrates that the electron density of the residual azide (**7**) is co-localized with the electron density of the N_2 fragment. Due to this effective compositional disorder, we restrained the metrics of the residual **7** and the N_2 molecule in order to obtain chemically meaningful metrics for **7**−N_2.

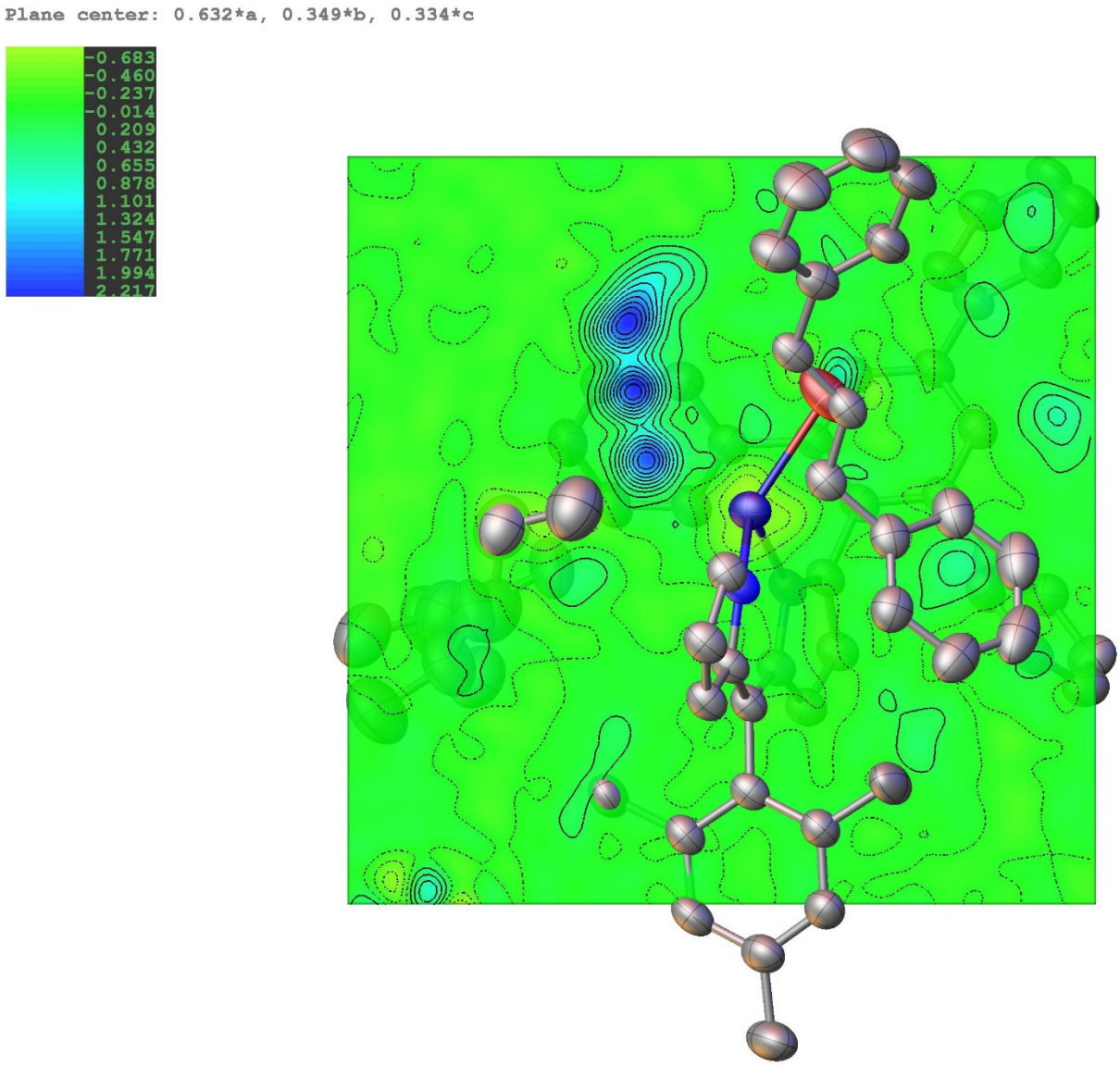


Figure S-31. Electron density map for **8**−N_2, which illustrates that the electron density of the residual azide (**8**) is co-localized with the electron density of the N_2 fragment. Due to this effective compositional disorder, we restrained the metrics of the residual **8** and the N_2 molecule in order to obtain chemically meaningful metrics for **8**−N_2.

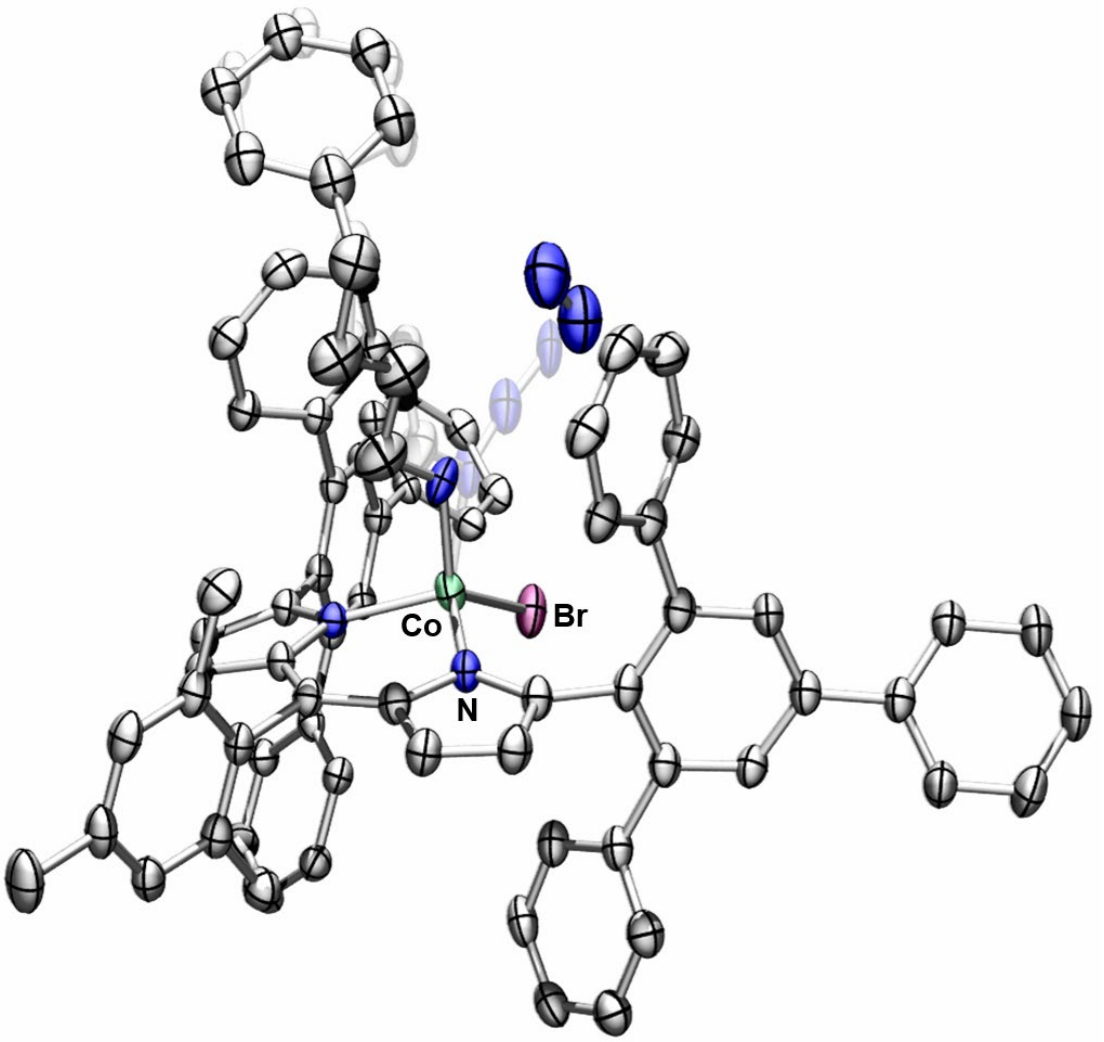


Figure S-32. Solid-state molecular structure for **7–N_2**. Thermal ellipsoid plot showing the dark structure (faded) and the irradiated structure (bold) generated from complex **7**.

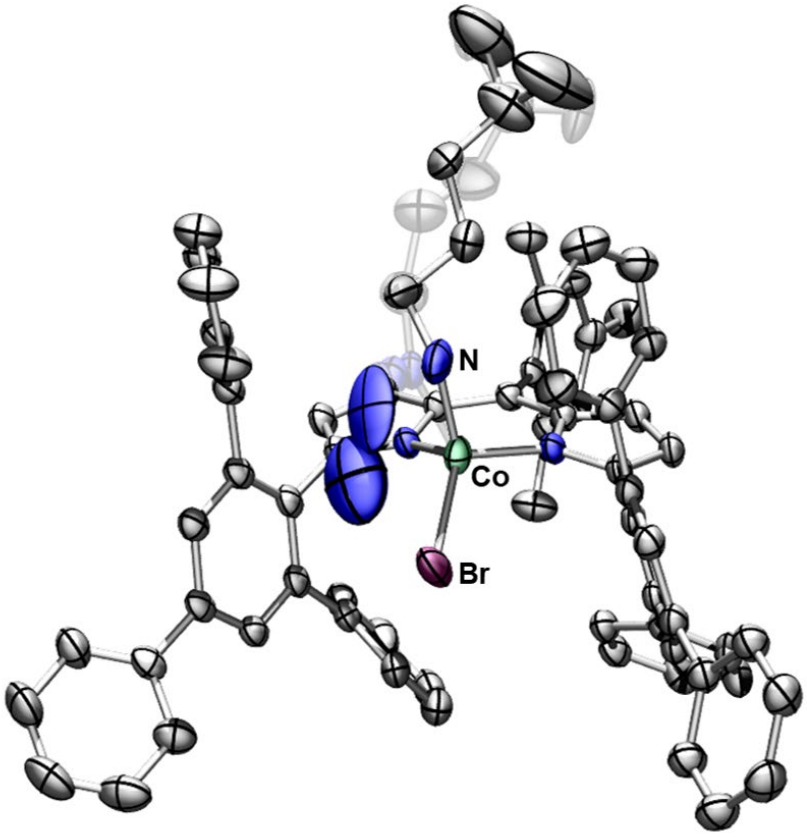


Figure S-33. Solid-state molecular structure for **8–N_2**. Thermal ellipsoid plot showing the dark structure (faded) and the irradiated structure (bold) generated from complex **8**.

Table S-3. X-ray diffraction experimental details[a,b]

	(^{Ar}L)CoBr(N_3(C_6H_4-*p*-^{t}Bu)) (3)	**(^{Ar}L)CoBr([3+2]annulation) (4)**	**(^{Ar}L)CoBr(NH_2(C_6H_4-*p*-^{t}Bu)) (5)**
Moiety Formula	$C_{76}H_{62}BrCoN_5 \cdot 2(C_7H_8)$	$C_{76}H_{62}BrCoN_3 \cdot 3.5(C_6H_6)$	$C_{76}H_{64}BrCoN_3 \cdot 2(C_6H_6)$
FW	1368.41	1429.50	1314.35
Crystal System	Monoclinic	Triclinic	Monoclinic
Space Group (Z)	$P2_1/n$ (4)	$P\bar{1}$ (2)	$P2_1/c$(4)
a (Å)	11.5371(4)	12.5766(4)	17.7144(19)
b (Å)	22.8606(10)	13.7287(5)	21.629(2)
c (Å)	27.3251(12)	22.5774(8)	18.715(2)
α (°)	90	100.712(1)	90
β (°)	94.279(4)	94.999(1)	108.264(2)
γ (°)	90	93.362(1)	90
Volume (Å^3)	7186.8(5)	3804.6(2)	6809.3(13)
Calc. ρ (mg/m^3)	1.265	1.248	1.282
μ (mm^{-1})	0.846	0.801	0.889
Crystal Size (mm)	0.20×0.10×0.06	0.35×0.20×0.08	0.40×0.20×0.15
Reflections	12706	13508	12048
Completeness (to 2θ)	100% 25.027°	99.6% 25.085°	99.9% 25.043°
GOF on F^2	1.083	1.014	1.029
R1, wR2[c] [I>2σ(I)]	0.0872, 0.1685	0.0552, 0.1230	0.0451, 0.1163

[a] λ = 0.71073 Å; [b] T = 100(2) K; [c] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

	$(^{Ar}L)CoBr(N_3R)$ $R = (CH_2)_4Ph$ (7)	$(^{Ar}L)CoBr(N_3R)$ $R = (CH_2)_3C(CH_3)$ (8)	$(^{Ar}L)CoBr(NHCHC_6H_5)$ (9)
Moiety Formula	$C_{76}H_{62}BrCoN_5$	$C_{72}H_{62}BrCoN_5 \cdot 0.5(C_6H_{14})$	$2(C_{73}H_{56}BrCoN_3) \cdot 3(C_7H_8)$
FW	1184.14	1179.19	1252.25
Crystal System	Triclinic	Monoclinic	Triclinic
Space Group (Z)	$P\bar{1}$ (2)	$P2_1/c$ (4)	$P\bar{1}$ (2)
a (Å)	11.8481(4)	11.5036(5)	11.7393(6)
b (Å)	12.2353 (3)	21.4756(11)	14.6478(7)
c (Å)	22.6467 (7)	25.3211(13)	19.8506(10)
α (°)	95.171(2)	90	81.004(1)
β (°)	101.347(3)	99.4205(16)	80.061(1)
γ (°)	107.834(3)	90	75.351(1)
Volume ($Å^3$)	3027.11(17)	6171.1(5)	3230.1(3)
Calc. ρ (mg/m^3)	1.300	1.269	1.288
μ (mm^{-1})	0.993	0.973	0.933
Crystal Size (mm)	0.25×0.20×0.05	0.39×0.25×0.16	0.18×0.10×0.06
Reflections	10711	10995	11459
Completeness (to 2θ)	99.8% 25.058°	99.4% 25.096°	99.9% 25.061°
GOF on F^2	1.011	1.016	1.006
R1, wR2[c] [I>2σ(I)]	0.0495, 0.1045	0.0605, 0.1713	0.0395, 0.0835

	[($^{t\text{Bu}}$L)CoBr]$_2$ (11)	($^{t\text{Bu}}$L)CoBr(thf) (12)	($^{t\text{Bu}}$L)CoBr(1,2,3-dihydrotriazole) (14-Br)	($^{t\text{Bu}}$L)CoBr(2-phenylpyrrolidine) (16-Br)
Moiety Formula	$C_{26}H_{33}BrCoN_2$	$C_{30}H_{41}BrCoN_2O$	$C_{32}H_{44}BrCoN_5$	$C_{36}H_{46}BrCoN_3$
FW	512.38	1168.97	637.56	659.60
Crystal System	Triclinic	Triclinic	Monoclinic	Triclinic
Space Group (Z)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P2_1/c$ (4)	$P\bar{1}$ (2)
a (Å)	9.8826(5)	14.3907(10)	10.5174(9)	9.3829(7)
b (Å)	10.8049(4)	14.9859(10)	18.4889(16)	13.2694(10)
c (Å)	13.3280(6)	15.2440(11)	17.0030(15)	14.2996(11)
α (°)	108.738(1)	92.015(1)	90	67.174(2)
β (°)	92.612(1)	98.561(1)	105.908(2)	84.707(2)
γ (°)	112.333(1)	115.785(1)	90	82.391(2)
Volume (Å^3)	1223.60(10)	2908.7(4)	3179.7(5)	1624.9(2)
Calc. ρ (mg/m^3)	1.391	1.335	1.332	1.348
μ (mm^{-1})	2.349	1.987	1.825	1.786
Crystal Size (mm)	0.25×0.20×0.15	0.40×0.20×0.18	0.30×0.19×0.07	0.20×0.18×0.06
Reflections	4306	10281	5637	5746
Completeness (to 2θ)	99.2% 25.072°	98.9% 25.048°	100% 25.045°	99.6% 25.077°
GOF on F^2	1.028	1.062	1.058	1.015
R1, wR2^c [I>2σ(I)]	0.0351, 0.0725	0.0269, 0.0607	0.0352, 0.0852	0.0546, 0.1212

	($^{t\text{Bu}}$L)CoCl(2,2-dimehtylpyrrolidine) (18)	($^{t\text{Bu}}$L)CoCl(NHCH(CH$_2$)$_2$CH$_3$) (20)	($^{\text{Ar}}$L)CoCl(NH$_2$(CH$_2$)$_3$CH$_3$) (21)
Moiety Formula	$2(C_{16}H_{23}Cl_{0.5}Co_{0.5}N_{1.5})$	$C_{30}H_{42}ClCoN_3$	$C_{30}H_{44}ClCoN_3$
FW	567.10	539.04	541.06
Crystal System	Orthorhombic	Monoclinic	Monoclinic
Space Group (Z)	*Pnma* (4)	$P2_1/n$ (4)	$P2_1/n$ (4)
a (Å)	19.6732(14)	13.892(2)	13.8661(8)
b (Å)	8.7859(8)	13.8768(18)	13.8215(9)
c (Å)	17.5128(12)	16.289(2)	16.3606(10)
α (°)	90	90	90
β (°)	90	111.131(2)	111.490(2)
γ (°)	90	90	90
Volume (Å^3)	3027.0(4)	2928.9(7)	2917.5(3)
Calc. ρ (mg/m^3)	1.244	1.222	1.232
μ (mm^{-1})	0.680	0.699	0.703
Crystal Size (mm)	0.20×0.15×0.13	0.40×0.18×0.09	0.50×0.30×0.10
Reflections	2879	5133	5194
Completeness (to 2θ)	99.7% 25.085°	98.8% 25.052°	99.7% 25.100°
GOF on F^2	1.181	1.001	1.084
R1, wR2^c [I>2σ(I)]	0.0685, 0.1450	0.0581, 0.1289	0.0445, 0.0813

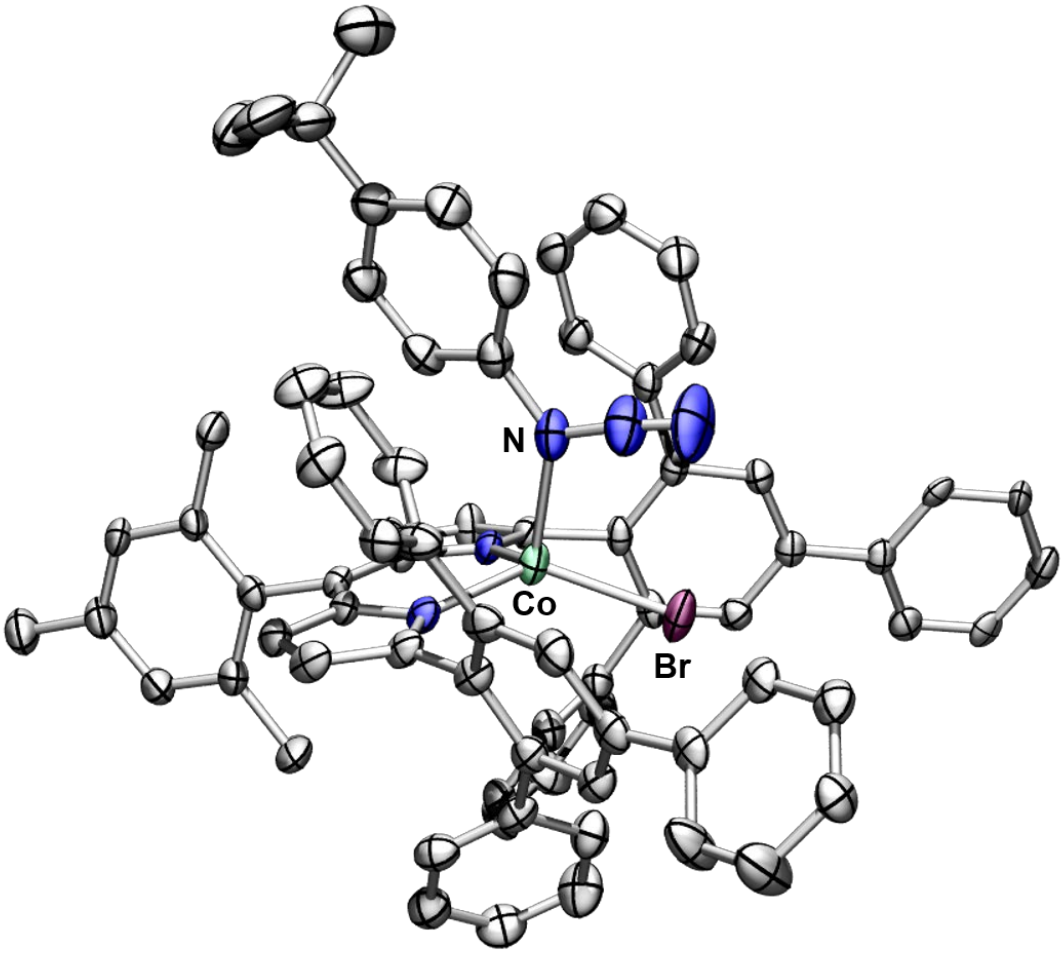


Figure S-34. Solid-state molecular structure for (^{Ar}L)CoBr(N_3(C_6H_4-*p*-^{t}Bu)) (**3**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity.

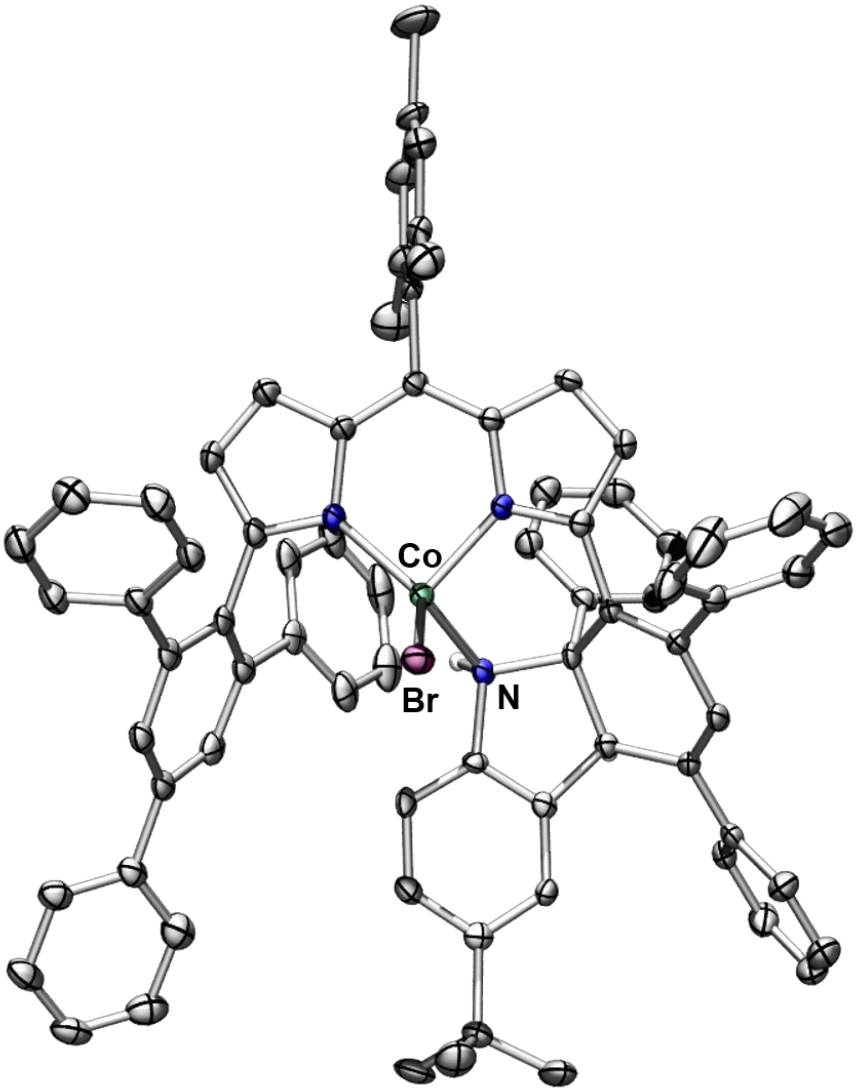


Figure S-35. Solid-state molecular structure for (^{Ar}L)CoBr([3+2]annulation) (**4**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity.

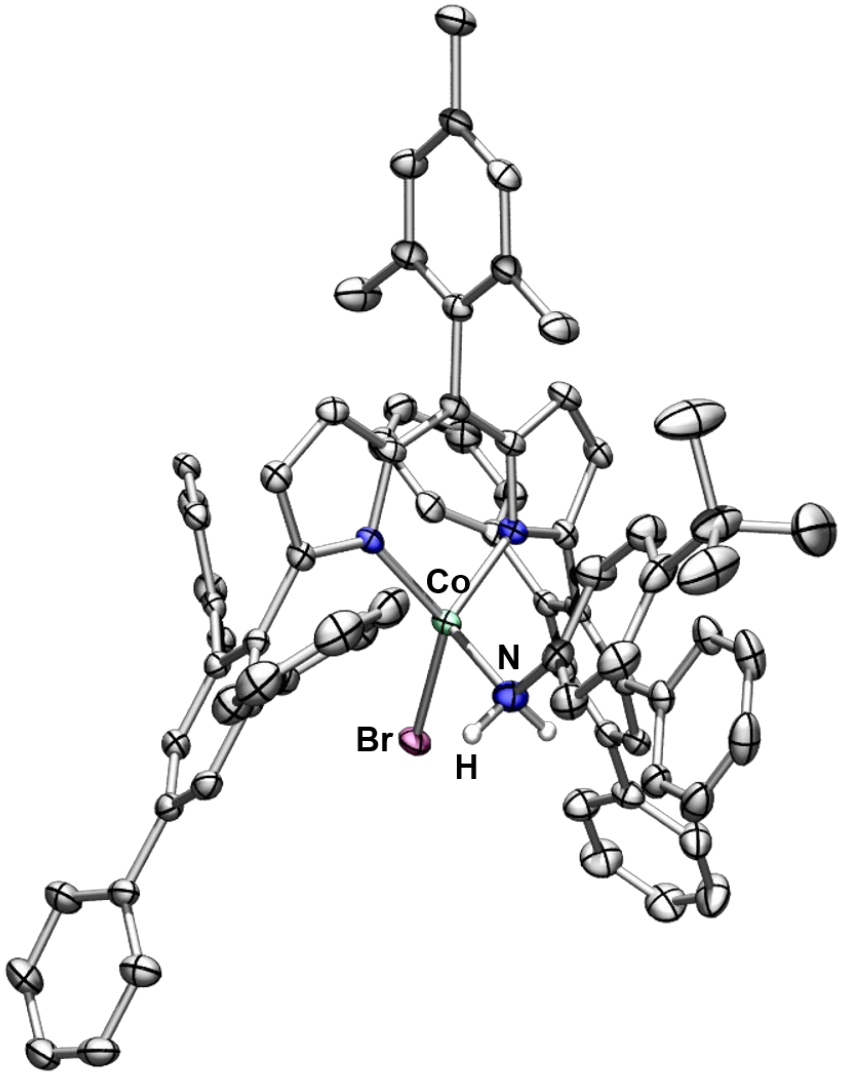


Figure S-36. Solid-state molecular structure for (^{Ar}L)CoBr(NH$_2$(C$_6$H$_4$-*p*-^{t}Bu)) (**5**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity, except of aniline N*H*$_2$.

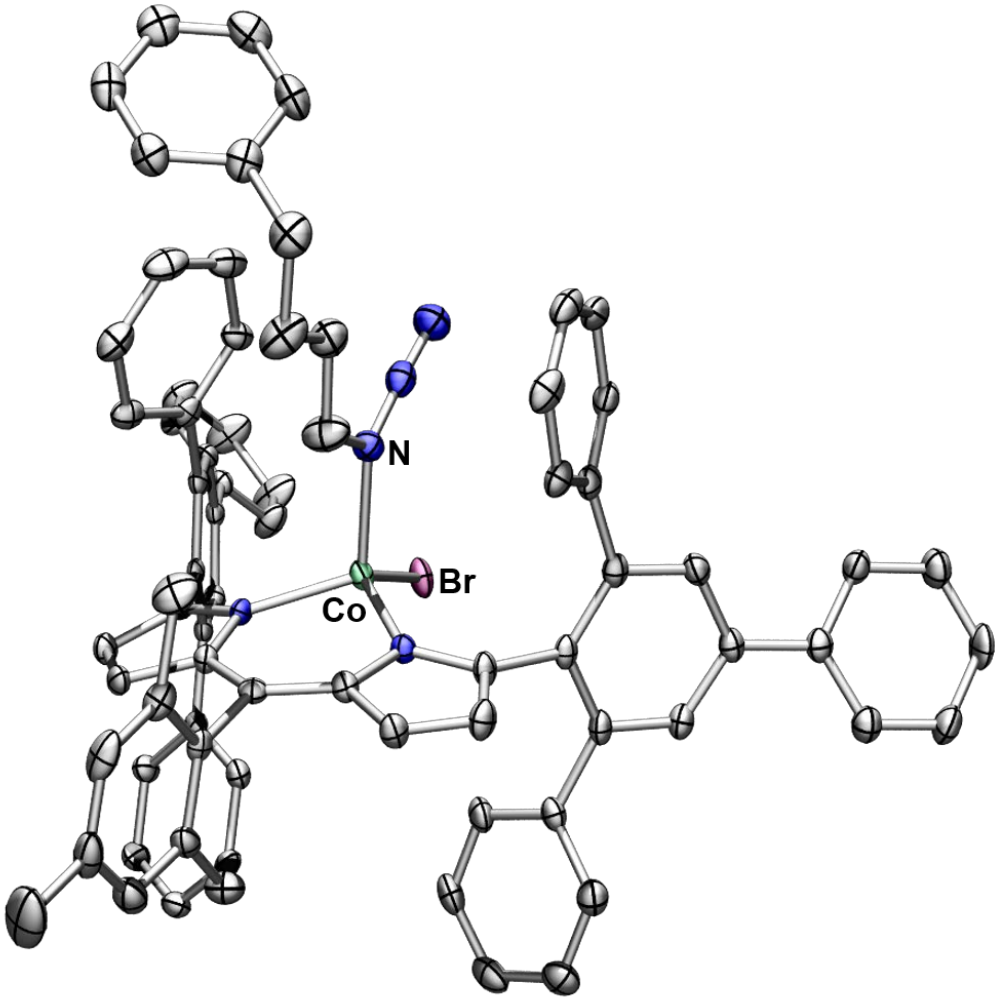


Figure S-37. Solid-state molecular structure for (^{Ar}L)CoBr(N_3R) (**7**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity.

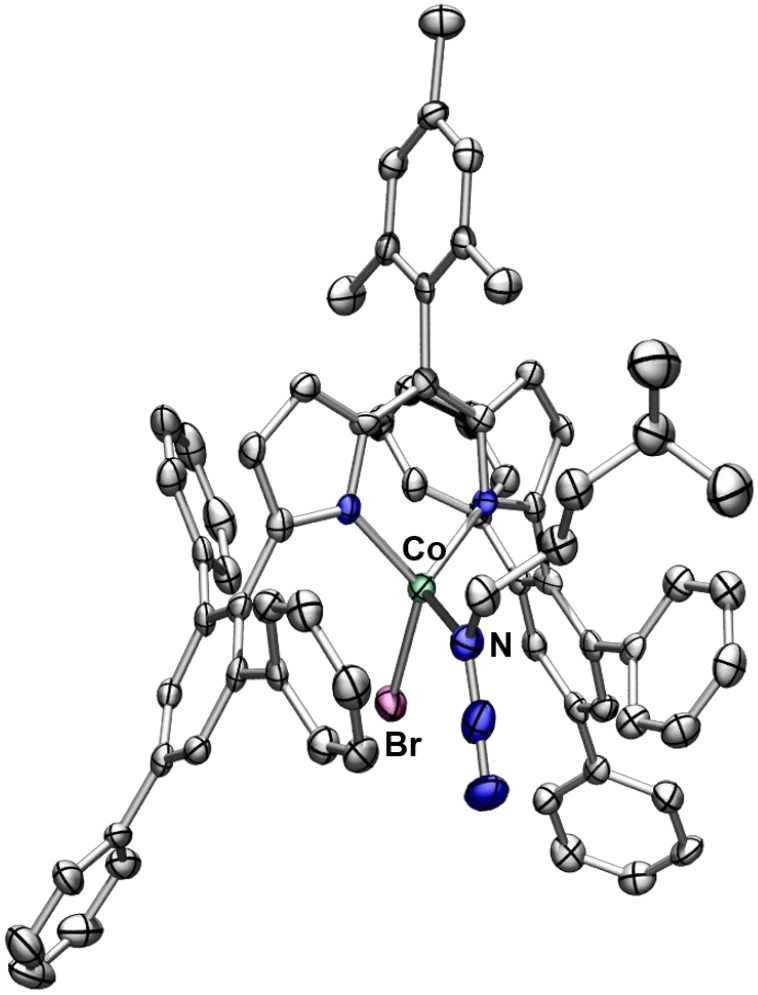


Figure S-38. Solid-state molecular structure for (^{Ar}L)CoBr(N_3R) (**8**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity.

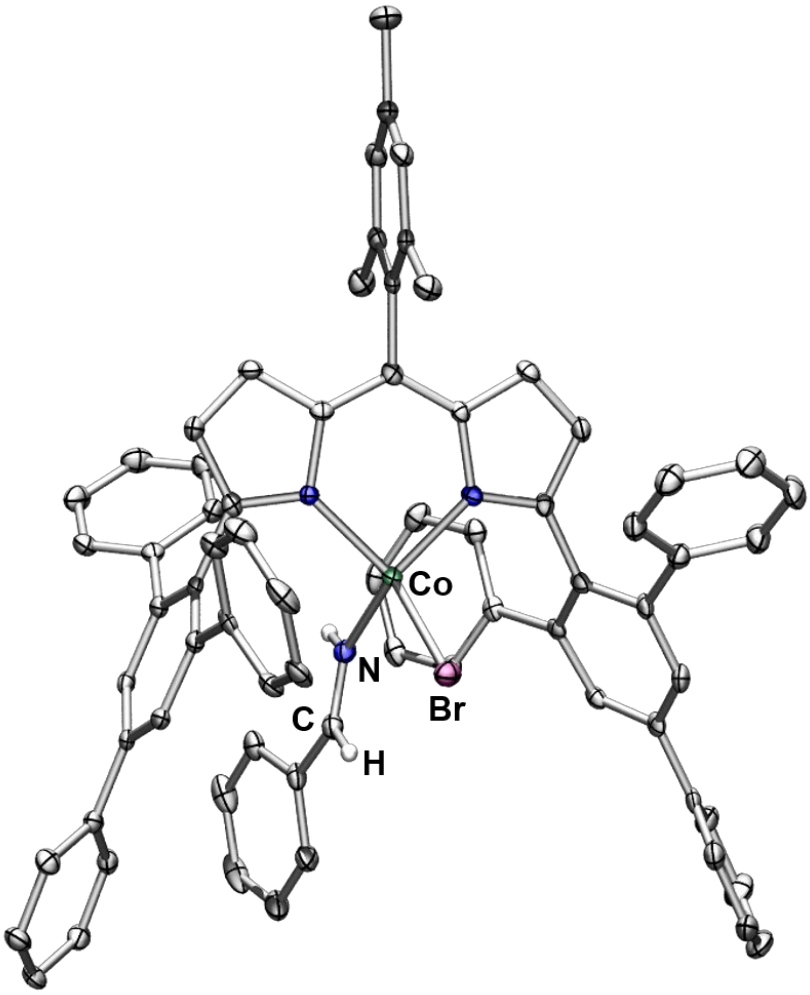


Figure S-39. Solid-state molecular structure for (^{Ar}L)CoBr(NHCHC$_6$H$_5$) (**9**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity, except for the imine *H*N=C*H*Ph.

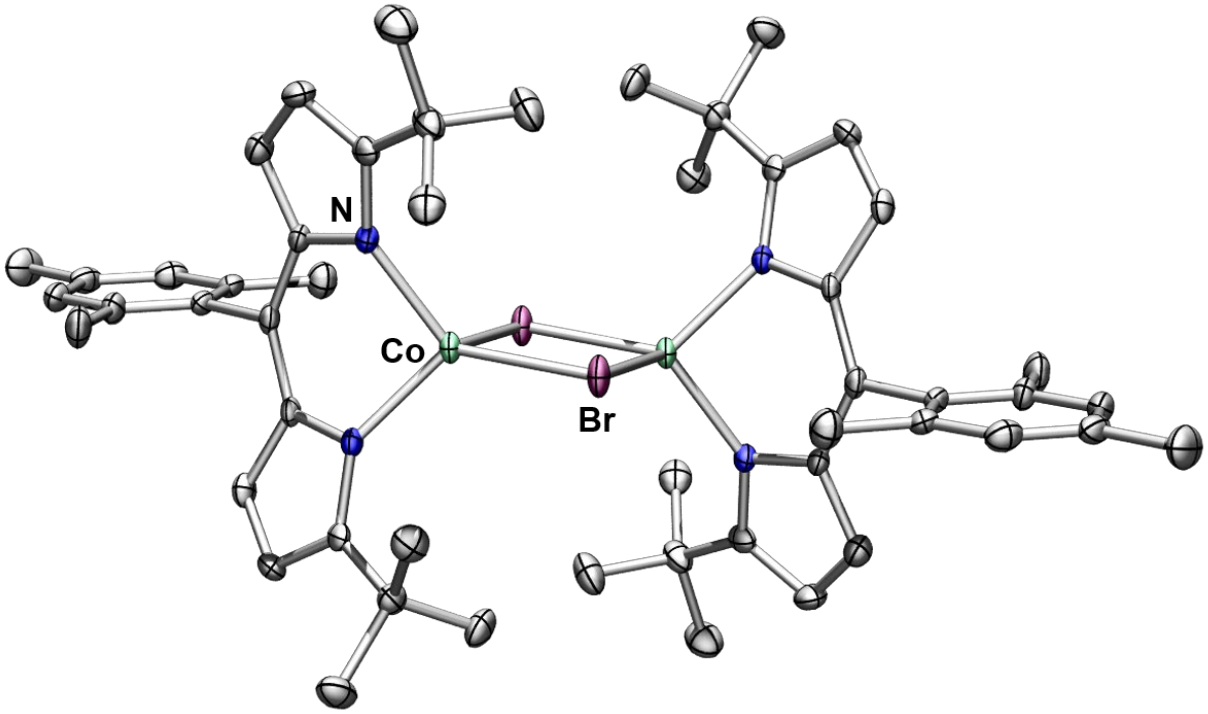


Figure S-40. Solid-state molecular structure for [($^{t\text{Bu}}$L)CoBr]$_2$ (**11**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity.

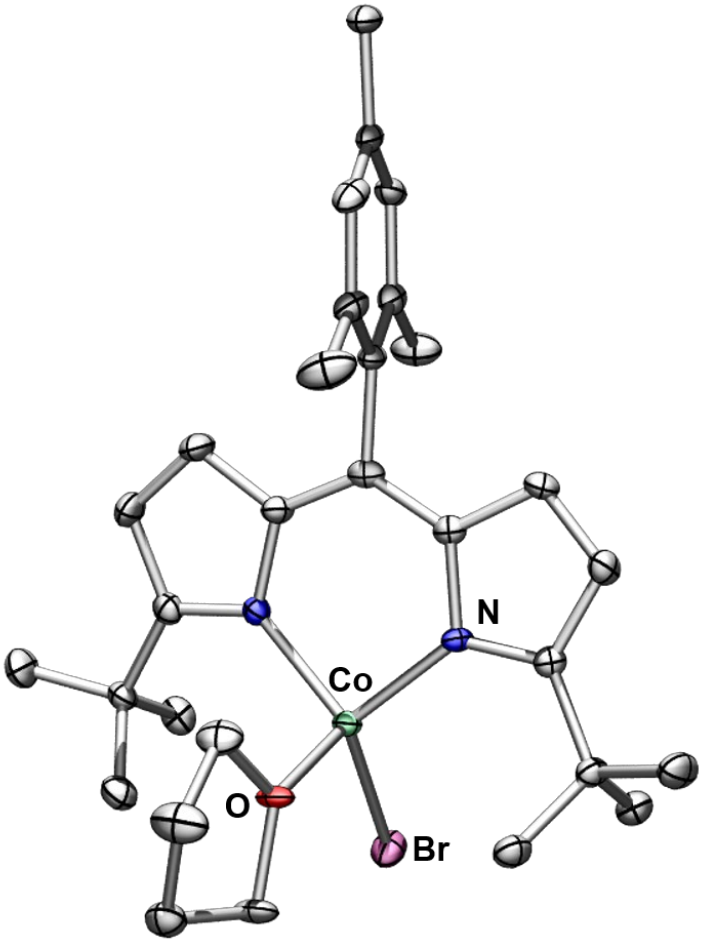


Figure S-41. Solid-state molecular structure for ($^{t\text{Bu}}$L)CoBr(thf) (**12**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity.

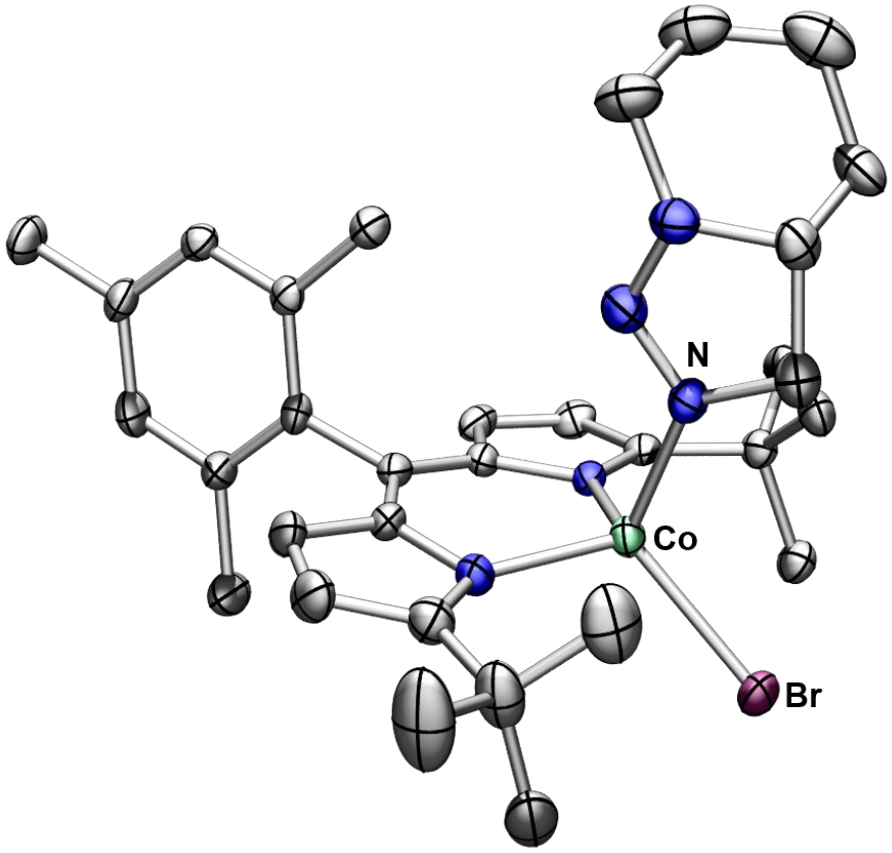


Figure S-42. Solid-state molecular structure for ($^{t\text{Bu}}$L)CoBr(1,2,3-dihydrotriazole) (**14-Br**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity.

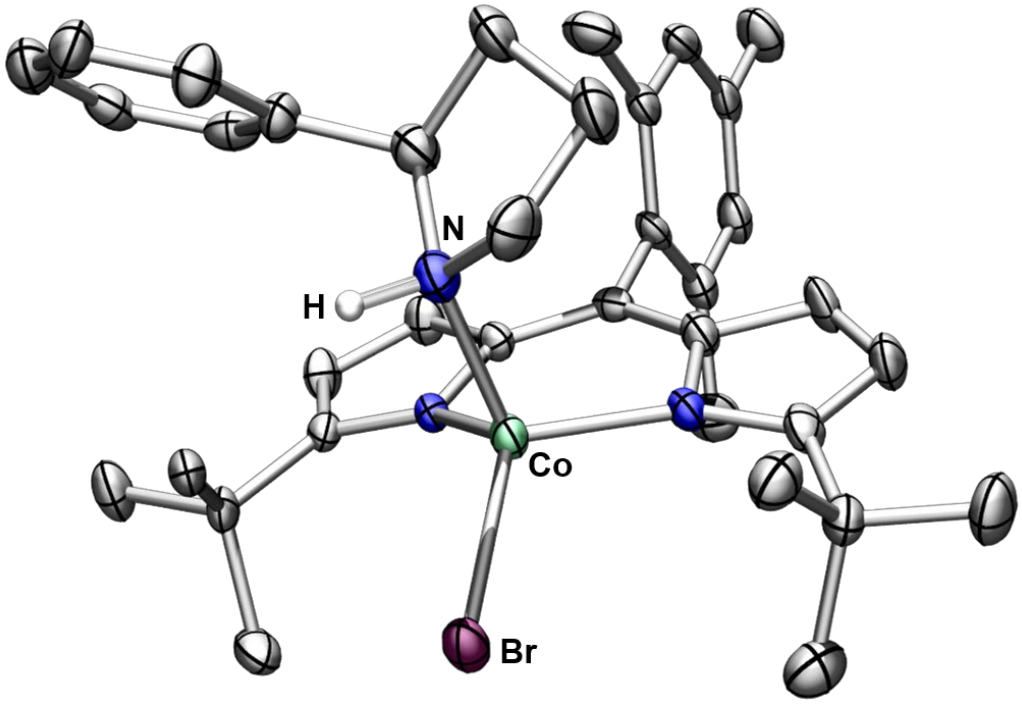


Figure S-43. Solid-state molecular structure for ($^{t\text{Bu}}$L)CoBr(2-phenylpyrrolidine) (**16-Br**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity, except for the pyrrolidine N*H*.

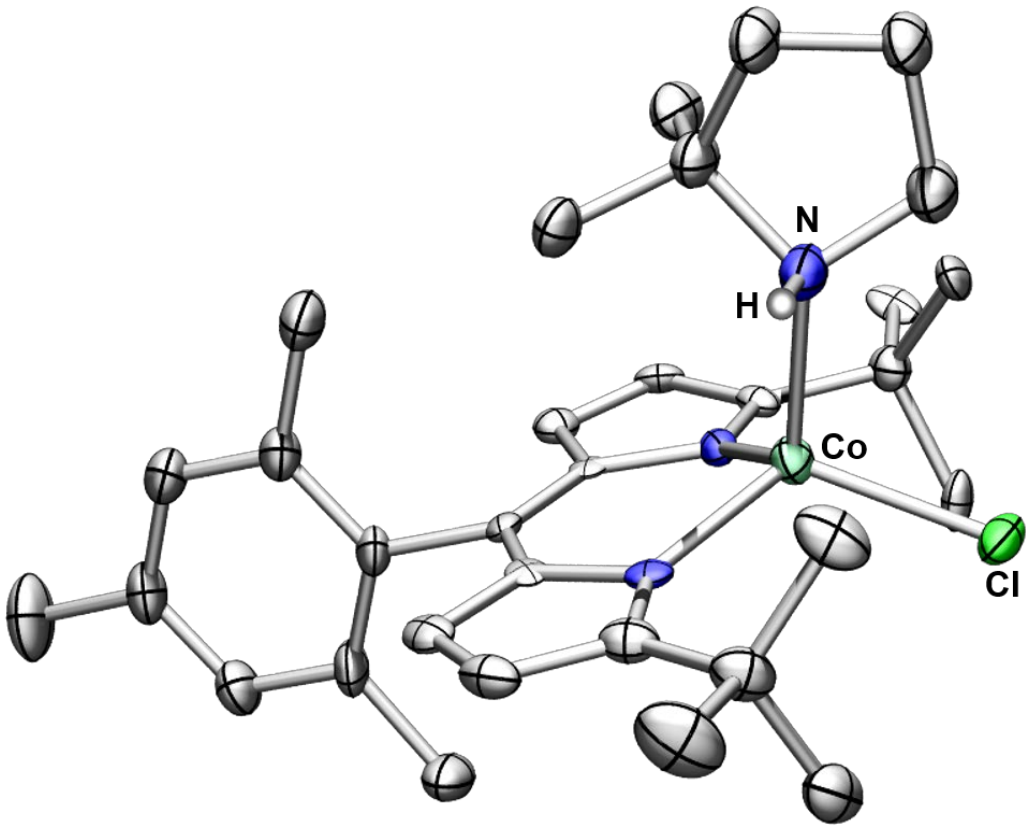


Figure S-44. Solid-state molecular structure for ($^{t\text{Bu}}$L)CoCl(2,2-dimethylpyrrolidine) (**18**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity, except for the pyrrolidine N*H*

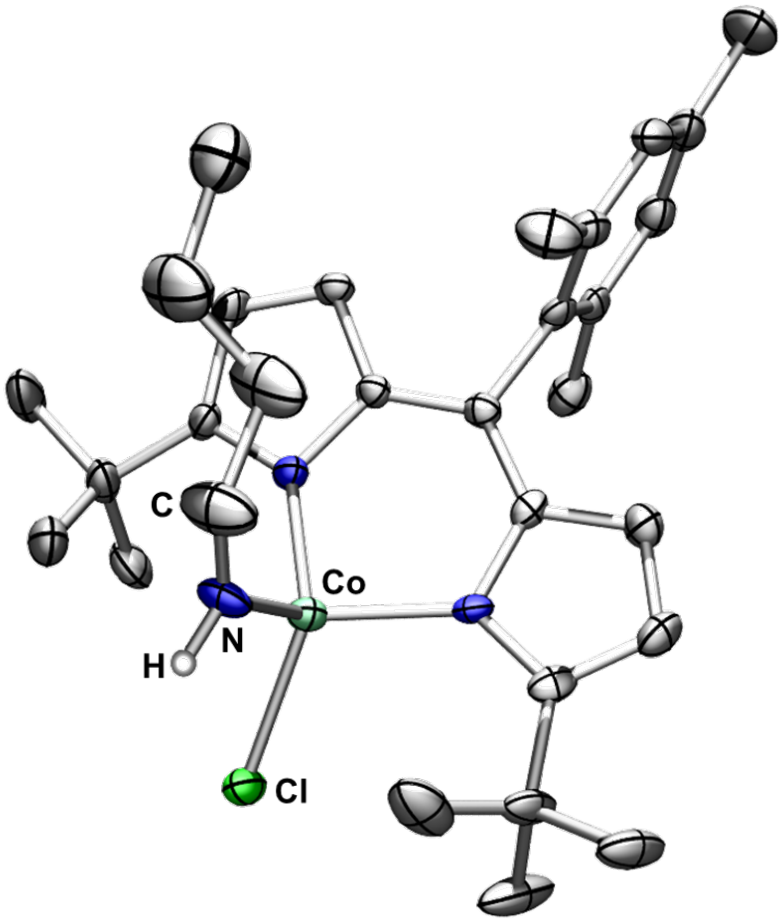


Figure S-45. Solid-state molecular structure for ($^{t\text{Bu}}$L)CoCl(NHCH(CH_2)CH_3) (**20**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity, except for the imine *H*N=C*H*R.

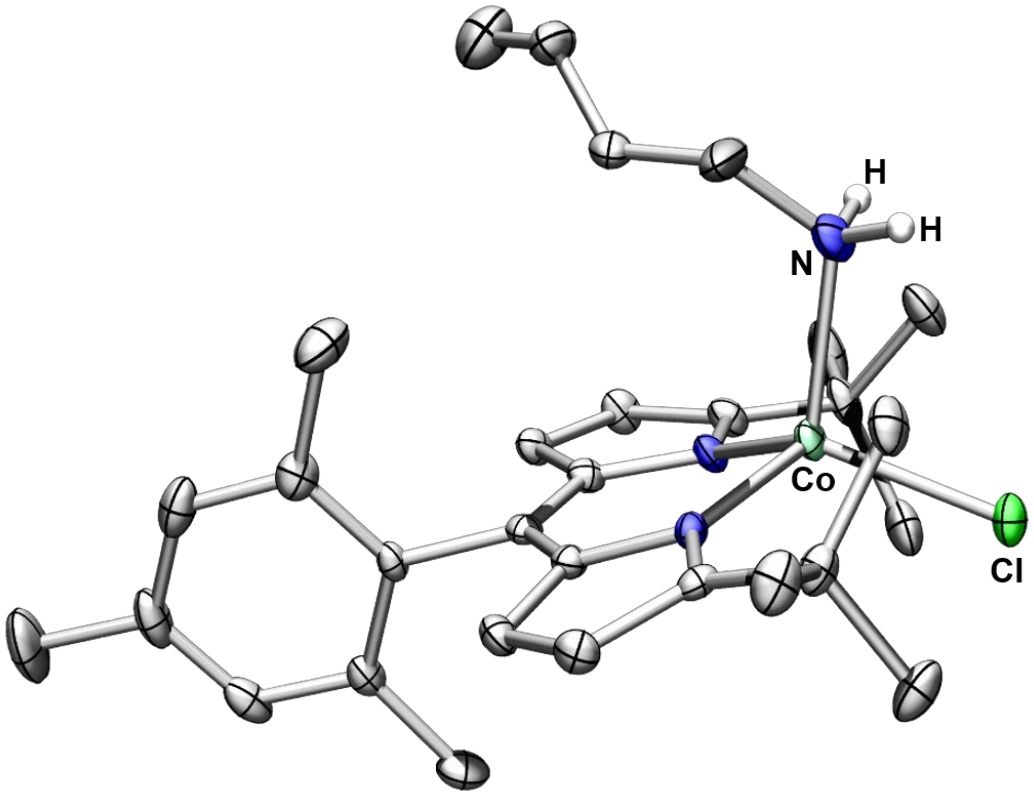


Figure S-46. Solid-state molecular structure for ($^{t\text{Bu}}$L)CoCl(*n*-BuNH$_2$) (**21**) with thermal ellipsoids at 50% probability level. Hydrogens omitted for clarity, except for the amine N*H*$_2$.

Computational Methods. Single point calculations and property calculations for complex **3** were carried out utilizing the ORCA 3.0.3[17] and package. All geometries were taken from the X-ray structure of compound **3** and the B3LYP[18-19] functional was used with the def2-TZVP (Co, N, Br) and def2-SV(P) (C, H) basis sets.[20-22] Additionally, the def2-TZVP/J (Co, N, Br) and def2-SVP/J (C, H) auxiliary basis sets were employed to utilize the RIJCOSX approximation for accelerating the calculation.[23] Geometry optimizations for complex **8–N$_2$** considering all possible electronic configuration scenarios were carried out using ORCA 4.0.1.2 program.[24] To minimize computational effort and facilitate convergence while retaining the overall structural environment of the molecule, the *para*-substituted phenyl groups of the 2,4,6-triphenylphenyl substituents were truncated to methyl units, and Br ancillary ligand was replaced with a Cl. The B3LYP[18-19] functional was used with the def2-TZVP (Co, N, Cl) and def2-SV(P) (C, H) basis sets.[20-22] Additionally, the def2-TZVP/J (Co, N, Cl) and def2-SVP/J (C, H) auxiliary basis sets were employed to utilize the RIJCOSX approximation for accelerating the calculation.[23]

Summary of results. We have performed theoretical studies on the proposed Co-nitrene complex with **8–N$_2$** as a model complex using ORCA (B3LYP functional, def2-TZVP for Co, N, Cl and def2-SVP/J for C, H). To minimize computational effort and facilitate convergence while retaining the overall structural environment of the molecule, the *para*-substituted phenyl groups of the 2,4,6-triphenylphenyl substituents were truncated to methyl units, and Br ancillary ligand was replaced with a Cl. As there is no direct spectroscopic evidence to assess either the formal oxidation state of the metal center (Co^{3+} *vs.* Co^{4+}) or the electronic configuration of the compound (the spin-state of Co and the nature of the nitrene (NR) unit (e.g., imido (NR^{2-}), iminyl ($^2NR^{1-}$), nitrene adduct (^3NR)), we have performed geometry optimizations for **8–N$_2$** considering all possible electronic configuration scenarios. First, in the case of Co(IV) imido (which is equivalent with the bound nitrene unit being a dianionic imido (NR^{2-})), we have considered the S = 1/2, 3/2, and 5/2 spin states (Co^{4+} = d^5). Among these, the S = 1/2 spin state is about 6.214 and 3.579 kcal/mol more stable with respect to the S = 3/2 and S = 5/2 states, respectively, suggesting that **8–N$_2$** might be best described as a doublet. However, we found that there is significant spin density localized on the N_α. Specifically, Mulliken spin population analysis suggests + 2.45 (α) spin density on the Co and – 1.55 (β) spin density on the N_α, indicating that the nitrene (NR) moiety is more likely an open-shell iminyl ($^2NR^{1-}$) as opposed to a closed-shell imido (NR^{2-}), and consequently, the

oxidation state of the Co would be 3+ rather than 4+. To this end, we have conducted a broken-symmetry calculation on **8–N$_2$** at S = 1 and S = 2 spin states for a d^6 Co(III) center along with an S = 1/2 nitrene moiety (We note that a low-spin S = 0 state Co(III) along with an S = 1/2 NR is equivalent to the previous S = 1/2 Co(IV) case as a computational input). As a result, in both cases, the calculation converged to the broken symmetry solution, suggesting anti-ferromagnetic coupling state between the Co and NR fragment to result in a net doublet (S_{Co} (1) – S_{NR} (1/2)) and quartet state (S_{Co} (2) – S_{NR} (1/2)), respectively. Furthermore, the anti-ferromagnetically coupled doublet state was found to be more stable than the overall quartet spin state by 5.513 kcal/mol. Therefore, we believe these computational results are in accord with our proposal suggesting that **8–N$_2$** is more likely a Co(III) iminyl as opposed to a Co(IV) imido. However, to better understand the exact spin configuration of the compound (e.g., low-spin Co(III) vs. intermediate-spin Co(III) vs. high-spin Co(III)), in-depth spectroscopic analysis using X-ray absorption or EPR spectroscopies are necessary and we are currently pursuing such spectroscopic characterization of this species.

Table S-4. Summary of the geometry optimized results of **8–N₂** as Co(IV) imido at the *S* = 1/2, 3/2, and 5/2 spin states.

	***S* = 1/2** model	***S* = 3/2** model	***S* = 5/2** model
Co–N_α (Å)	1.877	1.764	1.95
Spin density on Co	+ 2.453	+ 2.659	+ 2.742
Spin density on N_α	− 1.545	− 0.035	+ 1.744
Relative energy (kcal/mol)	0	+ 6.214	+ 3.579

Table S-5. Summary of the broken-symmetry[25] geometry optimized results of **8–N₂** as Co(III) iminyl at the *S* = 1 and *S* = 2 spin states.

	***S* = 1** Co and ***S* = 1/2** NR model	***S* = 2** Co and ***S* = 1/2** NR model
Co–N_α (Å)	1.883	1.764
Spin density on Co	+ 2.465	+ 2.659
Spin density on N_α	− 1.552	− 0.037
Relative energy (kcal/mol)	0	+ 5.513

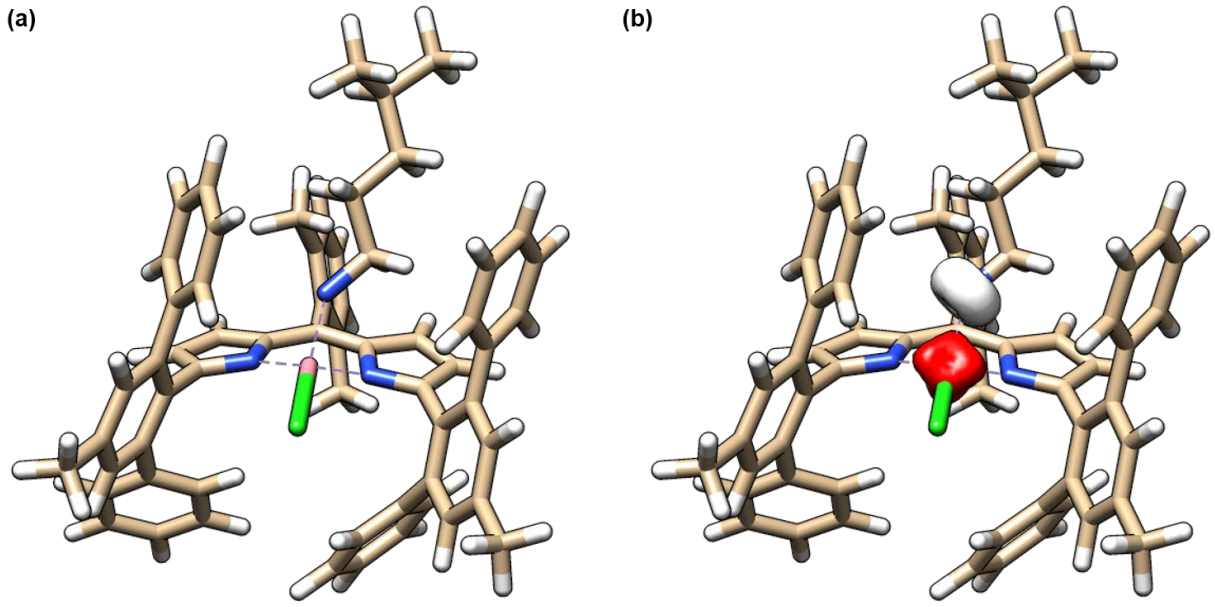


Figure S-47. Geometry optimized molecular structure and Mulliken spin density plot (α−β) of **8−N$_2$** at an S = 1/2 spin state of Co(IV).

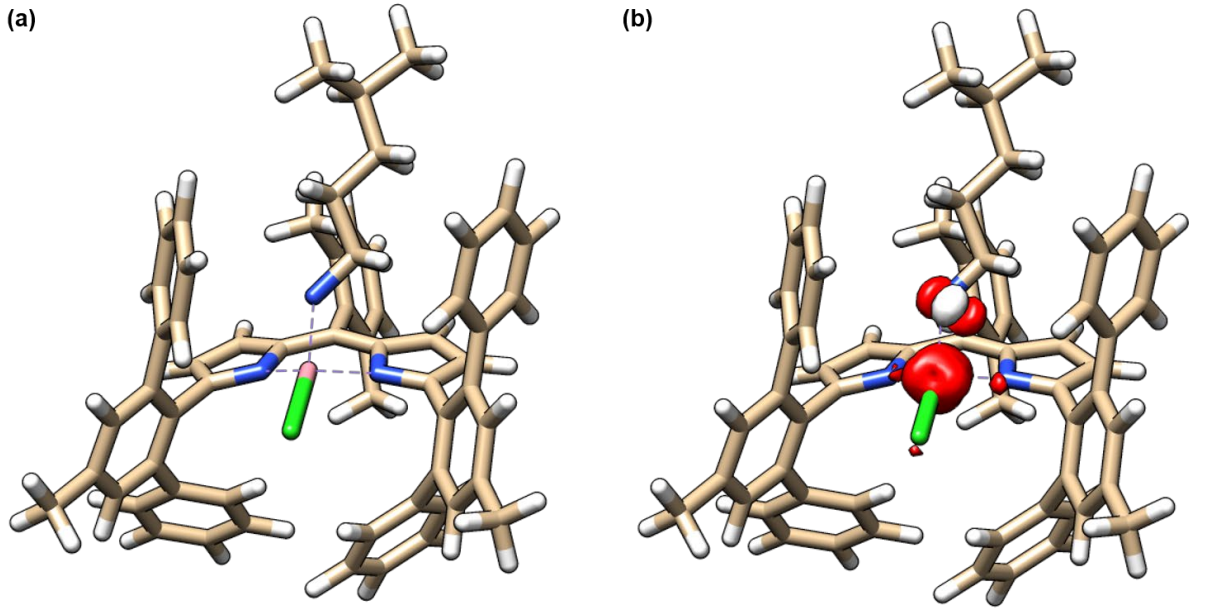


Figure S-48. Geometry optimized molecular structure and Mulliken spin density plot (α−β) of **8−N$_2$** at an S = 3/2 spin state of Co(IV).

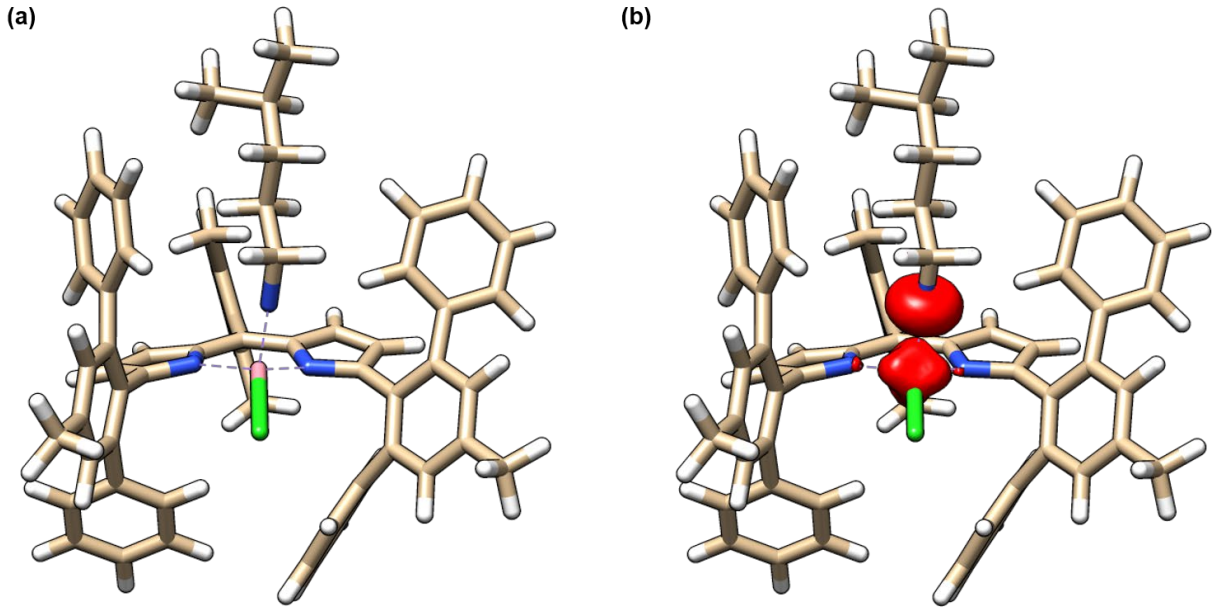


Figure S-49. Geometry optimized molecular structure and Mulliken spin density plot (α−β) of **8−N$_2$** at an S = 5/2 spin state of Co(IV).

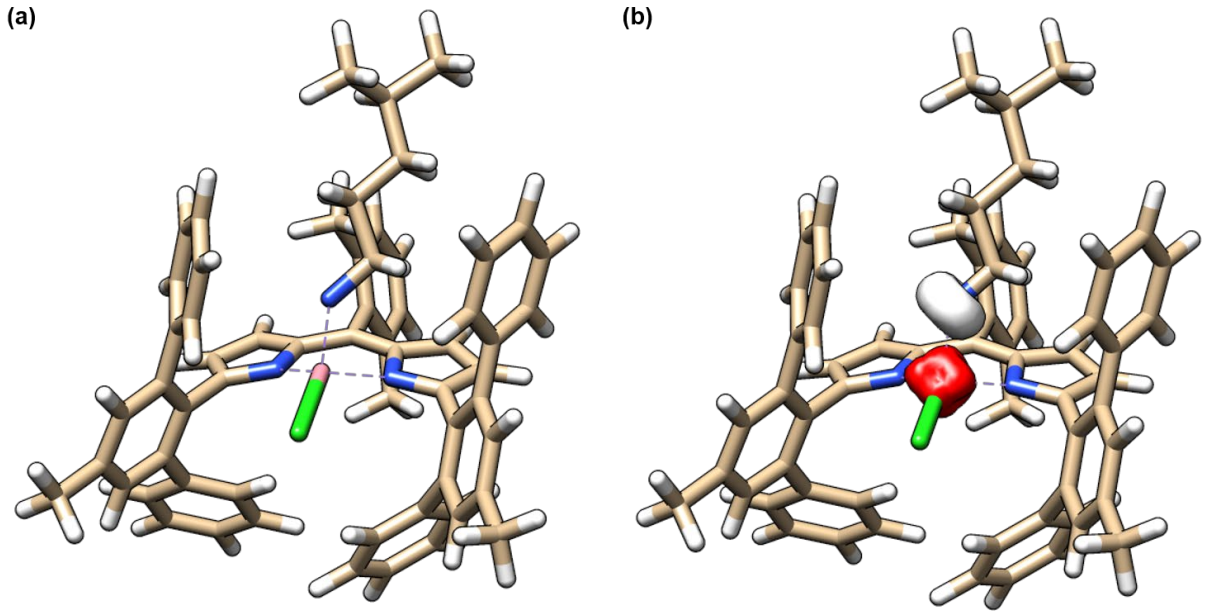


Figure S-50. Geometry optimized molecular structure and Mulliken spin density plot (α−β) of **8−N$_2$** at an S = 1 spin state of Co(III).

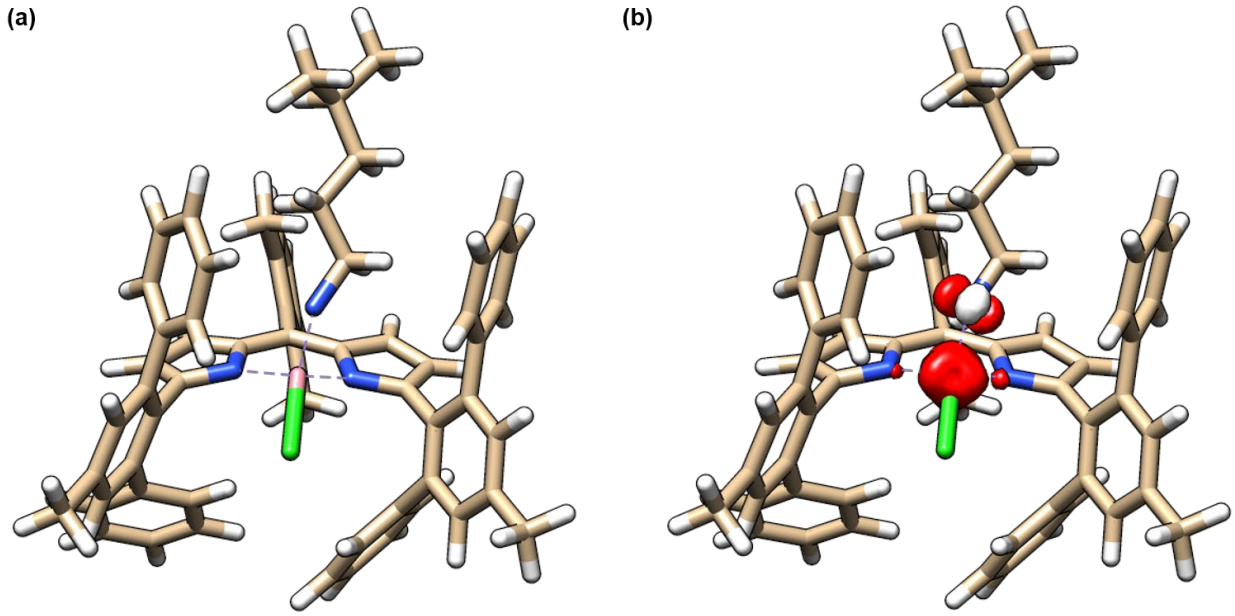


Figure S-51. Geometry optimized molecular structure and Mulliken spin density plot (α−β) of **8−N₂** at an *S* = 2 spin state of Co(III)

Table S-6. Coordinates of optimized molecular structure for the truncated Co-nitrenoid (**8-N₂**) at low-spin Co(IV) state.

Doublet (*S* = 1/2)

Co	6.181532	18.346355	7.941508
N	5.186259	19.891963	7.181055
N	5.703836	17.072267	6.467815
C	6.248266	15.927470	6.035387
N	4.981662	18.001664	9.343581
C	3.979178	19.612167	6.532219
C	8.648817	15.362445	5.620667
C	7.548478	15.389504	6.518886
C	4.507094	17.264032	5.766980
C	5.161939	21.184095	7.569959
C	5.406742	21.932379	10.584083
C	8.123159	17.151707	3.900301
C	3.180580	20.793001	6.551705
C	7.438383	22.196799	7.313491
C	7.470363	21.913653	5.844642
C	4.323632	16.153110	4.878732
C	2.335512	18.312329	5.178468
C	6.346910	21.876874	8.163983

C	3.674581	18.393660	5.868136
C	4.088006	22.417274	10.520435
C	9.888129	14.872586	6.055942
C	7.718298	14.887167	7.832739
C	8.986848	14.423613	8.226142
C	7.593818	22.870228	10.013195
C	6.438275	22.224426	9.538772
C	2.121354	18.962187	3.939077
C	0.847098	18.895336	3.353490
C	5.422096	15.332693	5.029356
C	10.085502	14.413134	7.364072
C	8.535199	15.842474	4.209149
C	6.608993	14.768029	8.826081
C	8.571113	22.840959	7.838146
C	8.672137	23.192185	9.185903
C	1.288553	17.583751	5.796877
C	8.031667	17.577360	2.571759
C	0.028492	17.549970	5.180970
C	5.852103	14.917589	11.145208
C	3.925313	21.775886	7.188902
C	6.831574	15.123789	10.171127
C	5.802740	21.254201	11.757060
C	4.375306	14.012605	9.461048
C	5.358480	14.215386	8.488226
C	6.545452	22.493356	4.958163
C	4.619876	14.354528	10.795813
C	8.871199	14.981560	3.148111
C	8.530164	21.158742	5.306513
C	6.688491	22.342183	3.574907
C	3.860419	18.627071	9.919328
C	1.712330	18.337033	11.261129
C	4.922920	21.083317	12.829511
C	2.965599	17.640805	10.710468
C	1.502865	16.833094	7.092502
C	8.349017	16.704736	1.525495
C	3.203882	22.242542	11.590696
C	7.761202	21.610381	3.052068
C	3.618757	21.586340	12.754595
C	8.676397	21.010182	3.923834
C	3.236717	19.691338	3.222238
C	8.773500	15.405091	1.818896
C	0.663793	17.404342	11.904155
C	1.239998	16.561770	13.052011
C	-0.548668	18.219880	12.381515
H	0.676277	19.398309	2.396350
H	-0.785122	16.996661	5.661823

H	1.977484	17.468882	7.859206
H	0.545951	16.460963	7.497332
H	2.171308	15.965303	6.949453
H	4.042538	18.994834	2.927153
H	2.859597	20.180859	2.308620
H	3.704408	20.462644	3.856240
H	3.479942	16.018766	4.202372
H	5.647971	14.410150	4.495947
H	9.199795	13.961618	3.371841
H	9.031664	14.714321	1.009983
H	8.268319	17.040749	0.485862
H	7.707916	18.600656	2.358659
H	7.884670	17.849517	4.707395
H	10.729146	14.879196	5.354365
H	9.105786	14.026070	9.237572
H	5.160798	13.908095	7.458586
H	3.419559	13.562699	9.172252
H	3.855113	14.179014	11.559534
H	6.055328	15.207097	12.182075
H	7.780306	15.588254	10.452078
H	3.754499	22.968144	9.639590
H	2.188624	22.645463	11.519156
H	2.931497	21.472636	13.599115
H	5.263939	20.557179	13.727293
H	6.818548	20.854510	11.823844
H	5.720733	23.091746	5.355079
H	5.966281	22.815975	2.902239
H	7.888174	21.512180	1.968312
H	9.509826	20.422493	3.525485
H	9.241752	20.680032	5.985548
H	9.386644	23.096756	7.154458
H	7.633372	23.148847	11.070562
H	3.650741	22.821817	7.322656
H	2.193725	20.900466	6.103540
H	4.215756	19.440889	10.587803
H	3.268407	19.120589	9.115493
H	3.566869	17.206806	11.526530
H	2.688465	16.802879	10.046504
H	2.021670	19.098876	12.003220
H	1.222977	18.896361	10.439069
H	0.313465	16.704106	11.119290
H	2.023515	15.866062	12.701660
H	1.686741	17.206811	13.833182
H	0.451072	15.954112	13.533207
H	-1.001772	18.795860	11.553306
H	-1.331892	17.565404	12.806110

H	-0.253742	18.940689	13.167879
Cl	8.312717	18.574888	8.494342
C	9.898695	23.881182	9.738153
H	9.629381	24.629327	10.504603
H	10.579433	23.151686	10.219326
H	10.469793	24.392952	8.944052
C	11.436251	13.906494	7.816053
H	11.703399	12.958910	7.310895
H	12.235044	14.633618	7.582294
H	11.455096	13.721125	8.903712
C	-0.196935	18.206436	3.970807
H	-1.186441	18.175448	3.502709

Table S-7. Coordinates of optimized molecular structure for the truncated Co-nitrenoid (**8-N_2**) at intermediate-spin Co(IV) state.

Quartet (S = 3/2)

Co	6.220597	18.384996	8.068425
N	5.214858	19.916191	7.189722
N	5.651378	17.038960	6.667357
C	6.159123	15.849809	6.305175
N	5.077328	18.211280	9.400098
C	4.022097	19.633699	6.515872
C	8.471748	15.210993	5.650748
C	7.496950	15.311575	6.680238
C	4.445043	17.206753	5.977825
C	5.226517	21.238065	7.462379
C	5.274778	22.069339	10.448494
C	7.950503	17.080172	4.026886
C	3.277573	20.842834	6.391399
C	7.500851	22.282981	7.302251
C	7.617879	21.955676	5.846066
C	4.203528	16.033282	5.193311
C	2.383037	18.330332	5.173916
C	6.373486	21.954436	8.099137
C	3.674740	18.381496	5.950790
C	3.943985	22.477676	10.245303
C	9.717915	14.633382	5.926415
C	7.813688	14.829608	7.972799
C	9.091755	14.287093	8.208958
C	7.481752	23.033172	9.985877
C	6.371261	22.344295	9.466592
C	2.315803	18.915660	3.885949
C	1.091227	18.896673	3.199871
C	5.279815	15.194697	5.386977

C	10.054737	14.170211	7.203381
C	8.239370	15.724664	4.265312
C	6.846391	14.805105	9.110595
C	8.586416	22.969366	7.870777
C	8.599013	23.357985	9.212494
C	1.243798	17.708456	5.740363
C	7.792115	17.557251	2.721994
C	0.038792	17.715469	5.020986
C	6.408459	15.128404	11.492428
C	4.038566	21.846573	6.968144
C	7.248619	15.254456	10.383215
C	5.599699	21.485282	11.691356
C	4.722137	14.113433	10.089665
C	5.561839	14.245063	8.979994
C	6.771722	22.535538	4.884703
C	5.144140	14.545770	11.352167
C	8.373276	14.865583	3.159604
C	8.678394	21.144273	5.402927
C	6.987879	22.318625	3.519461
C	3.889354	18.660693	9.992271
C	1.677806	18.223764	11.161200
C	4.638778	21.329792	12.694277
C	2.957325	17.586794	10.596417
C	1.293642	17.044918	7.098544
C	7.911521	16.689393	1.631306
C	2.979297	22.321026	11.245908
C	8.051738	21.516066	3.091571
C	3.322094	21.753957	12.477844
C	8.892117	20.922459	4.039341
C	3.530847	19.542394	3.234075
C	8.203683	15.340358	1.854872
C	0.635791	17.250425	11.751920
C	1.198475	16.407941	12.906909
C	-0.615694	18.023780	12.201537
H	1.033525	19.355589	2.207949
H	-0.845780	17.243897	5.461611
H	1.671615	17.736508	7.871647
H	0.290737	16.703772	7.407867
H	1.963754	16.167555	7.102881
H	4.366851	18.824053	3.160161
H	3.289936	19.893232	2.216422
H	3.909084	20.405369	3.807638
H	3.343174	15.873395	4.545013
H	5.467468	14.227373	4.922733
H	8.603766	13.808382	3.328590
H	8.304756	14.651841	1.009624

H	7.780499	17.067198	0.611517
H	7.577683	18.618910	2.562741
H	7.866691	17.769588	4.871318
H	10.453664	14.565992	5.117798
H	9.316619	13.903034	9.208320
H	5.227383	13.877028	8.006653
H	3.736895	13.651151	9.967648
H	4.492134	14.421733	12.223242
H	6.748586	15.488485	12.469315
H	8.231788	15.718268	10.499112
H	3.663326	22.956560	9.307341
H	1.956413	22.666777	11.063796
H	2.570109	21.648414	13.266243
H	4.924348	20.872518	13.647521
H	6.623684	21.143788	11.869703
H	5.952579	23.184098	5.207849
H	6.327903	22.792958	2.786187
H	8.230436	21.356187	2.022666
H	9.718255	20.280925	3.716489
H	9.331185	20.673198	6.142186
H	9.433034	23.227811	7.226803
H	7.451432	23.350588	11.032448
H	3.803990	22.910540	7.006508
H	2.312284	20.946471	5.898159
H	4.166375	19.399654	10.776676
H	3.342904	19.259593	9.225993
H	3.513218	17.046874	11.381290
H	2.709518	16.841933	9.820314
H	1.955368	18.960780	11.940355
H	1.189215	18.808934	10.356335
H	0.330602	16.553783	10.945930
H	2.015392	15.742191	12.575522
H	1.596752	17.055448	13.712078
H	0.412852	15.769244	13.352086
H	-1.062055	18.594389	11.365977
H	-1.390838	17.341957	12.597130
H	-0.366679	18.745461	13.002772
Cl	8.412375	18.539655	8.113882
C	9.773489	24.093023	9.814679
H	9.443941	24.828583	10.569961
H	10.463065	23.390082	10.322258
H	10.356653	24.628829	9.045441
C	11.420207	13.575936	7.464437
H	11.682741	12.821065	6.701414
H	12.204664	14.355944	7.428152
H	11.473907	13.090055	8.454156

C	-0.044029	18.313286	3.763511
H	-0.993785	18.320722	3.218564

Table S-8. Coordinates of optimized molecular structure for the truncated Co-nitrenoid (**8-N_2**) at high-spin Co(IV) state.

Sextet (S = 5/2)

Co	6.307190	18.595013	7.652618
N	5.162149	20.127499	6.956880
N	5.544725	17.155286	6.449617
C	5.994059	15.934279	6.103137
N	5.726175	18.278778	9.487293
C	3.940191	19.807870	6.345918
C	8.410153	15.287632	6.018844
C	7.180295	15.274251	6.722915
C	4.403489	17.409427	5.681178
C	5.113975	21.436198	7.277701
C	4.769041	22.843769	9.897497
C	8.527025	17.198296	4.340438
C	3.118881	20.978312	6.337256
C	7.464833	22.383988	7.190882
C	7.702676	21.981657	5.770158
C	4.172018	16.289024	4.824460
C	2.282633	18.506252	5.033246
C	6.236050	22.200913	7.883221
C	3.616500	18.578331	5.732076
C	4.212920	24.066401	10.321172
C	9.553895	14.721725	6.598066
C	7.105264	14.588302	7.963973
C	8.283826	14.048659	8.511574
C	7.116448	23.574968	9.701197
C	6.054545	22.851909	9.133802
C	2.113494	19.094787	3.757740
C	0.853023	19.022574	3.144246
C	5.183233	15.380350	5.070710
C	9.519634	14.123959	7.863555
C	8.507657	15.822591	4.622229
C	5.832052	14.290256	8.691902
C	8.497744	23.110916	7.807245
C	8.355987	23.698508	9.067387
C	1.204758	17.847338	5.674461
C	8.610375	17.649087	3.018271
C	-0.040605	17.806272	5.028894
C	4.648955	13.934017	10.805052
C	3.851668	21.993646	6.917097

C	5.777634	14.360395	10.099413
C	4.114512	21.656310	10.268053
C	3.567907	13.360291	8.726512
C	4.701236	13.780627	8.023575
C	6.799283	22.338692	4.751668
C	3.536944	13.427889	10.123032
C	8.594882	14.914356	3.551619
C	8.922125	21.385468	5.396365
C	7.115403	22.129301	3.405944
C	5.344549	18.024122	10.806683
C	3.476966	17.423062	12.424587
C	2.956243	21.689899	11.050419
C	3.845736	17.650125	10.952267
C	1.369006	17.193263	7.030659
C	8.675432	16.738260	1.959864
C	3.049409	24.102419	11.095890
C	8.342232	21.559791	3.048647
C	2.419029	22.911779	11.469873
C	9.240890	21.181174	4.051740
C	3.262119	19.780866	3.049646
C	8.672272	15.366091	2.230377
C	1.996522	17.093644	12.706581
C	1.542603	15.760226	12.093125
C	1.742338	17.093216	14.221223
H	0.715304	19.477779	2.158144
H	-0.880797	17.305827	5.521785
H	1.810443	17.888674	7.766917
H	0.395868	16.849865	7.422014
H	2.041733	16.318478	6.981022
H	4.123064	19.100786	2.921858
H	2.952597	20.136000	2.052327
H	3.630433	20.651109	3.619822
H	3.356122	16.200070	4.107881
H	5.351366	14.418548	4.587212
H	8.588129	13.839195	3.761541
H	8.728561	14.642366	1.410614
H	8.733516	17.099703	0.927320
H	8.621216	18.724988	2.821945
H	8.487409	17.918461	5.162967
H	10.495189	14.757239	6.039680
H	8.220561	13.507404	9.459553
H	4.718540	13.678260	6.937534
H	2.711750	12.956301	8.175661
H	2.657904	13.083078	10.675809
H	4.642111	13.991414	11.899418
H	6.642152	14.743819	10.650294

H	4.695534	25.002017	10.021443
H	2.631042	25.064655	11.409544
H	1.508481	22.936459	12.077021
H	2.465325	20.754899	11.340424
H	4.530682	20.699125	9.943312
H	5.854460	22.821631	5.014060
H	6.406219	22.436813	2.631197
H	8.600275	21.412618	1.994221
H	10.198133	20.720954	3.786216
H	9.624278	21.073947	6.172914
H	9.428934	23.261721	7.253141
H	6.962475	24.050509	10.674330
H	3.553032	23.031305	7.061747
H	2.114732	21.041724	5.921068
H	5.973317	17.196007	11.202894
H	5.574938	18.922043	11.424710
H	3.655837	16.746964	10.349063
H	3.232988	18.464128	10.521398
H	4.105912	16.608857	12.836693
H	3.744306	18.332598	12.997808
H	1.381901	17.898521	12.256237
H	1.654593	15.737785	10.995066
H	2.130714	14.919609	12.506339
H	0.478407	15.568026	12.324435
H	1.986750	18.070350	14.677440
H	0.685691	16.864050	14.452552
H	2.363607	16.327517	14.723195
Cl	8.522782	18.692611	7.834301
C	9.498409	24.445004	9.714335
H	9.135665	25.201801	10.431739
H	10.158790	23.752106	10.271935
H	10.124422	24.957482	8.962260
C	10.768857	13.567633	8.507594
H	11.435732	13.093675	7.765424
H	11.348382	14.371677	9.002437
H	10.524304	12.817450	9.279216
C	-0.219898	18.390902	3.774379
H	-1.198382	18.352158	3.283925

Table S-9. Coordinates of optimized molecular structure for the truncated Co-nitrenoid (**8-N_2**) at intermediate-spin Co(III) state. Broken-Symmetry calculation.

Quartet (S = 3/2)

(2, 1)

Co	6.180778	18.317814	8.003082

N	5.176850	19.873019	7.259372
N	5.728468	17.040019	6.511690
C	6.253184	15.887288	6.071689
N	4.971833	17.940741	9.396691
C	4.000923	19.596583	6.553570
C	8.568187	15.275365	5.382053
C	7.600058	15.357002	6.419473
C	4.497539	17.214071	5.862226
C	5.165905	21.183332	7.583649
C	5.108429	22.074873	10.559990
C	7.946156	17.114090	3.753948
C	3.237855	20.797866	6.467558
C	7.470665	22.168919	7.508107
C	7.646528	21.805695	6.066767
C	4.265121	16.077300	5.020454
C	2.367597	18.298921	5.197926
C	6.297888	21.889026	8.256926
C	3.688123	18.362423	5.926319
C	3.800955	22.537245	10.325316
C	9.825885	14.717674	5.648574
C	7.929680	14.867840	7.706927
C	9.217133	14.344714	7.932495
C	7.347529	22.985351	10.167852
C	6.244818	22.311176	9.613557
C	2.224894	18.907711	3.927760
C	0.971100	18.868027	3.297581
C	5.368550	15.260850	5.136962
C	10.177261	14.253266	6.921150
C	8.312234	15.777981	3.997299
C	6.960401	14.813260	8.842191
C	8.545670	22.842853	8.109187
C	8.506903	23.264420	9.440373
C	1.271406	17.637304	5.803595
C	7.754479	17.575450	2.448150
C	0.034695	17.625090	5.140872
C	6.501134	15.108367	11.222809
C	3.975619	21.790366	7.092773
C	7.352455	15.245282	10.123756
C	5.377618	21.474292	11.808443
C	4.825906	14.112498	9.793220
C	5.678136	14.252126	8.694059
C	6.881494	22.409397	5.053773
C	5.235139	14.534192	11.063617
C	8.489504	14.923820	2.893520
C	8.687858	20.935917	5.695316
C	7.162898	22.163069	3.705432

C	3.900130	18.594161	10.031329
C	1.696546	18.350994	11.289311
C	4.385802	21.353486	12.785731
C	2.919026	17.614539	10.722872
C	1.408038	16.941209	7.139555
C	7.918992	16.712077	1.359935
C	2.804463	22.413013	11.299042
C	8.208044	21.303219	3.348218
C	3.092354	21.827825	12.536656
C	8.964090	20.682691	4.348427
C	3.393233	19.572473	3.231682
C	8.288534	15.382909	1.587780
C	0.603803	17.453071	11.906583
C	1.128938	16.582792	13.058142
C	-0.583179	18.312040	12.371834
H	0.855140	19.343917	2.318756
H	-0.816553	17.121901	5.611379
H	1.840153	17.612258	7.901965
H	0.427599	16.591033	7.505570
H	2.077337	16.065170	7.074093
H	4.191715	18.842183	3.007396
H	3.073134	20.030331	2.280721
H	3.852545	20.360085	3.851656
H	3.388872	15.925983	4.391587
H	5.566742	14.324428	4.617068
H	8.778650	13.881819	3.065127
H	8.425862	14.697848	0.744905
H	7.760834	17.077384	0.339499
H	7.475635	18.621164	2.285465
H	7.822202	17.802915	4.594169
H	10.558569	14.665857	4.836025
H	9.453822	13.956325	8.927338
H	5.353015	13.891840	7.714676
H	3.842128	13.650985	9.656061
H	4.572612	14.406529	11.926310
H	6.832668	15.458411	12.206265
H	8.330770	15.714097	10.252235
H	3.565908	23.035640	9.385236
H	1.800951	22.799050	11.092032
H	2.315650	21.747333	13.303852
H	4.628965	20.883584	13.744733
H	6.383819	21.095198	12.011331
H	6.076526	23.098795	5.324829
H	6.568910	22.657608	2.930247
H	8.438999	21.119172	2.293354
H	9.774330	19.997669	4.078772

H	9.274954	20.446790	6.477094
H	9.427811	23.062189	7.499280
H	7.278706	23.323520	11.206068
H	3.726830	22.849221	7.159781
H	2.280227	20.907102	5.960996
H	4.313981	19.308583	10.777480
H	3.359948	19.214822	9.281587
H	3.464827	17.077356	11.516514
H	2.602658	16.851441	9.990189
H	2.033498	19.080878	12.050902
H	1.237556	18.952150	10.479357
H	0.237802	16.772903	11.111174
H	1.896459	15.864506	12.718706
H	1.579007	17.208710	13.853037
H	0.310646	15.998237	13.517888
H	-1.007683	18.902780	11.539005
H	-1.393667	17.686823	12.789409
H	-0.271183	19.022844	13.160910
Cl	8.304894	18.541477	8.601375
C	9.673621	23.980911	10.078493
H	9.335075	24.712637	10.833367
H	10.343370	23.264643	10.594035
H	10.281217	24.517461	9.328761
C	11.555253	13.684571	7.173212
H	11.838352	12.953733	6.394264
H	12.321233	14.483548	7.158807
H	11.616925	13.178433	8.152215
C	-0.121052	18.242745	3.899808
H	-1.094026	18.233088	3.397480

Table S-10. Coordinates of optimized molecular structure for the truncated Co-nitrenoid (**8-N_2**) at intermediate-spin Co(III) state. Broken-Symmetry calculation.

Sextet (S = 5/2)

(4, 1)

Co	6.220640	18.389496	8.064970
N	5.204872	19.908176	7.176731
N	5.659763	17.032271	6.673826
C	6.178826	15.846276	6.317957
N	5.081510	18.218291	9.400339
C	4.010775	19.612547	6.510943
C	8.502946	15.222392	5.690076
C	7.516362	15.318997	6.708480
C	4.455502	17.188725	5.978503
C	5.207013	21.231162	7.443885

C	5.276098	22.079513	10.424436
C	7.979534	17.074966	4.047757
C	3.254638	20.814488	6.387117
C	7.473879	22.289045	7.258186
C	7.581402	21.955787	5.802795
C	4.228091	16.011921	5.194639
C	2.380117	18.288409	5.177299
C	6.354960	21.958570	8.066470
C	3.673687	18.355816	5.949703
C	3.942763	22.484696	10.231795
C	9.751798	14.658990	5.982426
C	7.823073	14.845440	8.006857
C	9.103877	14.317299	8.259804
C	7.475079	23.049912	9.939209
C	6.363075	22.354351	9.432096
C	2.301751	18.867755	3.887314
C	1.075117	18.831752	3.205490
C	5.310292	15.182582	5.395663
C	10.079411	14.206581	7.265632
C	8.277941	15.723856	4.299027
C	6.841932	14.815389	9.132745
C	8.560737	22.983363	7.814604
C	8.583815	23.376835	9.154722
C	1.249919	17.655969	5.750349
C	7.824545	17.539786	2.738092
C	0.042443	17.646144	5.035203
C	6.371309	15.134978	11.508901
C	4.010277	21.827200	6.955628
C	7.225633	15.264944	10.411057
C	5.613466	21.500496	11.666281
C	4.706985	14.115630	10.083294
C	5.561191	14.250501	8.985166
C	6.712573	22.510939	4.846926
C	5.110680	14.548737	11.351513
C	8.425233	14.856464	3.201607
C	8.655693	21.166372	5.352483
C	6.920472	22.293111	3.480600
C	3.894827	18.672693	9.991704
C	1.683389	18.246658	11.164830
C	4.662154	21.347021	12.678640
C	2.962002	17.604250	10.604050
C	1.312479	17.000065	7.111740
C	7.956487	16.663560	1.655578
C	2.987742	22.330397	11.242002
C	7.999817	21.515364	3.045622
C	3.342947	21.768613	12.472879

C	8.862500	20.945227	3.987806
C	3.508116	19.504155	3.228792
C	8.258501	15.318920	1.892090
C	0.639032	17.278330	11.759566
C	1.198894	16.441119	12.919810
C	-0.611792	18.056144	12.203450
H	1.008621	19.285857	2.211865
H	-0.835316	17.166367	5.480623
H	1.673485	17.704477	7.881465
H	0.316816	16.638603	7.421571
H	2.001726	16.137819	7.121925
H	4.349396	18.792351	3.150949
H	3.259254	19.852677	2.212272
H	3.882612	20.370161	3.800261
H	3.372562	15.843512	4.542074
H	5.508420	14.215906	4.934417
H	8.663725	13.802777	3.380973
H	8.369718	14.624173	1.053229
H	7.827528	17.031489	0.631898
H	7.602257	18.598210	2.568998
H	7.885213	17.770767	4.885840
H	10.496807	14.594023	5.182118
H	9.321512	13.939398	9.263131
H	5.241117	13.881307	8.007536
H	3.724986	13.650135	9.947700
H	4.447276	14.422728	12.213649
H	6.697429	15.495295	12.490475
H	8.205469	15.732366	10.540420
H	3.652532	22.959862	9.294736
H	1.962736	22.674167	11.068298
H	2.598543	21.665387	13.268732
H	4.957379	20.893889	13.630922
H	6.639719	21.161639	11.836356
H	5.882419	23.142596	5.174991
H	6.242366	22.748682	2.752018
H	8.172870	21.356258	1.975685
H	9.701011	20.322750	3.659541
H	9.325856	20.713000	6.087314
H	9.400153	23.243966	7.162188
H	7.452583	23.370960	10.984841
H	3.766651	22.889222	6.991112
H	2.285720	20.907714	5.898898
H	4.175193	19.414947	10.771791
H	3.347809	19.269022	9.223922
H	3.517507	17.069393	11.392628
H	2.713008	16.853955	9.833655

H	1.961946	18.986999	11.940481
H	1.196608	18.828877	10.356716
H	0.333782	16.577887	10.956917
H	2.016288	15.773605	12.593227
H	1.595752	17.092330	13.722677
H	0.412022	15.804897	13.366292
H	-1.056515	18.622607	11.364203
H	-1.388405	17.377855	12.602266
H	-0.362507	18.782013	13.000785
Cl	8.410579	18.562751	8.099914
C	9.760860	24.118595	9.743527
H	9.435719	24.853397	10.501391
H	10.459263	23.419618	10.244465
H	10.333185	24.656281	8.967489
C	11.448805	13.630472	7.545986
H	11.739526	12.891520	6.777661
H	12.220657	14.423825	7.538196
H	11.490324	13.131358	8.529711
C	-0.051427	18.237631	3.775434
H	-1.002919	18.231235	3.233493

References.

(1) King, E. R.; Hennessy, E. T.; Betley, T. A., Catalytic C−H bond amination from high-spin iron imido complexes. *J. Am. Chem. Soc*. **2011**, *133* (13), 4917-4923.

(2) King, E. R.; Sazama, G. T.; Betley, T. A., Co(III) imidos exhibiting spin crossover and C–H bond activation. *J. Am. Chem. Soc*. **2012**, *134* (43), 17858-17861.

(3) Baek, Y.; Betley, T. A., Catalytic C–H amination mediated by dipyrrin cobalt imidos. *J. Am. Chem. Soc.* **2019**, *141* (19), 7797-7806.

(4) Smith, P. A. S.; Hall, J. H., Kinetic evidence for the formation of azene (electron-deficient nitrogen) intermediates from aryl azides. *J. Am. Chem. Soc*. **1962**, *84* (3), 480-485.

(5) Jin, L.-M.; Lu, H.; Cui, Y.; Lizardi, C. L.; Arzua, T. N.; Wojtas, L.; Cui, X.; Zhang, X. P., Selective radical amination of aldehydic C(sp^2)–H bonds with fluoroaryl azides via Co(II)-based metalloradical catalysis: synthesis of *N*-fluoroaryl amides from aldehydes under neutral and nonoxidative conditions. *Chem. Sci*. **2014**, *5* (6), 2422-2427.

(6) Hennessy, E. T.; Betley, T. A., Complex *N*-heterocycle synthesis via iron-catalyzed, direct C–H bond amination. *Science* **2013**, *340* (6132), 591-595.

(7) Stoll, S.; Schweiger, A., EasySpin, a comprehensive software package for spectral simulation and analysis in EPR. *J. Magn. Reson*. **2006**, *178* (1), 42-55.

(8) Johnson, E. R.; Keinan, S.; Mori-Sánchez, P.; Contreras-García, J.; Cohen, A. J.; Yang, W., Revealing noncovalent interactions. *J. Am. Chem. Soc*. **2010**, *132* (18), 6498-6506.

(9) Contreras-García, J.; Johnson, E. R.; Keinan, S.; Chaudret, R.; Piquemal, J.-P.; Beratan, D. N.; Yang, W., NCIPLOT: A program for plotting noncovalent interaction regions. *J. Chem. Theory Comput.* **2011**, *7* (3), 625-632.

(10) Intrieri, D.; Caselli, A.; Ragaini, F.; Macchi, P.; Casati, N.; Gallo, E., Insights into the mechanism of the ruthenium–porphyrin-catalysed allylic amination of olefins by aryl azides. *Eur. J. Inorg. Chem*. **2012**, 569-580.

(11) Fantauzzi, S.; Gallo, E.; Caselli, A.; Piangiolino, C.; Ragaini, F.; Cenini, S., The (porphyrin)ruthenium-catalyzed aziridination of olefins using aryl azides as nitrogen sources. *Eur. J. Org. Chem*. **2007**, 6053-6059.

(12) Yoshimoto, F. K.; Jung, I. J.; Goyal, S.; Gonzalez, E.; Guengerich, F. P., Isotope-labeling studies support the electrophilic compound I iron active species, FeO^{3+}, for the carbon–carbon bond cleavage reaction of the cholesterol side-chain cleavage enzyme, Cytochrome P450 11A1. *J. Am. Chem. Soc*. **2016**, *138* (37), 12124-12141.

(13) Renny, J. S.; Tomasevich, L. L.; Tallmadge, E. H.; Collum, D. B., Method of continuous variations: applications of Job plots to the study of molecular associations in organometallic chemistry. *Angew. Chem. Int. Ed*. **2013**, *52* (46), 11998-12013.

(14) Fielding, L., Determination of association constants (K_a) from solution NMR data. *Tetrahedron* **2000**, *56* (34), 6151-6170.

(15) APEX2 Software Suite; Bruker AXS: Madison, WI, 2014.

(16) (a) Sheldrick, G. M., SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr., Sect. A* **2015**, *71* (1), 3-8. (b) Sheldrick, G. M., Crystal structure refinement with SHELXL. *Acta Crystallogr.*, **2015**, C71, 3-8.

(17) Neese, F. ORCA - An ab initio, Density functional and semi-empirical electronic structure package; Version 3.0.3 ed. Universitat Bonn, Bonn, Germany, 2009.

(18) Lee, C.; Yang, W.; Parr, R. G., Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37* (2), 785-789.

(19) Becke, A. D., Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98* (7), 5648-5652.

(20) Weigend, F.; Ahlrichs, R., Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7* (18), 3297-3305.

(21) Schäfer, A.; Huber, C.; Ahlrichs, R., Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr. *J. Chem. Phys*. **1994**, *100* (8), 5829-5835.

(22) Schäfer, A.; Horn, H.; Ahlrichs, R., Fully optimized contracted Gaussian basis sets for atoms Li to Kr. *J. Chem. Phys*. **1992**, *97* (4), 2571-2577.

(23) Weigend, F., Accurate coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys*. **2006**, *8* (9), 1057-1065.

(24) Neese, F. ORCA - The ORCA program system, Wiley Interdiscip. Rev.: Comput. Mol. Sci., **2012**, *2*, 73.

(25) Kirchner, B.; Wennmohs, F.; Ye, S.; Neese, F., Theoretical bioinorganic chemistry: the electronic structure makes a difference. *Curr. Opin. Chem. Biol*. **2007**, *11* (2), 134-141.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 3_ArLCoBrN3Ar

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 3_ArLCoBrN3Ar

```
Bond precision:  C-C = 0.0081 A          Wavelength=0.71073

Cell:           a=11.5371(4)    b=22.8606(10)      c=27.3251(12)
                alpha=90        beta=94.279(4)     gamma=90
Temperature:    100 K

                Calculated                      Reported
Volume          7186.8(5)                       7186.8(5)
Space group     P 21/n                          P 21/n
Hall group      -P 2yn                          -P 2yn
Moiety formula  C76 H62 Br Co N5, 2(C7 H8)      C76H62BrCo,2(C7H8)
Sum formula     C90 H78 Br Co N5                C90 H78 Br Co N5
Mr              1368.41                         1368.41
Dx,g cm-3       1.265                           1.265
Z               4                               4
Mu (mm-1)       0.846                           0.846
F000            2860.0                          2860.0
F000'           2861.10
h,k,lmax        13,27,32                        13,27,32
Nref            12707                           12706
Tmin,Tmax       0.903,0.951                     0.661,0.745
Tmin'           0.844

Correction method= # Reported T Limits: Tmin=0.661 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 1.000          Theta(max)= 25.027

R(reflections)= 0.0860( 7291)     wR2(reflections)= 0.1631( 12706)

S = 1.091                 Npar= 1086
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT250_ALERT_2_B Large U3/U1 Ratio for Average U(i,j) Tensor .... 4.3 Note

Author Response: We cannot avoid this alert by using SIMU only to model the disorder in the structure. We have applied a stricter restraint by lowering down the parameter from SIMU 0.04 (default) to SIMU 0.02 or even to SIMU 0.01. As SIMU 0.01 assumes the default 1.4 distance criterion, it has been applied as a last-resort solution. We note that such Alert at B level can be avoided by applying EADP for the pair of disordered atoms and/or RIGU on the bonded atoms in disoder fragment.

Alert level C

RINTA01_ALERT_3_C The value of Rint is greater than 0.12
Rint given 0.166
PLAT020_ALERT_3_C The Value of Rint is Greater Than 0.12 ..... 0.166 Report
PLAT220_ALERT_2_C Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 3.2 Ratio
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 3.3 Note

Author Response: We cannot avoid this alert by using SIMU only to model the disorder in the structure. We have applied a stricter restraint by lowering down the parameter from SIMU 0.04 (default) to SIMU 0.02 or even to SIMU 0.01. As SIMU 0.01 assumes the default 1.4 distance criterion, it has been applied as a last-resort solution. We note that such Alert at B level can be avoided by applying EADP for the pair of disordered atoms and/or RIGU on the bonded atoms in disoder fragment.

PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 2.7 Note

Author Response: We cannot avoid this alert by using SIMU only to model the disorder in the structure. We have applied a stricter restraint by lowering down the parameter from SIMU 0.04 (default) to SIMU 0.02 or even to SIMU 0.01. As SIMU 0.01 assumes the default 1.4 distance criterion, it has been applied as a last-resort solution. We note that such Alert at B level can be avoided by applying EADP for the pair of disordered atoms and/or RIGU on the bonded atoms in disoder fragment.

PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 3.3 Note

Author Response: We cannot avoid this alert by using SIMU only to model the disorder in the structure. We have applied a stricter restraint by lowering down the parameter from SIMU 0.04 (default) to SIMU 0.02 or even to SIMU 0.01. As SIMU 0.01 assumes the default 1.4 distance criterion, it has been applied as a last-resort solution. We note that such Alert at B level can be avoided by applying EADP for the pair of disordered atoms and/or RIGU on the bonded atoms in disoder fragment.

```
PLAT341_ALERT_3_C Low Bond Precision on  C-C Bonds ..............     0.0081 Ang.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......     15.633 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      3.595 Check
```

Alert level G

```
FORMU01_ALERT_1_G  There is a discrepancy between the atom counts in the
           _chemical_formula_sum and _chemical_formula_moiety. This is
           usually due to the moiety formula being in the wrong format.
           Atom count from _chemical_formula_sum:   C90 H78 Br1 Co1 N5
           Atom count from _chemical_formula_moiety:C90 H78 Br1 Co1
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         23 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         71 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large      18.70 Why ?
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records          1 Report
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records          1 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records          4 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          6 Report
PLAT300_ALERT_4_G Atom Site Occupancy of C11S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C12S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C13S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C14S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C15S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C16S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C17S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H11S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H12S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H13S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H14S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H15S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H17A       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H17B       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H17C       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C21S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C22S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C23S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C24S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C25S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C26S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C27S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H21S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H22S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H23S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H24S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H25S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H27A       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H27B       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H27C       Constrained at        0.5 Check
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )        27% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )       100% Note
```

```
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  3  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  4  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  5  )       100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... Resd  2         11.62 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... Resd  3          7.50 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... Resd  4          7.50 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... Resd  5          3.37 Check
PLAT410_ALERT_2_G Short Intra H...H Contact  H17      ..H38A     .       2.04 Ang.
                                                     x,y,z  =      1_555 Check
PLAT410_ALERT_2_G Short Intra H...H Contact  H17      ..H38      .       1.98 Ang.
                                                     x,y,z  =      1_555 Check
PLAT410_ALERT_2_G Short Intra H...H Contact  H19      ..H34A     .       2.09 Ang.
                                                     x,y,z  =      1_555 Check
PLAT410_ALERT_2_G Short Intra H...H Contact  H19      ..H34      .       2.02 Ang.
                                                     x,y,z  =      1_555 Check
PLAT412_ALERT_2_G Short Intra XH3 .. XHn     H69      ..H74F     .       1.92 Ang.
                                                     x,y,z  =      1_555 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........          6 Note
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #         30 Check
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms ....          ! Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        933 Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          2 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          3 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   1 ALERT level B = A potentially serious problem, consider carefully
   9 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  59 ALERT level G = General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  14 ALERT type 2 Indicator that the structure model may be wrong or deficient
   8 ALERT type 3 Indicator that the structure quality may be low
  44 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

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Publication of your CIF in other journals

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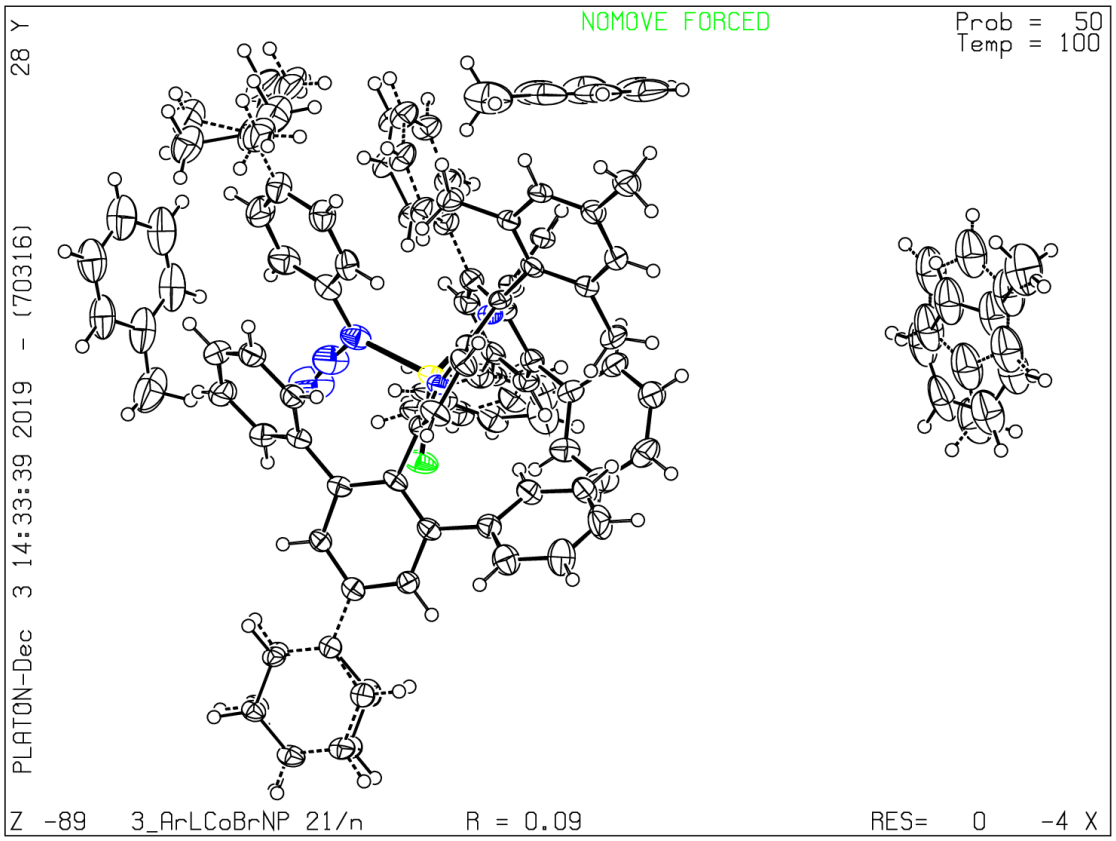
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 3_ArLCoBrN3Ar - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 4_ArLCoBrannulation

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 4_ArLCoBrannulation

```
Bond precision:  C-C = 0.0056 A          Wavelength=0.71073

Cell:          a=12.5766(4)       b=13.7287(5)     c=22.5774(8)
               alpha=100.712(1)   beta=94.999(1)   gamma=93.362(1)
Temperature:   100 K
```

	Calculated	Reported
Volume	3804.6(2)	3804.6(2)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C76 H62 Br Co N3, 3.5(C6 H6)	C76H62BrCoN3,3.5(C6H6)
Sum formula	C97 H83 Br Co N3	C97 H83 Br Co N3
Mr	1429.50	1429.50
Dx,g cm-3	1.248	1.248
Z	2	2
Mu (mm-1)	0.801	0.801
F000	1496.0	1496.0
F000’	1496.58	
h,k,lmax	15,16,26	14,16,26
Nref	13508	13453
Tmin,Tmax	0.825,0.938	0.698,0.745
Tmin’	0.756	

```
Correction method= # Reported T Limits: Tmin=0.698 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.996          Theta(max)= 25.085

R(reflections)= 0.0546( 8478)     wR2(reflections)= 0.1204( 13453)

S = 1.012                 Npar= 1037
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT220_ALERT_2_C Non-Solvent  Resd 1  C   Ueq(max)/Ueq(min) Range        3.5 Ratio
PLAT222_ALERT_3_C Non-Solv.  Resd 1  H   Uiso(max)/Uiso(min) Range        4.2 Ratio
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.8 Note
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.1 Note
PLAT420_ALERT_2_C D-H Without Acceptor       N3       --H3       .     Please Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      3.679 Check
PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min).         10 Note
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.597        45 Report
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite          3 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         36 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.001 Degree
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records          1 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          3 Report
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )         7% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  4  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  5  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  6  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  7  )       100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  4          7.69 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  5          4.31 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  6          3.01 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  7          2.99 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  C54      ..C22T           3.15 Ang.
                                              2-x,1-y,1-z  =      2_766 Check
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #         24 Check
PLAT793_ALERT_4_G Model has Chirality at N3          (Centro SPGR)         S Verify
PLAT793_ALERT_4_G Model has Chirality at C47         (Centro SPGR)         S Verify
PLAT793_ALERT_4_G Model has Chirality at C48         (Centro SPGR)         S Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............       481 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...         3 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         1 Info
```

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
8 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
23 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
9 ALERT type 2 Indicator that the structure model may be wrong or deficient
6 ALERT type 3 Indicator that the structure quality may be low
14 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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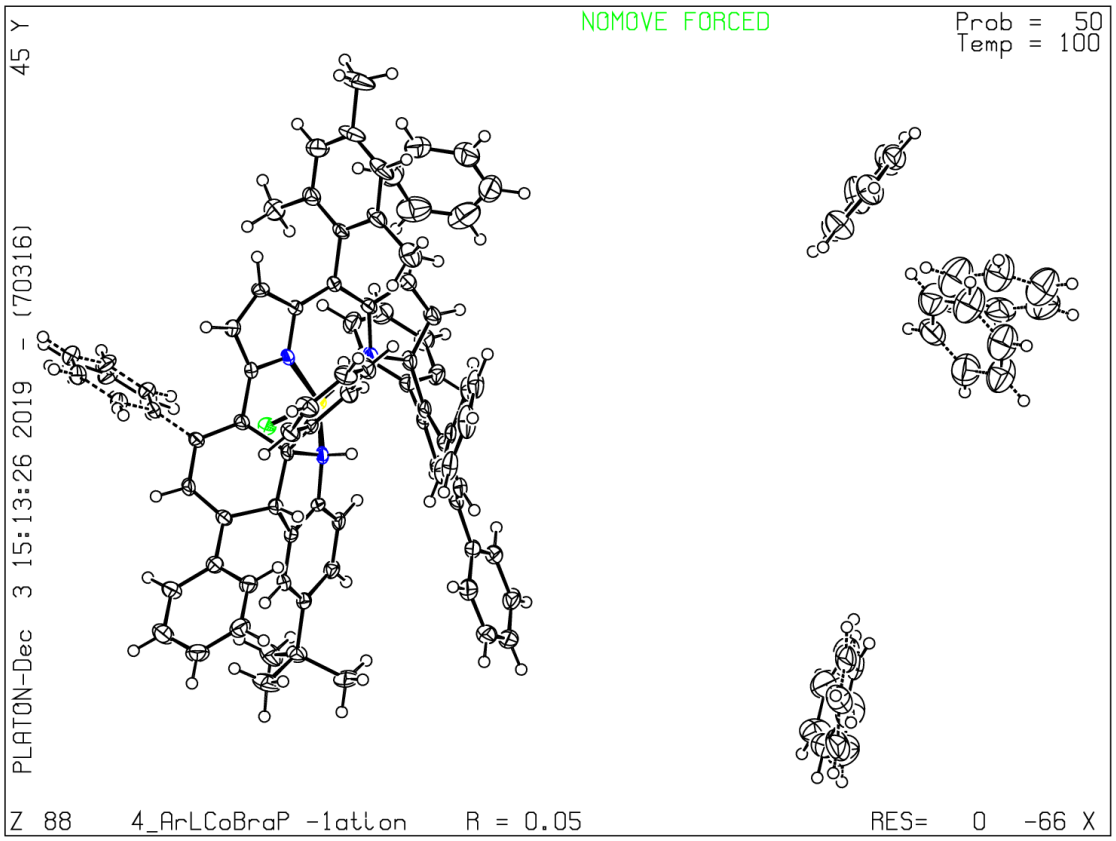
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 4_ArLCoBrannulation - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 5_ArLCoBrNH2Ar

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 5_ArLCoBrNH2Ar

```
Bond precision:  C-C = 0.0047 A          Wavelength=0.71073

Cell:           a=17.7144(19)    b=21.629(2)         c=18.715(2)
                alpha=90         beta=108.264(2)     gamma=90
Temperature:    100 K

                Calculated                   Reported
Volume          6809.3(12)                   6809.3(13)
Space group     P 21/c                       P 21/c
Hall group      -P 2ybc                      -P 2ybc
Moiety formula  C76 H64 Br Co N3, 2(C6 H6)   C76H64BrCoN3,2(C6H6)
Sum formula     C88 H76 Br Co N3             C88 H76 Br Co N3
Mr              1314.35                      1314.35
Dx,g cm-3       1.282                        1.282
Z               4                            4
Mu (mm-1)       0.889                        0.889
F000            2748.0                       2748.0
F000'           2749.08
h,k,lmax        21,25,22                     21,25,22
Nref            12056                        12048
Tmin,Tmax       0.808,0.915                  0.692,0.745
Tmin'           0.733

Correction method= # Reported T Limits: Tmin=0.692 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.999          Theta(max)= 25.043

R(reflections)= 0.0445( 8963)     wR2(reflections)= 0.1146( 12048)

S = 1.023                 Npar= 883
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
CRYSC01_ALERT_1_C The word below has not been recognised as a standard
           identifier.
           maroon
CRYSC01_ALERT_1_C No recognised colour has been given for crystal colour.
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....       3.69 Report
PLAT220_ALERT_2_C Non-Solvent  Resd 1  C   Ueq(max)/Ueq(min) Range        3.5 Ratio
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.9 Note
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.6 Note
PLAT331_ALERT_2_C Small Aver Phenyl C-C Dist C1S       -C6S      .       1.36 Ang.
PLAT420_ALERT_2_C D-H Without Acceptor       N3       --H3A      .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N3       --H3B      .     Please Check
PLAT905_ALERT_3_C Negative K value in the Analysis of Variance ...     -0.066 Report
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.596          7 Report
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         12 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large       7.21 Why ?
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          1 Report
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  3  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  4  )       100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... Resd  3           8.35 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... Resd  4           3.65 Check
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............       192 Note
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        51% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          1 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          4 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
  11 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  12 ALERT level G = General information/check it is not something unexpected

   3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  10 ALERT type 2 Indicator that the structure model may be wrong or deficient
   5 ALERT type 3 Indicator that the structure quality may be low
   5 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

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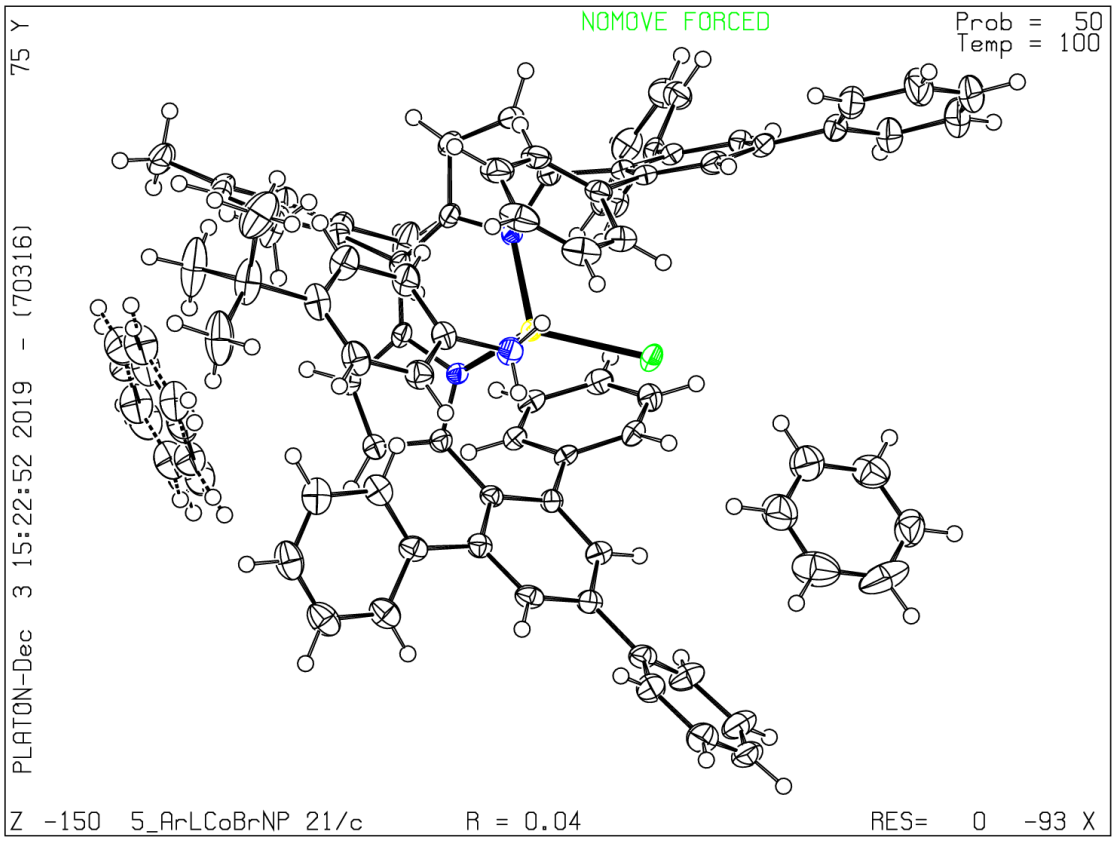
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 5_ArLCoBrNH2Ar - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 7_ArLCoBrN3R_1

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 7_ArLCoBrN3R_1

```
Bond precision:  C-C = 0.0053 A          Wavelength=0.71073

Cell:          a=11.8481(4)      b=12.2353(3)      c=22.6467(7)
               alpha=95.171(2)   beta=101.347(3)   gamma=107.834(3)
Temperature:   100 K
```

	Calculated	Reported
Volume	3024.10(17)	3024.11(17)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C76 H62 Br Co N5	C76H62BrCoN5
Sum formula	C76 H62 Br Co N5	C76 H62 Br Co N5
Mr	1184.14	1184.14
Dx,g cm-3	1.300	1.300
Z	2	2
Mu (mm-1)	0.993	0.993
F000	1230.0	1230.0
F000’	1230.48	
h,k,lmax	14,14,26	14,14,26
Nref	10711	10693
Tmin,Tmax	0.788,0.952	0.704,0.745
Tmin’	0.706	

```
Correction method= # Reported T Limits: Tmin=0.704 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.998          Theta(max)= 25.058

R(reflections)= 0.0495( 7395)     wR2(reflections)= 0.1045( 10693)

S = 1.011                 Npar= 751
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT910_ALERT_3_B Missing # of FCF Reflection(s) Below Theta(Min). 13 Note

Author Response: Reflections were blocked by the beamstop

Alert level C

PLAT220_ALERT_2_C Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 3.3 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for N3 --N4 . 6.3 s.u.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 2.648 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.596 6 Report

---

Alert level G

PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ Please Check
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Br1 --Co1 . 10.0 s.u.
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety ..... C9 Check
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still 42% Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ... 6 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 1 Info

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
6 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
5 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

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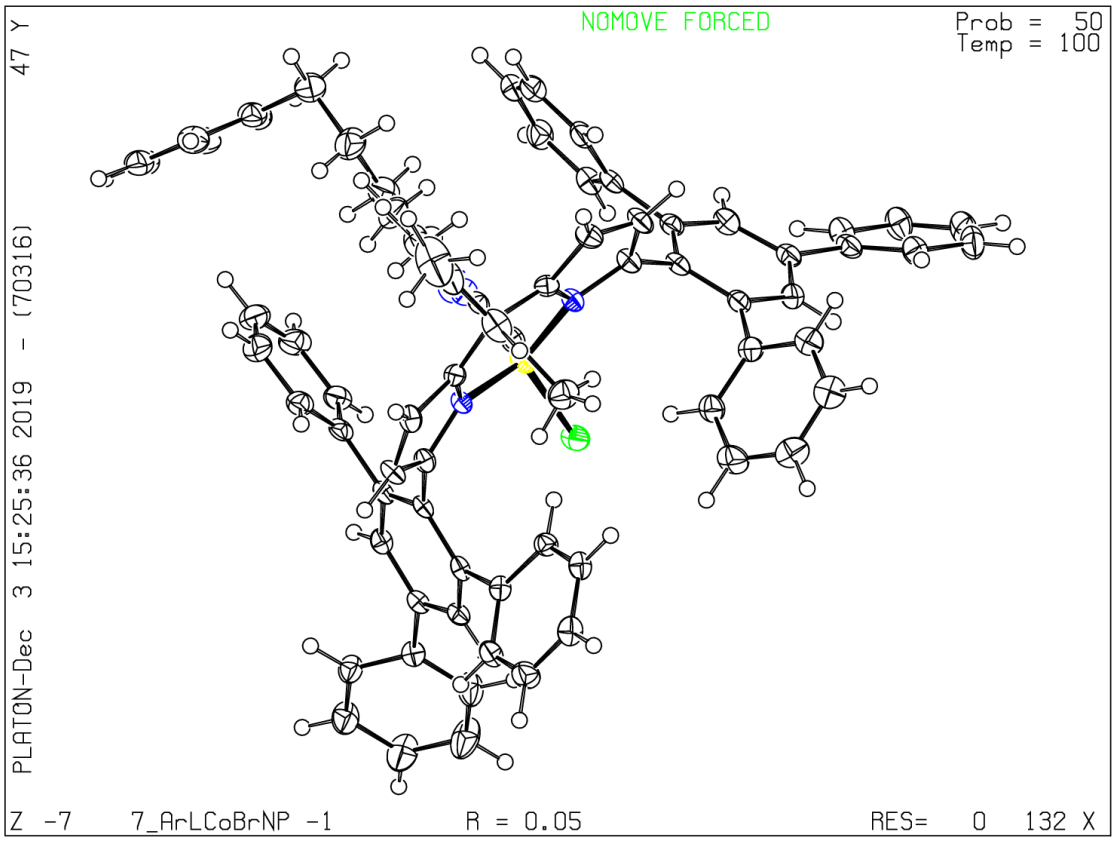
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 7_ArLCoBrN3R_1 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 8_ArLCoBrN3R2-initial

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 8_ArLCoBrN3R2-initial

```
Bond precision:  C-C = 0.0069 A          Wavelength=0.71073

Cell:           a=11.5036(5)    b=21.4756(11)       c=25.3211(13)
                alpha=90        beta=99.4205(16)    gamma=90
Temperature:    100 K

               Calculated                      Reported
Volume         6171.1(5)                       6171.1(5)
Space group    P 21/c                          P 21/c
Hall group     -P 2ybc                         -P 2ybc
Moiety formula C72 H62 Br Co N5, 0.5(C6 H14)   C72H62BrCoN5,0.5(C6H14)
Sum formula    C75 H69 Br Co N5                C75 H69 Br Co N5
Mr             1179.19                         1179.19
Dx,g cm-3      1.269                           1.269
Z              4                               4
Mu (mm-1)      0.973                           0.973
F000           2464.0                          2464.0
F000'          2464.96
h,k,lmax       13,25,30                        13,25,30
Nref           10995                           10930
Tmin,Tmax      0.749,0.856                     0.726,0.801
Tmin'          0.685

Correction method= # Reported T Limits: Tmin=0.726 Tmax=0.801
AbsCorr = MULTI-SCAN

Data completeness= 0.994          Theta(max)= 25.096

R(reflections)= 0.0604( 6924)     wR2(reflections)= 0.1713( 10930)

S = 1.017                 Npar= 790
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT220_ALERT_2_C Non-Solvent  Resd 1  C   Ueq(max)/Ueq(min) Range        3.3 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for    N3       --N4       .        7.0 s.u.
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C73 Check
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.8 Note
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.8 Note
PLAT341_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00695 Ang.
PLAT411_ALERT_2_C Short Inter H...H Contact  H17      ..H17      .       2.10 Ang.
                                            1-x,1-y,1-z  =      3_666 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      4.788 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.597         59 Report
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         12 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         12 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large      11.70 Why ?
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records          6 Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          1 Report
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records          2 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          1 Report
PLAT186_ALERT_4_G The CIF-Embedded .res File Contains ISOR Records          1 Report
PLAT187_ALERT_4_G The CIF-Embedded .res File Contains RIGU Records          1 Report
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )        100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  3  )        100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... Resd  2           4.84 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... Resd  3           5.16 Check
PLAT411_ALERT_2_G Short Inter H...H Contact  H28      ..H2SA     .       2.11 Ang.
                                          1-x,1/2+y,3/2-z  =      2_656 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H27      ..H1SA     .       1.97 Ang.
                                          1-x,1/2+y,3/2-z  =      2_656 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H27      ..H1SC     .       1.78 Ang.
                                           x,1/2-y,1/2+z  =      4_566 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          28 Note
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #          40 Check
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        279 Note
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        30% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          3 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          6 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          3 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   9 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  24 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  14 ALERT type 2 Indicator that the structure model may be wrong or deficient
   6 ALERT type 3 Indicator that the structure quality may be low
  12 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

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Publication of your CIF in other journals

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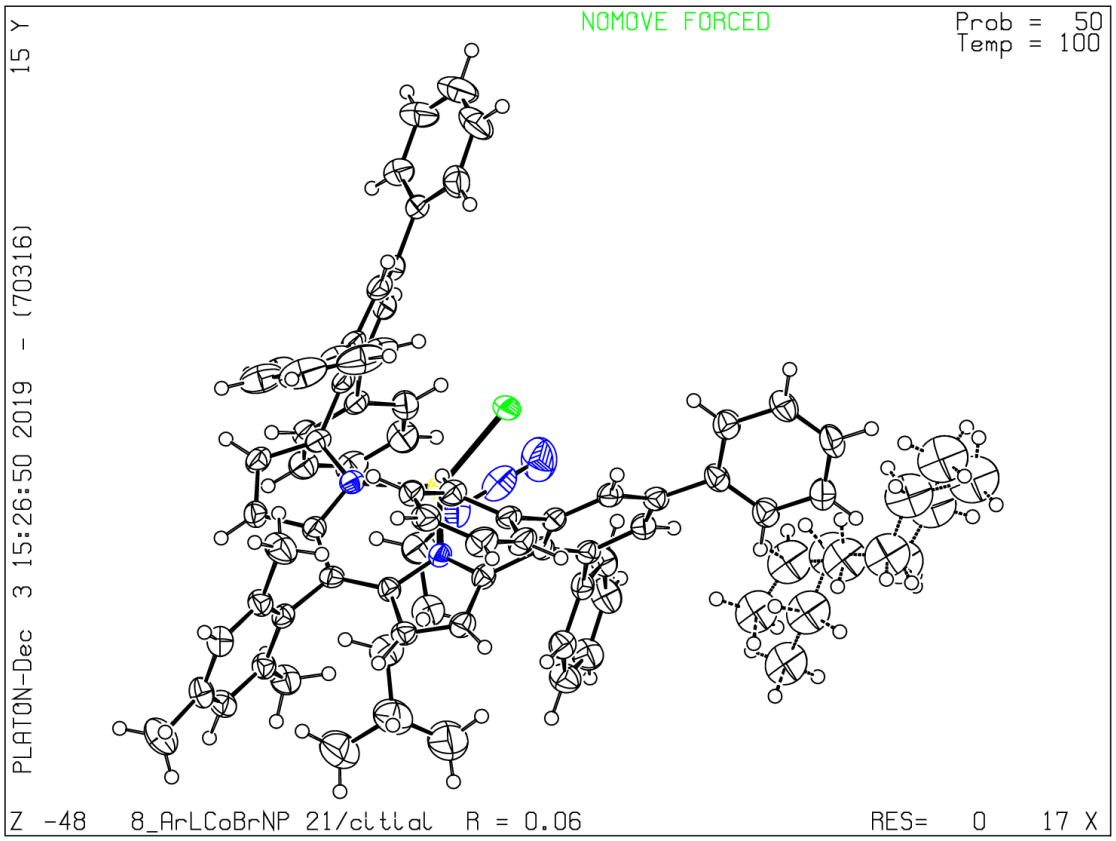
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 8_ArLCoBrN3R2-initial - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 9_ArLCoBrNHBn

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 9_ArLCoBrNHBn

```
Bond precision:  C-C = 0.0041 A          Wavelength=0.71073

Cell:          a=11.7393(6)      b=14.6478(7)     c=19.8506(10)
               alpha=81.004(1)   beta=80.061(1)   gamma=75.351(1)
Temperature:   100 K

               Calculated                        Reported
Volume         3230.1(3)                         3230.1(3)
Space group    P -1                              P -1
Hall group     -P 1                              -P 1
Moiety formula 2(C73 H56 Br Co N3), 3(C7 H8)     2(C73H56BrCoN3),3(C7H8)
Sum formula    C167 H136 Br2 Co2 N6              C83.50 H68 Br Co N3
Mr             2504.49                           1252.25
Dx,g cm-3      1.288                             1.288
Z              1                                 2
Mu (mm-1)      0.933                             0.933
F000           1304.0                            1304.0
F000'          1304.52
h,k,lmax       13,17,23                          13,17,23
Nref           11459                             11449
Tmin,Tmax      0.894,0.946                       0.684,0.745
Tmin'          0.845

Correction method= # Reported T Limits: Tmin=0.684 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.999          Theta(max)= 25.061

R(reflections)= 0.0395( 7982)     wR2(reflections)= 0.0833( 11449)

S = 1.009                 Npar= 826
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
CRYSC01_ALERT_1_C The word below has not been recognised as a standard
           identifier.
           maroon
CRYSC01_ALERT_1_C No recognised colour has been given for crystal colour.
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.2 Note
PLAT420_ALERT_2_C D-H Without Acceptor       N3       --H3       .     Please Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.596          8 Report
```

Alert level G

```
FORMU01_ALERT_1_G  There is a discrepancy between the atom counts in the
           _chemical_formula_sum and _chemical_formula_moiety. This is
           usually due to the moiety formula being in the wrong format.
           Atom count from _chemical_formula_sum:   C83.5 H68 Br1 Co1 N3
           Atom count from _chemical_formula_moiety:C167 H136 Br2 Co2 N6
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          7 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ...       0.50 Check
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.001 Degree
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          1 Report
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Br1      --Co1      .        9.0 s.u.
PLAT300_ALERT_4_G Atom Site Occupancy of C1S        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C2S        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C3S        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C4S        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C5S        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C6S        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C7S        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H7SA       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H1S        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H7SB       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H2S        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H7SC       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H3S        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H4S        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H5S        Constrained at        0.5 Check
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )       100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... Resd  2          7.50 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          3 Note
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #         15 Check
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        42 Note
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        45% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          1 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          1 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          5 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   5 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  31 ALERT level G = General information/check it is not something unexpected

   6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   6 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
  20 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

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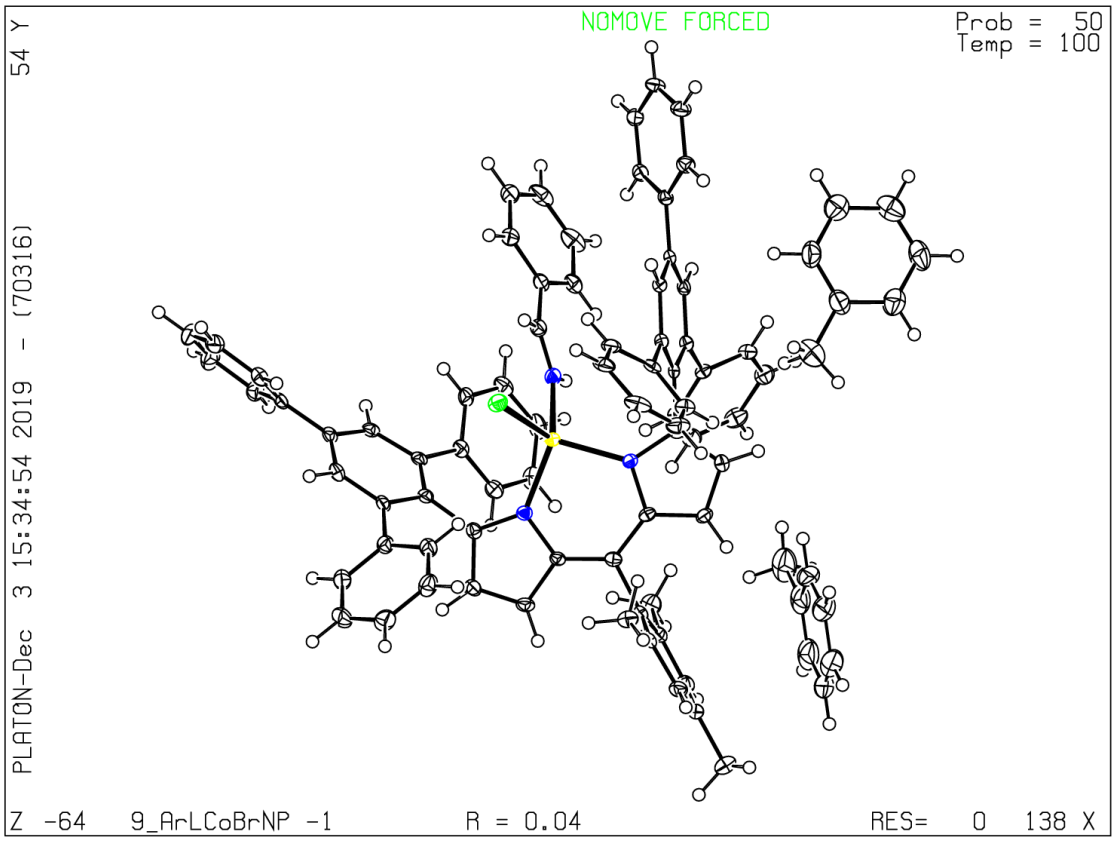
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 9_ArLCoBrNHBn - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 11_tBuLCoBr_dimer

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 11_tBuLCoBr_dimer

```
Bond precision:  C-C = 0.0051 A          Wavelength=0.71073

Cell:          a=9.8826(5)        b=10.8049(4)     c=13.3280(6)
               alpha=108.738(1)   beta=92.612(1)   gamma=112.333(1)
Temperature:   100 K
```

	Calculated	Reported
Volume	1223.60(10)	1223.60(10)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C52 H66 Br2 Co2 N4	C52H66Br2Co2N4
Sum formula	C52 H66 Br2 Co2 N4	C52 H66 Br2 Co2 N4
Mr	1024.75	1024.76
Dx,g cm-3	1.391	1.391
Z	1	1
Mu (mm-1)	2.349	2.349
F000	530.0	530.0
F000’	530.26	
h,k,lmax	11,12,15	11,12,15
Nref	4339	4306
Tmin,Tmax	0.575,0.703	0.705,0.745
Tmin’	0.550	

```
Correction method= # Reported T Limits: Tmin=0.705 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.992          Theta(max)= 25.072

R(reflections)= 0.0351( 3360)     wR2(reflections)= 0.0725( 4306)

S = 1.027                 Npar= 280
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.596         31 Report
```

Alert level G

```
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.001 Degree
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        55% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          2 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          6 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   5 ALERT level G = General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   1 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
   0 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

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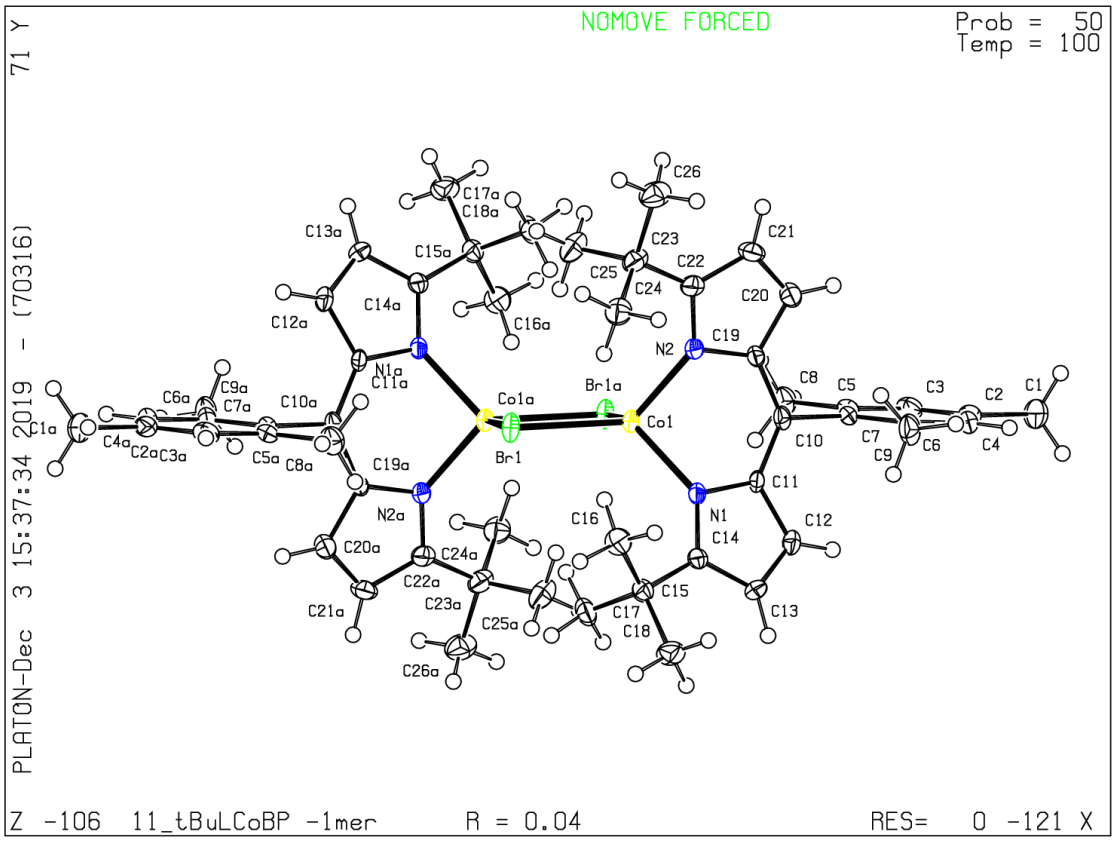
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 11_tBuLCoBr_dimer - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 12_tBuLCoBrthf

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 12_tBuLCoBrthf

```
Bond precision:  C-C = 0.0034 A          Wavelength=0.71073

Cell:          a=14.3907(10)     b=14.9859(10)    c=15.2440(11)
               alpha=92.015(1)   beta=98.561(1)   gamma=115.785(1)
Temperature:   100 K
```

	Calculated	Reported
Volume	2908.7(4)	2908.7(4)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C30 H41 Br Co N2 O	C30H4BrCoN2O
Sum formula	C30 H41 Br Co N2 O	C30 H41 Br Co N2 O
Mr	584.48	584.49
Dx,g cm-3	1.335	1.335
Z	4	4
Mu (mm-1)	1.987	1.987
F000	1220.0	1220.0
F000’	1220.58	
h,k,lmax	17,17,18	17,17,18
Nref	10281	10172
Tmin,Tmax	0.627,0.699	0.694,0.745
Tmin’	0.447	

```
Correction method= # Reported T Limits: Tmin=0.694 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.989          Theta(max)= 25.048

R(reflections)= 0.0269( 8521)     wR2(reflections)= 0.0608( 10172)

S = 1.063                 Npar= 649
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of .         47 Ang**3
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.596        110 Report
```

Alert level G

```
FORMU01_ALERT_1_G  There is a discrepancy between the atom counts in the
           _chemical_formula_sum and _chemical_formula_moiety. This is
           usually due to the moiety formula being in the wrong format.
           Atom count from _chemical_formula_sum:   C30 H41 Br1 Co1 N2 O1
           Atom count from _chemical_formula_moiety:C30 H4 Br1 Co1 N2 O1
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.001 Degree
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........          18 Note
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        72% Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         10 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   6 ALERT level G = General information/check it is not something unexpected

   3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   2 ALERT type 3 Indicator that the structure quality may be low
   1 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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Publication of your CIF in other journals

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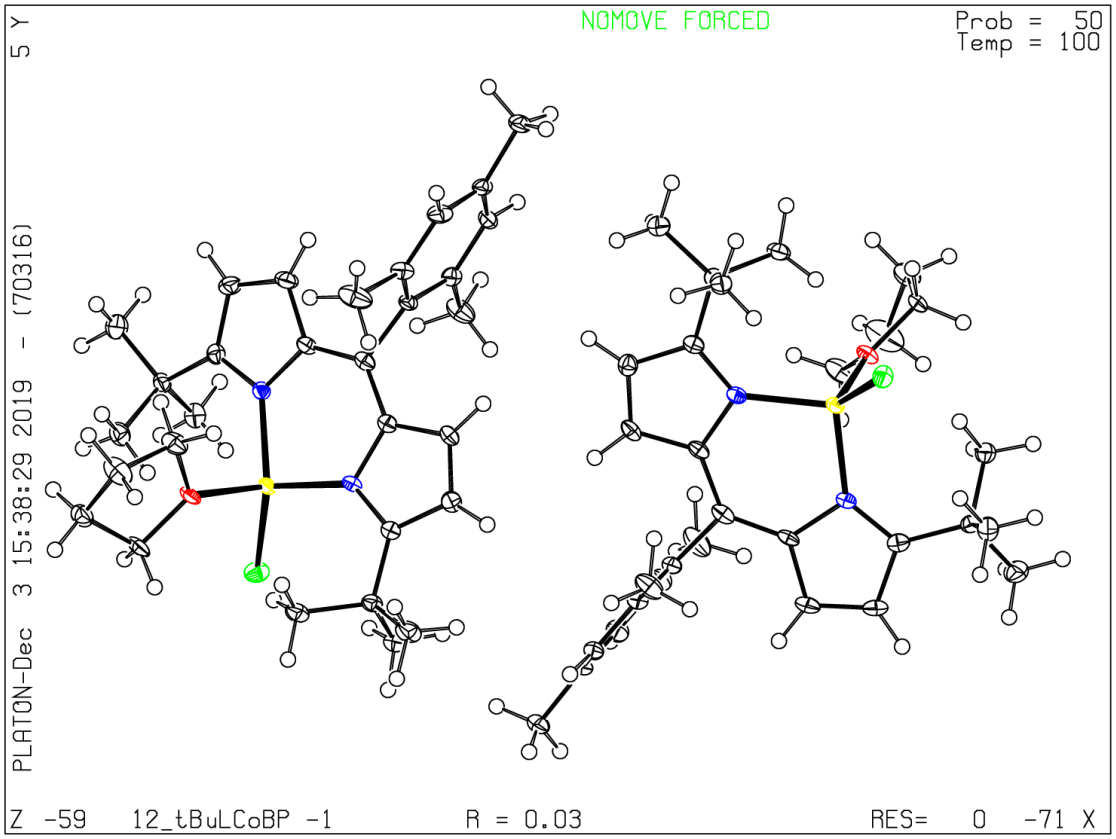
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 12_tBuLCoBrthf - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 14_tBuLCoBrtriazole

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 14_tBuLCoBrtriazole

```
Bond precision:  C-C = 0.0043 A          Wavelength=0.71073

Cell:           a=10.5174(9)    b=18.4889(16)       c=17.0030(15)
                alpha=90        beta=105.908(2)     gamma=90
Temperature:    100 K

                Calculated                Reported
Volume          3179.7(5)                 3179.7(5)
Space group     P 21/c                    P 21/c
Hall group      -P 2ybc                   -P 2ybc
Moiety formula  C32 H44 Br Co N5          C32H44BrCoN5
Sum formula     C32 H44 Br Co N5          C32 H44 Br Co N5
Mr              637.55                    637.56
Dx,g cm-3       1.332                     1.332
Z               4                         4
Mu (mm-1)       1.825                     1.825
F000            1332.0                    1332.0
F000'           1332.56
h,k,lmax        12,22,20                  12,22,20
Nref            5637                      5635
Tmin,Tmax       0.666,0.880               0.653,0.745
Tmin'           0.573

Correction method= # Reported T Limits: Tmin=0.653 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 1.000          Theta(max)= 25.045

R(reflections)= 0.0352( 4202)     wR2(reflections)= 0.0852( 5635)

S = 1.058                 Npar= 361
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....       2.38 Report
PLAT220_ALERT_2_C Non-Solvent  Resd 1  C   Ueq(max)/Ueq(min) Range        3.6 Ratio
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.596          4 Report
```

Alert level G

```
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT793_ALERT_4_G Model has Chirality at C28         (Centro SPGR)          R Verify
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        52% Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          3 Info
```

```
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   0 ALERT level B = A potentially serious problem, consider carefully
   3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
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   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
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   2 ALERT type 3 Indicator that the structure quality may be low
   1 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

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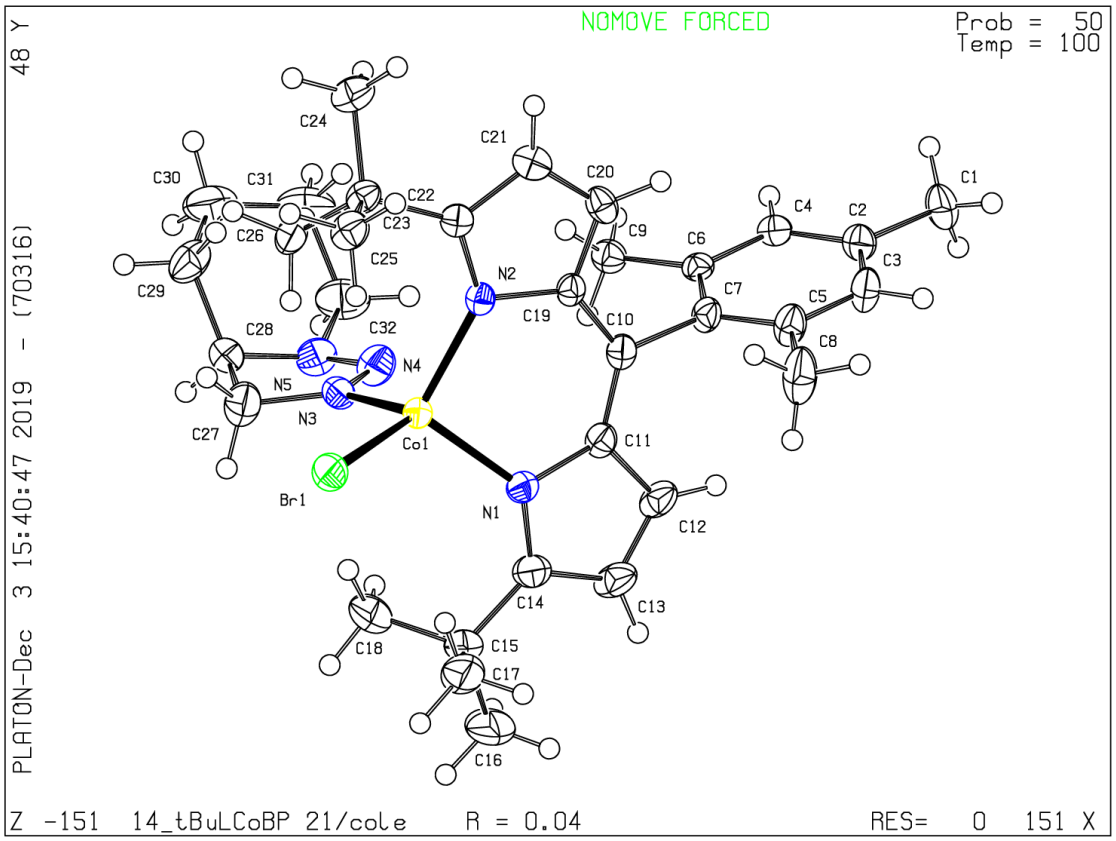
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 14_tBuLCoBrtriazole - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 16_tBuLCoBr2-phenylpyrrolidine

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 16_tBuLCoBr2-phenylpyrrolidine

```
Bond precision:  C-C = 0.0071 A          Wavelength=0.71073

Cell:          a=9.3829(7)       b=13.2694(10)    c=14.2996(11)
               alpha=67.174(2)   beta=84.707(2)   gamma=82.391(2)
Temperature:   100 K
```

	Calculated	Reported
Volume	1624.9(2)	1624.9(2)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C36 H46 Br Co N3	C36H46BrCoN3
Sum formula	C36 H46 Br Co N3	C36 H46 Br Co N3
Mr	659.59	659.60
Dx,g cm-3	1.348	1.348
Z	2	2
Mu (mm-1)	1.786	1.786
F000	690.0	690.0
F000’	690.30	
h,k,lmax	11,15,17	11,15,17
Nref	5767	5746
Tmin,Tmax	0.707,0.898	0.690,0.745
Tmin’	0.693	

```
Correction method= # Reported T Limits: Tmin=0.690 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.996          Theta(max)= 25.077

R(reflections)= 0.0546( 3735)     wR2(reflections)= 0.1210( 5746)

S = 1.014                 Npar= 383
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
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Alert level C

```
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....       2.40 Report
PLAT341_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00708 Ang.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.954 Check
PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min).         5 Note
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.596        16 Report
PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density.         0 Info
```

Alert level G

```
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.002 Degree
PLAT793_ALERT_4_G Model has Chirality at N3          (Centro SPGR)         S Verify
PLAT793_ALERT_4_G Model has Chirality at C30         (Centro SPGR)         R Verify
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        32% Note
```

```
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   0 ALERT type 5 Informative message, check
```

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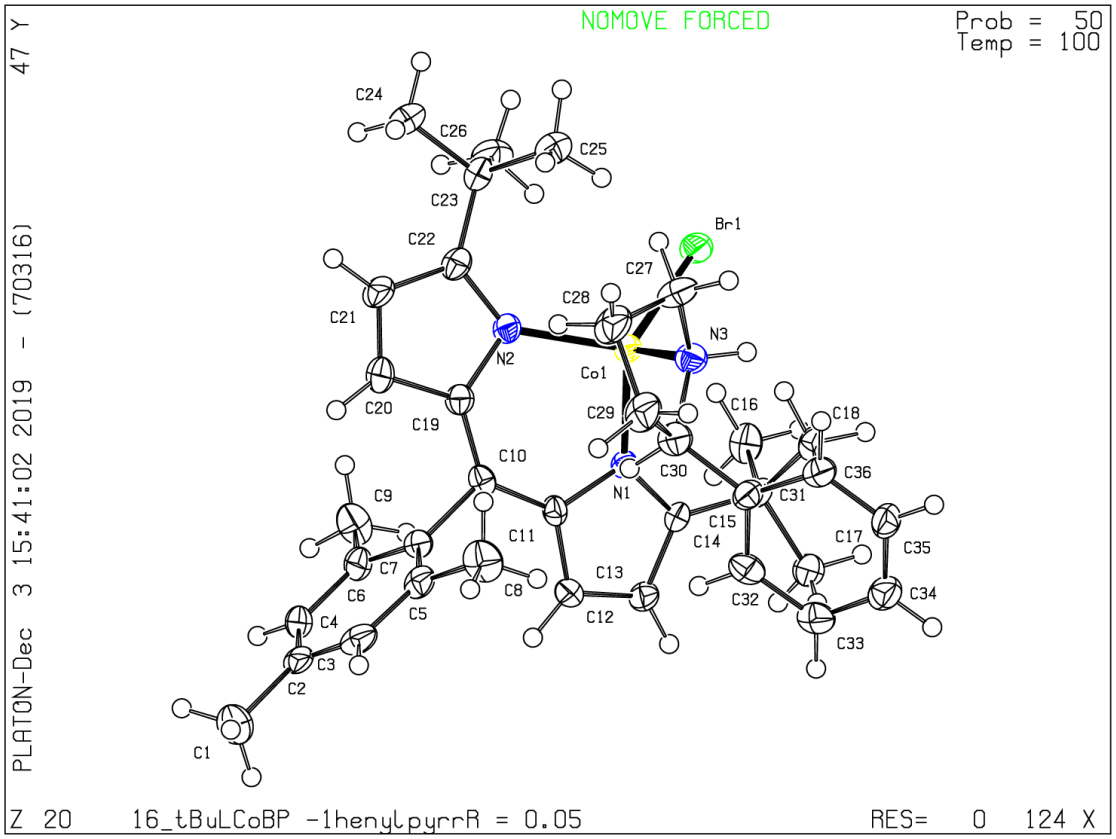
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 16_tBuLCoBr2-phenylpyrrolidine - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 18_tBuLCoCl22-dimethylpyrrolidine

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 18_tBuLCoCl22-dimethylpyrrolidine

```
Bond precision:  = 0.0000 A              Wavelength=0.71073

Cell:            a=19.6834(9)     b=8.7971(5)     c=17.5251(8)
                 alpha=90         beta=90         gamma=90
Temperature:     100 K

             Calculated      Reported
Volume       3034.6(3)       3034.6(3)
Space group  P n m a         P n m a
Hall group   -P 2ac 2n       -P 2ac 2n
Moiety       2(C16 H23 Cl0.50
formula      Co0.50 N1.50)   2(C16H23C10.50Co0.50N1.50)
Sum formula  C32 H46 Cl Co N3 C32 H46 Cl Co N3
Mr           567.10          567.10
Dx,g cm-3    1.241           1.241
Z            4               4
Mu (mm-1)    0.678           0.678
F000         1212.0          1212.0
F000'        1214.28
h,k,lmax     23,10,20        23,10,20
Nref         2887            2879
Tmin,Tmax    0.885,0.916     0.687,0.745
Tmin'        0.873

Correction method= # Reported T Limits: Tmin=0.687 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.997          Theta(max)= 25.056

R(reflections)= 0.0659( 2072)     wR2(reflections)= 0.1392( 2879)

S = 1.201                 Npar= 399
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT088_ALERT_3_B Poor Data / Parameter Ratio ..... 7.22 Note

Author Response: This structure is in a high symmetry space group (Pnma). It is full-molecule disorder along a mirror plane, and the 2,2-dimethylpyrrolidine moiety is further disorder in two positions. The restraints on bond lengths and atomic displacement parameters have been applied to improve the observed Data/Parameter ratio and stablize the model.

Alert level C

PLAT215_ALERT_3_C Disordered C10 has ADP max/min Ratio ..... 3.2 Note
PLAT220_ALERT_2_C Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 3.7 Ratio
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 8.871 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 2.576 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.596 6 Report

---

Alert level G

FORMU01_ALERT_1_G There is a discrepancy between the atom counts in the
_chemical_formula_sum and _chemical_formula_moiety. This is
usually due to the moiety formula being in the wrong format.
Atom count from _chemical_formula_sum: C32 H46 Cl1 Co1 N3
Atom count from _chemical_formula_moiety:C53 H46 Co1 N3
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 23 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 42 Report
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 2 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ Please Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 8.34 Why ?
PLAT174_ALERT_4_G The CIF-Embedded .res File Contains FLAT Records 1 Report
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records 3 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records 3 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records 1 Report
PLAT187_ALERT_4_G The CIF-Embedded .res File Contains RIGU Records 1 Report
PLAT300_ALERT_4_G Atom Site Occupancy of Co1 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Cl1 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of N1 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of N2 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C1 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C2 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C3 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C4 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C5 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C6 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C7 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C8 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C9 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C10 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C11 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C12 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C13 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C14 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C15 Constrained at 0.5 Check

```
PLAT300_ALERT_4_G Atom Site Occupancy of C16       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C17       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C21       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C22       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C23       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C24       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C25       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C26       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C27       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C28       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C29       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H3B       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H4        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H7A       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H7B       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H7C       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H8A       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H8B       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H8C       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H9A       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H9B       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H9C       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H11       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H12       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H15A      Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H15B      Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H15C      Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H16A      Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H16B      Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H16C      Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H17A      Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H17B      Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H17C      Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H23       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H25       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H27A      Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H27B      Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H27C      Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H28A      Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H28B      Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H28C      Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H29A      Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H29B      Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H29C      Constrained at       0.5 Check
PLAT301_ALERT_3_G Main Residue  Disorder .............(Resd  1  )      100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... Resd  1       41.50 Check
PLAT607_ALERT_4_G VOID Test Skipped Due to Severe Disorder .......         ! Info
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #      103 Check
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............      780 Note
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still      35% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).        2 Note
```

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
5 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
81 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

```
  4 ALERT type 2 Indicator that the structure model may be wrong or deficient
  9 ALERT type 3 Indicator that the structure quality may be low
 71 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
```

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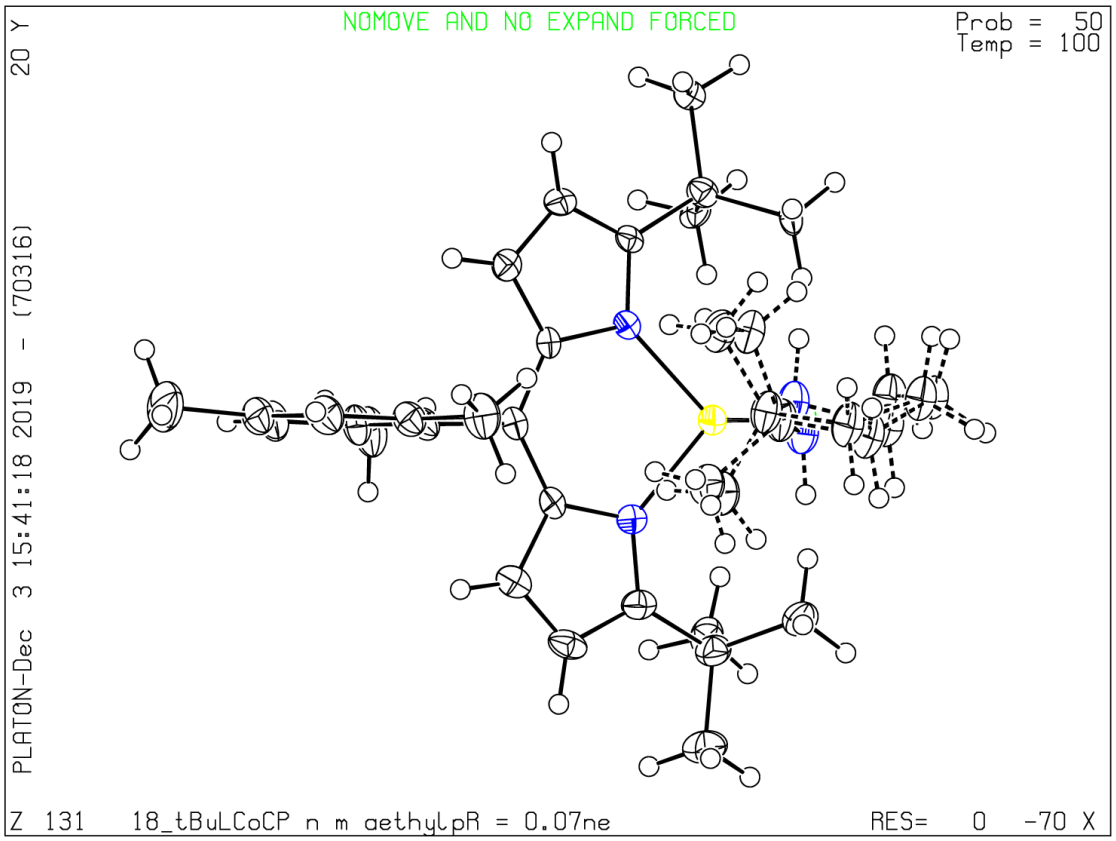
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 18_tBuLCoCl22-dimethylpyrrolidine - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 20_tBuLCoClnBu-imine

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 20_tBuLCoClnBu-imine

```
Bond precision:  C-C = 0.0064 A          Wavelength=0.71073

Cell:            a=13.892(2)    b=13.8768(18)       c=16.289(2)
                 alpha=90       beta=111.131(2)     gamma=90
Temperature:     100 K
```

	Calculated	Reported
Volume	2929.0(7)	2928.9(7)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C30 H42 Cl Co N3	C30H42ClCoN3
Sum formula	C30 H42 Cl Co N3	C30 H42 Cl Co N3
Mr	539.05	539.04
Dx,g cm-3	1.222	1.222
Z	4	4
Mu (mm-1)	0.699	0.699
F000	1148.0	1148.0
F000’	1150.26	
h,k,lmax	16,16,19	16,16,19
Nref	5193	5133
Tmin,Tmax	0.860,0.939	0.637,0.745
Tmin’	0.756	

```
Correction method= # Reported T Limits: Tmin=0.637 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.988          Theta(max)= 25.052

R(reflections)= 0.0577( 3010)     wR2(reflections)= 0.1286( 5133)

S = 0.996                 Npar= 379
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT220_ALERT_2_C NonSolvent Resd 1  C   Ueq(max) / Ueq(min) Range        3.4 Ratio
PLAT341_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00642 Ang.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      3.036 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.596         61 Report
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         16 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         12 Report
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          2 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records          2 Report
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records          1 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records          2 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          1 Report
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )        20% Note
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H17A     ..H29D     .       1.93 Ang.
                                       -1/2+x,1/2-y,-1/2+z  =      4_565 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          1 Note
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        157 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        3.2 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          0 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   4 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  14 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   5 ALERT type 2 Indicator that the structure model may be wrong or deficient
   6 ALERT type 3 Indicator that the structure quality may be low
   5 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

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Publication of your CIF in other journals

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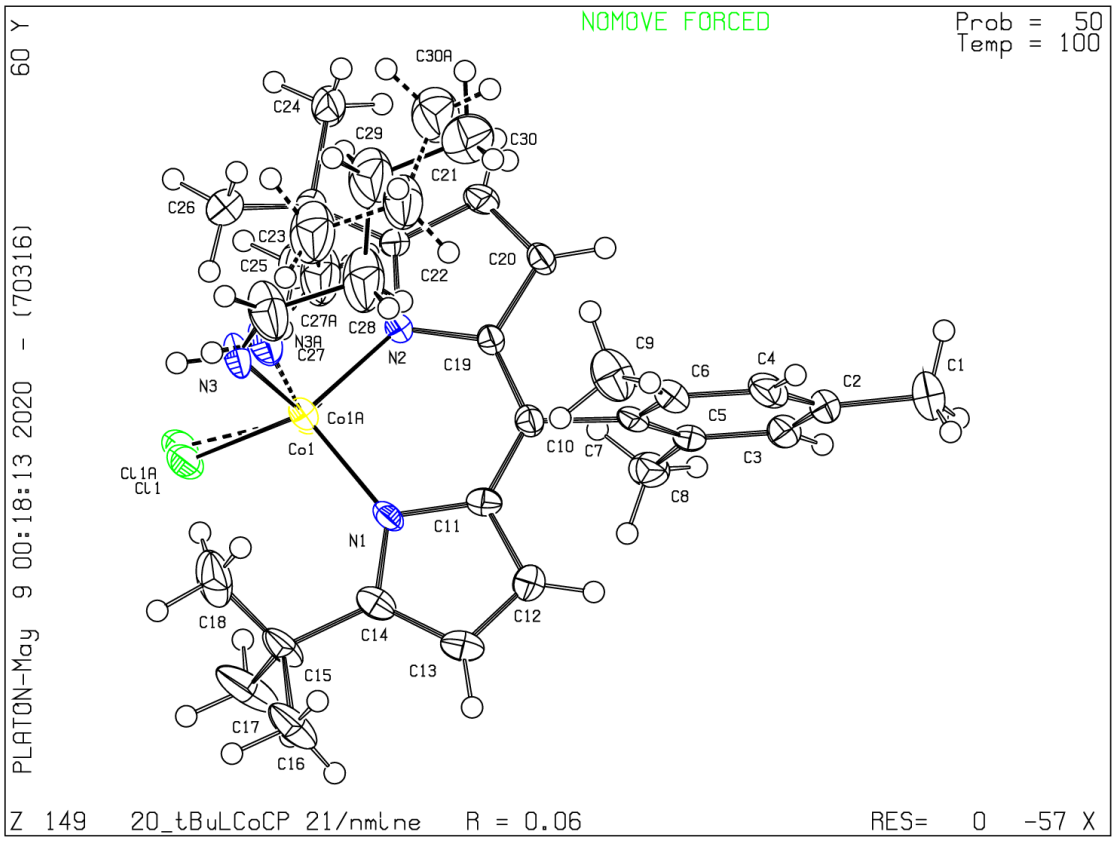
PLATON version of 22/04/2020; check.def file version of 09/03/2020

Datablock 20_tBuLCoClnBu-imine - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 21_tBuLCoClnBuNH2

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 21_tBuLCoClnBuNH2

```
Bond precision:  C-C = 0.0038 A          Wavelength=0.71073

Cell:           a=13.8661(8)    b=13.8215(9)        c=16.3606(10)
                alpha=90        beta=111.490(2)     gamma=90
Temperature:    100 K

                Calculated                Reported
Volume          2917.5(3)                 2917.5(3)
Space group     P 21/n                    P 21/n
Hall group      -P 2yn                    -P 2yn
Moiety formula  C30 H44 Cl Co N3          C30H44ClCoN3
Sum formula     C30 H44 Cl Co N3          C30 H44 Cl Co N3
Mr              541.06                    541.06
Dx,g cm-3       1.232                     1.232
Z               4                         4
Mu (mm-1)       0.702                     0.702
F000            1156.0                    1156.0
F000'           1158.26
h,k,lmax        16,16,19                  16,16,19
Nref            5208                      5194
Tmin,Tmax       0.777,0.932               0.670,0.745
Tmin'           0.704

Correction method= # Reported T Limits: Tmin=0.670 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.997          Theta(max)= 25.100

R(reflections)= 0.0442( 4011)     wR2(reflections)= 0.0810( 5194)

S = 1.083                 Npar= 373
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT220_ALERT_2_C Non-Solvent  Resd 1  C   Ueq(max)/Ueq(min) Range        3.2 Ratio
PLAT420_ALERT_2_C D-H Without Acceptor       N3       --H3B      .     Please Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      3.909 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.597         11 Report
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         11 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         10 Report
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          4 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records          1 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records          1 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          1 Report
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )        14% Note
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          2 Note
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        128 Note
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        52% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          3 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          5 Info
```

---

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1 ALERT type 5 Informative message, check

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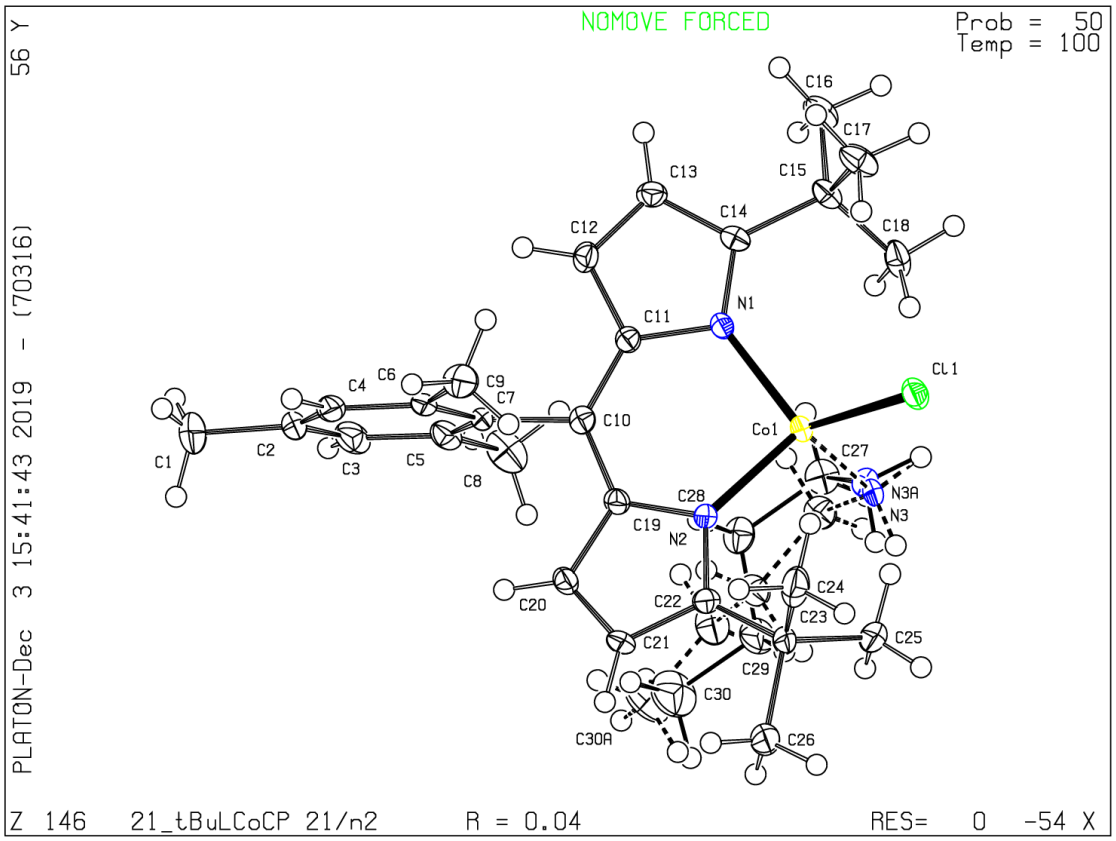
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 21_tBuLCoClnBuNH2 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 8-heat1

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 8-heat1

Bond precision: C-C = 0.0061 A Wavelength=0.71073

Cell: a=11.4915(6) b=21.4912(11) c=25.2006(13)
alpha=90 beta=99.2162(15) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	6143.4(6)	6143.4(6)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	2(C72 H62 Br Co N4.68), C6 H14	2(C72H62BrCoN4.68),C6H14
Sum formula	C150 H138 Br2 Co2 N9.36	C75 H69 Br Co N4.68
Mr	2349.40	1174.70
Dx,g cm-3	1.270	1.270
Z	2	4
Mu (mm-1)	0.977	0.977
F000	2455.0	2455.0
F000’	2456.00	
h,k,lmax	13,25,30	13,25,30
Nref	10906	10868
Tmin,Tmax	0.748,0.855	0.706,0.801
Tmin’	0.684	

Correction method= # Reported T Limits: Tmin=0.706 Tmax=0.801
AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 25.066

R(reflections)= 0.0571(7371) wR2(reflections)= 0.1622(10868)

S = 1.008 Npar= 801

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT077_ALERT_4_C Unitcell Contains Non-integer Number of Atoms ..     Please Check
PLAT220_ALERT_2_C Non-Solvent  Resd 1  C   Ueq(max)/Ueq(min) Range        3.1 Ratio
PLAT221_ALERT_2_C Solv./Anion  Resd 2  C   Ueq(max)/Ueq(min) Range        4.6 Ratio
PLAT223_ALERT_4_C Solv./Anion  Resd 2  H   Ueq(max)/Ueq(min) Range        5.8 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C26      --C27      .       0.17 Ang.
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        3.9 Note
PLAT260_ALERT_2_C Large Average Ueq of Residue Including       C1S      0.184 Check
PLAT341_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00605 Ang.
PLAT411_ALERT_2_C Short Inter H...H Contact  H17      ..H17      .       2.12 Ang.
                                              1-x,1-y,1-z  =      3_666 Check
PLAT413_ALERT_2_C Short Inter XH3 .. XHn     H26      ..H65B     .       2.14 Ang.
                                                1+x,y,z  =      1_655 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.826 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.596        35 Report
PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density.        0 Info
```

Alert level G

```
FORMU01_ALERT_1_G  There is a discrepancy between the atom counts in the
           _chemical_formula_sum and _chemical_formula_moiety. This is
           usually due to the moiety formula being in the wrong format.
           Atom count from _chemical_formula_sum:   C75 H69 Br1 Co1 N4.68
           Atom count from _chemical_formula_moiety:C150 H138 Br2 Co2 N9.36
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         20 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          6 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ...       0.50 Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large      11.75 Why ?
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records          9 Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          1 Report
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records          2 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records          2 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          1 Report
PLAT187_ALERT_4_G The CIF-Embedded .res File Contains RIGU Records          1 Report
PLAT230_ALERT_2_G Hirshfeld Test Diff for    N3       --N4       .        6.3 s.u.
PLAT300_ALERT_4_G Atom Site Occupancy of C1S        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C2S        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C3S        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C4S        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C5S        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C6S        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H1SA       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H1SB       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H1SC       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H2SA       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H2SB       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H3SA       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H3SB       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H4SA       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H4SB       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H5SA       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H5SB       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H6SA       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H6SB       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H6SC       Constrained at        0.5 Check
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )        14% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )       100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  1        140.68 Check
PLAT411_ALERT_2_G Short Inter H...H Contact  H2SB     ..H28      .       2.06 Ang.
                                       1-x,-1/2+y,3/2-z  =      2_646 Check
```

```
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H14      ..H75D     .       1.89 Ang.
                                            -x,1-y,1-z  =      3_566 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H44      ..H75F     .       1.63 Ang.
                                           1+x,1/2-y,1/2+z  =      4_666 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H1SB     ..H27      .       1.49 Ang.
                                            x,1/2-y,-1/2+z  =      4_565 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  C13      ..C75B             2.99 Ang.
                                            -x,1-y,1-z  =      3_566 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  C14      ..C75B             2.62 Ang.
                                            -x,1-y,1-z  =      3_566 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  C15      ..C75B             3.13 Ang.
                                            -x,1-y,1-z  =      3_566 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  C44      ..C75B             2.94 Ang.
                                           1+x,1/2-y,1/2+z  =      4_666 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .....          14 Note
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #      20 Check
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............     79 Note
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still     38% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).      3 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...      6 Note
```

---

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0 **ALERT level B** = A potentially serious problem, consider carefully
13 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
50 **ALERT level G** = General information/check it is not something unexpected

3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
20 ALERT type 2 Indicator that the structure model may be wrong or deficient
7 ALERT type 3 Indicator that the structure quality may be low
33 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

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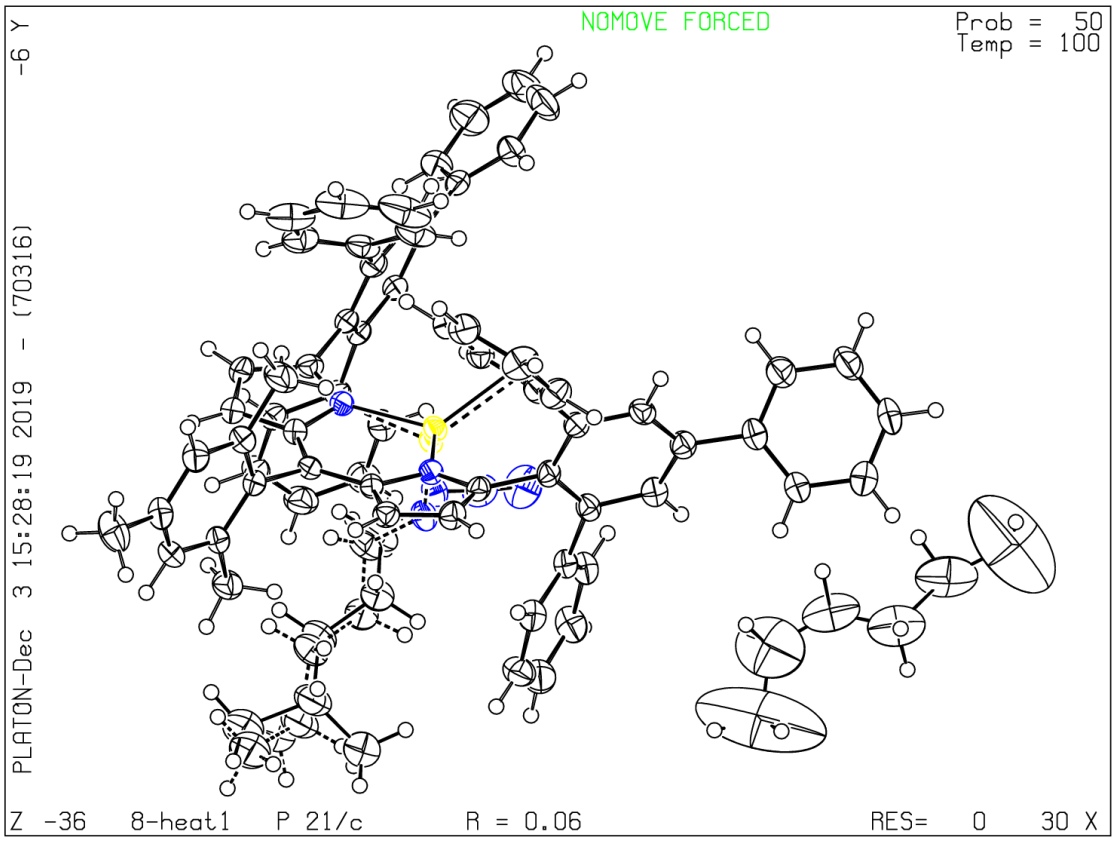
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 8-heat1 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 8-heat2

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 8-heat2

```
Bond precision:  C-C = 0.0062 A          Wavelength=0.71073

Cell:           a=11.4909(6)    b=21.4788(12)       c=25.2005(14)
                alpha=90        beta=99.2321(16)    gamma=90
Temperature:    100 K
```

	Calculated	Reported
Volume	6139.2(6)	6139.2(6)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	2(C72 H62 Br Co N4.66), C6 H14	2(C72H62BrCoN4.66),C6H14
Sum formula	C150 H138 Br2 Co2 N9.32	C75 H69 Br Co N4.66
Mr	2348.79	1174.42
Dx,g cm-3	1.271	1.271
Z	2	4
Mu (mm-1)	0.978	0.978
F000	2454.4	2454.0
F000’	2455.38	
h,k,lmax	13,25,30	13,25,30
Nref	10922	10882
Tmin,Tmax	0.747,0.855	0.678,0.801
Tmin’	0.684	

```
Correction method= # Reported T Limits: Tmin=0.678 Tmax=0.801
AbsCorr = MULTI-SCAN

Data completeness= 0.996          Theta(max)= 25.087

R(reflections)= 0.0580( 7428)     wR2(reflections)= 0.1662( 10882)

S = 1.040                 Npar= 801
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT077_ALERT_4_C Unitcell Contains Non-integer Number of Atoms ..     Please Check
PLAT221_ALERT_2_C Solv./Anion  Resd 2  C   Ueq(max)/Ueq(min) Range       4.6 Ratio
PLAT223_ALERT_4_C Solv./Anion  Resd 2  H   Ueq(max)/Ueq(min) Range       5.7 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C26      --C27      .      0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C73      --C74      .      0.17 Ang.
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....       3.8 Note
PLAT260_ALERT_2_C Large Average Ueq of Residue Including       C1S     0.188 Check
PLAT341_ALERT_3_C Low Bond Precision on  C-C Bonds ..............   0.00622 Ang.
PLAT411_ALERT_2_C Short Inter H...H Contact  H17      ..H17      .      2.11 Ang.
                                          1-x,1-y,1-z  =     3_666 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......     2.876 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.597        37 Report
PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density.         0 Info
```

Alert level G

```
FORMU01_ALERT_1_G  There is a discrepancy between the atom counts in the
           _chemical_formula_sum and _chemical_formula_moiety. This is
           usually due to the moiety formula being in the wrong format.
           Atom count from _chemical_formula_sum:   C75 H69 Br1 Co1 N4.66
           Atom count from _chemical_formula_moiety:C150 H138 Br2 Co2 N9.32
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite        20 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         6 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ    Please Check
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ...      0.50 Check
PLAT068_ALERT_1_G Reported F000 Differs from Calcd (or Missing)...    Please Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large     11.75 Why ?
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records         9 Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records         1 Report
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records         2 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records         2 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records         1 Report
PLAT187_ALERT_4_G The CIF-Embedded .res File Contains RIGU Records         1 Report
PLAT230_ALERT_2_G Hirshfeld Test Diff for    N3       --N4       .       9.8 s.u.
PLAT300_ALERT_4_G Atom Site Occupancy of C1S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C2S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C3S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C4S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C5S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C6S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H1SA       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H1SB       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H1SC       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H2SA       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H2SB       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H3SA       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H3SB       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H4SA       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H4SB       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H5SA       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H5SB       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H6SA       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H6SB       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H6SC       Constrained at       0.5 Check
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )        14% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )       100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... Resd  1        140.66 Check
PLAT411_ALERT_2_G Short Inter H...H Contact  H2SB     ..H28      .      2.05 Ang.
                                       1-x,-1/2+y,3/2-z  =     2_646 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H14      ..H75D     .      1.87 Ang.
```

```
                                                -x,1-y,1-z  =      3_566 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H21      ..H75D     .       1.99 Ang.
                                               1-x,1-y,1-z  =      3_666 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H21      ..H75F     .       1.89 Ang.
                                               1-x,1-y,1-z  =      3_666 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H44      ..H75E     .       2.04 Ang.
                                             1+x,1/2-y,1/2+z  =      4_666 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H1SB     ..H27      .       1.53 Ang.
                                              x,1/2-y,-1/2+z  =      4_565 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  C13      ..C75B             2.95 Ang.
                                                -x,1-y,1-z  =      3_566 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  C14      ..C75B             2.59 Ang.
                                                -x,1-y,1-z  =      3_566 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  C21      ..C75B             3.01 Ang.
                                               1-x,1-y,1-z  =      3_666 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  C44      ..C75B             3.02 Ang.
                                             1+x,1/2-y,1/2+z  =      4_666 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .....          14 Note
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #      20 Check
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............     79 Note
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still     38% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).      3 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...      6 Note
```

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
12 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
53 **ALERT level G** = General information/check it is not something unexpected

4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
20 ALERT type 2 Indicator that the structure model may be wrong or deficient
7 ALERT type 3 Indicator that the structure quality may be low
34 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

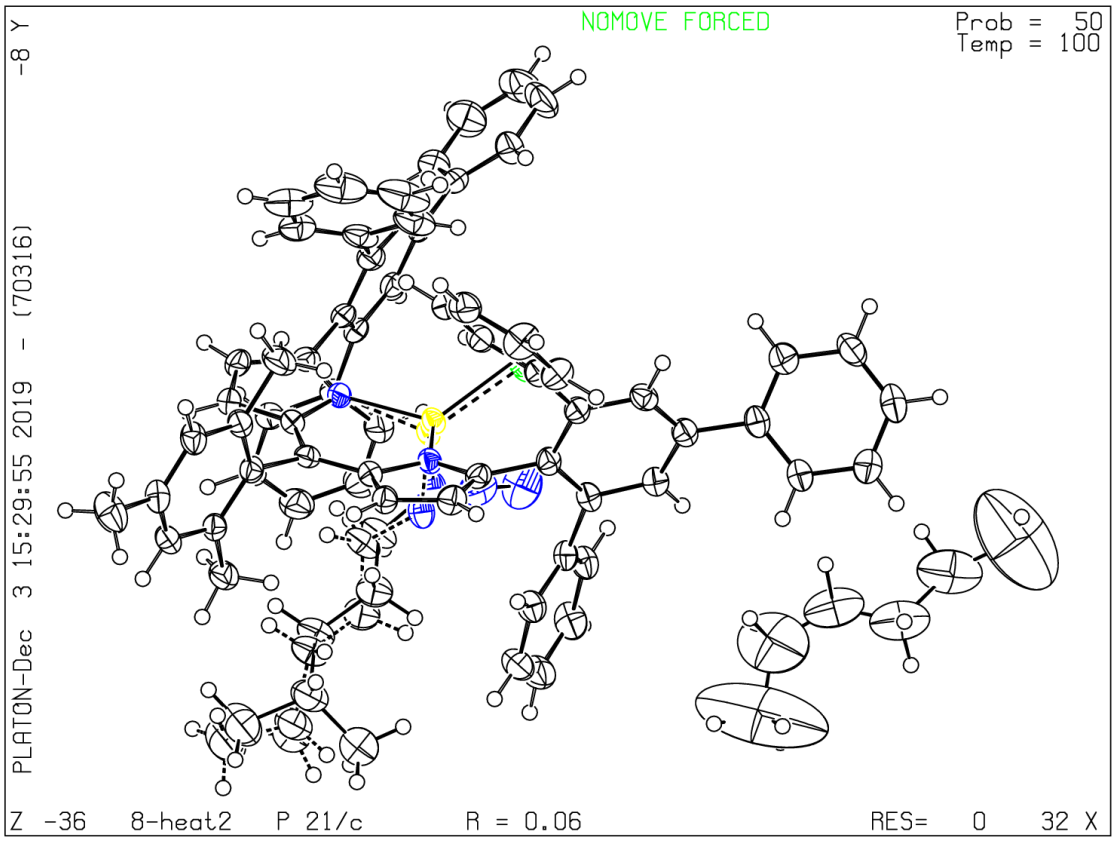
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 8-heat2 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 8-heat3

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 8-heat3

Bond precision: C-C = 0.0067 A Wavelength=0.71073

Cell: a=11.4836(7) b=21.4653(12) c=25.2099(14)
alpha=90 beta=99.2360(17) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	6133.7(6)	6133.6(6)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C72 H62 Br Co N4.62, 0.5(C6 H14)	C72H62BrCoN4.62,0.5(C6H14)
Sum formula	C75 H69 Br Co N4.62	C75 H69 Br Co N4.62
Mr	1173.92	1173.90
Dx,g cm-3	1.271	1.271
Z	4	4
Mu (mm-1)	0.979	0.979
F000	2453.5	2453.0
F000’	2454.43	
h,k,lmax	13,25,30	13,25,30
Nref	10952	10892
Tmin,Tmax	0.747,0.855	0.666,0.801
Tmin’	0.683	

Correction method= # Reported T Limits: Tmin=0.666 Tmax=0.801
AbsCorr = MULTI-SCAN

Data completeness= 0.995 Theta(max)= 25.120

R(reflections)= 0.0637(7459) wR2(reflections)= 0.1778(10892)

S = 1.106 Npar= 801

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT077_ALERT_4_C Unitcell Contains Non-integer Number of Atoms ..     Please Check
PLAT220_ALERT_2_C Non-Solvent  Resd 1  C   Ueq(max)/Ueq(min) Range       3.3 Ratio
PLAT223_ALERT_4_C Solv./Anion  Resd 2  H   Ueq(max)/Ueq(min) Range       5.0 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C26      --C27      .      0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C74      --C76      .      0.18 Ang.
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....       3.0 Note
PLAT260_ALERT_2_C Large Average Ueq of Residue Including       C1S     0.179 Check
PLAT341_ALERT_3_C Low Bond Precision on  C-C Bonds ..............   0.00673 Ang.
PLAT411_ALERT_2_C Short Inter H...H Contact  H17      ..H17      .      2.12 Ang.
                                            1-x,1-y,1-z  =     3_666 Check
PLAT413_ALERT_2_C Short Inter XH3 .. XHn     H26      ..H65B     .      2.14 Ang.
                                                1+x,y,z  =     1_655 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......     3.734 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.597        56 Report
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite        20 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         6 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ    Please Check
PLAT068_ALERT_1_G Reported F000 Differs from Calcd (or Missing)...    Please Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large     11.75 Why ?
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records         9 Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records         1 Report
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records         2 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records         2 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records         1 Report
PLAT187_ALERT_4_G The CIF-Embedded .res File Contains RIGU Records         1 Report
PLAT230_ALERT_2_G Hirshfeld Test Diff for    N3       --N4       .      10.2 s.u.
PLAT300_ALERT_4_G Atom Site Occupancy of C1S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C2S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C3S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C4S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C5S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C6S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H1SA       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H1SB       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H1SC       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H2SA       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H2SB       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H3SA       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H3SB       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H4SA       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H4SB       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H5SA       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H5SB       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H6SA       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H6SB       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H6SC       Constrained at       0.5 Check
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )        14% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )       100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  1       140.62 Check
PLAT411_ALERT_2_G Short Inter H...H Contact  H2SB     ..H28      .      2.03 Ang.
                                       1-x,-1/2+y,3/2-z  =     2_646 Check
```

```
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H21      ..H75D     .       1.75 Ang.
                                          1-x,1-y,1-z  =      3_666 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H44      ..H75E     .       1.74 Ang.
                                         1+x,1/2-y,1/2+z  =      4_666 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H44      ..H75F     .       1.73 Ang.
                                         1+x,1/2-y,1/2+z  =      4_666 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H1SB     ..H27      .       2.07 Ang.
                                          x,1/2-y,-1/2+z  =      4_565 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H1SC     ..H27      .       2.14 Ang.
                                        1-x,-1/2+y,3/2-z  =      2_646 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  C14      ..C75B             3.11 Ang.
                                             -x,1-y,1-z  =      3_566 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  C44      ..C75B             2.63 Ang.
                                         1+x,1/2-y,1/2+z  =      4_666 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .....          14 Note
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #      20 Check
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............     79 Note
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still     38% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).      3 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...      6 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.      1 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
  12 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  50 ALERT level G = General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  19 ALERT type 2 Indicator that the structure model may be wrong or deficient
   7 ALERT type 3 Indicator that the structure quality may be low
  34 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

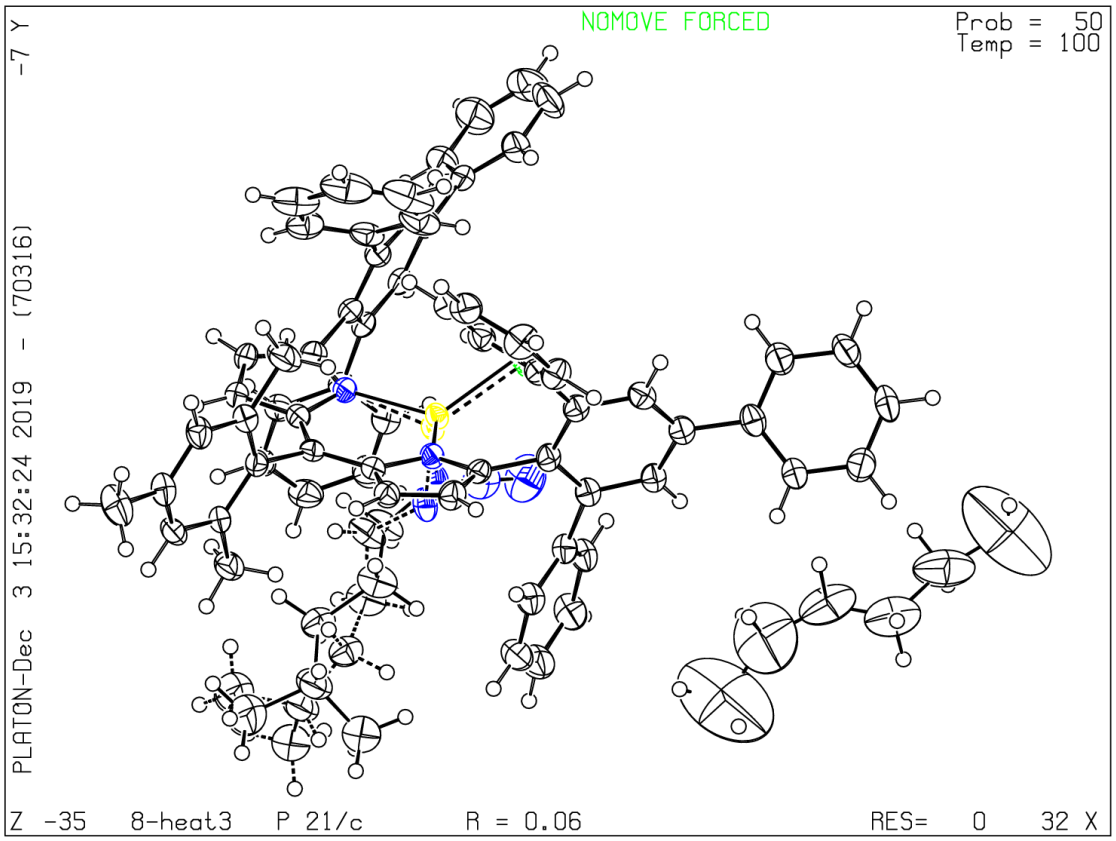
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 8-heat3 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 8-heat4

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 8-heat4

Bond precision: C-C = 0.0074 A Wavelength=0.71073

Cell: a=11.4804(7) b=21.4571(13) c=25.2287(15)
alpha=90 beta=99.2593(17) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	6133.8(6)	6133.8(6)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C72 H62 Br Co N4.60, 0.5(C6 H14)	C72H62BrCoN4.59 0.5(C6H14)
Sum formula	C75 H69 Br Co N4.60	C75 H69 Br Co N4.59
Mr	1173.53	1173.51
Dx,g cm-3	1.271	1.271
Z	4	4
Mu (mm-1)	0.979	0.979
F000	2452.7	2453.0
F000’	2453.64	
h,k,lmax	13,25,30	13,25,30
Nref	10919	10876
Tmin,Tmax	0.747,0.855	0.702,0.859
Tmin’	0.683	

Correction method= # Reported T Limits: Tmin=0.702 Tmax=0.859
AbsCorr = MULTI-SCAN

Data completeness= 0.996 Theta(max)= 25.095

R(reflections)= 0.0747(7301) wR2(reflections)= 0.1915(10876)

S = 1.165 Npar= 801

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT041_ALERT_1_C Calc. and Reported SumFormula    Strings  Differ     Please Check
PLAT077_ALERT_4_C Unitcell Contains Non-integer Number of Atoms ..     Please Check
PLAT220_ALERT_2_C Non-Solvent  Resd 1  C   Ueq(max)/Ueq(min) Range       3.8 Ratio
PLAT220_ALERT_2_C Non-Solvent  Resd 1  N   Ueq(max)/Ueq(min) Range       3.4 Ratio
PLAT223_ALERT_4_C Solv./Anion  Resd 2  H   Ueq(max)/Ueq(min) Range       4.3 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C74      --C76      .      0.19 Ang.
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....       3.7 Note
PLAT260_ALERT_2_C Large Average Ueq of Residue Including       C1S     0.188 Check
PLAT341_ALERT_3_C Low Bond Precision on  C-C Bonds ..............   0.00742 Ang.
PLAT411_ALERT_2_C Short Inter H...H Contact  H17      ..H17      .      2.10 Ang.
                                          1-x,1-y,1-z  =     3_666 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......     7.008 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......     2.295 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.597        41 Report
PLAT977_ALERT_2_C Check Negative Difference Density on H71C            -0.32 eA-3
PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density.        0 Info
```

Alert level G

```
FORMU01_ALERT_1_G  There is a discrepancy between the atom counts in the
           _chemical_formula_sum and _chemical_formula_moiety. This is
           usually due to the moiety formula being in the wrong format.
           Atom count from _chemical_formula_sum:   C75 H69 Br1 Co1 N4.59
           Atom count from _chemical_formula_moiety:C78 H76 Br1 Co1 N40590.50
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite        20 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         6 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT068_ALERT_1_G Reported F000 Differs from Calcd (or Missing)...     Please Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large      11.75 Why ?
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records         9 Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records         1 Report
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records         2 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records         2 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records         1 Report
PLAT186_ALERT_4_G The CIF-Embedded .res File Contains ISOR Records         1 Report
PLAT187_ALERT_4_G The CIF-Embedded .res File Contains RIGU Records         1 Report
PLAT230_ALERT_2_G Hirshfeld Test Diff for    N3       --N4       .      12.8 s.u.
PLAT300_ALERT_4_G Atom Site Occupancy of C1S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C2S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C3S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C4S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C5S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C6S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H1SA       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H1SB       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H1SC       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H2SA       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H2SB       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H3SA       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H3SB       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H4SA       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H4SB       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H5SA       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H5SB       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H6SA       Constrained at       0.5 Check
```

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PLAT300_ALERT_4_G Atom Site Occupancy of H6SB       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H6SC       Constrained at        0.5 Check
PLAT301_ALERT_3_G Main Residue  Disorder .............(Resd  1  )        13% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )       100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... Resd  1        140.60 Check
PLAT411_ALERT_2_G Short Inter H...H Contact  H2SB     ..H28      .       2.04 Ang.
                                          1-x,-1/2+y,3/2-z  =      2_646 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H14      ..H75D     .       1.75 Ang.
                                              -x,1-y,1-z  =      3_566 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H44      ..H75F     .       1.83 Ang.
                                            1+x,1/2-y,1/2+z  =      4_666 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H1SB     ..H27      .       1.57 Ang.
                                             x,1/2-y,-1/2+z  =      4_565 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  C13      ..C75B             2.85 Ang.
                                              -x,1-y,1-z  =      3_566 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  C14      ..C75B             2.47 Ang.
                                              -x,1-y,1-z  =      3_566 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  C15      ..C75B             3.08 Ang.
                                              -x,1-y,1-z  =      3_566 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  C44      ..C75B             3.01 Ang.
                                            1+x,1/2-y,1/2+z  =      4_666 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .....         14 Note
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #         20 Check
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............       115 Note
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still       39% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          3 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          6 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
  15 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  51 ALERT level G = General information/check it is not something unexpected

   4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  20 ALERT type 2 Indicator that the structure model may be wrong or deficient
   8 ALERT type 3 Indicator that the structure quality may be low
  34 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

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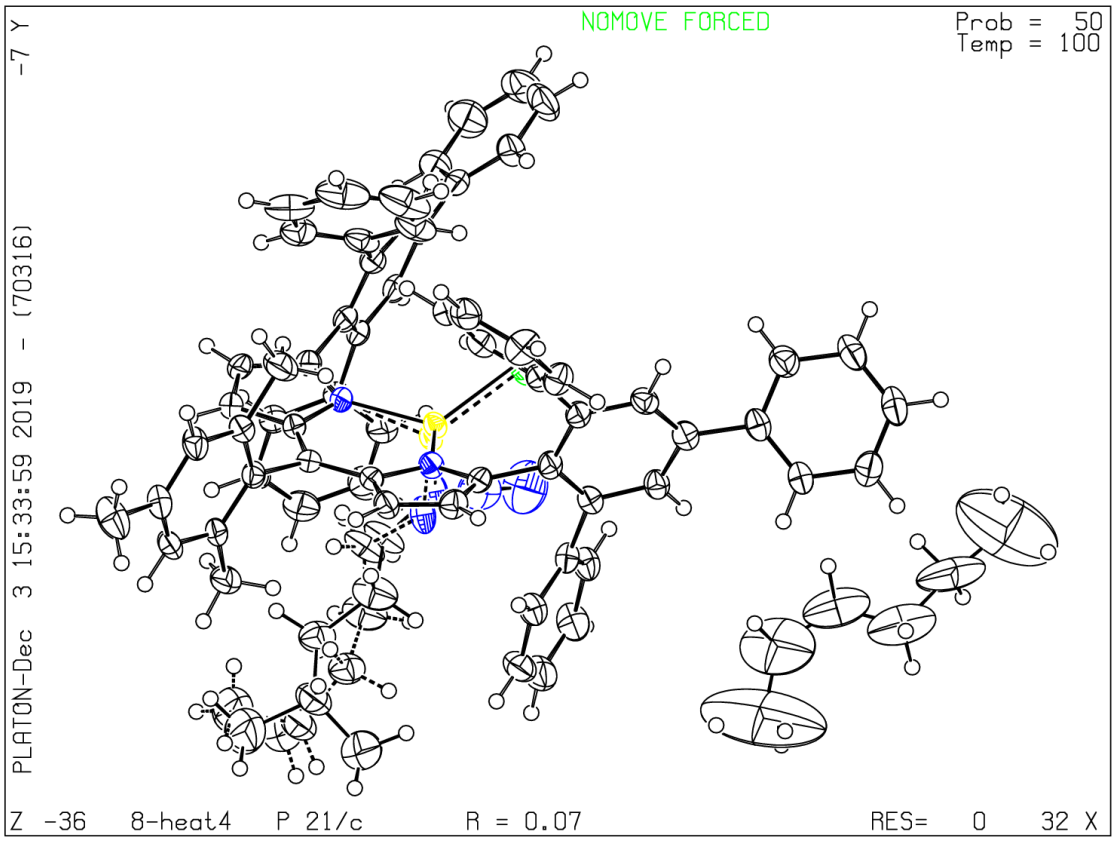
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 8-heat4 - ellipsoid plot



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 7_start

```
Bond precision:  C-C = 0.0088 A          Wavelength=0.41328

Cell:          a=11.725(3)       b=12.350(3)       c=22.789(5)
               alpha=87.920(4)   beta=89.927(13)   gamma=72.544(5)
Temperature:   100 K
```

	Calculated	Reported
Volume	3145.7(13)	3145.7(13)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C76 H62 Br Co N5, 0.5(C6 H6)	C76 H62 Br Co N5, C3 H3
Sum formula	C79 H65 Br Co N5	C79 H65 Br Co N5
Mr	1223.19	1223.20
Dx,g cm-3	1.291	1.291
Z	2	2
Mu (mm-1)	0.234	0.515
F000	1272.0	1272.0
F000’	1272.78	
h,k,lmax	14,15,28	14,15,28
Nref	13592	12428
Tmin,Tmax		0.617,0.744
Tmin’		

```
Correction method= # Reported T Limits: Tmin=0.617 Tmax=0.744
AbsCorr = MULTI-SCAN

Data completeness= 0.914          Theta(max)= 15.251

R(reflections)= 0.0863( 8871)     wR2(reflections)= 0.2485( 12428)

S = 1.049                 Npar= 779
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full value Low . 0.939 Why?

Author Response: Data was collected at a synchrotron source as a series of phi scans and this is the completeness that was obtained by this acquisition sequence. The geometry of the experiment (cryostat, LED fiber optic, detector, and beam path) prevented acquisition of omega scans.

Alert level C

RINTA01_ALERT_3_C The value of Rint is greater than 0.12
Rint given 0.138
PLAT020_ALERT_3_C The Value of Rint is Greater Than 0.12 ..... 0.138 Report
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0088 Ang.

Alert level G

ABSMU01_ALERT_1_G Calculation of _exptl_absorpt_correction_mu
not performed for this radiation type.
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ Please Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 14.35 Why ?
PLAT092_ALERT_4_G Check: Wavelength Given is not Cu,Ga,Mo,Ag,In Ka 0.41328 Ang.
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 3 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT984_ALERT_1_G The Br-f'= 0.2880 Deviates from the B&C-Value 0.2863 Check
PLAT985_ALERT_1_G The Br-f"= 0.9627 Deviates from the B&C-Value 0.9639 Check
PLAT985_ALERT_1_G The Co-f"= 0.3155 Deviates from the B&C-Value 0.3559 Check

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Publication of your CIF in other journals

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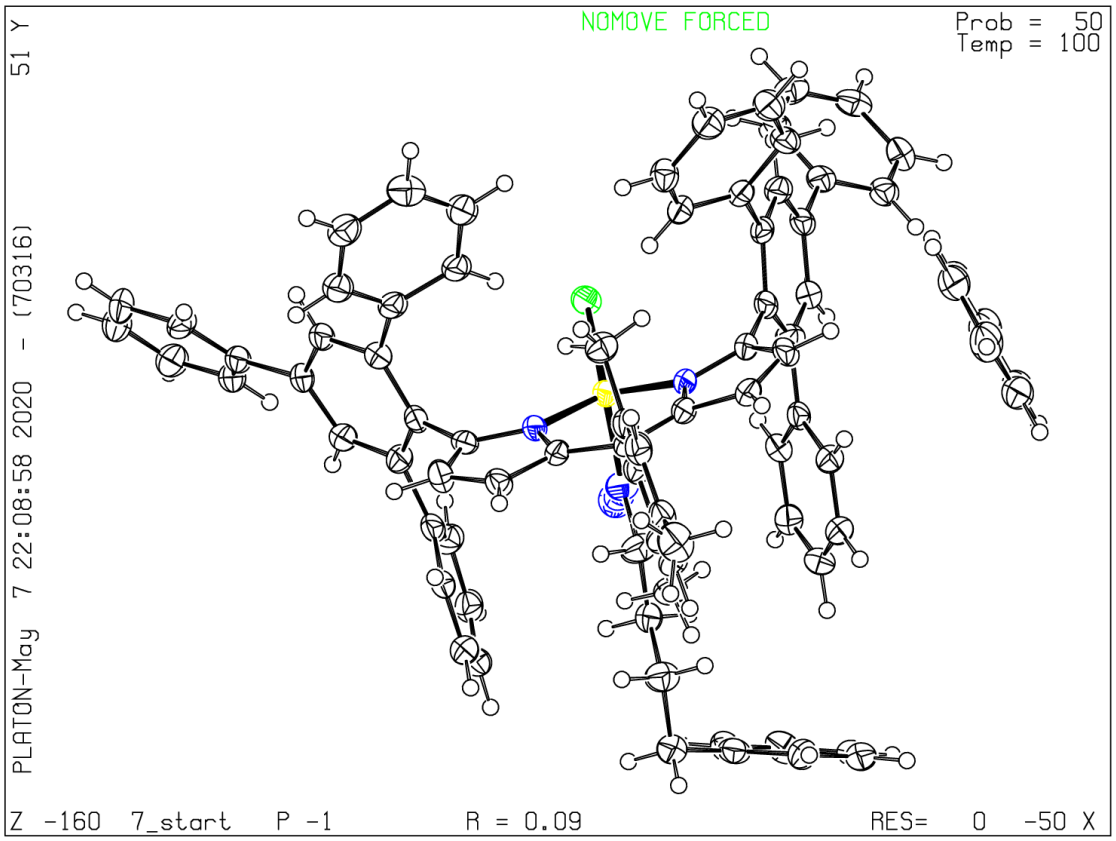
PLATON version of 22/04/2020; check.def file version of 09/03/2020

Datablock 7_start - ellipsoid plot



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 7-N2

Bond precision: C-C = 0.0050 A Wavelength=0.41328

Cell: a=11.866(3) b=12.306(3) c=22.704(5)
alpha=87.988(4) beta=89.482(4) gamma=72.256(4)
Temperature: 100 K

	Calculated	Reported
Volume	3155.6(13)	3155.6(11)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C76 H62 Br Co N3.62, 0.5(C6 H6), 0.572(N2)	C76 H62 Br Co N3.63, 0.57(N2), C3 H3
Sum formula	C79 H65 Br Co N4.77	C79 H65 Br Co N4.77
Mr	1219.94	1219.97
Dx,g cm-3	1.284	1.284
Z	2	2
Mu (mm-1)	0.233	0.954
F000	1268.8	1269.0
F000’	1269.53	
h,k,lmax	14,15,28	14,15,28
Nref	13237	12235
Tmin,Tmax		0.617,0.744
Tmin’		

Correction method= # Reported T Limits: Tmin=0.617 Tmax=0.744
AbsCorr = MULTI-SCAN

Data completeness= 0.924 Theta(max)= 15.104

R(reflections)= 0.0536(8997) wR2(reflections)= 0.1511(12235)

S = 1.022 Npar= 889

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full value Low . 0.936 Why?

Author Response: Data was collected at a synchrotron source as a series of phi scans and this is the completeness that was obtained by this acquisition sequence. The geometry of the experiment (cryostat, LED fiber optic, detector, and beam path) prevented acquisition of omega scans.

Alert level C

PLAT077_ALERT_4_C Unitcell Contains Non-integer Number of Atoms .. Please Check
PLAT220_ALERT_2_C NonSolvent Resd 1 C Ueq(max) / Ueq(min) Range 3.2 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C1_2 --C2_2 . 0.16 Ang.

Alert level G

ABSMU01_ALERT_1_G Calculation of _exptl_absorpt_correction_mu
not performed for this radiation type.
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 23 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 23 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ Please Check
PLAT092_ALERT_4_G Check: Wavelength Given is not Cu,Ga,Mo,Ag,In Ka 0.41328 Ang.
PLAT152_ALERT_1_G The Supplied and Calc. Volume s.u. Differ by ... 2 Units
PLAT154_ALERT_1_G The s.u.’s on the Cell Angles are Equal ..(Note) 0.004 Degree
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records 3 Report
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records 1 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records 1 Report
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records 3 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records 3 Report
PLAT230_ALERT_2_G Hirshfeld Test Diff for N1A --C1_2 . 5.2 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Br1 --Co1 . 10.3 s.u.
PLAT301_ALERT_3_G Main Residue Disorder .....(Resd 1) 13% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd 3) 100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd 1) 143.62 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd 3) 1.14 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 42 Note
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 174 Note
PLAT984_ALERT_1_G The Br-f’= 0.2880 Deviates from the B&C-Value 0.2863 Check
PLAT985_ALERT_1_G The Br-f"= 0.9627 Deviates from the B&C-Value 0.9639 Check
PLAT985_ALERT_1_G The Co-f"= 0.3155 Deviates from the B&C-Value 0.3559 Check

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3 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
23 **ALERT level G** = General information/check it is not something unexpected

7 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
5 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
12 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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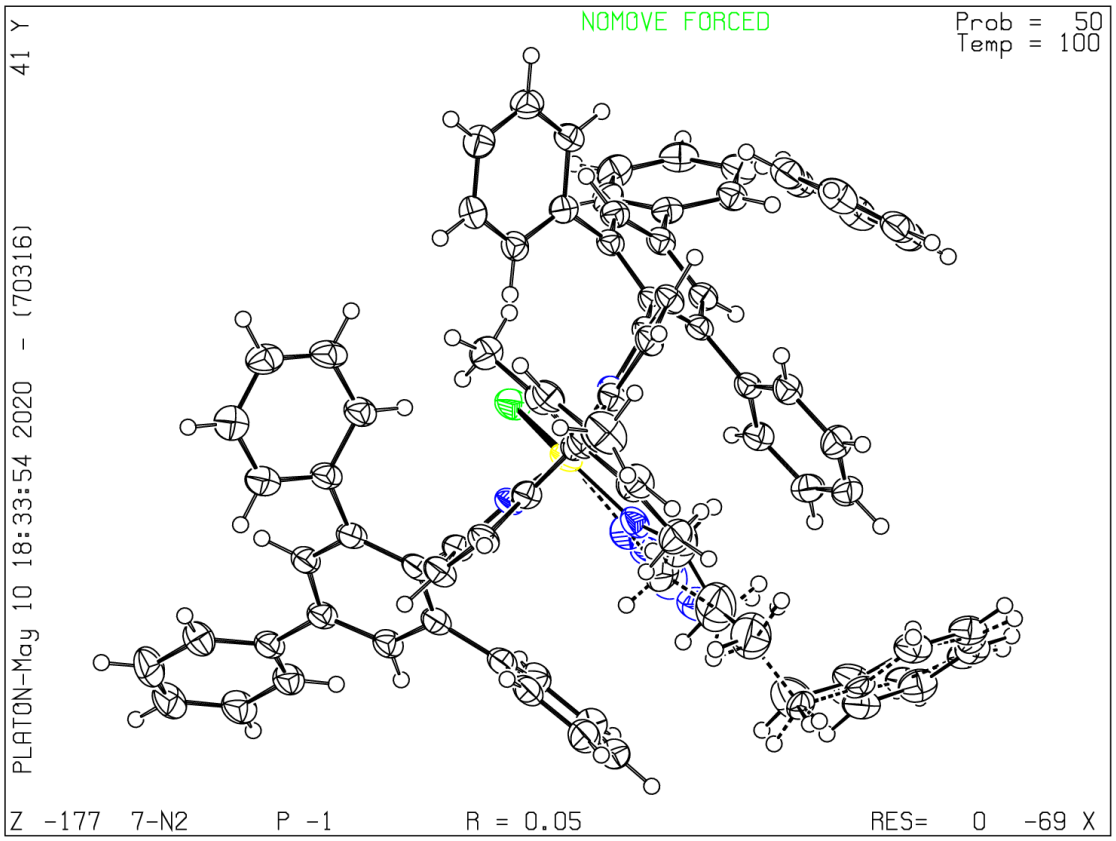
PLATON version of 22/04/2020; check.def file version of 09/03/2020

Datablock 7-N2 - ellipsoid plot



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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 8_start

```
Bond precision:  C-C = 0.0051 A          Wavelength=0.41328

Cell:            a=11.4854(11)     b=21.580(2)        c=25.393(3)
                 alpha=90          beta=98.729(2)     gamma=90
Temperature:     100 K
```

	Calculated	Reported
Volume	6220.9(11)	6220.8(10)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C72 H62 Br Co N5 [+ solvent]	C72 H62 Br Co N5
Sum formula	C72 H62 Br Co N5 [+ solvent]	C72 H62 Br Co N5
Mr	1136.10	1136.10
Dx,g cm-3	1.213	1.213
Z	4	4
Mu (mm-1)	0.234	0.963
F000	2364.0	2364.0
F000’	2365.58	
h,k,lmax	14,27,31	14,26,31
Nref	12994	12277
Tmin,Tmax		0.701,0.736
Tmin’		

```
Correction method= # Reported T Limits: Tmin=0.701 Tmax=0.736
AbsCorr = MULTI-SCAN

Data completeness= 0.945          Theta(max)= 15.080

R(reflections)= 0.0546( 9027)     wR2(reflections)= 0.1630( 12277)

S = 1.043                 Npar= 717
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full value Low . 0.953 Why?

Author Response: Data was collected at a synchrotron source as a series of phi scans and this is the completeness that was obtained by this acquisition sequence. The geometry of the experiment (cryostat, LED fiber optic, detector, and beam path) prevented acquisition of omega scans.

Alert level C

PLAT220_ALERT_2_C NonSolvent Resd 1 C Ueq(max) / Ueq(min) Range 6.0 Ratio
PLAT222_ALERT_3_C NonSolvent Resd 1 H Uiso(max)/Uiso(min) Range 7.0 Ratio
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C3 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C4 Check
PLAT360_ALERT_2_C Short C(sp3)-C(sp3) Bond C4 - C6 . 1.38 Ang.
PLAT411_ALERT_2_C Short Inter H...H Contact H68 ..H68 . 2.13 Ang.
1-x,1-y,1-z = 3_666 Check

Alert level G

ABSMU01_ALERT_1_G Calculation of _exptl_absorpt_correction_mu
not performed for this radiation type.
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 10 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 6 Report
PLAT092_ALERT_4_G Check: Wavelength Given is not Cu,Ga,Mo,Ag,In Ka 0.41328 Ang.
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records 5 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records 1 Report
PLAT187_ALERT_4_G The CIF-Embedded .res File Contains RIGU Records 1 Report
PLAT606_ALERT_4_G VERY LARGE Solvent Accessible VOID(S) in Structure ! Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 44 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ... 1 Note
PLAT984_ALERT_1_G The Br-f'= 0.2880 Deviates from the B&C-Value 0.2863 Check
PLAT985_ALERT_1_G The Br-f"= 0.9627 Deviates from the B&C-Value 0.9639 Check
PLAT985_ALERT_1_G The Co-f"= 0.3155 Deviates from the B&C-Value 0.3559 Check

---

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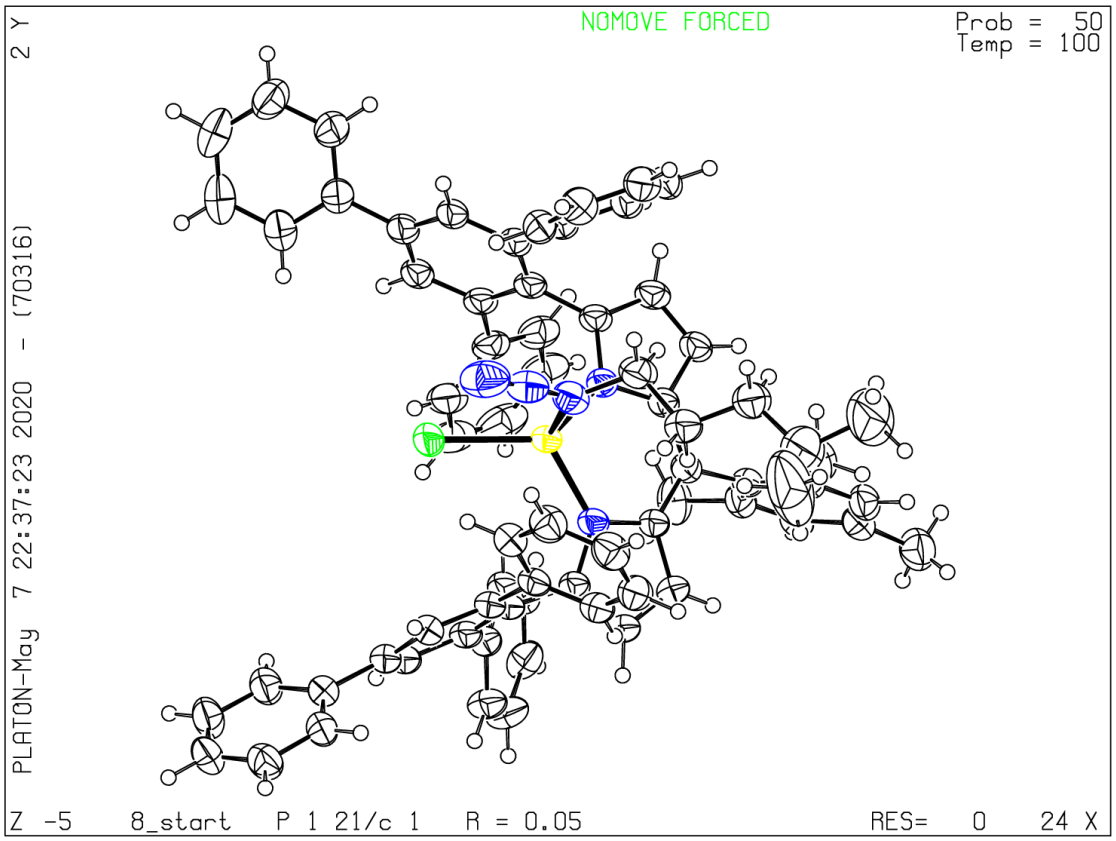
Datablock 8_start - ellipsoid plot



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 8-N2

Bond precision: C-C = 0.0047 A Wavelength=0.41328

Cell: a=11.4265(9) b=21.5332(18) c=25.652(2)
alpha=90 beta=98.6512(17) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	6239.8(9)	6239.9(9)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C72 H62 Br Co N3.69, 0.22(N2) [+ solvent]	C72 H62 Br Co N3.69, 0.22(N2)
Sum formula	C72 H62 Br Co N4.13 [+ solvent]	C72 H62 Br Co N4.08
Mr	1123.91	1123.25
Dx,g cm-3	1.196	1.196
Z	4	4
Mu (mm-1)	0.233	0.959
F000	2339.6	2338.0
F000’	2341.24	
h,k,lmax	14,27,32	13,26,31
Nref	12936	12257
Tmin,Tmax		0.703,0.744
Tmin’		

Correction method= # Reported T Limits: Tmin=0.703 Tmax=0.744
AbsCorr = MULTI-SCAN

Data completeness= 0.948 Theta(max)= 15.039

R(reflections)= 0.0518(9409) wR2(reflections)= 0.1471(12257)

S = 1.017 Npar= 803

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full value Low . 0.952 Why?

Author Response: Data was collected at a synchrotron source as a series of phi scans and this is the completeness that was obtained by this acquisition sequence. The geometry of the experiment (cryostat, LED fiber optic, detector, and beam path) prevented acquisition of omega scans.

Alert level C

PLAT077_ALERT_4_C Unitcell Contains Non-integer Number of Atoms .. Please Check
PLAT220_ALERT_2_C NonSolvent Resd 1 C Ueq(max) / Ueq(min) Range 5.5 Ratio
PLAT222_ALERT_3_C NonSolvent Resd 1 H Uiso(max)/Uiso(min) Range 6.2 Ratio
PLAT260_ALERT_2_C Large Average Ueq of Residue Including N1N 0.173 Check

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Alert level G

FORMU01_ALERT_1_G There is a discrepancy between the atom counts in the
_chemical_formula_sum and _chemical_formula_moiety. This is
usually due to the moiety formula being in the wrong format.
Atom count from _chemical_formula_sum: C72 H62 Br1 Co1 N4.08
Atom count from _chemical_formula_moiety:C72 H62 Br1 Co1 N4.13
FORMU01_ALERT_2_G There is a discrepancy between the atom counts in the
_chemical_formula_sum and the formula from the _atom_site* data.
Atom count from _chemical_formula_sum:C72 H62 Br1 Co1 N4.08
Atom count from the _atom_site data: C72 H62 Br1 Co1 N4.13
ABSMU01_ALERT_1_G Calculation of _exptl_absorpt_correction_mu
not performed for this radiation type.
CELLZ01_ALERT_1_G Difference between formula and atom_site contents detected.
CELLZ01_ALERT_1_G ALERT: check formula stoichiometry or atom site occupancies.
From the CIF: _cell_formula_units_Z 4
From the CIF: _chemical_formula_sum C72 H62 Br Co N4.08
TEST: Compare cell contents of formula and atom_site data

atom	Z*formula	cif sites	diff
C	288.00	288.00	0.00
H	248.00	248.00	0.00
Br	4.00	4.00	0.00
Co	4.00	4.00	0.00
N	16.32	16.52	-0.20

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 18 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 17 Report
PLAT041_ALERT_1_G Calc. and Reported SumFormula Strings Differ Please Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 5.32 Why ?
PLAT092_ALERT_4_G Check: Wavelength Given is not Cu,Ga,Mo,Ag,In Ka 0.41328 Ang.
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records 4 Report
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records 1 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records 1 Report
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records 2 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records 3 Report
PLAT301_ALERT_3_G Main Residue Disorder .....(Resd 1) 10% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd 2) 100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd 1) 139.69 Check

```
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  2  )       0.44 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H6A_2    ..H43B     .       2.14 Ang.
                                              x,1/2-y,1/2+z  =      4_566 Check
PLAT431_ALERT_2_G Short Inter HL..A Contact  Br1      ..N2N      .       3.16 Ang.
                                             x,y,z  =      1_555 Check
PLAT606_ALERT_4_G VERY LARGE Solvent Accessible VOID(S) in Structure        ! Info
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........          38 Note
PLAT860_ALERT_3_G Number of Least-Squares Restraints ............        117 Note
PLAT984_ALERT_1_G The Br-f'=    0.2880 Deviates from the B&C-Value     0.2863 Check
PLAT985_ALERT_1_G The Br-f"=    0.9627 Deviates from the B&C-Value     0.9639 Check
PLAT985_ALERT_1_G The Co-f"=    0.3155 Deviates from the B&C-Value     0.3559 Check
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   1 ALERT level B = A potentially serious problem, consider carefully
   4 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  27 ALERT level G = General information/check it is not something unexpected

   8 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   8 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
  12 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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