Supporting Information For:

Synthesis of a Cobalt(IV) Ketimide with a Squashed Tetrahedral Geometry

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Experimental

General. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions under an atmosphere of nitrogen or argon. THF, hexane, diethyl ether and toluene were dried using a Vacuum Atmospheres DRI-SOLV solvent purification system. C_6D_6, DME, and 12-crown-4 were dried over activated 4Å molecular sieves for 24 h before use. $Li(N=C^tBu_2)$[1] was synthesized according to the previously reported procedures, while all other reagents were purchased from commercial suppliers and used as received.

^1H, $^{13}C\{^1H\}$, and $^7Li\{^1H\}$ NMR spectra were recorded on a Varian UNITY INOVA 400 or Varian UNITY INOVA 500 spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra are referenced to external $SiMe_4$ using the residual protio solvent peaks as internal standards (^1H NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). $^7Li\{^1H\}$ NMR spectra were referenced to external LiCl in D_2O. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer with a NXR FT Raman Module. while UV-vis/NIR experiments were performed on a UV-3600 Shimadzu spectrophotometer. GC/MS analyses were performed with a Hewlett Packard 5970B GC/MSD. Elemental analyses were performed by the Microanalytical Laboratory at UC Berkeley.

Cyclic Voltammetry Measurements. CV experiments were performed with a CH Instruments 600c Potentiostat, and the data were processed using CHI software (version 6.29). All experiments were performed in a glove box using a 20 mL glass vial as the cell. The working electrode consisted of a platinum disk embedded in glass (2 mm

diameter), the counter electrode was a platinum wire, and the reference electrode consisted of AgCl plated on Ag wire. Solutions employed during CV studies were typically 1 mM in the metal complex and 0.1 M in $[Bu_4N][PF_6]$. All potentials are reported versus the $[Cp_2Fe]^{0/+}$ couple. For all trials, $i_{p,a}/i_{p,c} = 1$ for the $[Cp_2Fe]^{0/+}$ couple, while $i_{p,c}$ increased linearly with the square root of the scan rate (i.e. $\sqrt{\nu}$).

Magnetism Measurements. Magnetism data were recorded using a Quantum Design MPMS 5XL SQUID magnetometer. Complexes **1**, **2**, **3**, and **4** were analyzed using 30-55 mg of powdered crystalline material loaded into a NMR tube, which was subsequently flame sealed. The solid was kept in place with ~45 mg quartz wool packed on either side of the sample. The data was corrected for the contribution of the NMR tube holder and 90 mg of quartz wool. Data for complex **1-4** were collected using a 1 T field between 4 K and 300K. Diamagnetic corrections ($\chi_{dia} = -5.79 \times 10^{-4}$ cm^3·mol^{-1} for **1**, $\chi_{dia} = -4.72 \times 10^{-4}$ cm^3·mol^{-1} for **2**, $\chi_{dia} = -6.97 \times 10^{-4}$ cm^3·mol^{-1} for **3**, $\chi_{dia} = -4.68 \times 10^{-4}$ cm^3·mol^{-1} for **4**) were made using Pascal's constants.[2]

$[Li(THF)]_2[Co(N=C(^tBu)_2)_4]$ (1). To a white suspension of $Li(N=C^tBu_2)$ (638.4 mg, 4.34 mmol) in THF (5 mL) was added $CoCl_2$ (139.4 mg, 1.07 mmol). The solution immediately turned orange-red. This solution was allowed to stir for 1 h, whereupon the solvent was removed in vacuo and Et_2O (5 mL) was added to the resulting green solid. This solution was filtered through a Celite column supported on glass wool (0.5 cm × 2 cm) and the volume of the solution was reduced in vacuo to 2 mL. Storage at -25 °C for 24 h resulted in the deposition of green crystals, which were isolated by decanting off the supernatant (568.4 mg, 68 % yield). Anal. Calcd for $CoN_4C_{44}H_{88}O_2Li_2$: C, 67.93; H, 11.40; N, 7.20. Found: C, 67.85; H, 11.24; N, 7.41. ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): δ

27.2 (br s, **2**), 17.6 (br s, **1**), 1.29 (LiN=C^{t}Bu$_2$). ^{1}H NMR (THF-d_8, -66 °C, 500 MHz): δ 33.8 (br s, **2**). ^{7}Li{^{1}H} NMR (THF-d_8, -66 °C, 500 MHz): δ 304 (br s, **1**), 2.4 (s, LiN=C^{t}Bu$_2$), -159 (br s, **2**). ^{1}H NMR (THF-d_8, -57 °C, 500 MHz): δ 31.7 (br s, **2**), 21.3 (v br s, **1**). ^{7}Li{^{1}H} NMR (THF-d_8, -57 °C, 500 MHz): δ 286 (br s, **1**), 2.4 (s, LiN=C^{t}Bu$_2$), -146 (br s, **2**). ^{1}H NMR (THF-d_8, -40 °C, 500 MHz): δ 28.6 (br s, **2**), 21.5 (br s, **1**). ^{7}Li{^{1}H} NMR (THF-d_8, -40 °C, 500 MHz): δ 254 (br s, **1**), 2.4 (s, LiN=C^{t}Bu$_2$), -131 (br s, **2**). ^{1}H NMR (THF-d_8, -24 °C, 500 MHz): δ 26.5 (br s, **2**), 20.2 (br s, **1**). ^{7}Li{^{1}H} NMR (THF-d_8, -24 °C, 500 MHz): δ 229 (br s, **1**), 2.4 (s, LiN=C^{t}Bu$_2$), -119 (br s, **2**). ^{1}H NMR (THF-d_8, 8 °C, 500 MHz): δ 23.4 (br s, **2**), 18.0 (br s, **1**). ^{7}Li{^{1}H} NMR (THF-d_8, 8 °C, 500 MHz): δ 186 (br s, **1**), 2.4 (s, LiN=C^{t}Bu$_2$), -92 (br s, **2**). ^{1}H NMR (THF-d_8, 23 °C, 500 MHz): δ 22.4 (br s, **2**), 17.1 (br s, **1**). ^{7}Li{^{1}H} NMR (THF-d_8, 23 °C, 500 MHz): δ 169 (br s, **1**), 2.4 (s, LiN=C^{t}Bu$_2$), -76 (br s, **2**). ^{1}H NMR (THF-d_8, 33 °C, 500 MHz): δ 21.8 (br s, **2**), 16.6 (br s, **1**). ^{7}Li{^{1}H} NMR (THF-d_8, 33 °C, 500 MHz): δ 158 (br s, **1**), 2.4 (s, LiN=C^{t}Bu$_2$), -64 (br s, **2**). ^{1}H NMR (THF-d_8, 46 °C, 500 MHz): δ 21.1 (br s, **2**), 15.9 (br s, **1**). ^{7}Li{^{1}H} NMR (THF-d_8, 46 °C, 500 MHz): δ 144 (br s, **1**), 2.4 (s, LiN=C^{t}Bu$_2$), -48 (br s, **2**). UV-Vis (C_4H_8O, 2.78 × 10^{-4} M): 522 nm (ε = 2887 L·mol^{-1}·cm^{-1}) IR (hexane, cm^{-1}): 1640(s), 1620(s), 1610(s) (N=C).

[Li(12-crown-4)][Co(N=C^{t}Bu$_2$)$_3$] (2). To a white suspension of Li(N=C^{t}Bu$_2$) (469.3 mg, 3.19 mmol) in THF (3 mL) was added $CoCl_2$ (136.2 mg, 1.05 mmol). The solution immediately turned red-orange. This solution was allowed to stir for 2 h, whereupon the solvent was removed in vacuo and Et_2O (5 mL) was added to the resulting red-orange oil. This solution was filtered through a Celite column supported on glass wool (0.5 cm × 2 cm) and the volume of the solution was reduced in vacuo to 1 mL. This solution was

subsequently layered with a solution of 12-crown-4 (196.2 mg, 1.11 mmol) in hexanes (5 mL). Storage at -25 °C for 24 h resulted in the formation of yellow-green crystals, which were isolated by decanting off the supernatant (639.3 mg, 91% Yield). Anal. Calcd for $CoN_3C_{35}H_{70}O_4Li$: C, 63.42; H, 10.64; N, 6.34. Found: C, 62.93; H, 10.45; N, 6.00. ^{1}H NMR (Et_2O, 25 °C, 500 MHz): δ 27.2 (br s). ^{7}Li{^{1}H} NMR (Et_2O, 25 °C, 500 MHz): δ 226.6 (br s). ^{1}H NMR (DME, 25 °C, 500 MHz): δ 24.6 (br s). ^{7}Li{^{1}H} NMR (DME, 25 °C, 500 MHz): δ -293 (br s). ^{1}H NMR (THF-d_8, -57 °C, 500 MHz): δ 32.0 (br s), 3.4 (br s, 12-crown-4). ^{7}Li{^{1}H} NMR (THF-d_8, -57 °C, 500 MHz): δ -147 (br s). ^{1}H NMR (THF-d_8, -35 °C, 500 MHz): δ 28.6 (br s), 3.4 (br s, 12-crown-4). ^{7}Li{^{1}H} NMR (THF-d_8, -35 °C, 500 MHz): δ -128 (br s). ^{1}H NMR (THF-d_8, -15 °C, 500 MHz): δ 26.0 (br s), 3.7 (br s, 12-crown-4), 3.5 (s, 12-crown-4). ^{7}Li{^{1}H} NMR (THF-d_8, -15 °C, 500 MHz): δ -113 (br s). ^{1}H NMR (THF-d_8, 5 °C, 500 MHz): δ 23.9 (br s), 4.2 (br s, 12-crown-4), 3.5 (s, 12-crown-4). ^{7}Li{^{1}H} NMR (THF-d_8, 5 °C, 500 MHz): δ -96 (br s). ^{1}H NMR (THF-d_8, 23 °C, 500 MHz): δ 22.6 (br s), 4.9 (br s, 12-crown-4), 3.6 (s, 12-crown-4). ^{7}Li{^{1}H} NMR (THF-d_8, 23 °C, 500 MHz): δ -75 (br s). ^{1}H NMR (THF-d_8, 29 °C, 500 MHz): δ 22.3 (br s), 5.1 (br s, 12-crown-4), 3.6 (s, 12-crown-4). ^{7}Li{^{1}H} NMR (THF-d_8, 29 °C, 500 MHz): δ -69 (br s). ^{1}H NMR (THF-d_8, 38 °C, 500 MHz): δ 21.7 (br s), 5.6 (br s, 12-crown-4), 3.6 (s, 12-crown-4). ^{7}Li{^{1}H} NMR (THF-d_8, 38 °C, 500 MHz): δ -56 (br s). ^{1}H NMR (THF-d_8, 46 °C, 500 MHz): δ 21.3 (br s), 6.0 (br s, 12-crown-4), 3.6 (s, 12-crown-4). ^{7}Li{^{1}H} NMR (THF-d_8, 46 °C, 500 MHz): δ -46 (br s). UV-Vis ($C_4H_{10}O$, 2.16×10^{-4} M): 490 nm (ε = 2243 $L \cdot mol^{-1} \cdot cm^{-1}$). IR ($Et_2O$, cm^{-1}): 1640(s), 1620(s), 1600(s) (N=C).

[Li(12-crown-4)$_2$][Co(N=C^{t}Bu$_2$)$_4$] (3). To an orange solution of [Li(THF)]$_2$[Co(N=C^{t}Bu$_2$)$_4$] (278.6 mg, 0.36 mmol) in Et_2O (2 mL) was added a solution of I_2 (45.4 mg, 0.18 mmol) in Et_2O (3 mL). The solution immediately turned deep blue. The reaction was allowed to stir for 30 min whereupon DME (1 mL) was added. This resulted in the deposition of $LiI(DME)_2$ as a white solid. Storage at -25 °C for 24 h resulted in the further deposition of white solid. The solution was then filtered through a Celite column supported on glass wool (0.5 cm × 2 cm). A solution of 12-crown-4 (126.9 mg, 0.72 mmol) in pentane (3 mL) was added to the filtrate. Storage at -25 °C for 24 h resulted in the deposition of a dark blue solid, which was isolated by decanting off the supernatant (180.0 mg, 51 % yield). Anal. Calcd for $CoN_4C_{52}H_{104}O_8Li$: C, 63.78; H, 10.70; N, 5.72. Found: C, 63.41; H, 10.93; N, 5.6. ^{1}H NMR (pyridine-d_5, 25 °C, 500 MHz): δ 29.0 (br s), 19.3 (br s), 3.65 (12-crown-4). ^{7}Li{^{1}H} NMR (pyridine-d_5, 25 °C, 500 MHz): δ 391 (br s), 2.4 (br s). ^{1}H NMR (pyridine-d_5, -35 °C, 500 MHz): δ 35.9 (br s), 25.9 (br s), 3.6 (br s, 12-crown-4). ^{7}Li{^{1}H} NMR (pyridine-d_5, -35 °C, 500 MHz): δ 511 (br s), 4 (br s). ^{1}H NMR (pyridine-d_5, -25 °C, 500 MHz): δ 34.8, 24.8 (br s), 3.6 (br s, 12-crown-4) ^{7}Li{^{1}H} NMR (pyridine-d_5, -25 °C, 500 MHz): δ 493 (br s), 4 (br s). ^{1}H NMR (pyridine-d_5, -9 °C, 500 MHz): δ 33.2 (br s), 23.2 (br s), 3.6 (br s, 12-crown-4) ^{7}Li{^{1}H} NMR (pyridine-d_5, -9 °C, 500 MHz): δ 459 (br s), 4 (br s). ^{1}H NMR (pyridine-d_5, 23 °C, 500 MHz): δ 30.3 (br s), 20.7 (br s), 3.6 (br s, 12-crown-4) ^{7}Li{^{1}H} NMR (pyridine-d_5, 23 °C, 500 MHz): δ 391 (br s), 3 (br s). ^{1}H NMR (pyridine-d_5, 34 °C, 500 MHz): δ 29.5 (br s), 20.0 (br s), 3.6 (br s, 12-crown-4). ^{7}Li{^{1}H} NMR (pyridine-d_5, 34 °C, 500 MHz): δ 369 (br s), 3 (br s). ^{1}H NMR (pyridine-d_5, 41 °C, 500 MHz): δ 28.9 (br s), 19.6 (br s), 3.6 (br s, 12-crown-4) ^{7}Li{^{1}H} NMR (pyridine-d_5, 41 °C, 500 MHz): δ

356 (br s), 4 (br s). ^{1}H NMR (pyridine-d_5, 47 °C, 500 MHz): δ 28.5 (br s), 19.3 (br s), 3.6 (br s, 12-crown-4). ^{7}Li{^{1}H} NMR (pyridine-d_5, 47 °C, 500 MHz): δ 342 (br s), 4 (br s). ^{1}H NMR (pyridine-d_5, 53 °C, 500 MHz): δ 28.0 (br s), 18.9 (br s), 3.6 (br s, 12-crown-4). ^{7}Li{^{1}H} NMR (pyridine-d_5, 53 °C, 500 MHz): δ 3 (br s). UV-Vis ($C_4H_{10}O$, 1.25×10^{-4} M): 328 nm (ε = 10210 L·mol^{-1}·cm^{-1}), 555 nm (ε = 3197 L·mol^{-1}·cm^{-1}). IR (KBr, cm^{-1}): 1650(s), 1620(s) (N=C).

Co(N=C^{t}Bu$_2$)$_4$ (4). To an orange solution of **1** (298.5 mg, 3.84 mmol) in Et_2O (4 mL) was added a solution of I_2 (96.8 mg, 3.81 mmol) dissolved in Et_2O (2 mL). The solution immediately turned dark blue. After stirring for 30 min the solution was stored at -25 °C for 24 h, resulting in the deposition of dark blue crystals. These were isolated by decanting off the supernatant (199.9 mg, 85 % yield). Anal. Calcd for $CoN_4C_{36}H_{72}$: C, 69.75; H, 11.71; N, 9.04. Found: C, 69.60; H, 12.02; N, 9.01. ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): δ 41.2 (br s, Me). UV-Vis (C_7H_8, 4.76×10^{-5} M): 336 nm (ε = 16143 L·mol^{-1}·cm^{-1}), 561 nm (ε = 5721 L·mol^{-1}·cm^{-1}). IR (KBr, cm^{-1}): 1650(s), 1600(s) (N=C).

X-ray Crystallography. Data for **1**, **2**, **3**, and **4** were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromater with a Mo Kα X-ray source (α = 0.71073 Å). The crystals of **1**, **2**, **3** and **4** were mounted on a cryoloop under Paratone-N oil, and all data were collected at 100(2) K using an Oxford nitrogen gas cryostream system. A hemisphere of data was collected using ω scans with 0.5º frame widths. Frame exposures of 20, 25, 10, and 40, seconds were used for **1**, **2**, **3**, and **4** respectively. Data collection and cell parameter determination were conducted using the SMART program.[3] Integration of the data frames and final cell parameter refinement were performed using SAINT software.[4]

Absorption correction of the data for **1**, **2**, **3**, and **4** was carried out using the multi-scan method SADABS.[5] Subsequent calculations were carried out using SHELXTL.[6] Structure determination was done using direct or Patterson methods and difference Fourier techniques. All hydrogen atom positions were idealized and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[6]

Further crystallographic details for complexes **1**-**4** can be found in Table S1.

Table S1. Crystallographic details for complexes **1-4**

	1	**2**	**3**	**4**
empirical formula	$CoN_4C_{44}H_{88}O_2Li_2$	$CoN_3C_{35}H_{70}O_4Li$	$CoN_4C_{52}H_{104}O_8Li$	$CoN_4C_{36}H_{72}$
Crystal habit, color	Block, Green	Block, Yellow	Block, Black	Block, Blue
crystal size (mm)	0.20 × 0.10 × 0.05	0.20 × 0.10 × 0.10	0.30 × 0.20 × 0.20	0.40 × 0.15 × 0.02
crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
space group	$P2_1/n$	P-1	P-1	P-1
vol ($Å^3$)	4664.3(11)	1895.4(3)	2877.23(15)	1924.4(3)
a (Å)	12.4875(18)	10.8516(11)	13.5073(4)	11.3082(9)
b (Å)	19.709(2)	13.2752(14)	13.5432(4)	11.5753(10)
c (Å)	19.089(3)	13.4533(12)	16.3252(5)	16.4021(14)
α (deg)	90.00	82.003(6)	88.668(2)	70.220(3)
β (deg)	96.876(7)	87.087(7)	74.519(2)	78.481(3)
γ (deg)	90.00	81.136(7)	89.944(2)	73.509(3)
Z	4	2	2	2
fw (g/mol)	777.99	662.81	979.26	619.91
Density (calcd) (Mg/m^3)	1.108	1.161	1.130	1.070
abs coeff (mm^{-1})	0.405	0.490	0.349	0.473
F_{000}	1716	726	1076	686
Total no. reflections	33023	14057	31151	31564
Unique reflections	6736	6577	14294	6849
R_{int}	0.0557	0.0711	0.0350	0.0703
final R indices [$I > 2\sigma(I)$]	R1 = 0.0498	R1 = 0.0500	R1 = 0.0512	R1 = 0.0610
	wR2 = 0.1520	wR2 = 0.1481	wR2 = 0.1599	wR2 = 0.1755
largest diff peak and hole ($e^- Å^{-3}$)	0.769, -0.520	0.288, -0.363	1.292, -0.227	1.544, -0.482
GOF	0.989	0.810	0.959	0.977

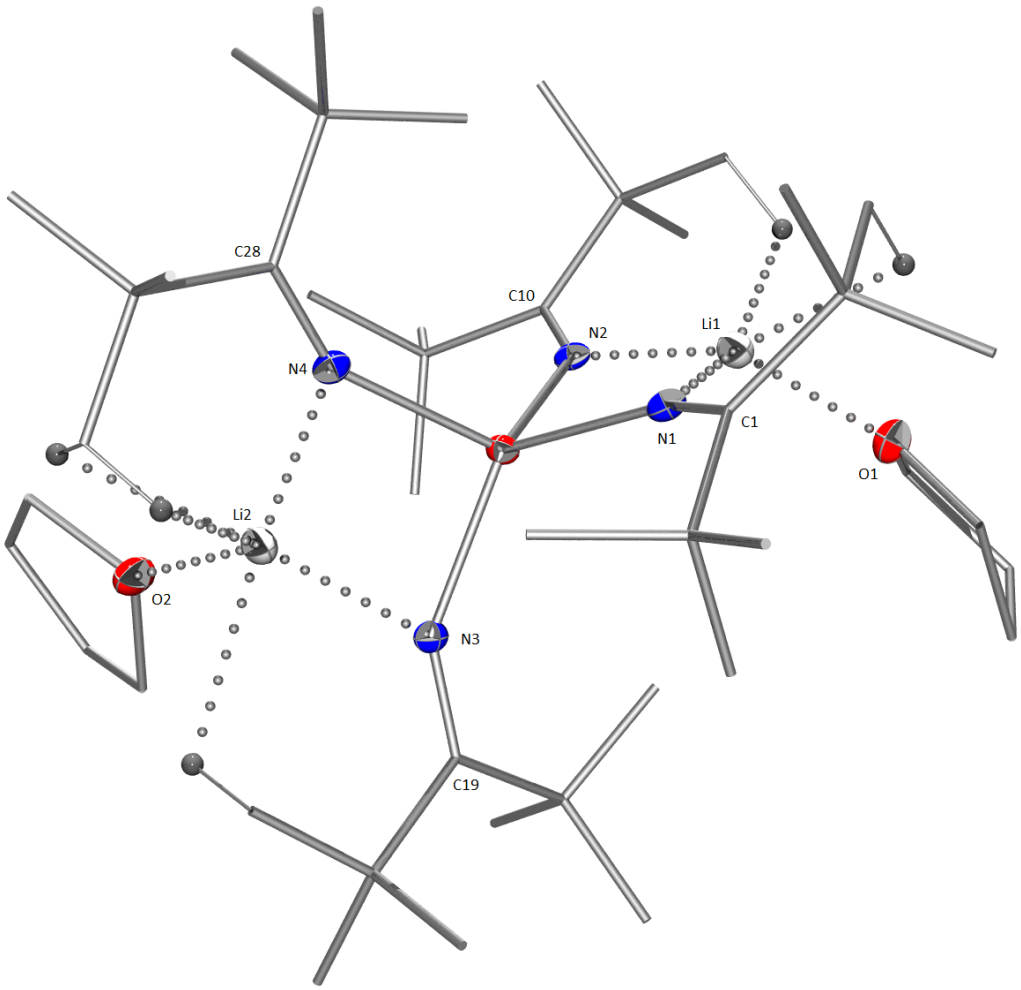


Figure S1. Solid state molecular structure of $[Li(THF)]_2[Co(N=C^tBu_2)_4]$ (**1**) with 40% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Co1 – N1 = 2.021(2), Co1 – N2 = 2.006(2), N1 – Co1 – N2 = 94.47(10), N1 – Co1 – N3 = 117.78(9), Co1 – N1 – C1 = 148.1(2), Co1 – N2 – C10 = 145.4(2).

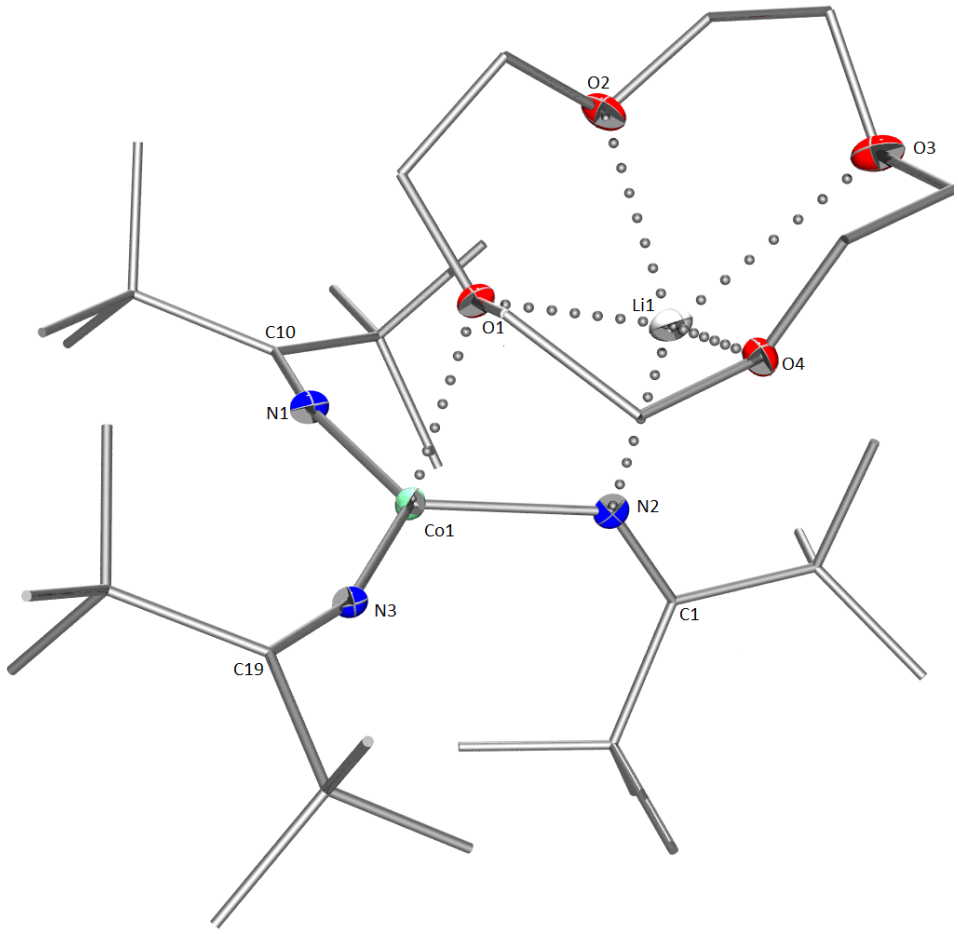


Figure S2. Solid state molecular structure of [Li(12-crown-4)][Co(N=C^{t}Bu$_2$)$_3$] (**2**) with 40% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Co1 – N1 = 1.875(3), Co1 – N2 = 2.019(3), Co1 – N3 = 1.882(3), Co1 – O1 = 2.391(2), N1 – Co1 – N2 = 111.49(13), N1 – Co1 – N3 = 130.26(13), Co1 – N1 – C10 = 163.5(3), Co1 – N2 – C1 = 129.9(3).

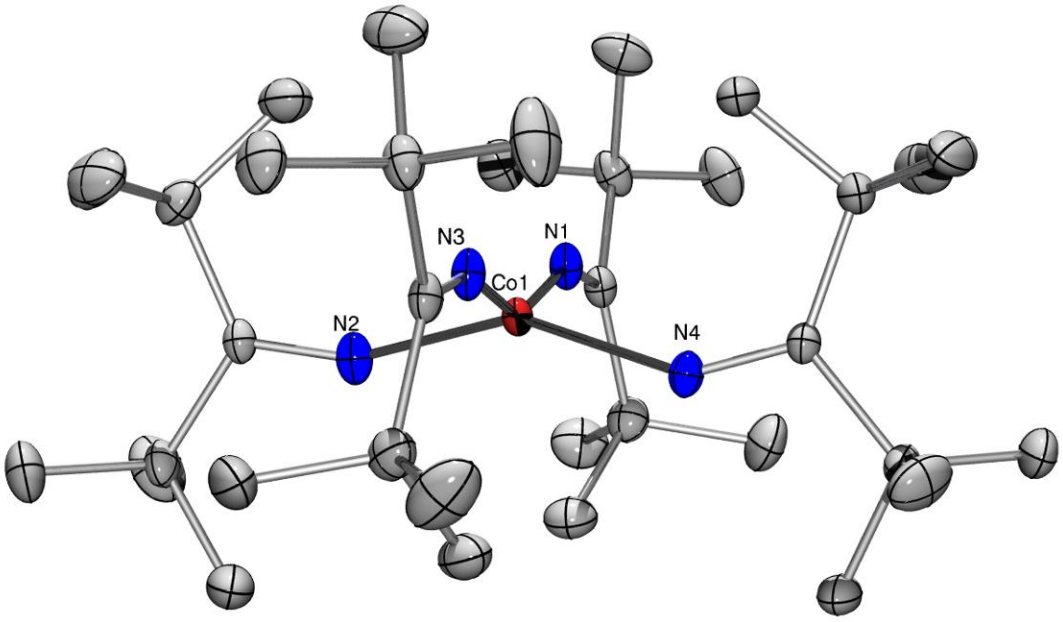


Figure S3. Solid state molecular structure of $[Li(12\text{-crown-}4)_2][Co(N{=}C^tBu_2)_4]$ (**3**) with 40% probability ellipsoids. $[Li(12\text{-crown-}4)_2]^+$ cation excluded for clarity. Selected bond lengths (Å) and angles (deg): Co1 – N1 = 1.8407(19), Co1 – N2 = 1.8201(18), Co1 – N3 = 1.8332(18), Co1 – N4 = 1.8722(18), N1 – Co1 – N3 = 150.32(9), N2 – Co1 – N4 = 148.70(9), Co1 – N1 – C1 = 153.71(18), Co1 – N2 – C10 = 158.31(18), Co1 – N3 – C19 = 156.16(18), Co1 – N4 – C28 = 147.75(17).

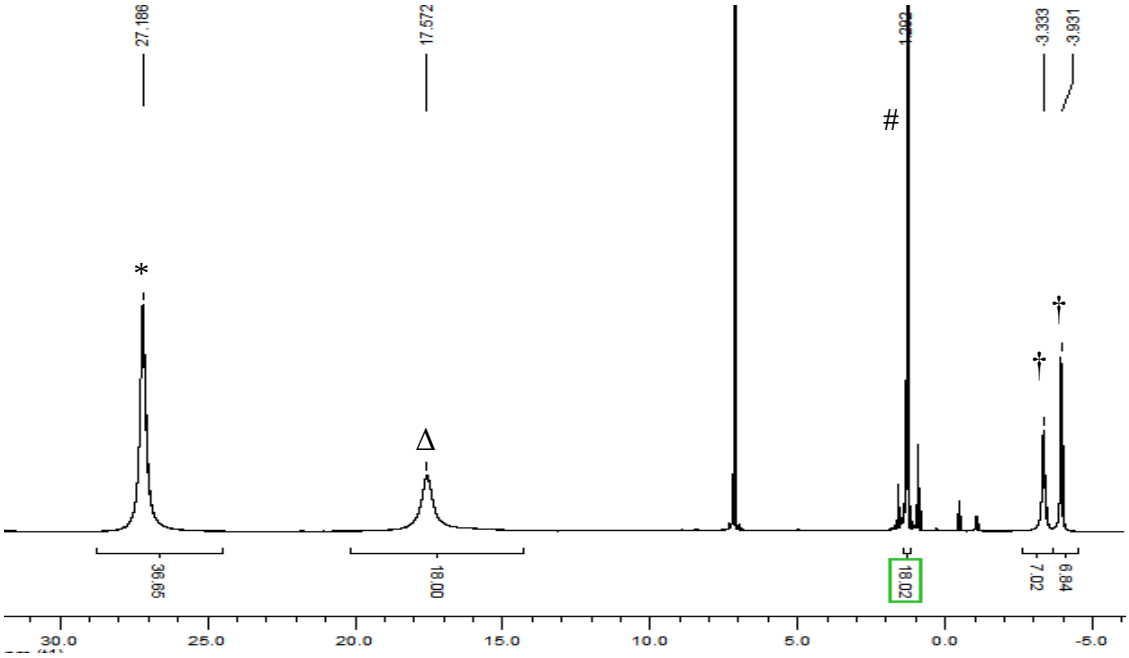


Figure S4. ^{1}H NMR spectrum of **1** in C_6D_6. Asterisk indicates the paramagnetic resonances assigned to the *tert*-butyl groups of **2**. # indicates the resonance assigned to free ligand. Δ indicates the resonances associated to $[Li(THF)]_2[Co(N{=}C^tBu_2)_4]$ (**1**). † indicates the resonances for the α- and β- protons of THF.

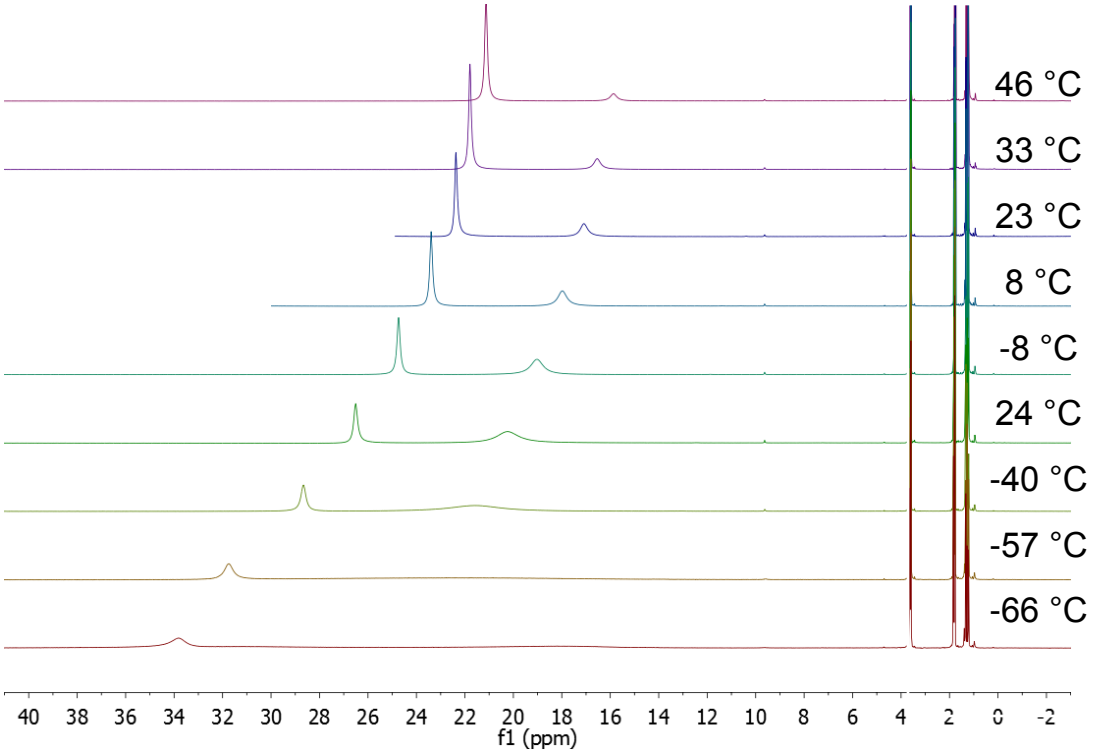


Figure S5. Variable temperature ^{1}H NMR spectra of $[Li(THF)]_2[Co(N{=}C^tBu_2)_4]$ (**1**) in THF-d_8. The ^{1}H NMR spectrum of **1** in THF-d_8 (23 °C) consists of two paramagnetically broadened resonances at 22.4 ppm (**2**) and 17.0 ppm (**1**), and a single diamagnetic resonance 1.29 ppm, assignable to $LiN{=}C^tBu_2$, which is obscured by the β-protons of the THF solvent.

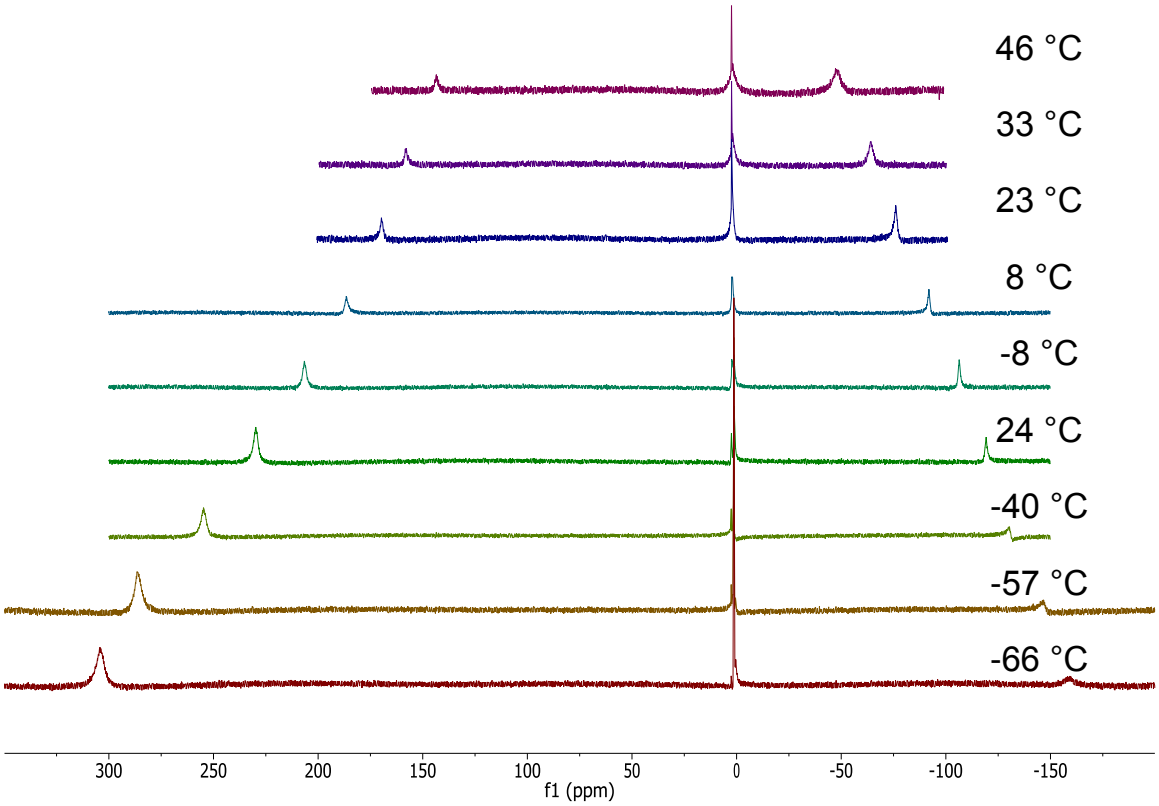


Figure S6. Variable temperature ^{7}Li NMR spectra of $[Li(THF)]_2[Co(N{=}C^tBu_2)_4]$ (**1**) in THF-d_8. The ^{7}Li NMR spectrum of **1** in THF-d_8 (23 °C) consists of two paramagnetically broadened resonances at 170 ppm (**1**) and -76 ppm (**2**), and a single diamagnetic resonance 2.4 ppm, assignable to $LiN{=}C^tBu_2$.

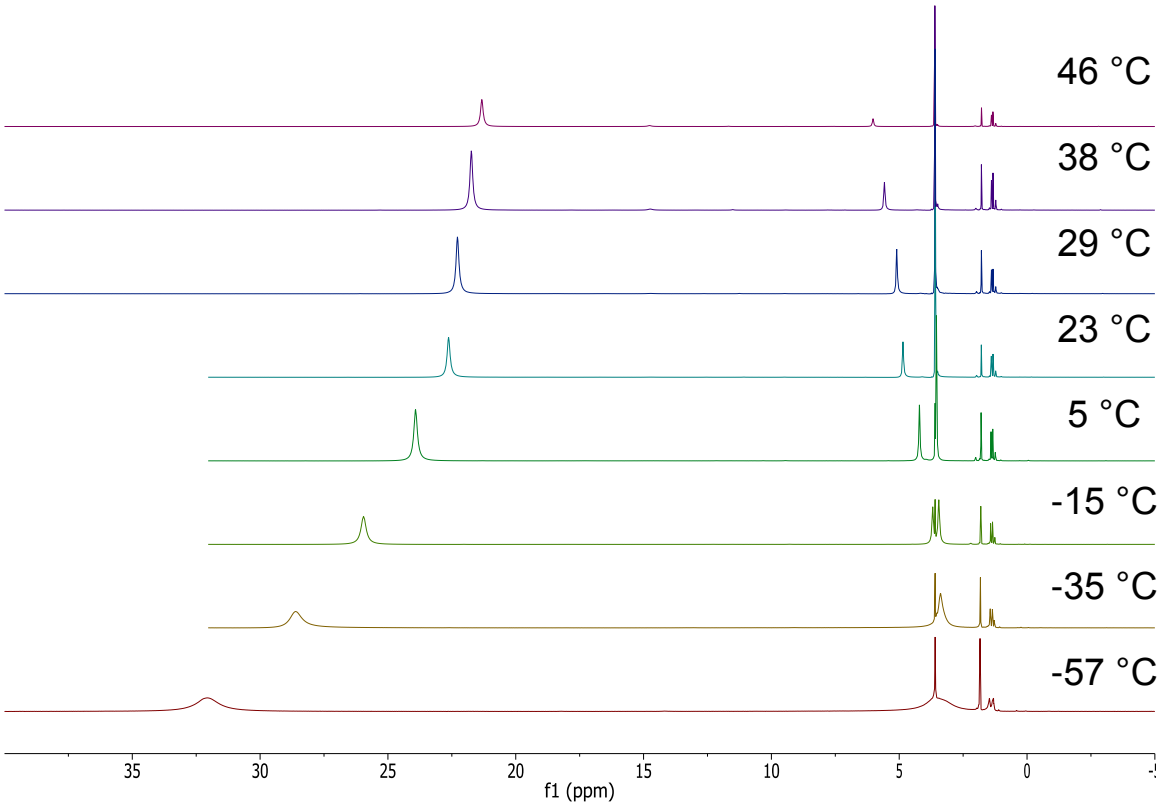


Figure S7. Variable temperature ^{1}H NMR spectra of [Li(12-crown-4)][Co(N=C^{t}Bu$_2$)$_3$] (**2**) in THF-d_8. The ^{1}H NMR spectrum of **2** in THF-d_8 (-57 °C) consists of a paramagnetically broadened resonance at 32.5 ppm (**2**) and a single broad resonance 3.4 ppm, assignable to 12-crown-4, which is partially obscured by the α-protons of the THF solvent. Upon warming, the resonance assignable to 12-crown-4 splits into two resonances, and at 23 °C these are observed at 4.9 and 3.6 ppm.

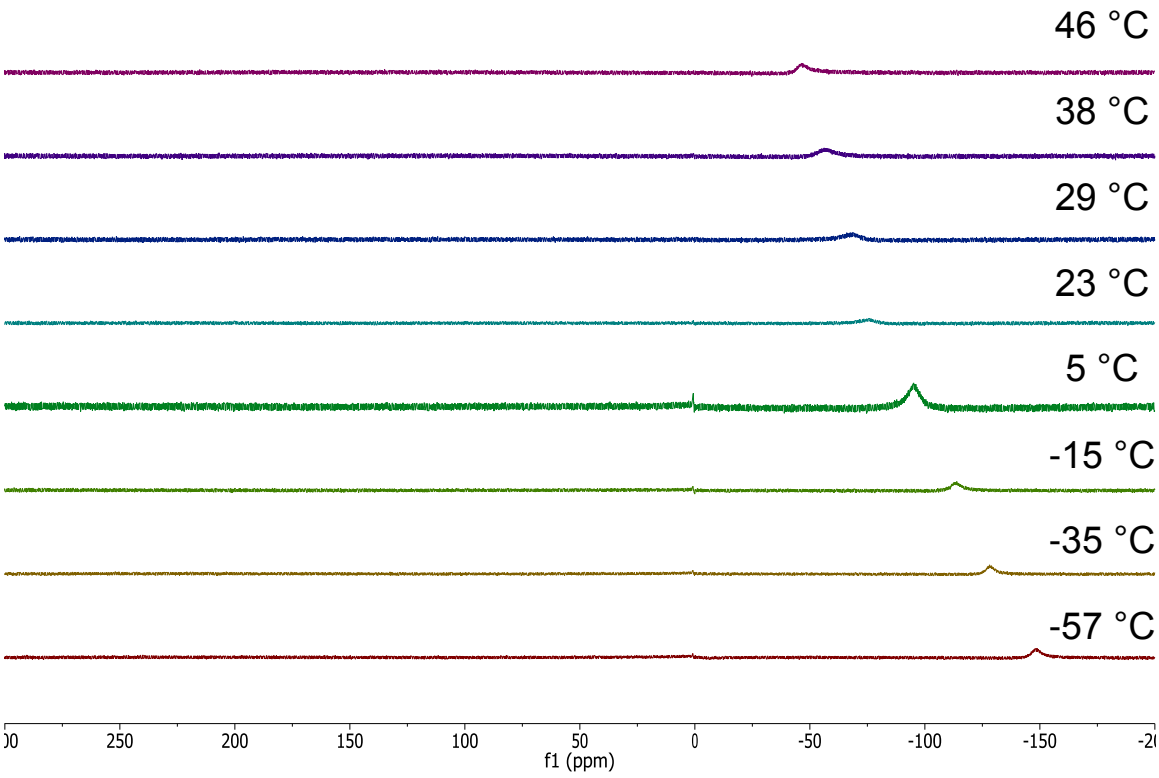


Figure S8. Variable temperature ^{7}Li NMR spectra of [Li(12-crown-4)][Co(N=C^{t}Bu$_2$)$_3$] (**2**) in THF-d_8. The ^{7}Li NMR spectrum of **2** in THF-d_8 (23 °C) consists of a single paramagnetically broadened resonance at -76 ppm.

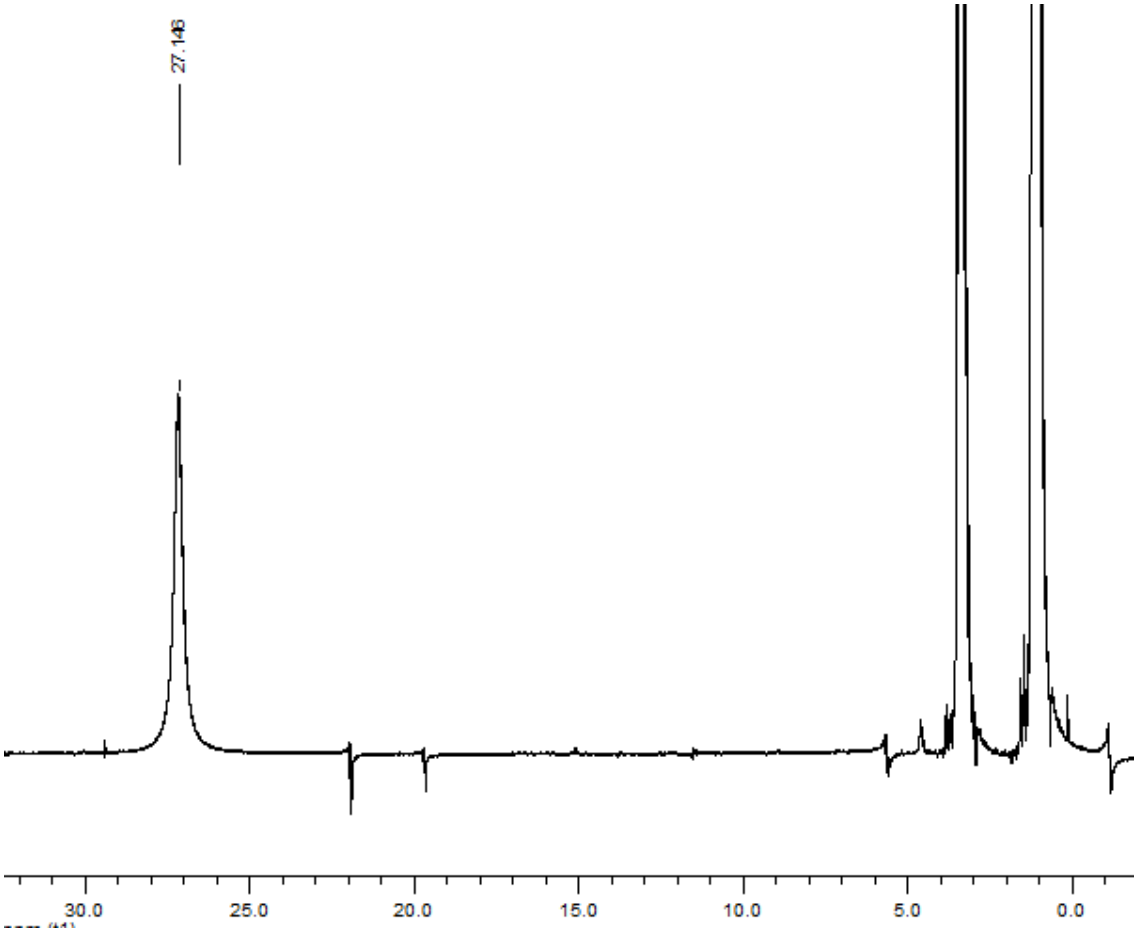


Figure S9. ^{1}H NMR spectrum of **2** in protio-Et_2O.

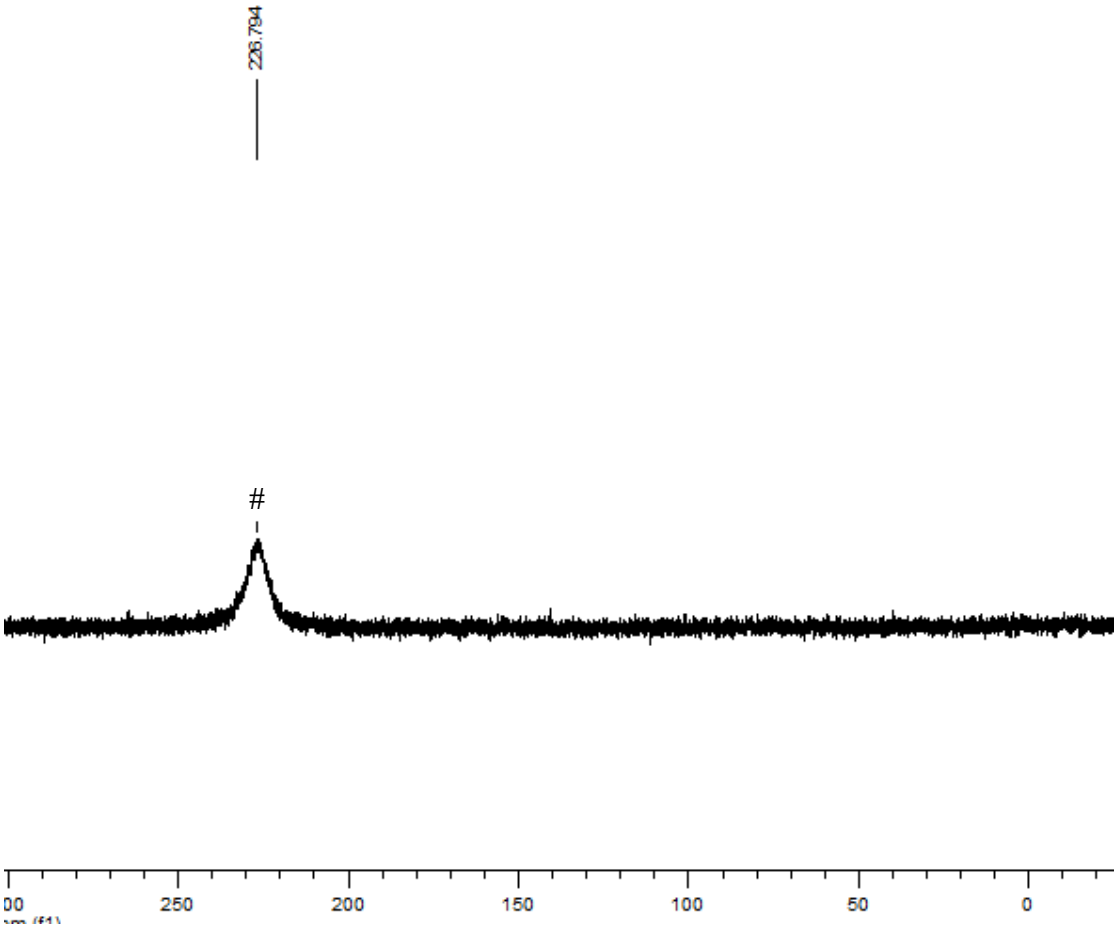


Figure S10. $^{7}Li\{^{1}H\}$ NMR spectrum of **2** in protio-Et_2O.

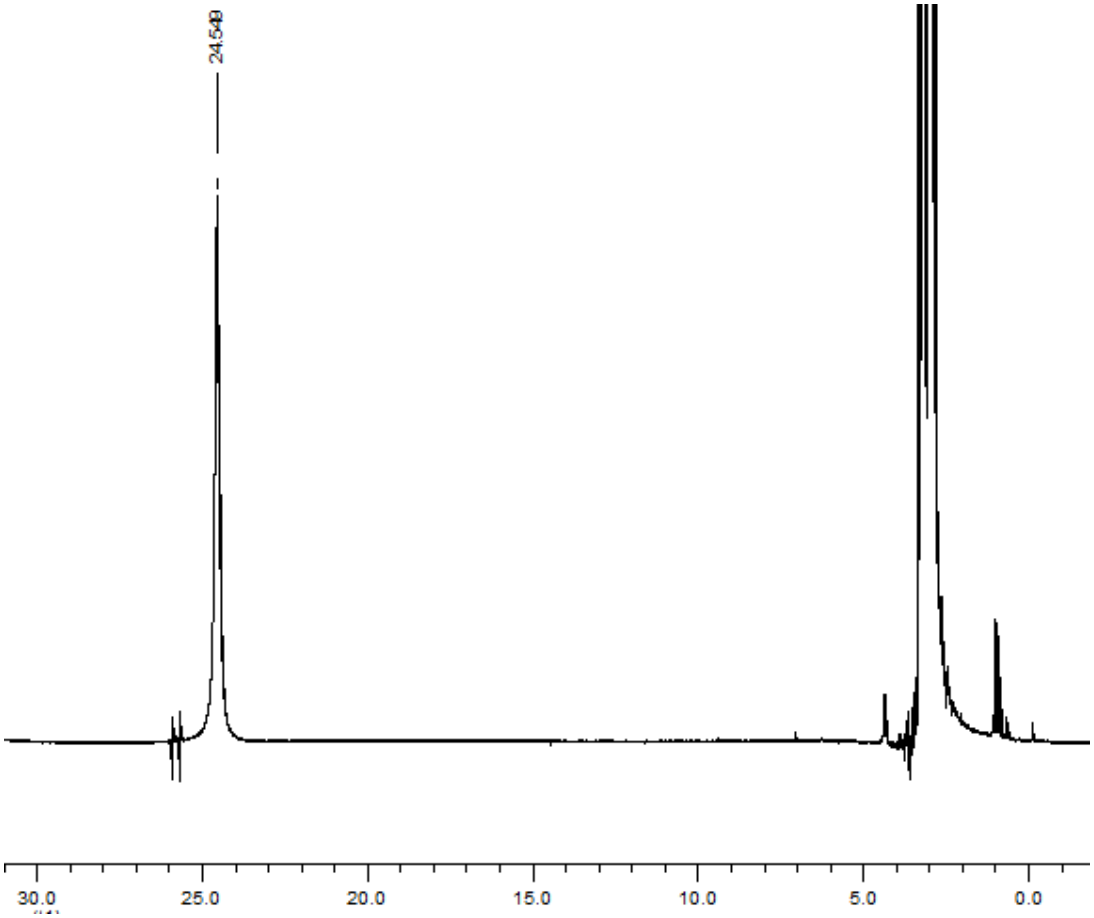


Figure S11. ^{1}H NMR spectrum of **2** in protio-DME.

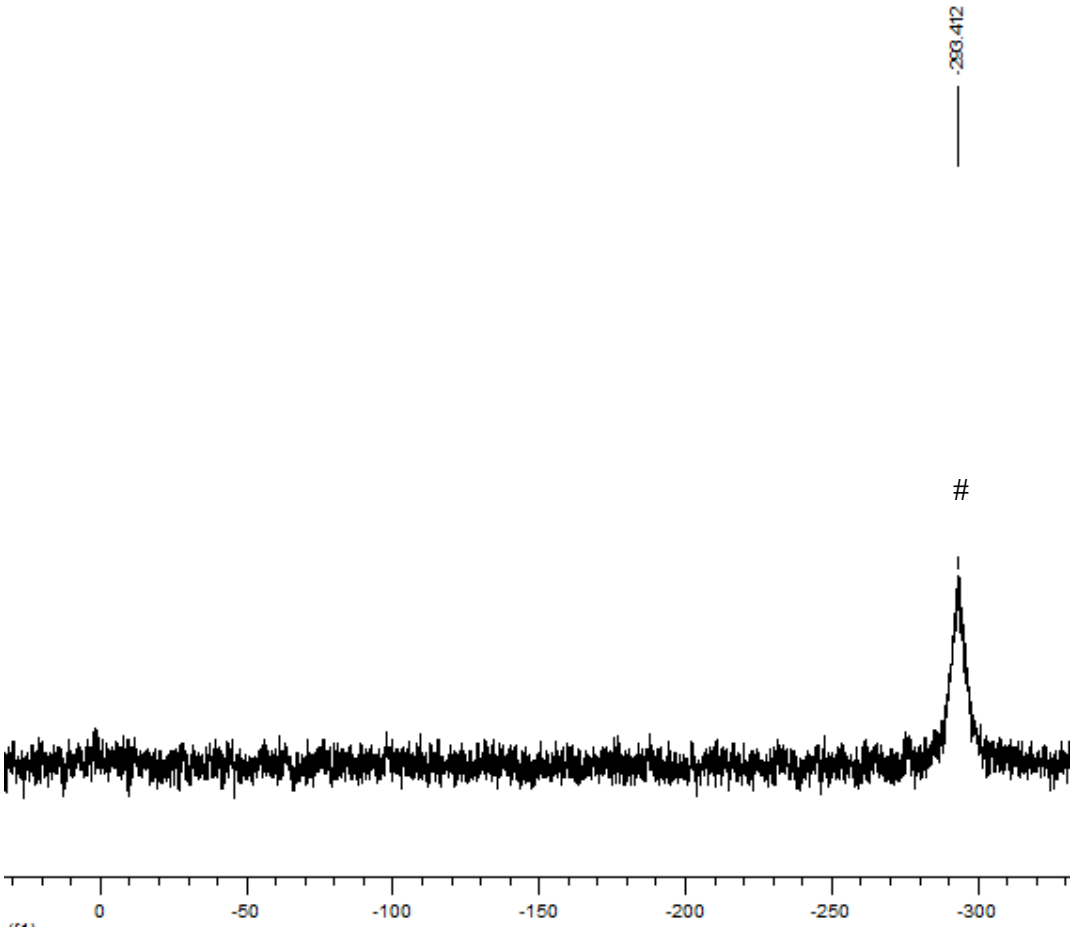


Figure S12. $^{7}Li\{^{1}H\}$ NMR spectrum of **2** in protio-DME.

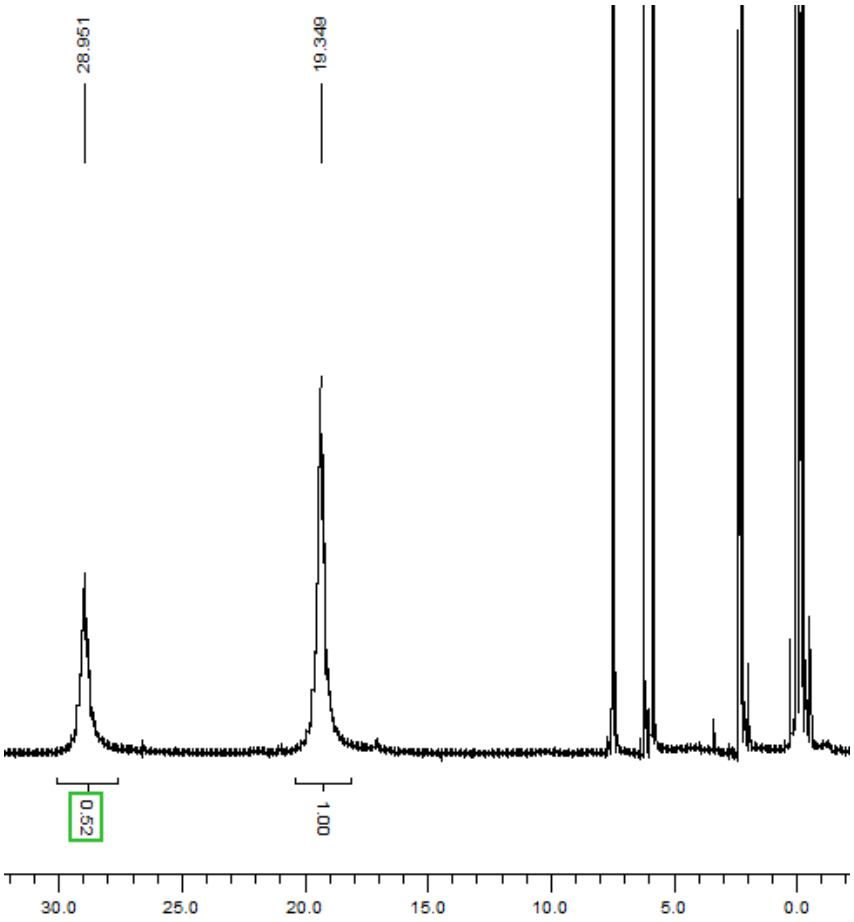
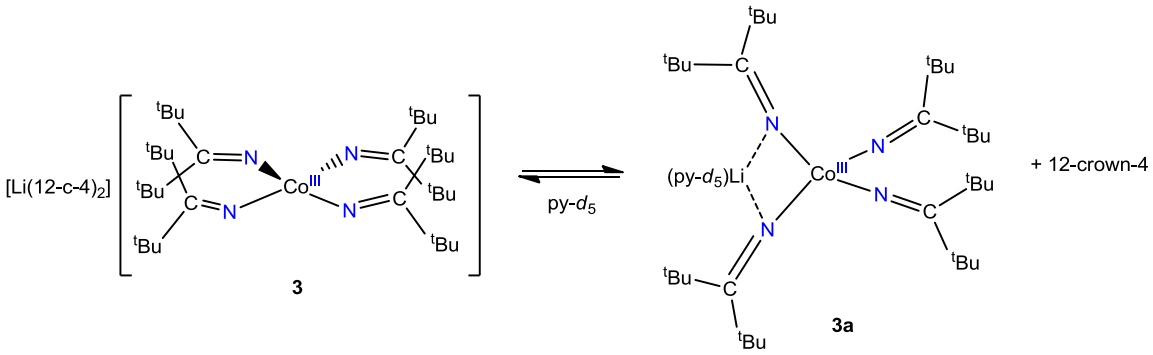


Figure S13 ^{1}H NMR spectrum of [Li(12-crown-4)$_2$][Co(N=C^{t}Bu$_2$)$_4$] (**3**) in pyridine-d_5.

The ^{1}H NMR spectrum of **3** in pyridine-d_5 consists of two paramagnetically broadened resonances at 29.0 and 19.3 ppm, and a single diamagnetic resonance 3.65 ppm, assignable to 12-crown-4. These resonances are consistent between independently prepared batches of **3**. The presence of two resonances in this spectrum can be rationalized by invoking an equilibrium between **3** and the close contact ion pair **3a** (Scheme S1), formed by loss of 12-crown-4 and coordination of Li^+ by the nitrogen atoms of the ketimide ligands. Note that the isostructural Fe analogue of **3a**, [Li(DME)][Fe(N=C^{t}Bu$_2$)$_4$], has been structurally characterized.[7]

Scheme S1



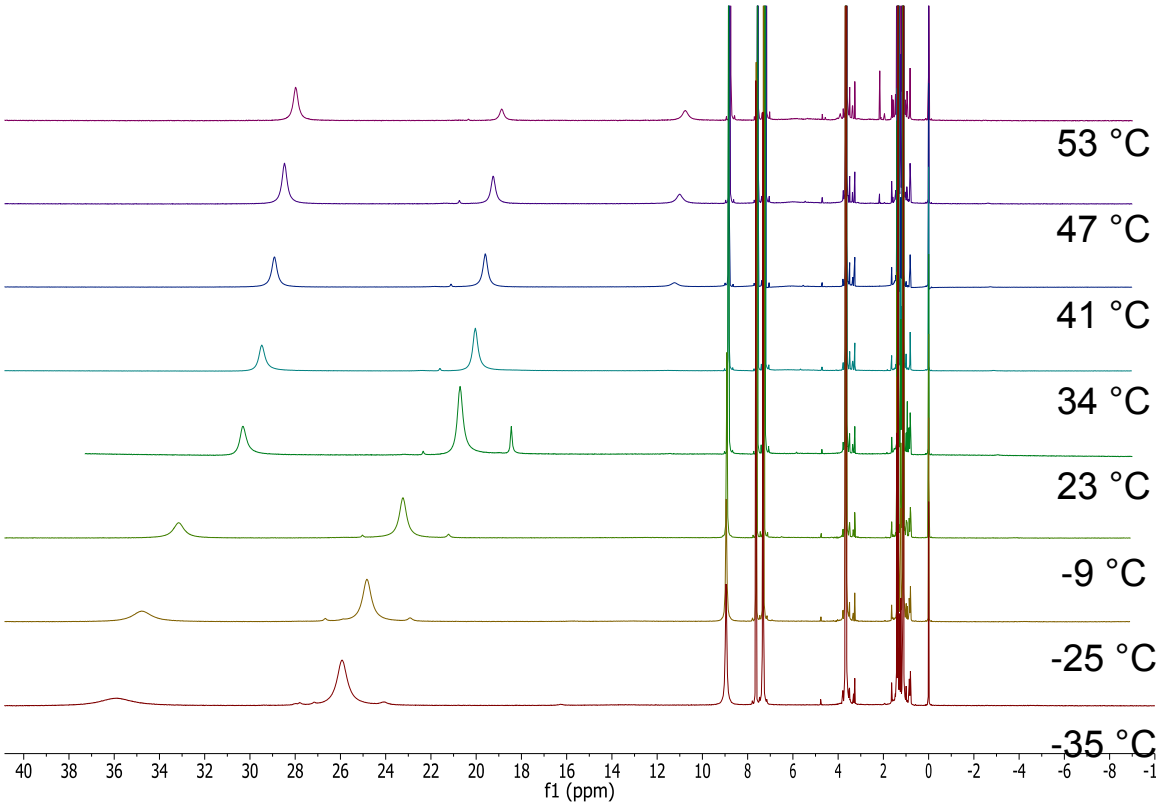


Figure S14. Variable temperature ^{1}H variable temperature NMR spectra of [Li(12-crown-4)$_2$][Co(N=C^{t}Bu$_2$)$_4$] (**3**) in pyridine-d_5. Upon warming from -35 °C, the resonance at 26 ppm decreases in intensity, while the resonance at 36 ppm increases in intensity. We have tentatively assigned the resonance at 26 ppm to complex **3a** and the resonance at 36 ppm to complex **3**. These assignments are supported by the variable temperature ^{7}Li NMR spectra (vide infra). The broad peak at 12 ppm is assignable to a decomposition product, formed upon warming, while the sharp resonance at 19 ppm is assignable to an unidentified impurity.

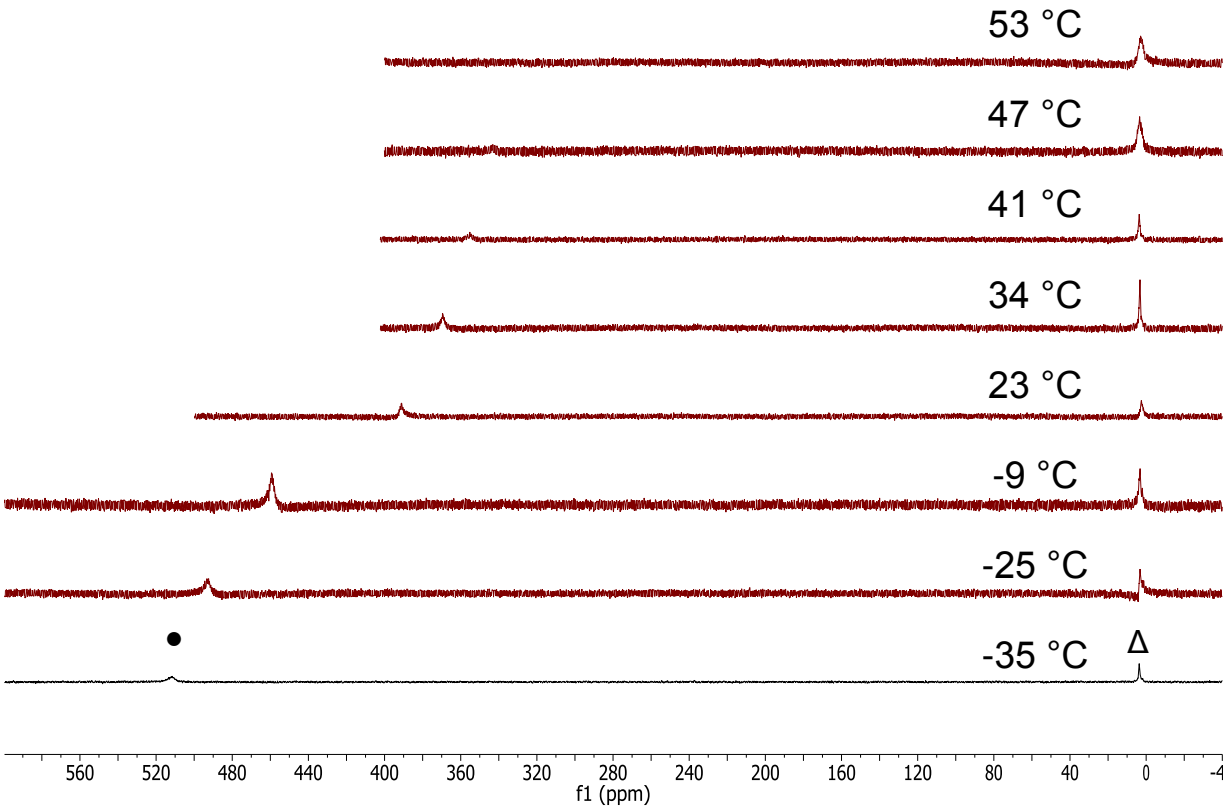


Figure S15. Variable temperature $^{7}Li\{^{1}H\}$ variable temperature NMR spectra of [Li(12-crown-4)$_2$][Co(N=C^{t}Bu$_2$)$_4$] (**3**) in pyridine-d_5. At -35 °C the spectrum consists of two resonances. Given the large chemical shift, the resonance at 510 ppm (●) is assignable to the close contact ion pair **3a**. The resonance at 0 ppm (Δ) is assignable to the [Li(12-crown-4)$_2$]$^+$ ion found in complex **3**. Upon warming, the resonance at 510 ppm shifts upfield and decreases in intensity, relative to the resonance at 0 ppm. Accordingly, we have assigned the resonance at 510 ppm to complex **3a** and the resonance at 0 ppm to complex **3**.

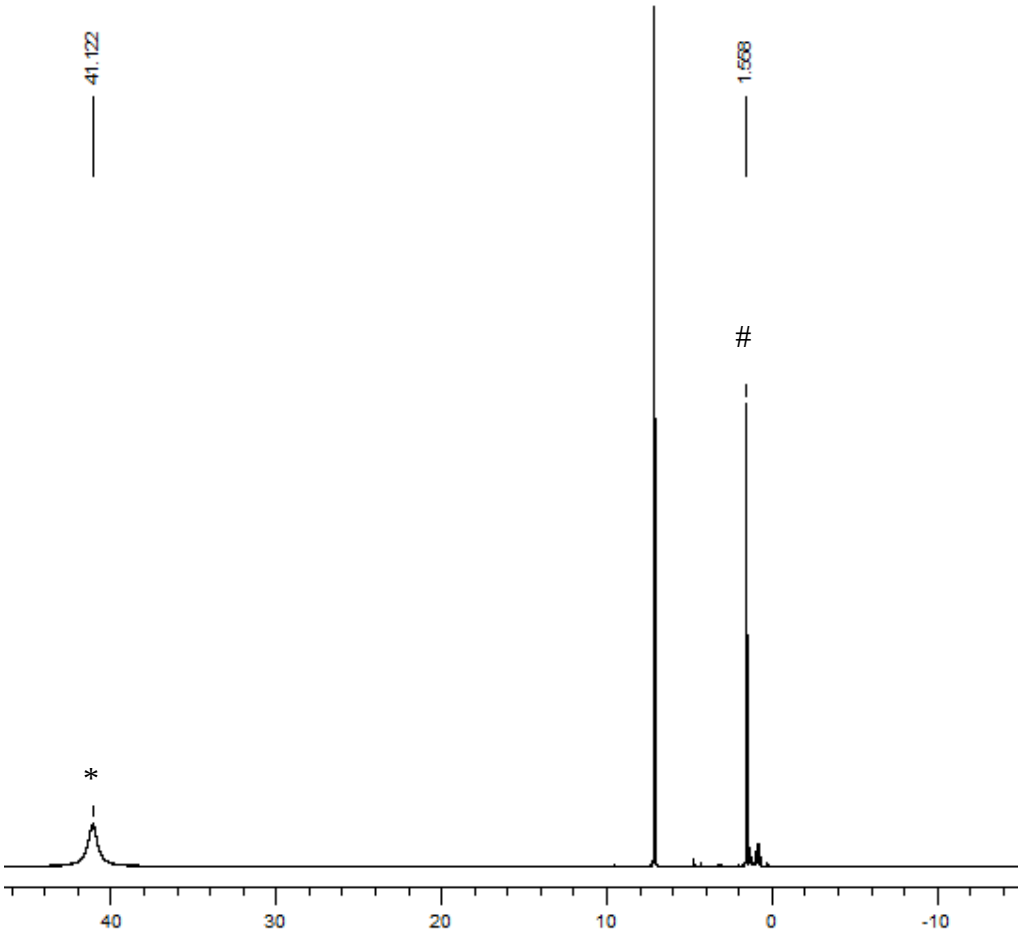


Figure S16. ^{1}H NMR spectrum of **4** in C_6D_6. Asterisk indicates resonance assignable to complex **4.** # indicates resonance assignable to a thermal decomposition product.

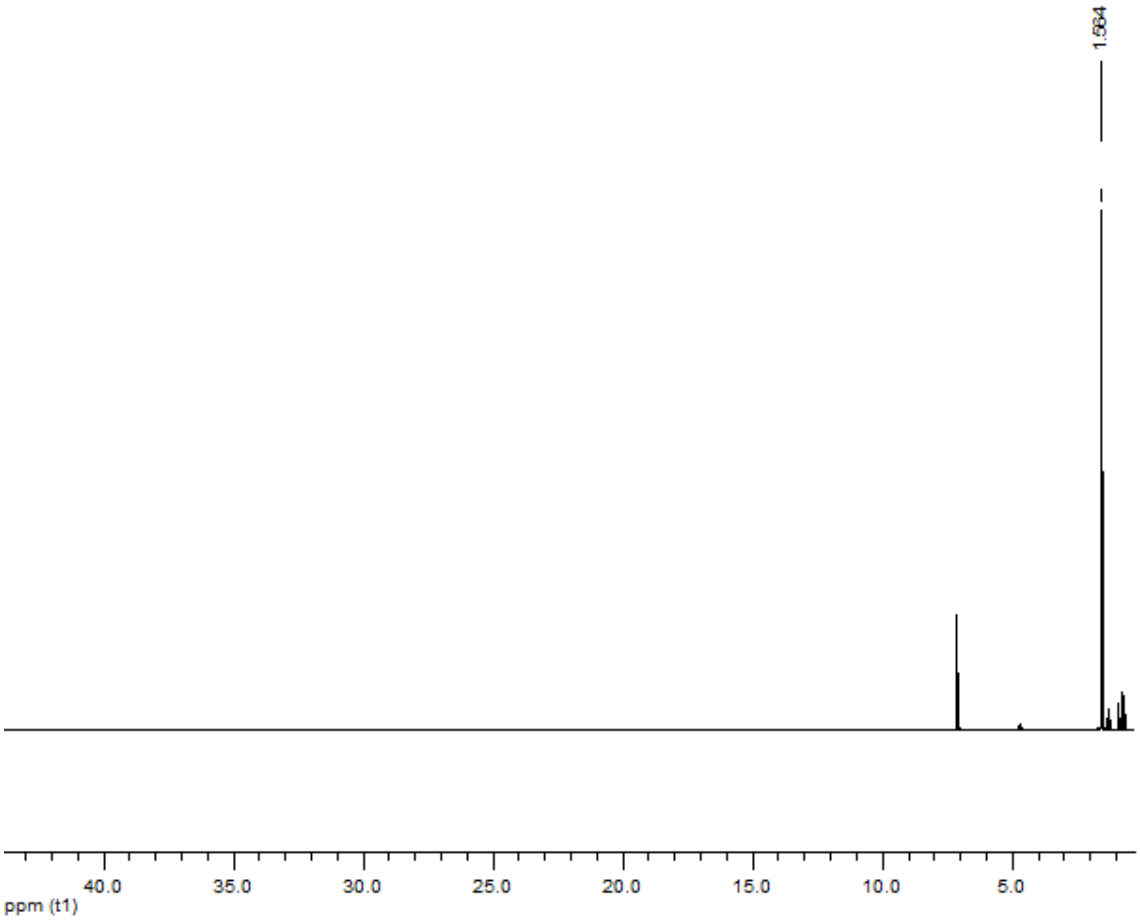


Figure S17. ^{1}H NMR spectrum of complex **4** in C_6D_6 after standing at 25 °C for 4 h.

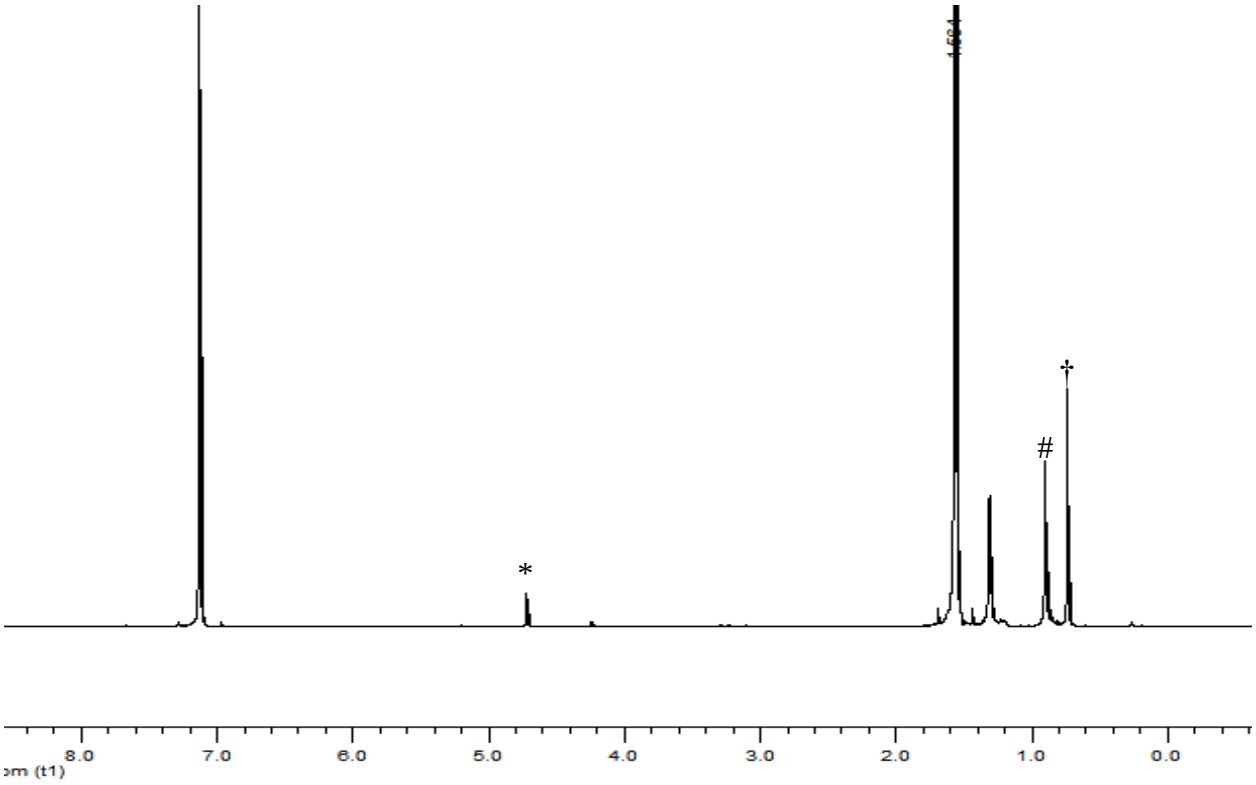


Figure S18. Partial ^{1}H NMR spectrum of complex **4** in C_6D_6 after standing at 25 °C for 4 h (vide supra). Asterisk indicates resonance assignable to the vinyl protons of isobutylene. # indicates resonance assignable to the methyl protons of isobutane. † indicates resonance assignable to the methyl protons of *tert*-butylcyanide.

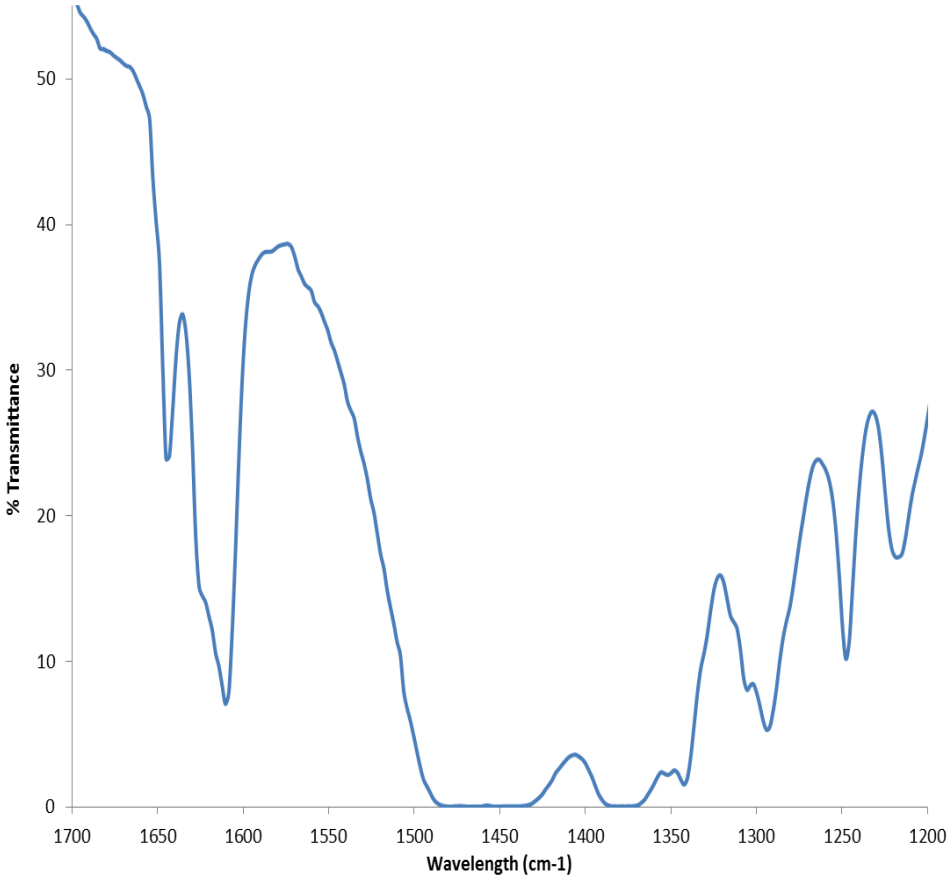


Figure S19. IR spectrum of $[Li(THF)]_2[Co(N=C^tBu_2)_4]$ (**1**) (hexanes).

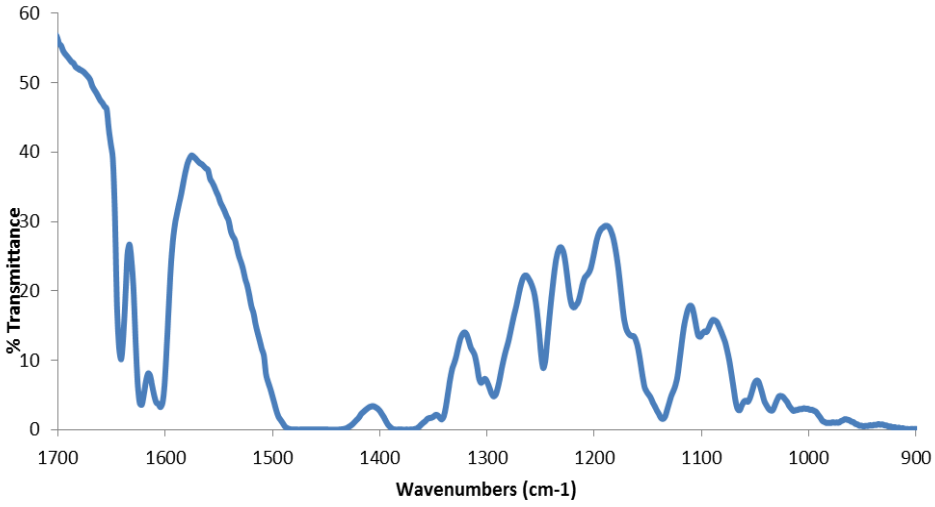


Figure S20. IR spectrum of $[Li(12\text{-crown-4})][Co(N=C^tBu_2)_3]$ (**2**) (Et_2O).

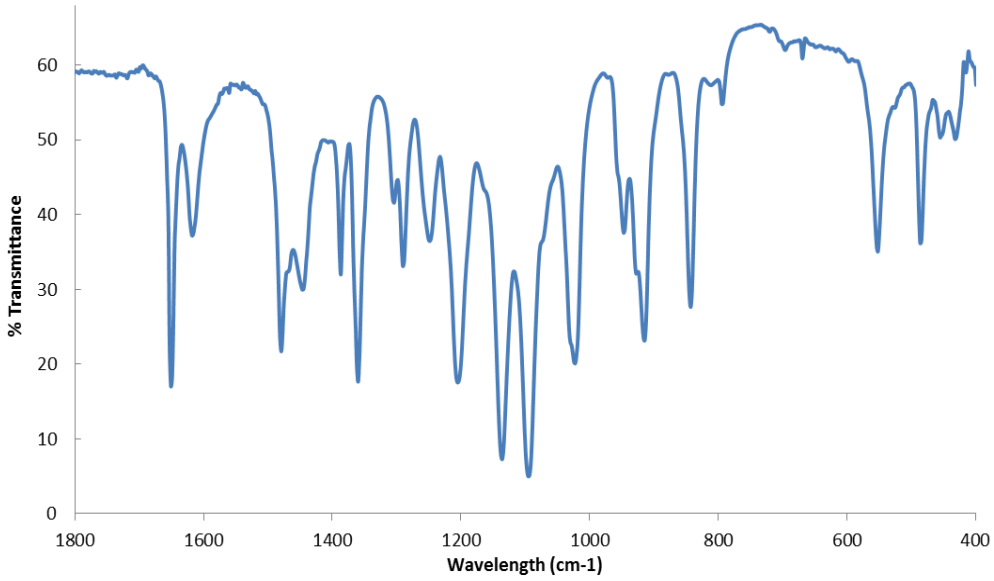


Figure S21. IR spectrum of $[Li(12\text{-crown-4})_2][Co(N{=}C^tBu_2)_4]$ (**3**) (KBr mull).

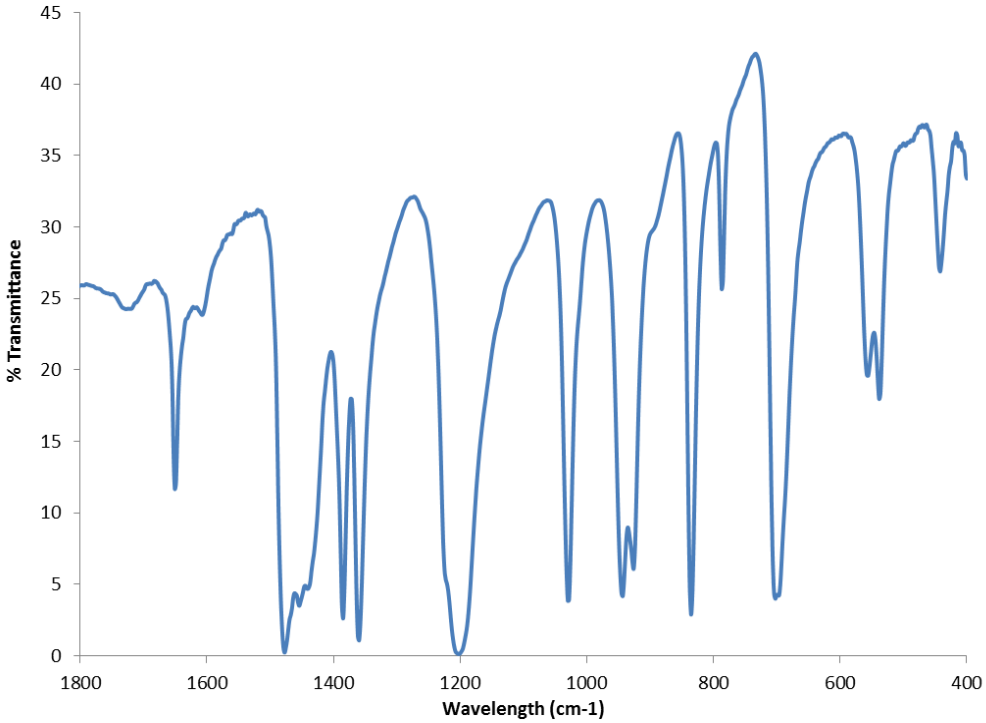


Figure S22. IR spectrum of $Co(N{=}C^tBu_2)_4$ (**4**) (KBr mull).

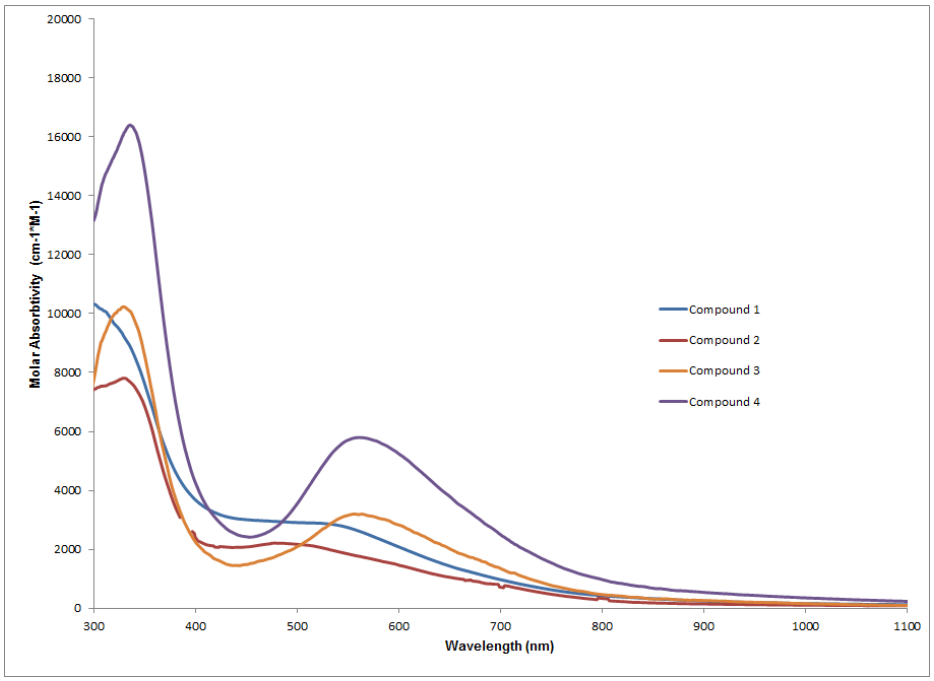


Figure S23. Near-IR-UV-Vis spectra of **1** (C_4H_8O, $2.78 \cdot \times 10^{-4}$ M), **2** ($C_4H_{10}O$, $2.16 \cdot \times 10^{-4}$ M), **3** ($C_4H_{10}O$, $7.08 \cdot \times 10^{-5}$ M), **4** (C_7H_8, $4.76 \cdot \times 10^{-5}$ M).

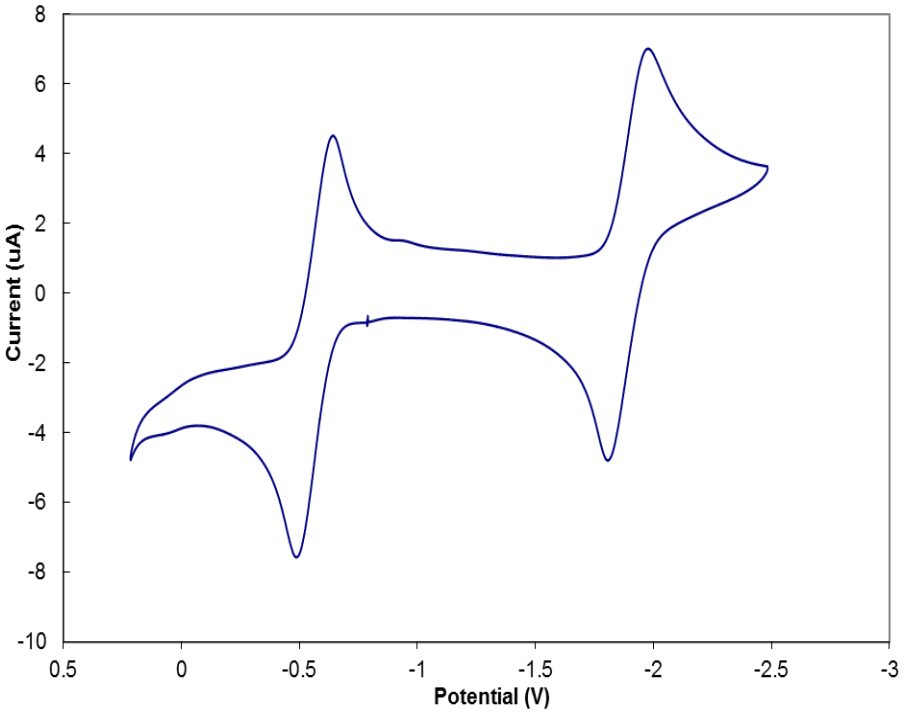


Figure S24. Cyclic voltammogram of the Co(IV)/Co(III) and Co(III)/Co(II) redox features for complex **4** (200 mV/s scan rate), referenced to Fc/Fc^{+}. The experiment was performed in THF with 0.1 M $[NBu_4][PF_6]$ as supporting electrolyte.

The cyclic voltammogram of **4** in THF consists of two reversible reduction features at -1.82 V and -0.46 V (vs. Fc/Fc^{+}), attributable to the Co(III)/Co(II) and Co(IV)/Co(III) redox couples, respectively. For comparison, $Fe(N=C^{t}Bu_2)_4$ exhibits reversible redox features at -1.63 and -0.53 V (vs. Fc/Fc^{+}), attributable to the Fe(II)/Fe(III) and Fe(III)/Fe(IV) redox couples, respectively,[7] while $Co(1\text{-norbornyl})_4$ exhibits Co(IV)/Co(III) and Co(V)/Co(IV) redox couples at -2.02 V and -0.65 V (vs. Fc/Fc^{+}), respectively.[8] These latter data, in particular, suggest that 1-norbornyl is a substantially stronger donor than $[N=C^{t}Bu_2]^{-}$.

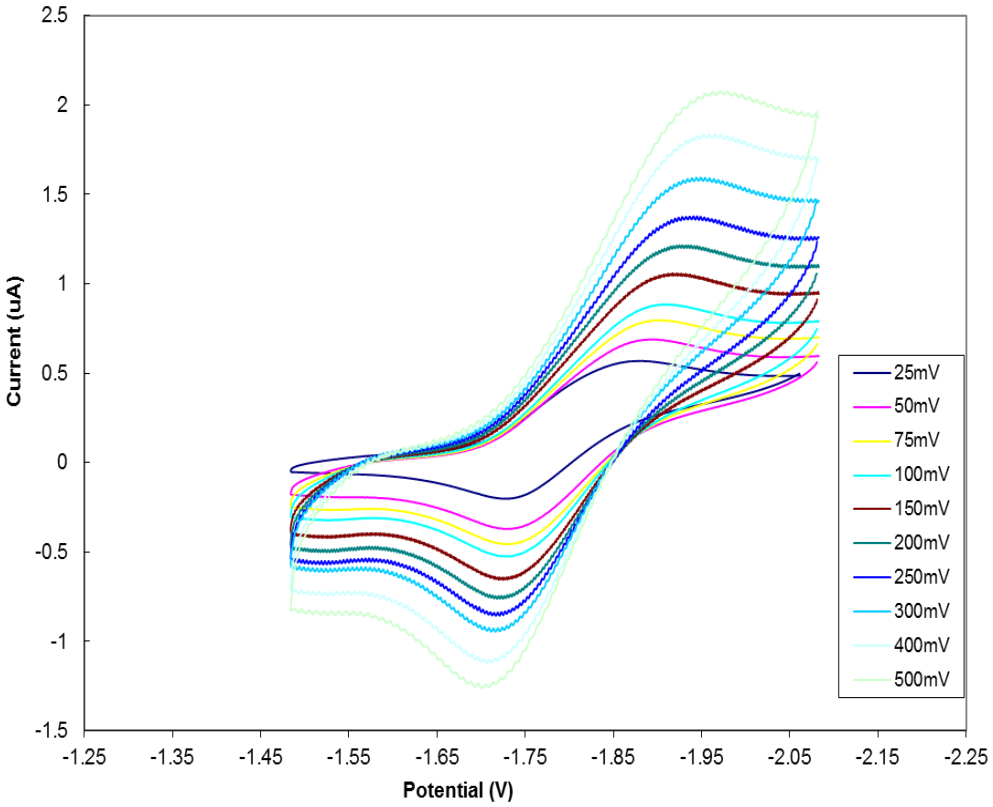


Figure S25. Co(II)/(III) couple for complex **4** measured in THF with 0.1 M $[NBu_4][PF_6]$ as supporting electrolyte (vs. Fc/Fc^+).

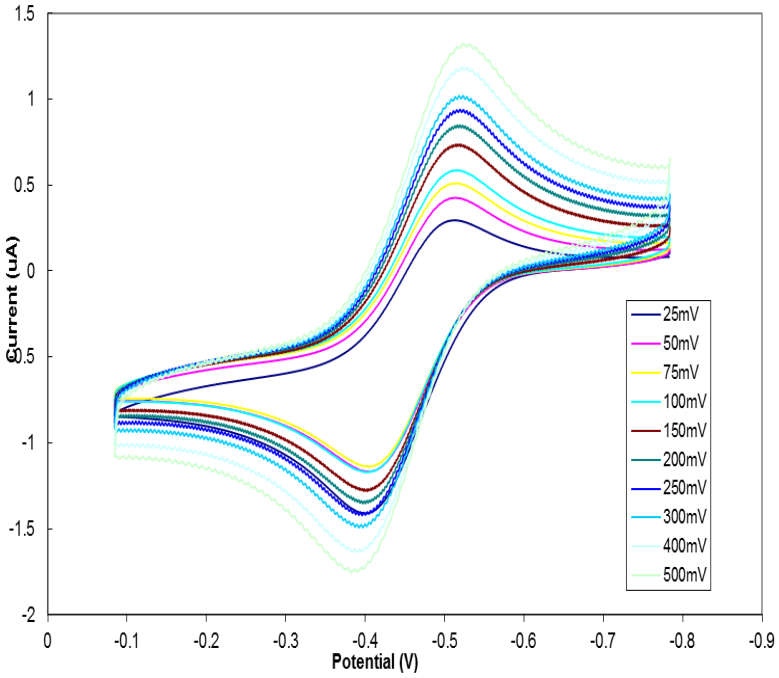


Figure S26. Co(III)/(IV) couple for complex **4** measured in THF with 0.1 M $[NBu_4][PF_6]$ as supporting electrolyte (vs. Fc/Fc^+).

Table S2. Electrochemical parameters for $Co(N=C^tBu_2)_4$ (**4**) in THF (vs. Fc/Fc^+, $[NBu_4][PF_6]$ as supporting electrolyte).

Reduction feature 1	**Scan rate, V/s**	$E_{p,c}$, V	$E_{p,a}$, V	ΔE_p [a]	$i_{p,c}/i_{p,a}$
	0.025	-0.513	-0.400	0.113	0.78
	0.05	-0.513	-0.406	0.107	0.82
	0.075	-0.519	-0.406	0.113	0.86
	0.1	-0.517	-0.402	0.115	0.90
	0.15	-0.516	-0.403	0.113	0.93
	0.2	-0.519	-0.397	0.122	0.97
	0.25	-0.520	-0.396	0.124	0.98
	0.3	-0.524	-0.392	0.132	0.97
	0.4	-0.522	-0.389	0.133	1.00
	0.5	-0.532	-0.382	0.150	1.01
Reduction feature 2	**Scan rate, V/s**	$E_{p,c}$, V	$E_{p,a}$, V	ΔE_p [a]	$i_{p,c}/i_{p,a}$
	0.025	-1.880	-1.725	0.155	1.50
	0.05	-1.896	-1.728	0.168	1.48
	0.075	-1.901	-1.734	0.167	1.40
	0.1	-1.906	-1.728	0.178	1.38
	0.15	-1.917	-1.725	0.192	1.24
	0.2	-1.925	-1.718	0.207	1.21
	0.25	-1.941	-1.721	0.220	1.14
	0.3	-1.944	-1.716	0.228	1.08
	0.4	-1.959	-1.706	0.253	1.09
	0.5	-1.971	-1.701	0.270	1.07
Ferrocene	**Scan rate, V/s**	$E_{p,c}$, V	$E_{p,a}$, V	ΔE_p [a]	$i_{p,c}/i_{p,a}$
	0.025	0.103	-0.055	0.158	0.90
	0.05	0.091	-0.074	0.165	0.97
	0.075	0.094	-0.087	0.181	0.99
	0.1	0.096	-0.096	0.192	0.99
	0.15	0.105	-0.109	0.214	0.99
	0.2	0.114	-0.118	0.232	0.99
	0.25	0.116	-0.122	0.238	1.00
	0.3	0.122	-0.137	0.259	1.00
	0.4	0.126	-0.150	0.276	0.99
	0.5	0.135	-0.171	0.306	0.99

[a] ΔE_p is defined as the potential difference between the cathodic wave and the anodic wave generated after the change in sweep direction.

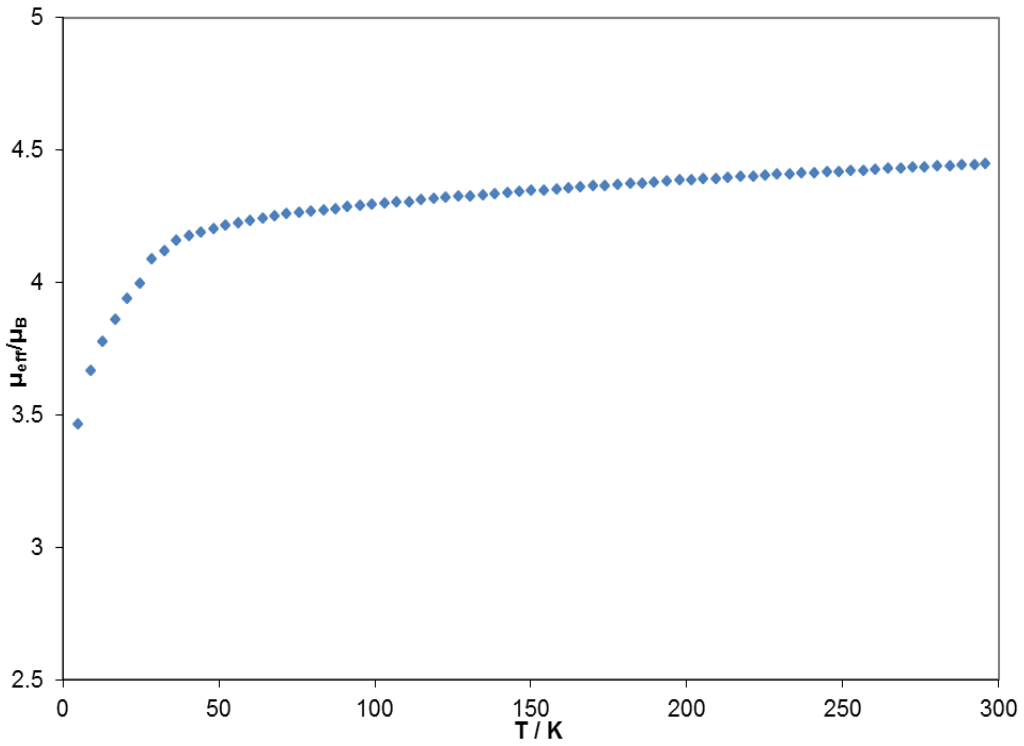


Figure S27. Temperature dependence of μ_{eff} for **1** from 4 K to 300 K (χ_{dia} = -5.79 × 10^{-4} $cm^3 \cdot mol^{-1}$, mass = 35.8 mg, M = 778.0 g/mol).

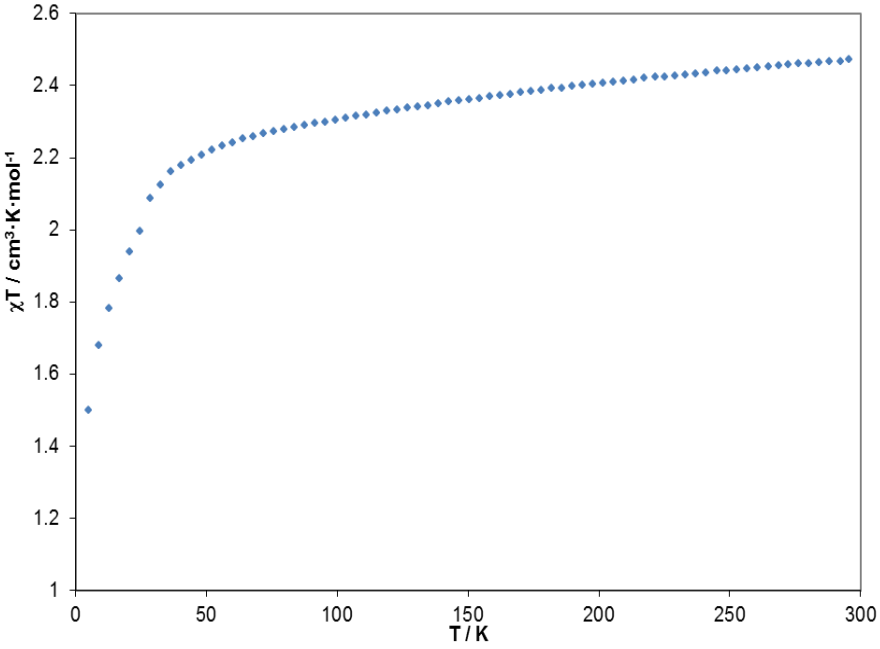


Figure S28. Temperature dependence of χT for **1** from 4 K to 300 K (χ_{dia} = -5.79 × 10^{-4} $cm^3 \cdot mol^{-1}$, mass = 35.8 mg, M = 778.0 g/mol).

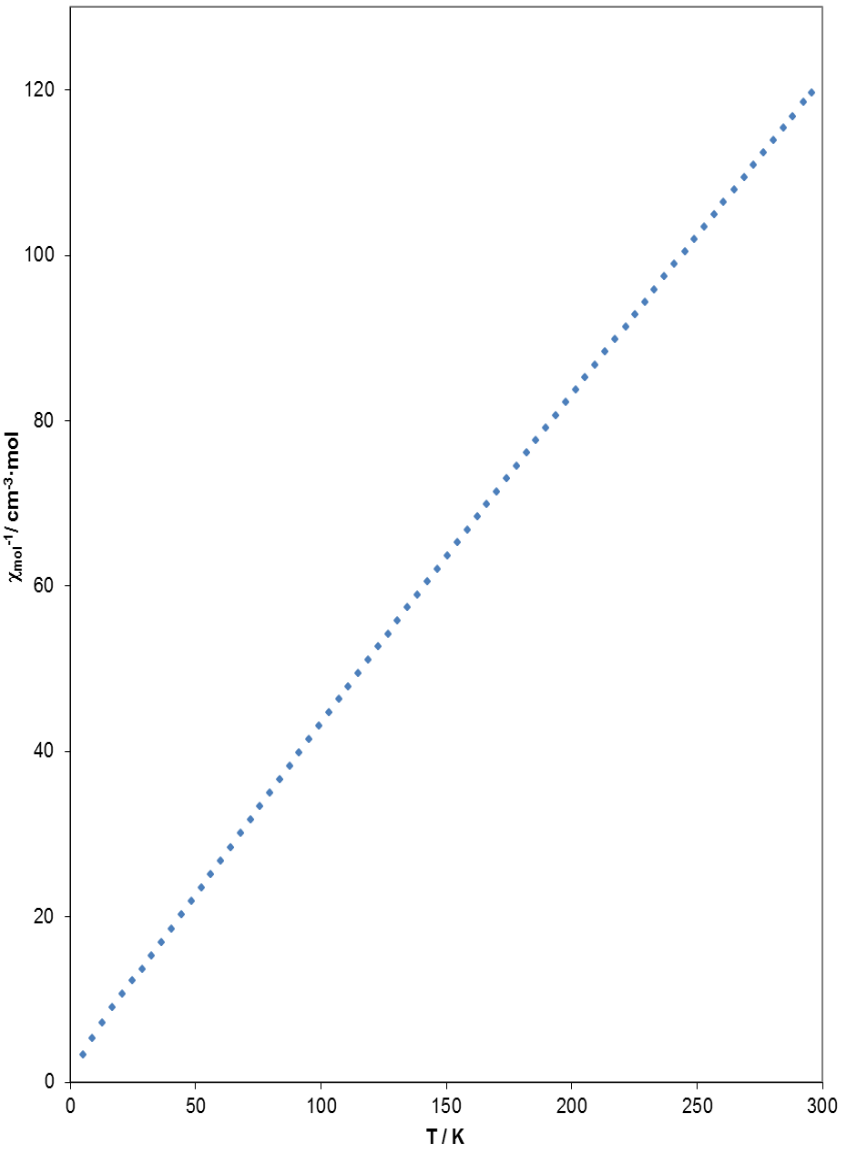


Figure S29. Temperature dependence of χ^{-1} for **1** from 4 K to 300 K (χ_{dia} = -5.79 × 10^{-4} cm^3·mol^{-1}, mass = 35.8 mg, M = 778.0 g/mol).

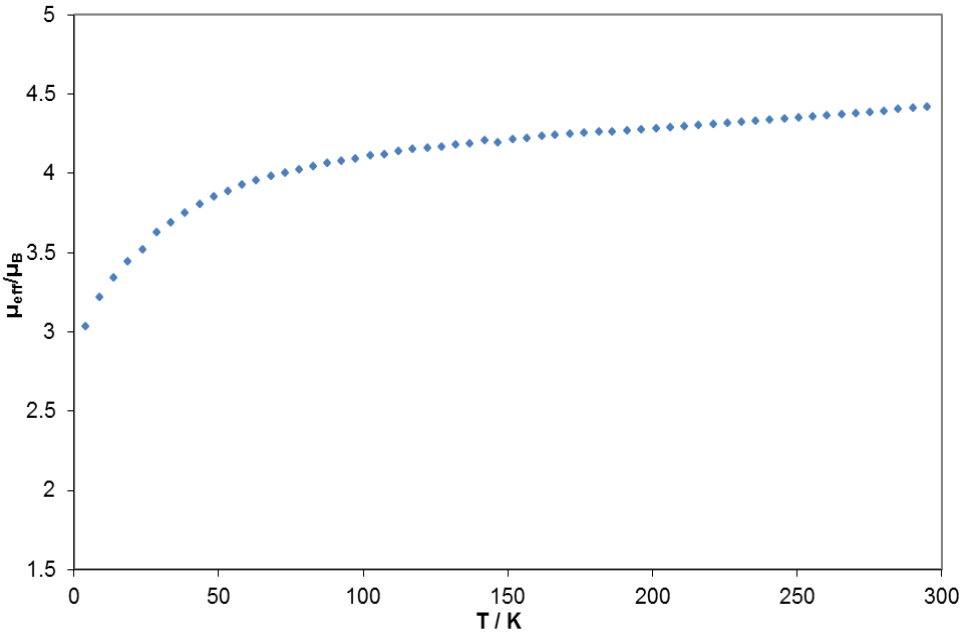


Figure S30. Temperature dependence of μ_{eff} for **2** from 4 K to 300 K (χ_{dia} = -4.72 × 10^{-4} $cm^3 \cdot mol^{-1}$, mass = 47.0 mg, M = 662.8 g/mol).

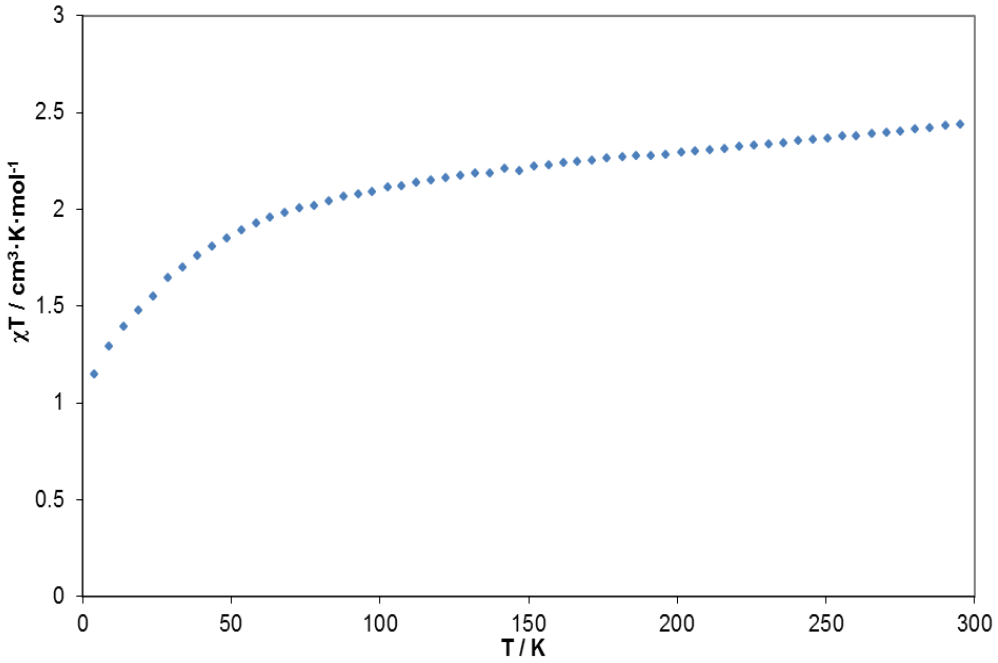


Figure S31. Temperature dependence of χT for **2** from 4 K to 300 K (χ_{dia} = -4.72 × 10^{-4} $cm^3 \cdot mol^{-1}$, mass = 47.0 mg, M = 662.8 g/mol).

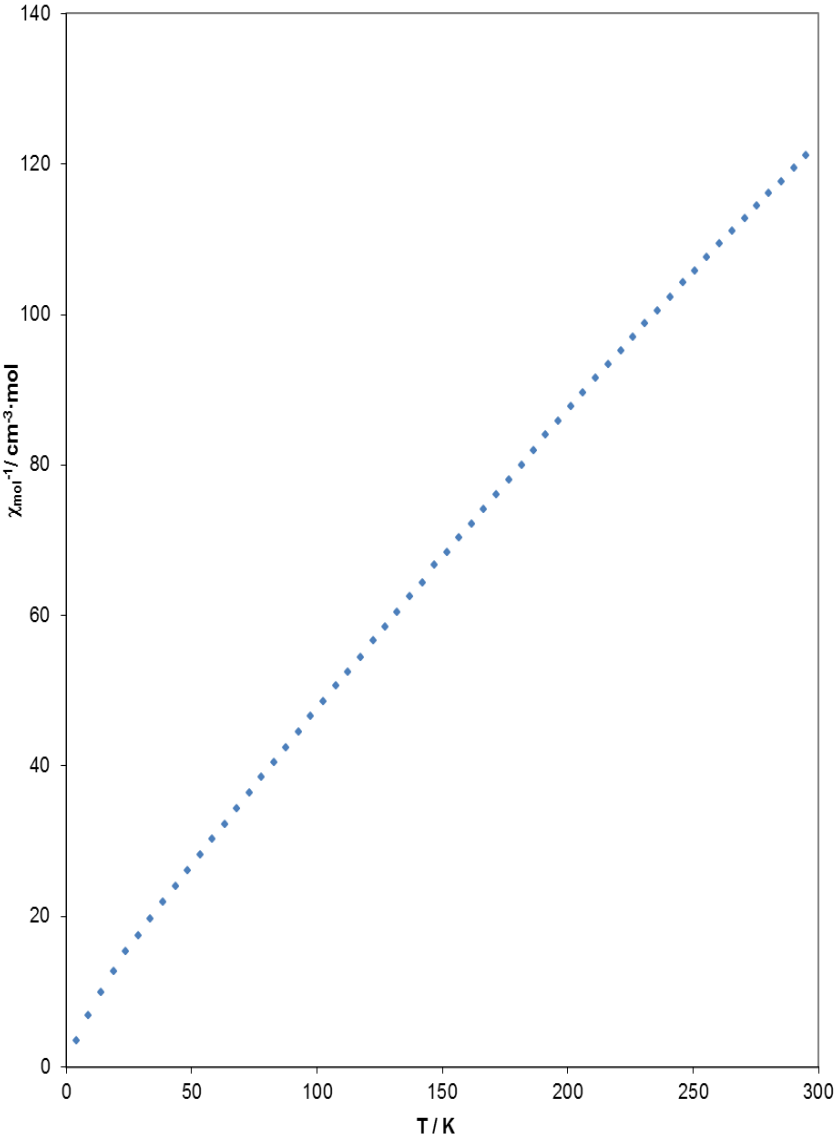


Figure S32. Temperature dependence of χ^{-1} for **2** from 4 K to 300 K (χ_{dia} = -4.72 × 10^{-4} $cm^3 \cdot mol^{-1}$, mass = 47.0 mg, M = 662.8 g/mol).

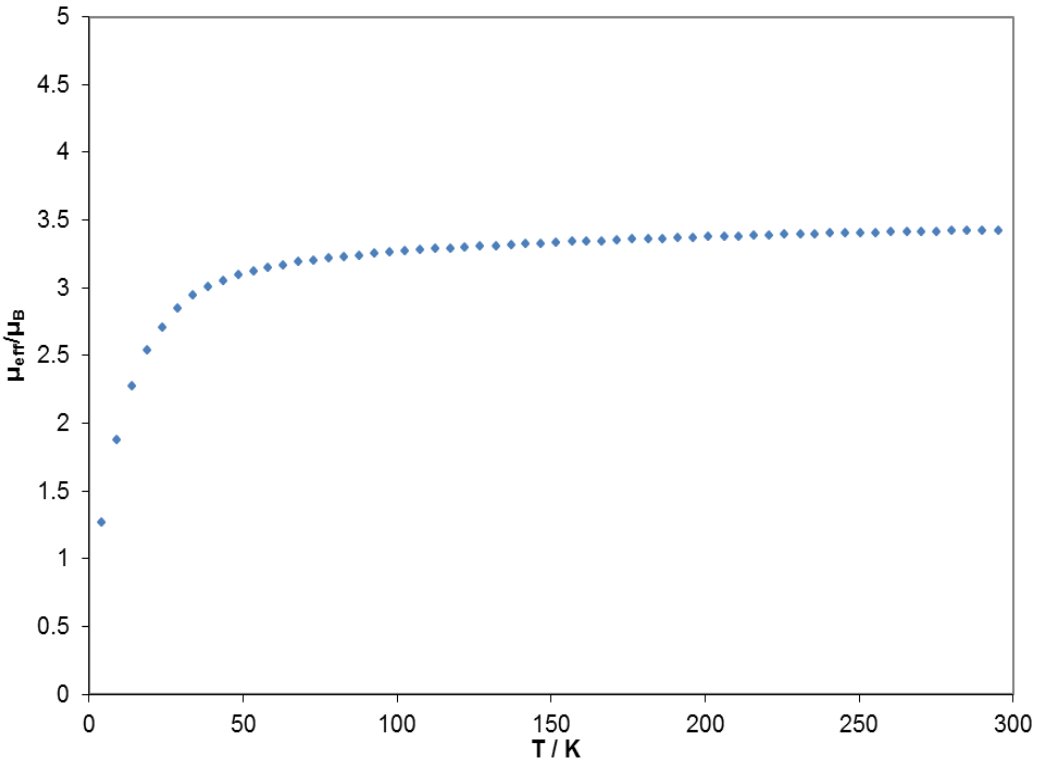


Figure S33. Temperature dependence of μ_{eff} for **3** from 4 K to 300 K (χ_{dia} = -6.97 × 10^{-4} $cm^3 \cdot mol^{-1}$, mass = 53.0 mg, M = 979.3 g/mol). Analysis of **3** by SQUID magnetometry yields an effective magnetic moment of 3.41 B.M. at 300 K, consistent with an intermediate spin S = 1 ground state.

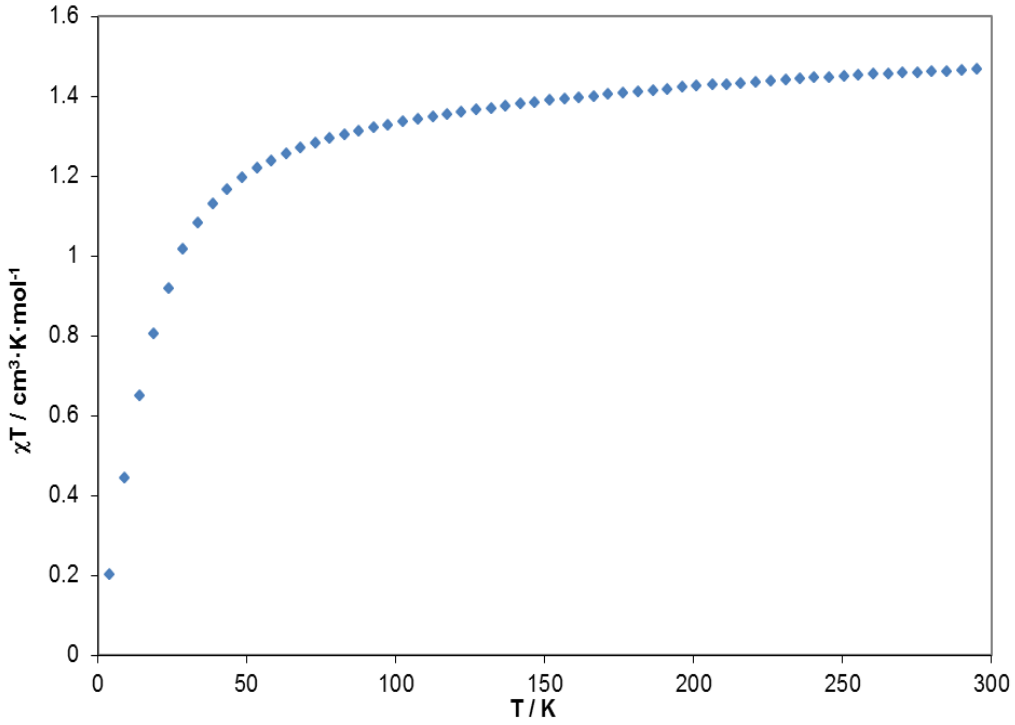


Figure S34. Temperature dependence of χT for **3** from 4 K to 300 K (χ_{dia} = -6.97 × 10^{-4} $cm^3 \cdot mol^{-1}$, mass = 53.0 mg, M = 979.3 g/mol).

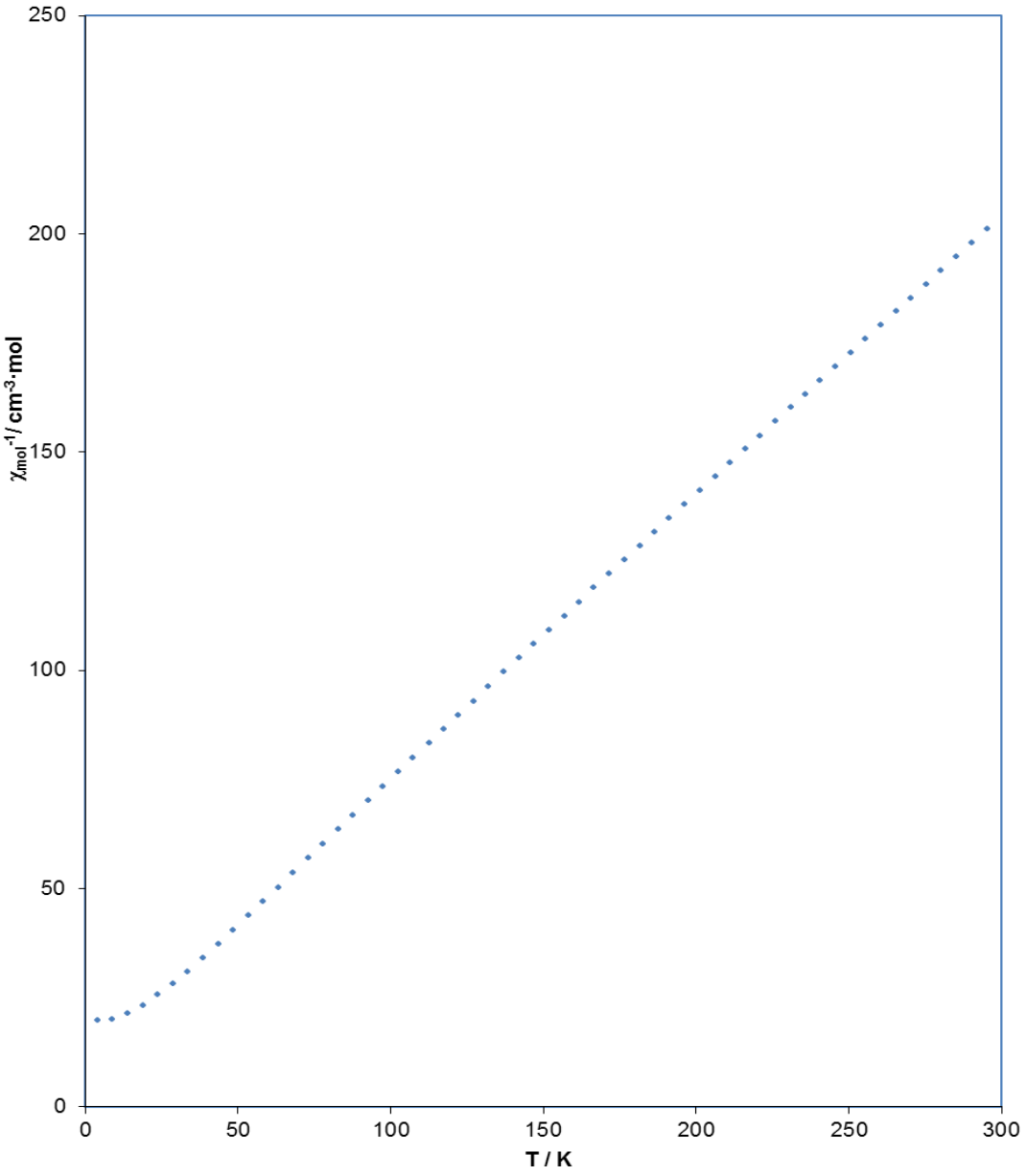


Figure S35. Temperature dependence of χ^{-1} for **3** from 4 K to 300 K (χ_{dia} = -6.97 × 10^{-4} cm^3·mol^{-1}, mass = 53.0 mg, M = 979.3 g/mol).

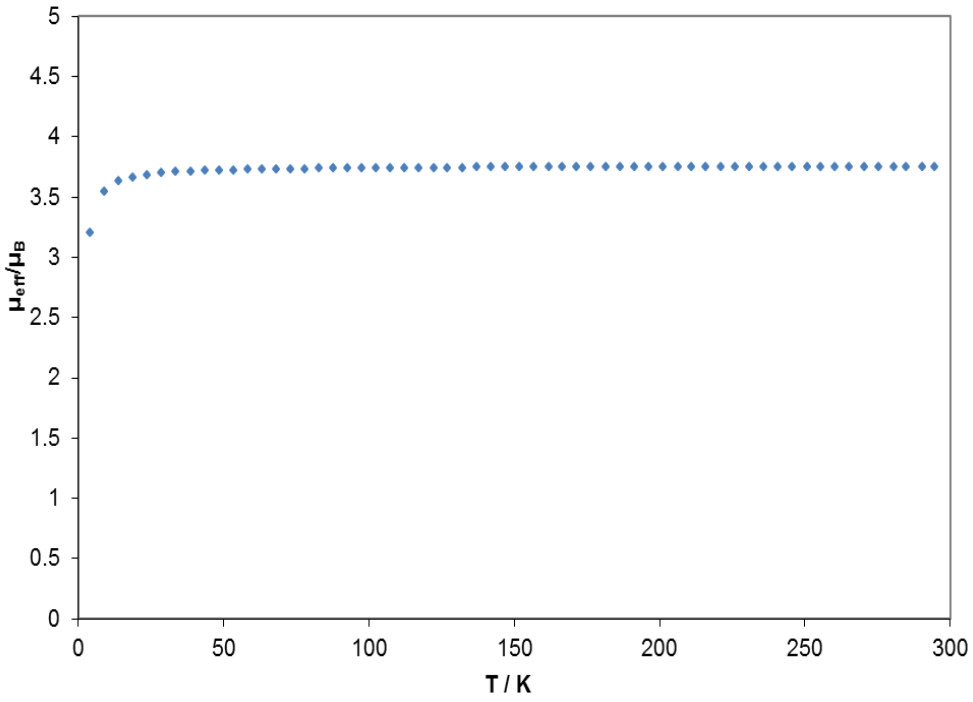


Figure S36. Temperature dependence of μ_{eff} for **4** from 4 K to 300 K (χ_{dia} = -4.68 × 10^{-4} $cm^3 \cdot mol^{-1}$, mass = 35.2 mg, M = 619.5 g/mol).

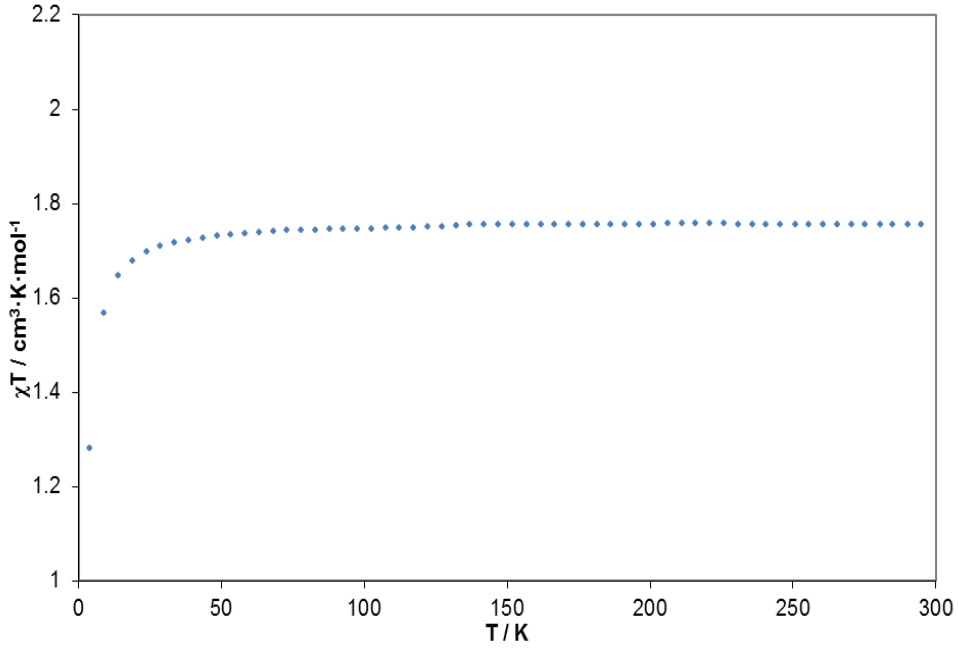


Figure S37. Temperature dependence of χT for **4** from 4 K to 300 K (χ_{dia} = -4.68 × 10^{-4} $cm^3 \cdot mol^{-1}$, mass = 35.2 mg, M = 619.5 g/mol).

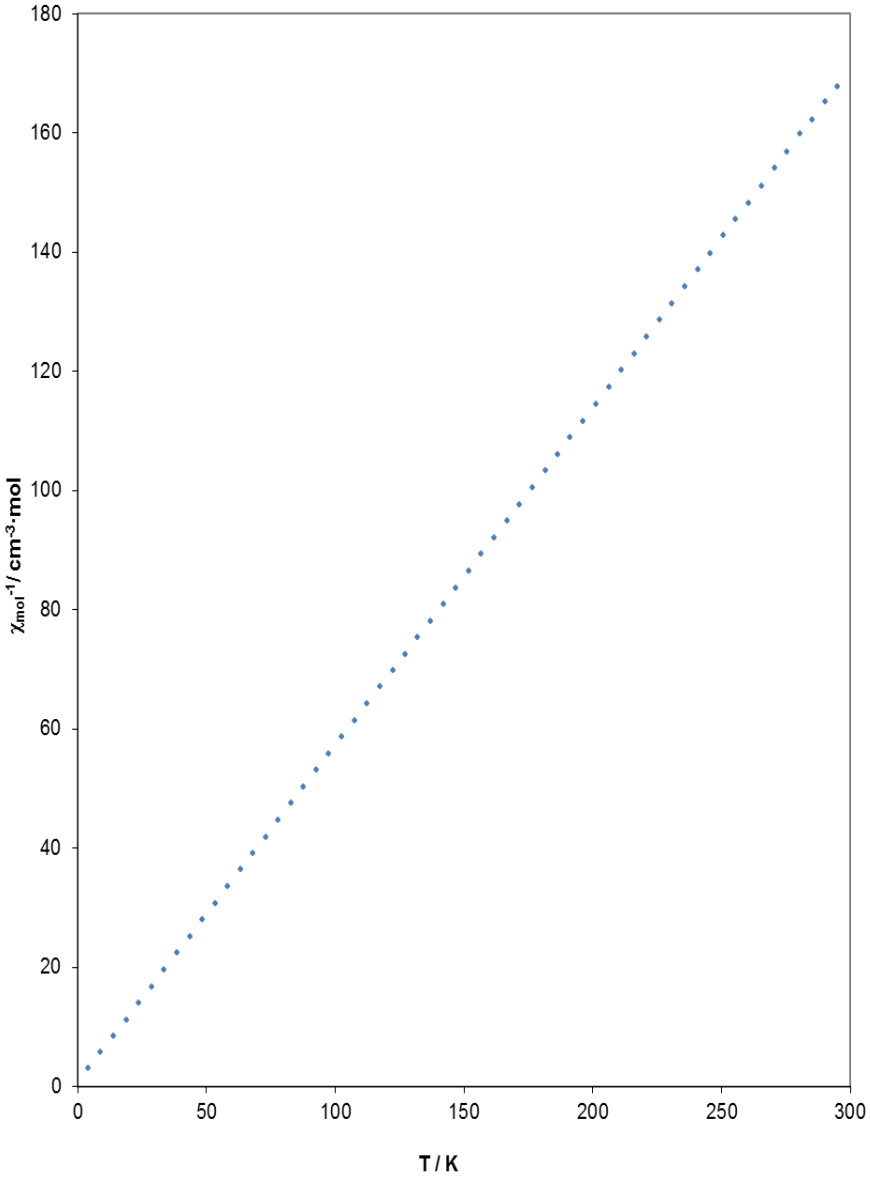


Figure S38. Temperature dependence of χ^{-1} for **4** from 4 K to 300 K (χ_{dia} = -4.68 × 10^{-4} $cm^3 \cdot mol^{-1}$, mass = 35.2 mg, M = 619.5 g/mol).

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S1. Input and Results of Computational Studies

S1.1. Computational Details.

Density Functional Theory calculations were performed with the Amsterdam Density Functional (ADF) program suite[1,2] version 2007.01.[3] For all atoms, the triple-ζ Slater-type orbital TZ2P ADF basis set was utilized without frozen cores. The local density approximation (LDA) of Vosko, Wilk and Nusair,[4] (VWN) was coupled with the generalized gradient approximation (GGA) corrections described by Becke[5] and Perdew[6,7] for electron exchange and correlation, respectively. Calculated molecular structures and molecular orbitals were visualized with the ADFView graphical routine of the ADF-GUI.[8] Crystallographic atomic coordinates were used as input where appropriate.

For the symmetry-constrained calculations on T_d and D_{4h} isomers, the N-M-N angles were constrained to the idealized values of 109.5˚ and 180˚, respectively. All other metrical parameters were allowed to optimize. For the unconstrained D_{2d} isomers, crystallographic atomic coordinates were used as input and all geometrical parameters were subject to full optimization. All calculations were performed using the spin-unrestricted formalism for direct energetic comparison of various spin states (ΔE^{SCF}). Isomeric variation vs. total bonding energy (E^{SCF}) is reported as a function of the average of the two N-M-N angles (˚) that bisect the primary molecular 2-fold axis (C_2 in D_{2d} and D_{4h} symmetry).

For each complex, two different T_d-symmetric isomers were calculated. The initial series of calculations constrained all N-M-N angles to 109.5˚, while allowing all other parameters to optimize. These calculations allowed free-rotation of the ketimide ligands with respect to the M-N bond vector and are denoted 'symmetry unconstrained'. In a second series of calculations, the N-M-N angles were constrained to 109.5˚ and the point symmetry of the molecule was confined to D_{2d}. In this configuration, all ketimide-nitrogen lone pairs are oriented mutually parallel. All other parameters were allowed to optimize. These calculations represent idealized T_d symmetry ($D_{2d} = T_d$ at $\theta = 109.5^\circ$)[9] and are denoted 'symmetry constrained'. For each complex, the 'symmetry-constrained' T_d isomer was found to be 8-21 kcal/mol higher in energy than the 'symmetry-unconstrained' isomer. For comparative purposes, only the energy 'symmetry-unconstrained' T_d isomer is compared with those of the D_{2d} ($\theta \neq 109.5^\circ$) and D_{4h} isomers.

Energy decomposition analysis (EDA)[10] was performed on the model complexes $[Co(NC{=}CH_2)_4]^n$ ($n = 0, -1$) in idealized D_{2d} symmetry using metrical parameters derived from geometry-optimization calculation. EDA calculations were constructed from a closed-shell [tetra(ketimide)]$^{4-}$ fragment in the geometry of the complex and either a Co^0 or Co^{1-} atomic fragment. The ΔE_{elstat}, ΔE_{Pauli} and ΔE_{orb} contributions to the total interaction energy, ΔE_{int}, are listed in Section S1.6. Energy decomposition of the orbital contributions (ΔE_{orb}) by irreducible representation for the metal-ketimide interactions are also listed in Section S1.6.

S1.2. Hardware Specifics. DFT calculations were performed on a home-built 72-CPU (1 x 8 master, 8 x 8 slave) Rocks 4.3 Linux cluster featuring Intel Xeon E5335 Quad-Core 2.00 GHz processors. Job control was implemented with the Sun Grid Engine v. 5.3.

S1.3. Sample Input File.

All ADF 2007.01 input files follow the general structure outlined below for $Co(CN^tBu_2)_4$ (S = 3/2). A complete listing of all input files is found in section S1.7.

S1.3.1. Input File for $Co(CN^tBu_2)_4$ (S = 3/2, Unconstrained).

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MAXMEMORYUSAGE 23000

UNRESTRICTED

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SCF
 Iterations 250
DIIS
END

XC
 LDA VWN
 GGA Becke Perdew
END

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2 N        2.893770000000       3.175610000000       2.828580000000
3 N        5.404115000000       5.280159000000       3.584369000000
4 N        3.001420000000       4.967260000000       4.815330000000
5 N        5.277894000000       2.648157000000       4.030308000000
6 C        1.989950000000       2.509380000000       2.291280000000
7 C        1.227800000000       1.500440000000       3.199540000000
8 C        2.242600000000       0.802720000000       4.096120000000
9 H        1.778030000000       0.168421000000       4.680980000000
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11 H       2.891830000000       0.321335000000       3.541480000000
12 C       0.411977000000       0.428715000000       2.513320000000
13 H       0.984674000000      -0.074537100000       1.897280000000
14 H      -0.320011000000       0.845122000000       2.010990000000
15 H       0.041361800000      -0.180470000000       3.185950000000
16 C       0.261536000000       2.327710000000       4.080780000000
17 H      -0.416475000000       2.751200000000       3.515090000000
18 H       0.766714000000       3.020180000000       4.558230000000
19 H      -0.174882000000       1.737570000000       4.729630000000
20 C       1.620180000000       2.845680000000       0.823441000000
21 C       0.202667000000       3.315690000000       0.684585000000
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28 H       1.717260000000       1.784320000000      -0.990963000000
29 C       2.564050000000       3.943640000000       0.321183000000
30 H       2.293620000000       4.220220000000      -0.578786000000
31 H       3.481590000000       3.599190000000       0.295808000000
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34	C	6.805825000000	6.883631000000	2.459561000000
35	C	6.461380000000	8.379916000000	2.606675000000
36	H	6.581722000000	8.829012000000	1.743913000000
37	H	7.052357000000	8.786804000000	3.271752000000
38	H	5.529516000000	8.473267000000	2.896305000000
39	C	8.293720000000	6.727332000000	2.174528000000
40	H	8.517211000000	5.775429000000	2.113230000000
41	H	8.810388000000	7.138109000000	2.897838000000
42	H	8.513180000000	7.169037000000	1.327090000000
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44	H	6.352263000000	6.838497000000	0.445939000000
45	H	5.092781000000	6.500693000000	1.373063000000
46	H	6.232059000000	5.402007000000	1.141665000000
47	C	7.060752000000	6.177857000000	5.110676000000
48	C	7.703273000000	7.532112000000	5.430956000000
49	H	8.076556000000	7.510643000000	6.336626000000
50	H	7.024655000000	8.236567000000	5.372723000000
51	H	8.419885000000	7.714860000000	4.787332000000
52	C	8.124478000000	5.082210000000	5.153585000000
53	H	8.545240000000	5.068907000000	6.039333000000
54	H	8.805802000000	5.260676000000	4.471650000000
55	H	7.706776000000	4.213424000000	4.978887000000
56	C	6.040154000000	5.889616000000	6.209433000000
57	H	5.675640000000	4.987744000000	6.088371000000
58	H	5.314131000000	6.545410000000	6.158863000000
59	H	6.477138000000	5.950655000000	7.084455000000
60	C	2.169920000000	5.718750000000	5.392900000000
61	C	1.781920000000	5.348840000000	6.865720000000
62	C	2.251340000000	6.453240000000	7.846020000000
63	H	1.733650000000	7.269820000000	7.689140000000
64	H	3.203290000000	6.635690000000	7.699360000000
65	H	2.114140000000	6.150720000000	8.767960000000
66	C	0.302452000000	5.102430000000	7.033210000000
67	H	0.014296800000	4.404550000000	6.407180000000
68	H	-0.189406000000	5.929640000000	6.847280000000
69	H	0.120312000000	4.813440000000	7.951810000000
70	C	2.524090000000	4.090200000000	7.283410000000
71	H	2.271100000000	3.849200000000	8.198360000000
72	H	3.489930000000	4.252050000000	7.242660000000
73	H	2.289710000000	3.357040000000	6.676200000000
74	C	1.581330000000	6.914420000000	4.596210000000
75	C	2.674740000000	7.521520000000	3.749200000000
76	H	2.300730000000	8.240280000000	3.198130000000
77	H	3.059940000000	6.831830000000	3.169200000000
78	H	3.375090000000	7.887740000000	4.329860000000
79	C	0.947818000000	8.010620000000	5.401260000000
80	H	1.611390000000	8.393980000000	6.010780000000
81	H	0.199941000000	7.646190000000	5.919150000000
82	H	0.616933000000	8.708820000000	4.796870000000
83	C	0.553295000000	6.297000000000	3.655190000000
84	H	-0.132200000000	5.832290000000	4.180020000000

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85 H       0.998170000000       5.657830000000       3.059880000000
86 H       0.133449000000       7.002840000000       3.122360000000
87 C       6.102014000000       1.712876000000       3.923038000000
88 C       6.509121000000       0.976496000000       5.234804000000
89 C       8.038808000000       0.928736000000       5.421761000000
90 H       8.250260000000       0.509763000000       6.281458000000
91 H       8.398618000000       1.840505000000       5.404904000000
92 H       8.440188000000       0.405341000000       4.696918000000
93 C       5.941945000000       1.729785000000       6.436234000000
94 H       4.963706000000       1.752059000000       6.376469000000
95 H       6.288739000000       2.646083000000       6.440831000000
96 H       6.207875000000       1.275778000000       7.262217000000
97 C       5.933082000000      -0.439533000000       5.279244000000
98 H       6.082290000000      -0.824919000000       6.168058000000
99 H       6.377480000000      -0.994129000000       4.603440000000
100 H      4.971792000000      -0.407944000000       5.093820000000
101 C      6.679433000000       1.350519000000       2.520858000000
102 C      7.941153000000       2.159256000000       2.289460000000
103 H      8.638196000000       1.859988000000       2.908565000000
104 H      7.752678000000       3.108520000000       2.441172000000
105 H      8.246722000000       2.029977000000       1.366934000000
106 C      6.953244000000      -0.137341000000       2.301720000000
107 H      7.250815000000      -0.282163000000       1.379193000000
108 H      6.132077000000      -0.648021000000       2.464158000000
109 H      7.651746000000      -0.435499000000       2.920824000000
110 C      5.667880000000       1.764454000000       1.440490000000
111 H      5.496604000000       2.726686000000       1.506385000000
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S1.4. Results for calculated $Co(NC^tBu_2)_4$ ($S = 3/2$).

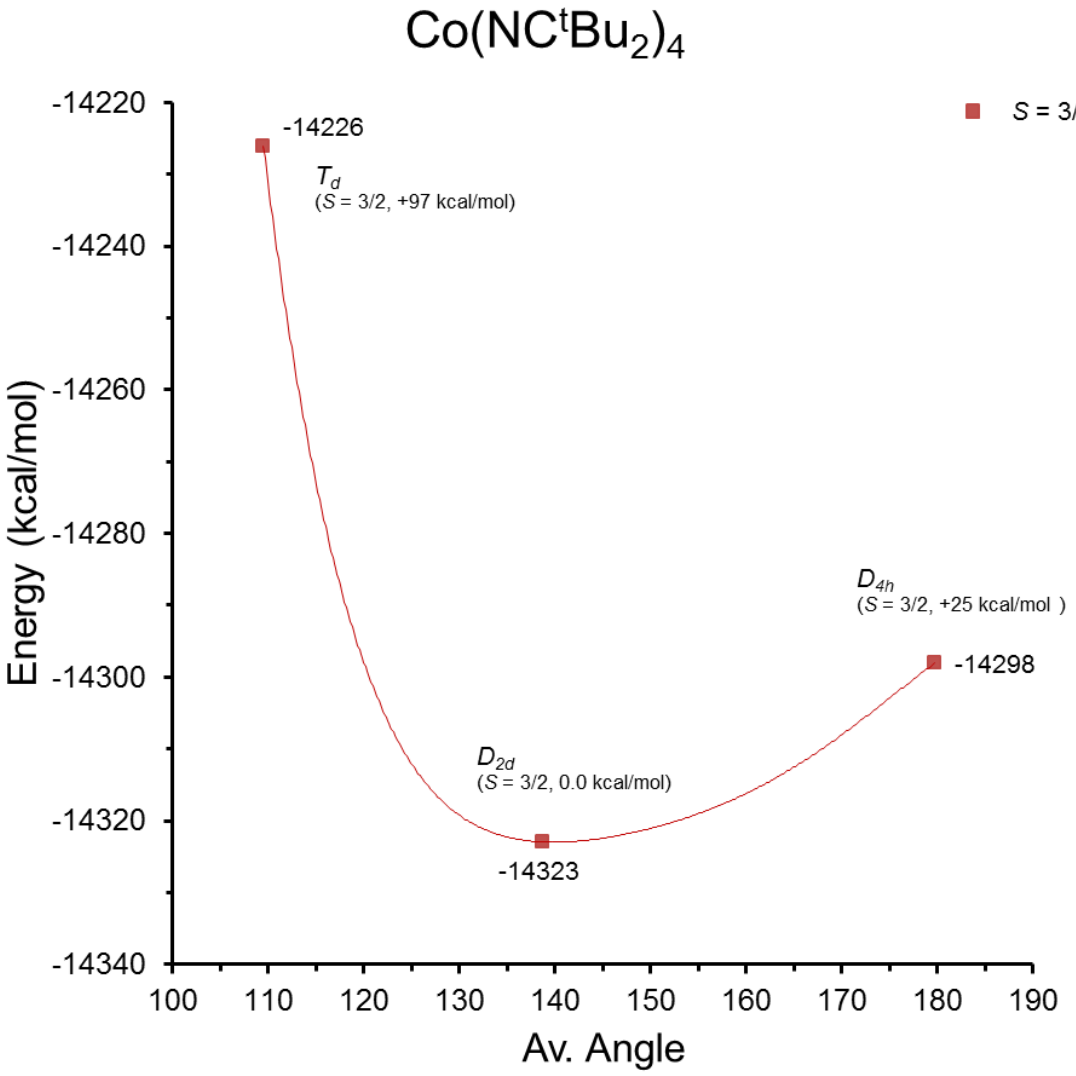

Figure S1.1. Plot of the average N-Co-N bond angle vs the potential energy (E^{SCF}) for $Co(NC^tBu_2)_4$ ($S = 3/2$). The values relating to T_d and D_{4h} symmetries are from constrained geometry optimizations while the value for the D_{2d} symmetry is from an unconstrained geometry optimization. Relative Energy (ΔE^{SCF}) for each isomer and spin state is listed in parentheses. The best fit of three points is plotted and is not a quantitative potential energy surface.

Table S1.1. Comparison of Relative Energy Differences Between the T_d, T_d (symmetry constrained), D_{2d} and D_{4h} Geometries of $Co(NC^tBu_2)_4$ ($S = 3/2$).

Geometry	Relative Energy, $S = 3/2$ (kcal/mol)
D_{2d}	0.0
T_d	97
T_d (sym)	118
D_{4h}	25

S1.4.1 Results for D_{2d} Unconstrained $Co(NC^tBu_2)_4$ ($S = 3/2$).

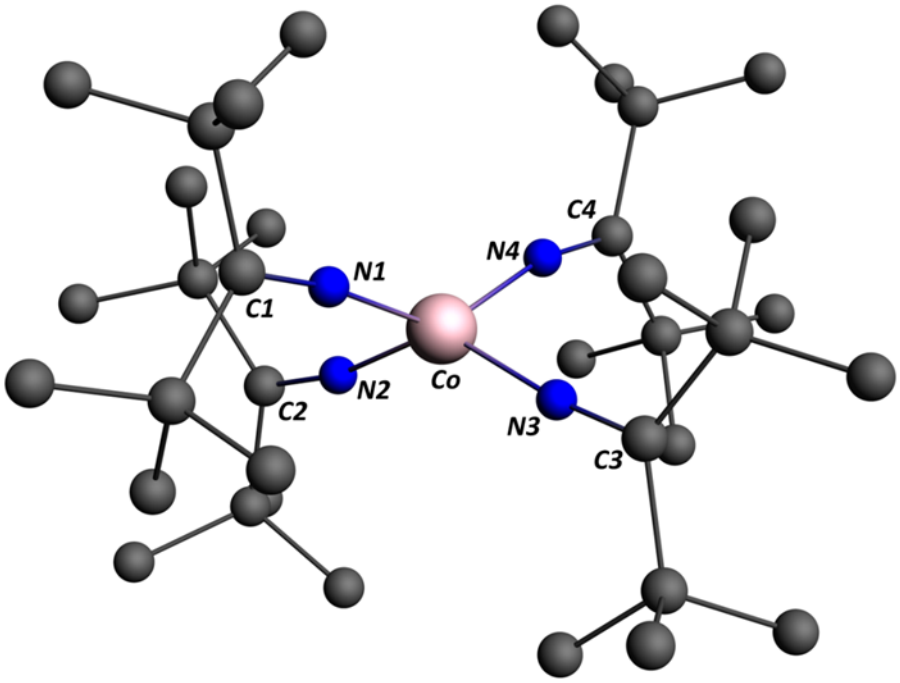

Figure S1.2. Optimized molecular structure of D_{2d} unconstrained $Co(NC^tBu_2)_4$ ($S = 3/2$). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Co-N1, 1.806; Co-N2, 1.803; Co-N3, 1.805; Co-N4, 1.802; N1-Co-N4, 139.1; N2-Co-N3, 138.2; Co-N1-C1, 172.0; Co-N2-C2, 169.2; Co-N3-C3, 173.1; Co-N4-C4, 165.9.

Table S1.2. Comparison of Calculated vs. Experimental Structures for $Co(NC^tBu_2)_4$ (**4**, X-ray).

Parameter/Complex	$Co(NC^tBu_2)_4$ (Calc)	$Co(NC^tBu_2)_4$ (4, Exp)	% Difference
Co-N1	1.806 Å	1.800(3) Å	0.3
Co-N2	1.803 Å	1.789(3) Å	0.8
Co-N3	1.805 Å	1.792(3) Å	0.7
Co-N4	1.802 Å	1.794(3) Å	0.4
N1-Co-N4	139.1°	139.17(15)°	0.0
N2-Co-N3	138.2°	137.57(15)°	0.4
Co-N1-C1	172.0°	171.9(3)°	0.0
Co-N2-C2	169.2°	167.9(3)°	0.7
Co-N3-C3	173.1°	172.9(3)°	0.1

Co-N4-C4	165.9°	165.1(3)°	0.4

S1.4.2 Optimized Cartesian Coordinates for D_{2d} Unconstrained Co(NC^{t}Bu$_2$)$_4$ (S = 3/2).

1.Co	4.149986	4.023271	3.810427
2.N	2.885614	3.175365	2.837979
3.N	5.417926	5.285193	3.592159
4.N	3.009240	4.983394	4.828444
5.N	5.286288	2.637753	4.006201
6.C	1.965080	2.500513	2.308810
7.C	1.175796	1.470535	3.214391
8.C	2.187233	0.754214	4.130465
9.H	1.654567	0.080697	4.819437
10.H	2.770288	1.473773	4.715704
11.H	2.892324	0.151625	3.539711
12.C	0.369946	0.377465	2.485534
13.H	1.014223	-0.293003	1.901038
14.H	-0.409424	0.777875	1.824575
15.H	-0.136493	-0.238261	3.246153
16.C	0.211534	2.293912	4.096581
17.H	-0.559645	2.800850	3.499318
18.H	0.772010	3.056165	4.652020
19.H	-0.296540	1.633537	4.817363
20.C	1.602363	2.804691	0.804935
21.C	0.147255	3.310650	0.685613
22.H	-0.000326	4.226265	1.275835
23.H	-0.592188	2.569728	1.012564
24.H	-0.068188	3.552477	-0.367335
25.C	1.808724	1.569184	-0.101739
26.H	1.073276	0.778059	0.077222
27.H	2.814912	1.144695	0.028411
28.H	1.712548	1.877511	-1.155079
29.C	2.527318	3.919666	0.279244
30.H	2.248977	4.162909	-0.757418
31.H	3.578238	3.604954	0.290875
32.H	2.448590	4.829882	0.885888
33.C	6.372963	6.094491	3.731330
34.C	6.824290	6.906132	2.456222
35.C	6.468299	8.405292	2.600731
36.H	6.647882	8.912917	1.639439
37.H	7.068250	8.917284	3.361230
38.H	5.405702	8.532400	2.852724
39.C	8.334945	6.747548	2.173641
40.H	8.603757	5.691106	2.028463
41.H	8.969109	7.155545	2.969905
42.H	8.585697	7.285483	1.245607
43.C	6.068255	6.371753	1.223522
44.H	6.393562	6.928285	0.331397

45.H	4.983820	6.491963	1.332653
46.H	6.268402	5.305190	1.060716
47.C	7.099766	6.206606	5.128836
48.C	7.736543	7.575017	5.445613
49.H	8.199239	7.517307	6.443592
50.H	6.986630	8.377653	5.479833
51.H	8.524467	7.865830	4.740540
52.C	8.193796	5.115062	5.175168
53.H	8.664550	5.102050	6.171396
54.H	8.983699	5.284165	4.431366
55.H	7.749787	4.128618	4.988183
56.C	6.082020	5.917106	6.247205
57.H	5.620353	4.932092	6.122404
58.H	5.275459	6.663052	6.247745
59.H	6.586985	5.952226	7.224453
60.C	2.183880	5.732872	5.412224
61.C	1.789154	5.377640	6.897382
62.C	2.231384	6.483137	7.883566
63.H	1.666832	7.414214	7.766186
64.H	3.301792	6.707054	7.768657
65.H	2.074014	6.128783	8.914854
66.C	0.269453	5.127081	7.032450
67.H	-0.062089	4.320676	6.363268
68.H	-0.335458	6.016358	6.820761
69.H	0.046673	4.815303	8.065251
70.C	2.509864	4.080125	7.312445
71.H	2.220332	3.818536	8.341428
72.H	3.599419	4.199093	7.277319
73.H	2.246953	3.243677	6.653351
74.C	1.547281	6.926789	4.592143
75.C	2.655979	7.567706	3.734427
76.H	2.227443	8.360217	3.101452
77.H	3.142170	6.822706	3.095092
78.H	3.430013	8.019657	4.371417
79.C	0.897664	8.061812	5.408582
80.H	1.630015	8.592691	6.031662
81.H	0.073220	7.726618	6.049167
82.H	0.479784	8.796817	4.702345
83.C	0.486300	6.315635	3.649783
84.H	-0.336259	5.844683	4.206744
85.H	0.948651	5.552920	3.009152
86.H	0.055864	7.100722	3.007310
87.C	6.105656	1.686803	3.908464
88.C	6.518348	0.939946	5.238482
89.C	8.051988	0.877952	5.412872
90.H	8.285562	0.408087	6.381331
91.H	8.493960	1.884618	5.418003
92.H	8.551167	0.289181	4.633476

93.C	5.947579	1.707204	6.447144
94.H	4.853013	1.759363	6.409629
95.H	6.327479	2.735232	6.488997
96.H	6.240813	1.191136	7.373900
97.C	5.926732	-0.488886	5.289775
98.H	6.109961	-0.915779	6.288874
99.H	6.373509	-1.167212	4.554938
100.H	4.839419	-0.468559	5.129241
101.C	6.714076	1.329138	2.495776
102.C	8.009719	2.148264	2.290427
103.H	8.804201	1.867844	2.993651
104.H	7.804579	3.220962	2.408876
105.H	8.390270	1.982382	1.269505
106.C	7.014825	-0.168619	2.282627
107.H	7.398971	-0.307006	1.259719
108.H	6.106870	-0.781449	2.376401
109.H	7.771922	-0.563196	2.971008
110.C	5.715521	1.750371	1.402877
111.H	5.500609	2.823523	1.452838
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113.H	6.133317	1.516969	0.411977

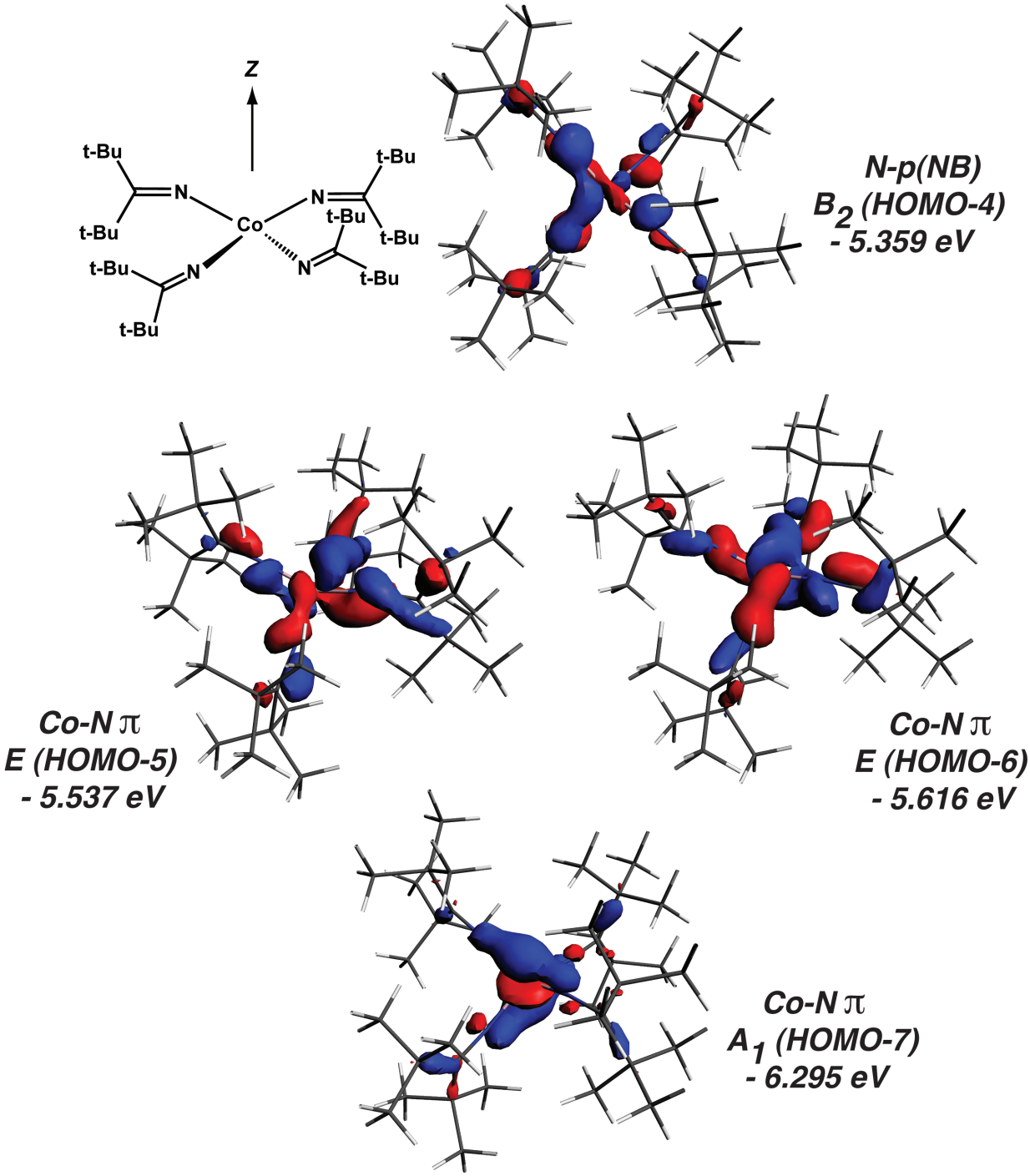

Figure S1.3. Calculated Co-ketimide π-bonding molecular orbitals for D_{2d} unconstrained $Co(NC^tBu_2)_4$ (S = 3/2) (HOMO-7 – HOMO-4). Symmetry labels have been added to correspond with idealized D_{2d} symmetry.

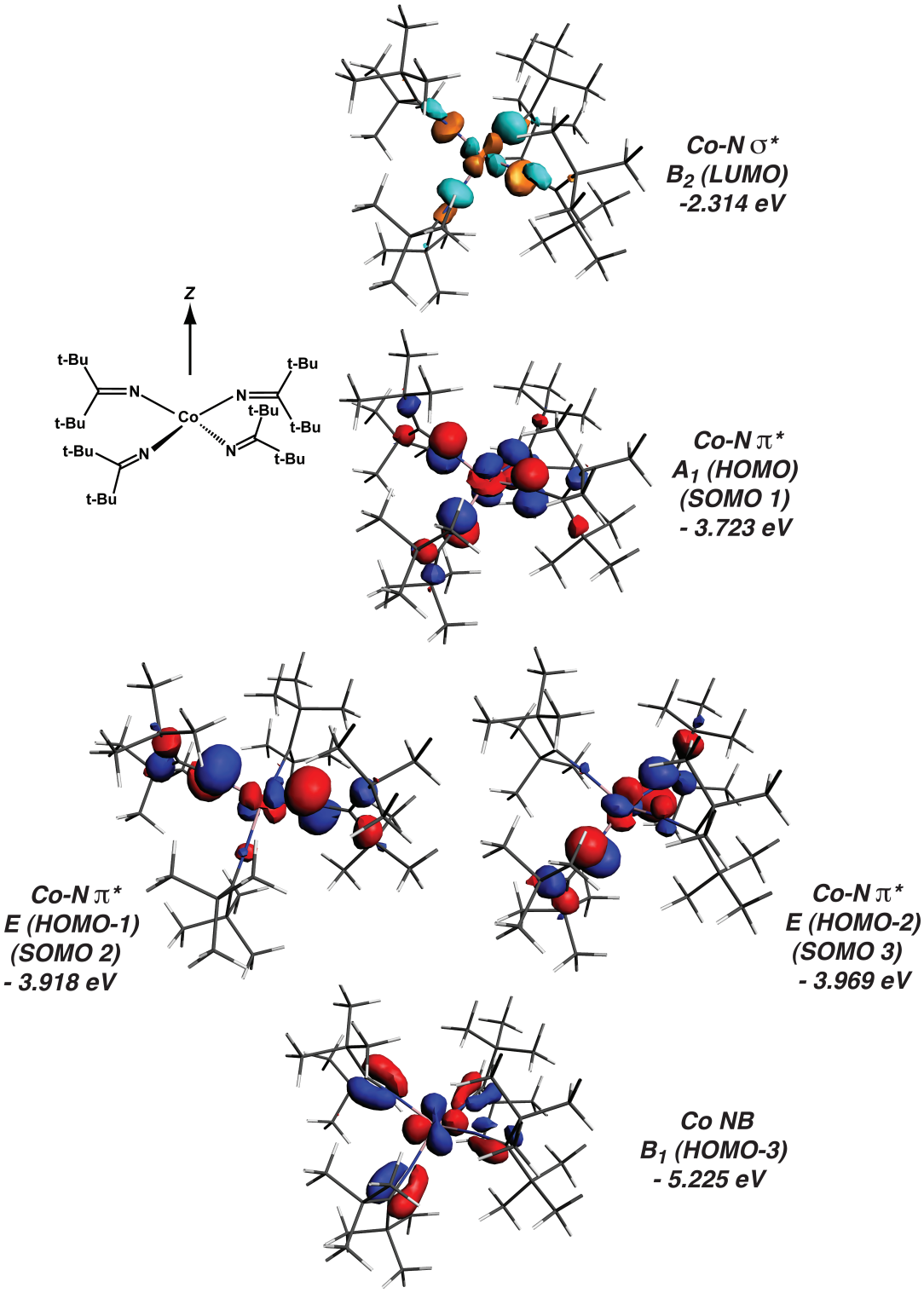

Figure S1.4. Calculated Co-ketimide π-antibonding and σ-antibonding molecular orbitals for D_{2d} unconstrained $Co(NC^tBu_2)_4$ (S = 3/2) (HOMO-3 – LUMO). Symmetry labels have been added to correspond with idealized D_{2d} symmetry.

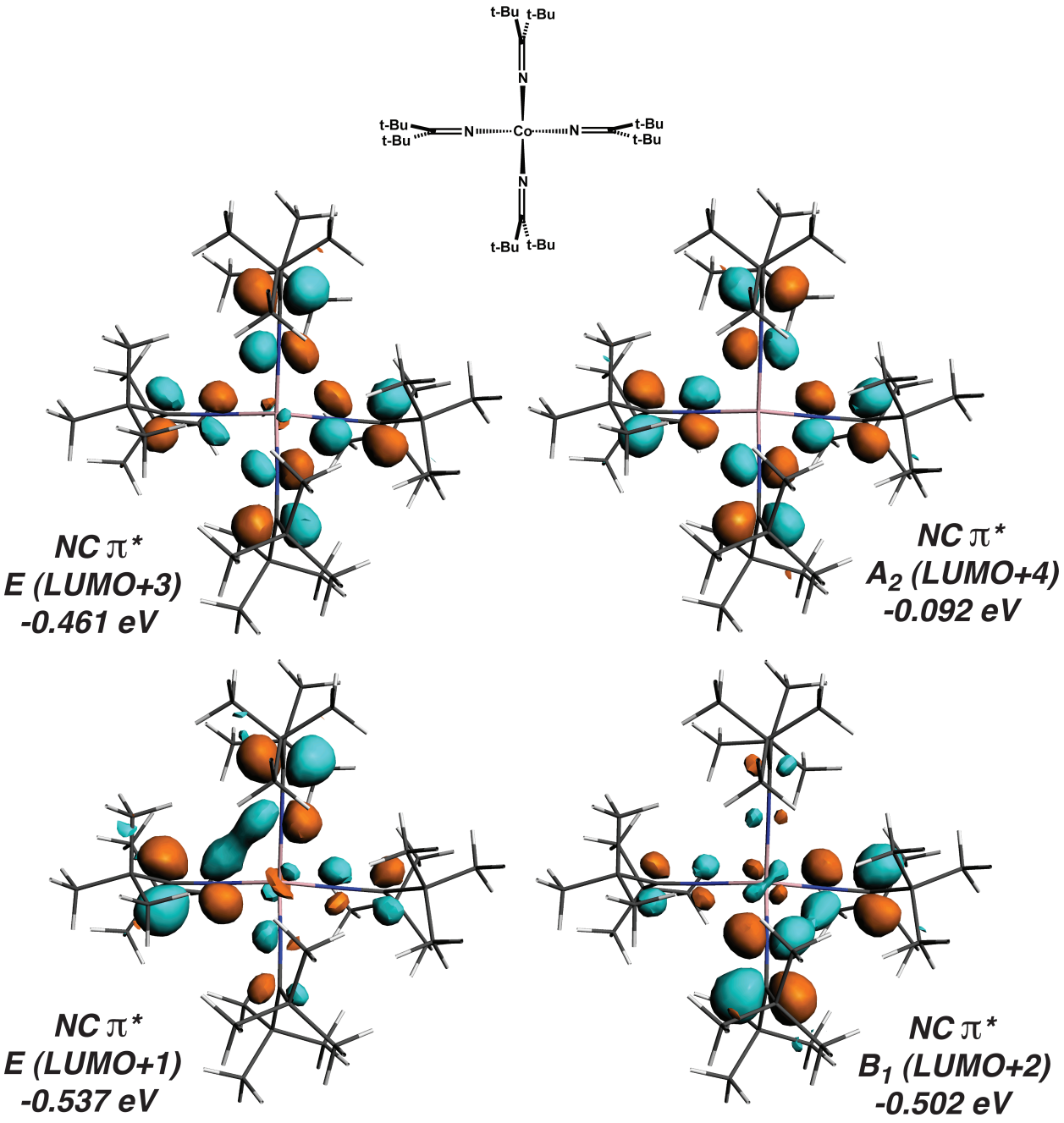

Figure S1.5. Calculated ketimide NC π-antibonding (π*) molecular orbitals for D_{2d} unconstrained $Co(NC^tBu_2)_4$ (S = 3/2) (LUMO+1 – LUMO+4). Symmetry labels have been added to correspond with idealized D_{2d} symmetry.

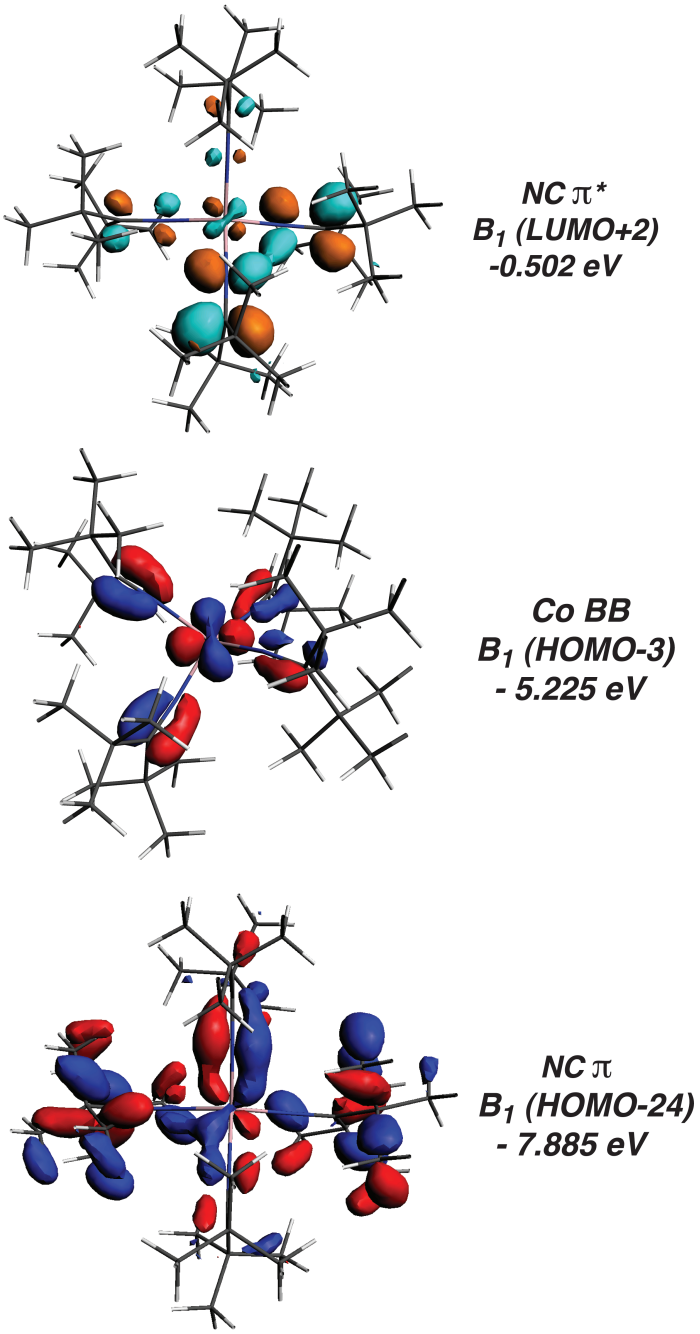

Figure S1.6. Calculated b_1-symmetric molecular orbitals for D_{2d} unconstrained $Co(NC^tBu_2)_4$ (S = 3/2) showing the three-orbital interaction describing the Co-to-ketimide π-back bonding interaction. Symmetry labels have been added to correspond with idealized D_{2d} symmetry.

S1.4.3. Results for T_d Constrained $Co(NC^tBu_2)_4$ ($S = 3/2$).

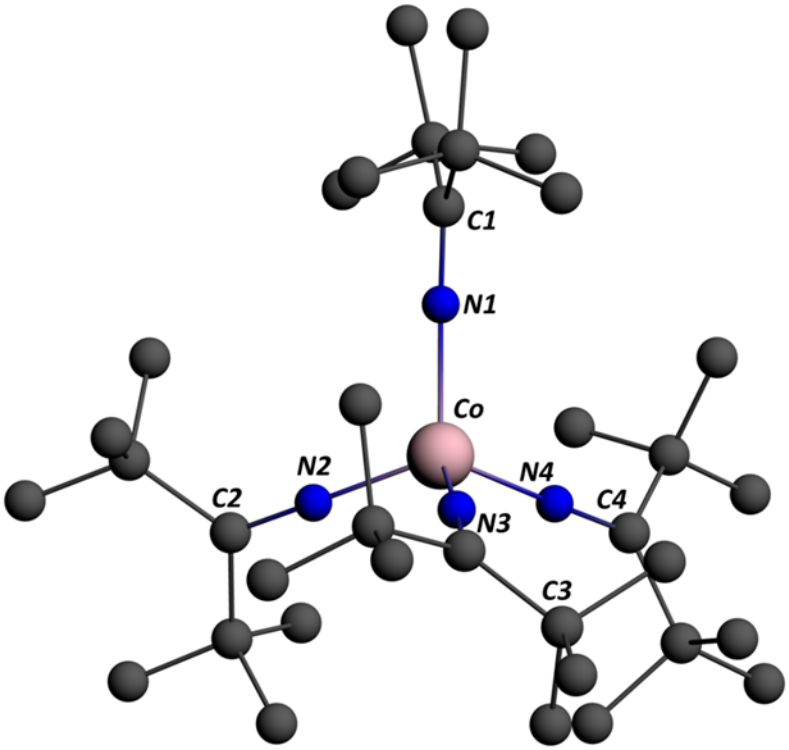

Figure S1.7. Optimized molecular structure of T_d constrained $Co(NC^tBu_2)_4$ ($S = 3/2$). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Co-N1, 1.937; Co-N2, 1.888; Co-N3, 1.901; Co-N4, 1.944; N1-Co-N3, 109.5; N2-Co-N4, 109.5; Co-N1-C1, 175.2; Co-N2-C2, 177.0; Co-N3-C3, 176.7; Co-N4-C4, 178.7.

S1.4.4. Optimized Cartesian Coordinates for T_d Constrained $Co(NC^tBu_2)_4$ ($S = 3/2$).

1.Co	0.022231	-0.003982	0.009771
2.N	-0.210817	0.479046	1.833546
3.N	-1.008257	-1.599369	-0.372969
4.N	-0.587238	1.449279	-1.128484
5.N	1.849917	-0.340277	-0.323552
6.C	-0.298690	0.827023	3.048679
7.C	-1.728293	-2.622018	-0.530359
8.C	-1.010584	2.383097	-1.869558
9.C	3.061462	-0.563169	-0.611971
10.C	-0.875523	3.893970	-1.375774
11.C	-1.698586	1.979338	-3.266019
12.C	3.972251	0.661588	-1.083731
13.C	3.599521	-2.075698	-0.501592
14.C	-0.883484	2.264887	3.417197
15.C	0.210545	-0.185660	4.187122
16.C	-2.585797	-3.236650	0.660426
17.C	-1.721744	-3.254556	-2.019605

18.C	3.459464	1.140259	-2.479609
19.H	2.776026	1.994712	-2.391062
20.H	4.305219	1.446712	-3.115158
21.H	2.920113	0.345419	-3.011147
22.C	5.491585	0.418563	-1.237189
23.H	5.946940	1.384475	-1.501728
24.H	5.971076	0.075513	-0.313145
25.H	5.742785	-0.281214	-2.041614
26.C	3.829856	1.776413	-0.013070
27.H	2.900404	2.344199	-0.131716
28.H	3.833450	1.347406	0.998868
29.H	4.679026	2.475243	-0.081636
30.C	5.109989	-2.347170	-0.691272
31.H	5.454888	-2.126372	-1.707387
32.H	5.753166	-1.823996	0.024208
33.H	5.253143	-3.427786	-0.536535
34.C	2.894452	-2.936661	-1.587780
35.H	2.050228	-3.483692	-1.160991
36.H	2.511118	-2.330661	-2.417073
37.H	3.585182	-3.680994	-2.012500
38.C	3.243962	-2.584639	0.921187
39.H	3.436099	-1.808807	1.674736
40.H	2.188822	-2.874470	1.002716
41.H	3.865505	-3.458942	1.176095
42.C	-3.497779	-4.442638	0.358488
43.H	-4.014886	-4.677556	1.299818
44.H	-4.262874	-4.241382	-0.399941
45.H	-2.936401	-5.338349	0.075384
46.C	-1.562915	-3.739880	1.711463
47.H	-0.640430	-4.112548	1.244432
48.H	-1.282561	-2.933077	2.380540
49.H	-1.985849	-4.554891	2.317730
50.C	-3.511884	-2.124586	1.229163
51.H	-2.998494	-1.472041	1.946048
52.H	-3.907738	-1.489041	0.424885
53.H	-4.373501	-2.585526	1.737663
54.C	1.759013	-0.323469	4.074251
55.H	2.040751	-1.201143	3.477629
56.H	2.218095	0.551619	3.597501
57.H	2.205826	-0.439712	5.073319
58.C	-0.470493	-1.536644	3.913729
59.H	-1.514564	-1.384570	3.606230
60.H	0.053617	-2.077663	3.122456
61.H	-0.484723	-2.166885	4.816746
62.C	-0.125985	0.121627	5.664249
63.H	0.213422	-0.745861	6.249560
64.H	0.380899	1.000381	6.069990
65.H	-1.204672	0.223144	5.837528

66.C	-1.051189	2.675447	4.898692
67.H	-1.750625	2.045205	5.457492
68.H	-0.101452	2.724314	5.442593
69.H	-1.467931	3.694332	4.891741
70.C	0.103600	3.310611	2.826968
71.H	1.144661	2.972719	2.928621
72.H	-0.067912	3.487029	1.762873
73.H	0.012282	4.271967	3.359620
74.C	-2.305337	2.343158	2.804241
75.H	-2.272662	2.486070	1.723739
76.H	-2.863125	1.413824	2.992886
77.H	-2.878183	3.172142	3.252111
78.C	-0.265923	-3.325900	-2.508181
79.H	0.151947	-2.343806	-2.759217
80.H	0.363127	-3.769778	-1.730571
81.H	-0.197524	-3.977468	-3.393931
82.C	-2.276907	-4.683327	-2.185821
83.H	-1.789541	-5.410235	-1.523565
84.H	-3.359576	-4.750204	-2.057039
85.H	-2.055864	-4.980573	-3.220982
86.C	-2.559955	-2.310179	-2.917712
87.H	-3.320118	-1.760882	-2.347832
88.H	-1.914750	-1.566827	-3.401196
89.H	-3.076979	-2.876606	-3.706738
90.C	-0.674309	1.095124	-4.024895
91.H	0.331414	1.538280	-3.987734
92.H	-0.603290	0.086156	-3.603567
93.H	-0.962672	1.014844	-5.086360
94.C	-3.025000	1.206871	-2.974006
95.H	-2.983260	0.185838	-3.364420
96.H	-3.238399	1.135321	-1.900402
97.H	-3.880557	1.700598	-3.457740
98.C	-2.073153	3.112198	-4.246542
99.H	-2.477539	2.636266	-5.153317
100.H	-2.857622	3.768468	-3.855270
101.H	-1.217648	3.726392	-4.551466
102.C	-1.258600	5.051267	-2.321463
103.H	-0.685978	5.087010	-3.254729
104.H	-2.328198	5.048151	-2.558520
105.H	-1.061373	5.982047	-1.767684
106.C	-1.818131	4.071194	-0.146417
107.H	-2.409826	3.169920	0.037333
108.H	-1.254517	4.288541	0.765521
109.H	-2.519077	4.904532	-0.292387
110.C	0.610588	4.107466	-1.004820
111.H	0.913441	3.494085	-0.148841
112.H	1.257748	3.837507	-1.853006
113.H	0.796322	5.167499	-0.769203

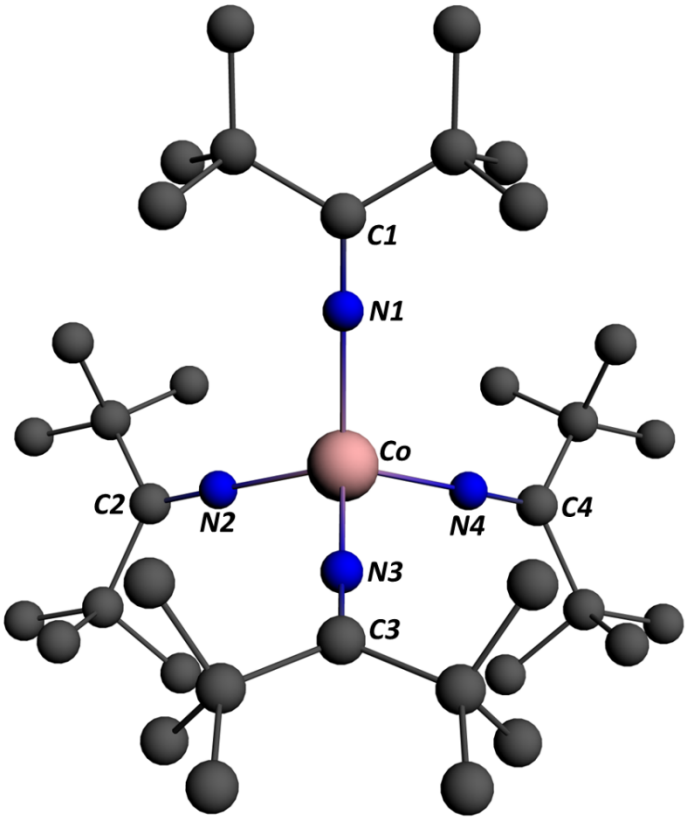

Figure S1.8. Optimized molecular structure of T_d constrained (symmetry constrained) $Co(NC^tBu_2)_4$ (S = 3/2). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Co-N1, 2.129; Co-N2, 2.129; Co-N3, 2.129; Co-N4, 2.129; N1-Co-N3, 109.5; N2-Co-N4, 109.5; Co-N1-C1, 178.7; Co-N2-C2, 178.7; Co-N3-C3, 178.7; Co-N4-C4, 178.7.

S1.4.5. Optimized Cartesian Coordinates for T_d Constrained (Symmetry Constrained) $Co(NC^tBu_2)_4$ (S = 3/2).

1.N	1.228999	-1.228999	-1.228930
2.Co	0.000000	0.000000	0.000000
3.N	1.228999	1.228999	1.228930
4.N	-1.228999	1.228999	-1.228930
5.N	-1.228999	-1.228999	1.228930
6.C	1.948828	-1.948828	-1.984455
7.C	1.948828	1.948828	1.984455
8.C	-1.948828	1.948828	-1.984455
9.C	-1.948828	-1.948828	1.984455
10.C	2.316863	-4.314492	-3.369716
11.C	-3.219685	0.106530	-3.231278
12.C	-4.250291	1.202966	-1.210879
13.C	3.219685	-0.106530	-3.231278
14.C	4.314492	2.316863	3.369716

15.C	3.219685	0.106530	3.231278
16.C	-3.219685	-0.106530	3.231278
17.C	-2.316863	4.314492	-3.369716
18.C	3.415926	1.434976	2.472432
19.C	-0.106530	-3.219685	3.231278
20.C	-4.314492	-2.316863	3.369716
21.C	1.434976	3.415926	2.472432
22.C	1.202966	4.250291	1.210879
23.C	-0.106530	3.219685	-3.231278
24.C	-1.434976	3.415926	-2.472432
25.C	-1.202966	-4.250291	1.210879
26.C	4.250291	1.202966	1.210879
27.C	-3.415926	1.434976	-2.472432
28.C	-4.250291	-1.202966	1.210879
29.C	-2.316863	-4.314492	3.369716
30.C	-1.434976	-3.415926	2.472432
31.C	-1.202966	4.250291	-1.210879
32.C	2.316863	4.314492	3.369716
33.C	-3.415926	-1.434976	2.472432
34.C	-4.314492	2.316863	-3.369716
35.C	0.106530	3.219685	3.231278
36.C	1.434976	-3.415926	-2.472432
37.C	0.106530	-3.219685	-3.231278
38.C	4.250291	-1.202966	-1.210879
39.C	3.415926	-1.434976	-2.472432
40.C	1.202966	-4.250291	-1.210879
41.C	4.314492	-2.316863	-3.369716
42.H	4.615273	3.252627	2.885381
43.H	3.901587	2.539702	4.357962
44.H	5.238951	1.739754	3.529705
45.H	1.739754	5.238951	3.529705
46.H	3.252627	4.615273	2.885381
47.H	2.539702	3.901587	4.357962
48.H	2.539702	-3.901587	-4.357962
49.H	1.739754	-5.238951	-3.529705
50.H	3.252627	-4.615273	-2.885381
51.H	5.238951	-1.739754	-3.529705
52.H	3.901587	-2.539702	-4.357962
53.H	4.615273	-3.252627	-2.885381
54.H	-1.739754	5.238951	-3.529705
55.H	-3.252627	4.615273	-2.885381
56.H	-2.539702	3.901587	-4.357962
57.H	-4.615273	3.252627	-2.885381
58.H	-5.238951	1.739754	-3.529705
59.H	-3.901587	2.539702	-4.357962
60.H	-4.615273	-3.252627	2.885381
61.H	-5.238951	-1.739754	3.529705
62.H	-3.901587	-2.539702	4.357962

63.H	-1.739754	-5.238951	3.529705
64.H	-3.252627	-4.615273	2.885381
65.H	-2.539702	-3.901587	4.357962
66.H	-0.812176	5.244887	-1.481933
67.H	-0.477920	3.749066	-0.579230
68.H	-2.126299	4.395721	-0.630804
69.H	-3.749066	0.477920	-0.579230
70.H	-5.244887	0.812176	-1.481933
71.H	-4.395721	2.126299	-0.630804
72.H	-2.620983	0.260471	-4.141097
73.H	-4.204725	-0.276242	-3.544483
74.H	-2.724425	-0.649781	-2.611193
75.H	0.276242	4.204725	-3.544483
76.H	-0.260471	2.620983	-4.141097
77.H	0.649781	2.724425	-2.611193
78.H	2.126299	-4.395721	-0.630804
79.H	0.812176	-5.244887	-1.481933
80.H	0.477920	-3.749066	-0.579230
81.H	-0.276242	-4.204725	-3.544483
82.H	0.260471	-2.620983	-4.141097
83.H	-0.649781	-2.724425	-2.611193
84.H	5.244887	-0.812176	-1.481933
85.H	4.395721	-2.126299	-0.630804
86.H	3.749066	-0.477920	-0.579230
87.H	4.204725	-0.276242	3.544483
88.H	2.724425	-0.649781	2.611193
89.H	2.620983	0.260471	4.141097
90.H	5.244887	0.812176	1.481933
91.H	4.395721	2.126299	0.630804
92.H	3.749066	0.477920	0.579230
93.H	4.204725	0.276242	-3.544483
94.H	2.724425	0.649781	-2.611193
95.H	2.620983	-0.260471	-4.141097
96.H	0.260471	2.620983	4.141097
97.H	-0.649781	2.724425	2.611193
98.H	-0.276242	4.204725	3.544483
99.H	0.477920	3.749066	0.579230
100.H	2.126299	4.395721	0.630804
101.H	0.812176	5.244887	1.481933
102.H	-2.620983	-0.260471	4.141097
103.H	-4.204725	0.276242	3.544483
104.H	-2.724425	0.649781	2.611193
105.H	-4.395721	-2.126299	0.630804
106.H	-3.749066	-0.477920	0.579230
107.H	-5.244887	-0.812176	1.481933
108.H	0.649781	-2.724425	2.611193
109.H	0.276242	-4.204725	3.544483
110.H	-0.260471	-2.620983	4.141097

111.H	-2.126299	-4.395721	0.630804
112.H	-0.812176	-5.244887	1.481933
113.H	-0.477920	-3.749066	0.579230

S1.4.6. Results for D_{4h} Constrained $Co(NC^tBu_2)_4$ ($S = 3/2$).

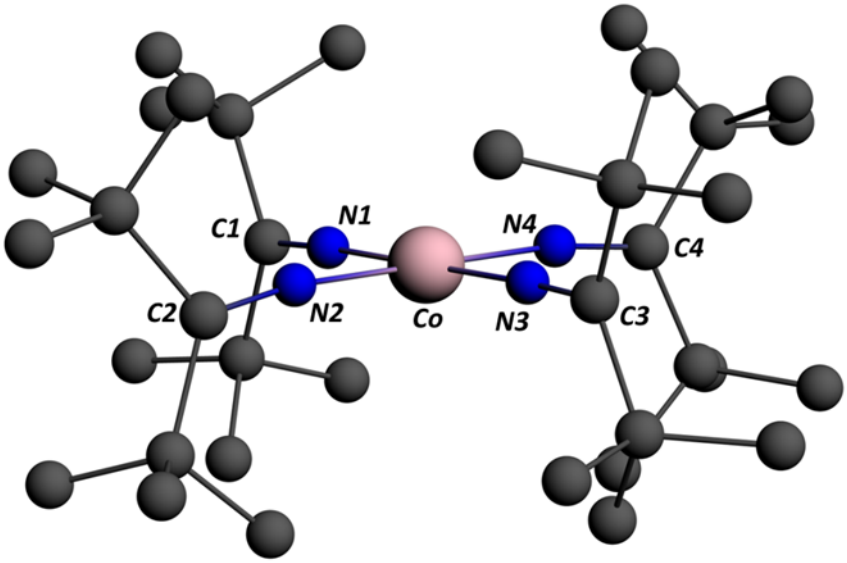

Figure S1.9. Optimized molecular structure of D_{4h} constrained $Co(NC^tBu_2)_4$ ($S = 3/2$). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Co-N1, 1.838; Co-N2, 1.838; Co-N3, 1.837; N1-Co-N3, 179.8; N2-Co-N4, 179.7; Co-N1-C1, 175.6; Co-N2-C2, 171.4; Co-N3-C3, 176.6; Co-N4-C4, 172.1.

S1.4.7. Optimized Cartesian Coordinates for D_{4h} Constrained $Co(NC^tBu_2)_4$ ($S = 3/2$).

1.Co	0.000187	-0.000254	-0.000104
2.N	1.862536	-0.000417	-0.001159
3.N	-0.000128	-1.862239	-0.004485
4.N	-1.862996	0.000382	0.000417
5.N	-0.000167	1.862275	-0.000100
6.C	0.000793	-3.130657	-0.002636
7.C	3.130942	-0.002647	0.000080
8.C	-3.132258	0.000754	-0.000393
9.C	0.001454	3.130569	0.003908
10.C	-3.928982	0.010085	-1.336162
11.C	-3.928261	-0.009181	1.335749
12.C	0.000431	3.931756	-1.326756
13.C	0.003281	3.923301	1.337268
14.C	3.930304	0.009682	-1.332686
15.C	3.925817	-0.014313	1.333587
16.C	0.000052	-3.929251	-1.334051
17.C	0.001162	-3.925958	1.328481
18.C	0.185772	5.426878	-1.064295

19.H	0.208912	5.975627	-1.985420
20.H	-0.627602	5.794892	-0.445429
21.H	1.111423	5.592361	-0.543640
22.C	-1.334773	3.711903	-2.046264
23.H	-1.292093	2.805679	-2.635133
24.H	-2.134819	3.622639	-1.323873
25.H	-1.543545	4.549277	-2.700680
26.C	1.145473	3.430142	-2.210479
27.H	2.035578	3.281579	-1.615516
28.H	0.872621	2.488410	-2.670894
29.H	1.357595	4.154217	-2.987646
30.C	0.988749	5.100170	1.263822
31.H	0.467682	5.992546	0.943588
32.H	1.437322	5.277016	2.219595
33.H	1.765004	4.874690	0.540442
34.C	0.428221	2.990598	2.470182
35.H	-0.320223	2.223810	2.617999
36.H	1.370127	2.518464	2.224067
37.H	0.543525	3.554793	3.387887
38.C	-1.411469	4.460384	1.615940
39.H	-1.869103	3.889469	2.411933
40.H	-1.359240	5.500958	1.912768
41.H	-2.021839	4.378378	0.727519
42.C	-3.566952	1.270925	-2.123513
43.H	-3.479511	2.116075	-1.454422
44.H	-2.623407	1.128049	-2.632828
45.H	-4.336867	1.479841	-2.856259
46.C	-3.557528	-1.231673	-2.148507
47.H	-2.630627	-1.060133	-2.678178
48.H	-3.434506	-2.081950	-1.491752
49.H	-4.340126	-1.449940	-2.864272
50.C	-5.430466	0.000806	-1.113784
51.H	-5.988042	0.007449	-2.003331
52.H	-5.700178	-0.877468	-0.542648
53.H	-5.708576	0.867130	-0.529614
54.C	-5.430016	0.018748	1.114397
55.H	-5.687711	0.897379	0.538744
56.H	-5.720409	-0.847005	0.534407
57.H	-5.987615	0.026124	2.003918
58.C	-3.580123	-1.281052	2.115625
59.H	-3.449929	-2.111670	1.434670
60.H	-2.662845	-1.131840	2.668949
61.H	-4.378349	-1.514523	2.809774
62.C	-3.542000	1.224002	2.156401
63.H	-2.577769	1.068609	2.621350
64.H	-3.488384	2.095017	1.516357
65.H	-4.283818	1.397050	2.926737
66.C	-1.251464	-4.818243	1.403700

67.H	-0.962608	-5.861385	1.364017
68.H	-1.780717	-4.633283	2.325233
69.H	-1.906542	-4.604266	0.569583
70.C	-0.009064	-2.940905	2.496215
71.H	0.872982	-2.317618	2.460647
72.H	-0.886131	-2.309648	2.438025
73.H	-0.024519	-3.481389	3.434951
74.C	1.259682	-4.801334	1.414155
75.H	1.350654	-5.222131	2.404928
76.H	1.196982	-5.609345	0.706679
77.H	2.136582	-4.209632	1.191201
78.C	-0.019646	-5.435542	-1.062076
79.H	-0.110561	-5.982970	-1.984011
80.H	0.895271	-5.729741	-0.574770
81.H	-0.849760	-5.683517	-0.420015
82.C	1.258684	-3.574076	-2.131493
83.H	1.086823	-2.679457	-2.716470
84.H	2.085174	-3.396995	-1.457982
85.H	1.516186	-4.387429	-2.798749
86.C	-1.242125	-3.548883	-2.146063
87.H	-2.101926	-3.471399	-1.494237
88.H	-1.087812	-2.595306	-2.634427
89.H	-1.438105	-4.303036	-2.898347
90.C	3.436997	-1.136957	-2.217579
91.H	3.319215	-2.036044	-1.629031
92.H	2.481279	-0.880387	-2.657417
93.H	4.150999	-1.325828	-3.009788
94.C	5.426528	-0.159981	-1.085039
95.H	5.976627	-0.168648	-1.997699
96.H	5.784286	0.646695	-0.451095
97.H	5.604826	-1.090169	-0.573358
98.C	3.698523	1.344500	-2.047330
99.H	2.780230	1.303698	-2.616753
100.H	3.626385	2.145296	-1.322884
101.H	4.522706	1.551158	-2.718246
102.C	5.245019	-0.779192	1.183462
103.H	6.004715	-0.118738	0.785464
104.H	5.575758	-1.171491	2.114713
105.H	5.103878	-1.596069	0.482229
106.C	3.084801	-0.700156	2.408163
107.H	2.209456	-0.104771	2.629547
108.H	2.768179	-1.674886	2.060406
109.H	3.669952	-0.820593	3.312101
110.C	4.225894	1.432790	1.759210
111.H	4.096039	2.102935	0.920861
112.H	3.552171	1.727202	2.552854
113.H	5.245788	1.508451	2.116863

S1.5. Results for Calculated $[Co(NC^tBu_2)_4]^-$ ($S = 0$ and $S = 1$).

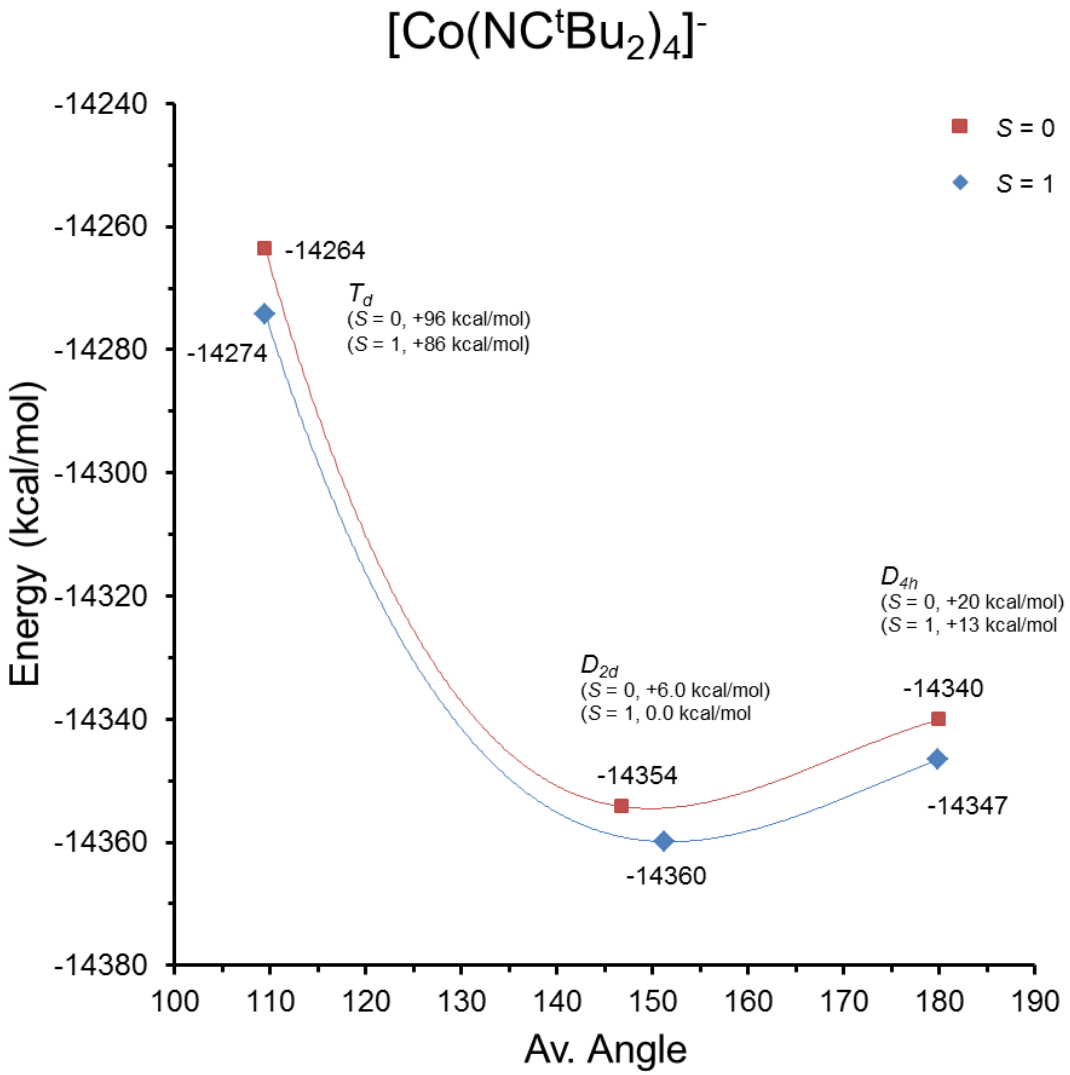

Figure S1.10. Plot of the average N-Co-N bond angle vs the potential energy for $[Co(NC^tBu_2)_4]^-$ ($S = 0$ and $S = 1$). The values relating to T_d and D_{4h} symmetries are from constrained geometry optimizations while the value for the D_{2d} symmetry is from an unconstrained geometry optimization. Relative Energy (ΔE^{SCF}) for each isomer and spin state is listed in parentheses. The best fit of three points is plotted and is not a quantitative potential energy surface.

Table S1.3. Comparison of Relative Energy Differences Between the Various Geometries and Spin States of $[Co(NC^tBu_2)_4]^-$.

Geometry	**Relative Energy, $S = 0$ (kcal/mol)**	**Relative Energy, $S = 1$ (kcal/mol)**
D_{2d}	6.0	0.0
T_d	96	86
T_d (sym)	115	99
D_{4h}	20	13

S1.5.1 Results for D_{2d} Unconstrained $[Co(NC^tBu_2)_4]^-$ ($S = 0$ and $S = 1$).

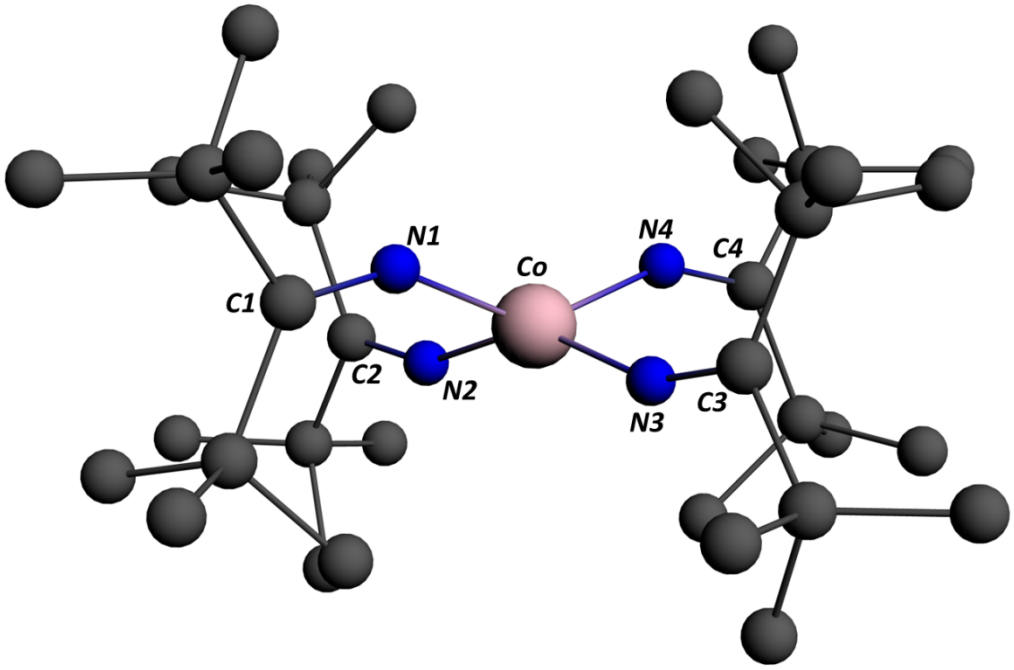

Figure S1.11. Optimized molecular structure of D_{2d} unconstrained $[Co(NC^tBu_2)_4]^-$ ($S = 0$). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Co-N1, 1.885; Co-N2, 1.821; Co-N3, 1.825; Co-N4, 1.860; N1-Co-N4, 143.0; N2-Co-N3, 150.7; Co-N1-C1, 147.4; Co-N2-C2, 155.2; Co-N3-C3, 156.0; Co-N4-C4, 150.9.

Table S1.4. Comparison of Calculated vs. Experimental Structures for $[Co(NC^tBu_2)_4]^-$ ($S = 0$) and $[Li(12\text{-crown-}4)_2][Co(NC^tBu_2)_4]$ (**3**, X-ray).

Parameter/Complex	**$[Co(NC^tBu_2)_4]^-$ ($S = 0$, Calc)**	**$[Li(12\text{-crown-}4)_2][Co(NC^tBu_2)_4]$ (3, Exp)**	**% Difference**
Co-N1	1.885 Å	1.8722(18) Å	0.7
Co-N2	1.821 Å	1.8201(18) Å	0.0
Co-N3	1.825 Å	1.8332(18) Å	0.4
Co-N4	1.860 Å	1.8407(19) Å	1.0
N1-Co-N4	143.0°	148.70(9)°	3.8
N2-Co-N3	150.7°	150.32(9)°	0.3
Co-N1-C1	147.4°	147.75(17)°	0.2
Co-N2-C2	155.2°	153.71(18)°	1.0
Co-N3-C3	156.0°	158.31(18)°	1.5
Co-N4-C4	150.9°	156.16(18)°	3.3

S1.5.2 Optimized Cartesian Coordinates for D_{2d} Unconstrained $[Co(NC^tBu_2)_4]^-$ ($S = 0$).

1.Co	5.165422	3.509672	4.027057
2.N	3.458719	3.461096	4.826159
3.N	5.126540	1.745327	3.563826
4.C	7.469185	3.731256	1.606982
5.H	7.198910	4.781076	1.777808
6.H	6.568973	3.133602	1.790073
7.H	7.772423	3.608937	0.552812
8.C	5.007885	7.498943	2.563210
9.C	5.438416	5.963390	6.261670
10.H	5.428816	6.356493	7.292850
11.H	6.449876	5.613045	6.021618
12.H	4.775705	5.091401	6.207814
13.C	2.205576	3.506576	4.664252
14.C	1.318788	3.347482	5.983623
15.C	2.185988	3.682748	7.213802
16.H	2.511060	4.731814	7.194979
17.H	3.089562	3.064812	7.240329
18.H	1.599998	3.516378	8.133809
19.C	0.872407	1.872456	6.131075
20.H	0.376049	1.723261	7.106263
21.H	1.746251	1.206993	6.088071
22.H	0.168808	1.560659	5.348305
23.C	0.077552	4.264453	6.063089
24.H	-0.437085	4.096704	7.025102
25.H	-0.656259	4.081779	5.267662
26.H	0.363424	5.326192	6.024377
27.C	1.499164	3.688661	3.253687
28.C	0.292286	2.749798	3.020606
29.H	-0.107510	2.925222	2.006905
30.H	-0.533920	2.903995	3.726174
31.H	0.596957	1.693843	3.075397
32.C	1.043074	5.156769	3.068105
33.H	1.888035	5.839076	3.236162
34.H	0.227342	5.443874	3.744567
35.H	0.686294	5.305093	2.033460
36.C	2.502595	3.383343	2.129144
37.H	1.998745	3.480373	1.152086
38.H	2.905624	2.367815	2.224626
39.H	3.356992	4.069081	2.157130
40.N	6.984475	3.541632	4.411626
41.C	8.191625	3.477022	4.043849
42.C	8.625870	3.298924	2.525445
43.C	8.907201	1.805098	2.234368
44.H	9.078959	1.662854	1.152535
45.H	8.040783	1.195448	2.524885
46.H	9.790874	1.424446	2.763790

47.C	9.856354	4.132799	2.098563
48.H	10.774862	3.875374	2.641562
49.H	9.673868	5.210226	2.225293
50.H	10.053087	3.956165	1.026941
51.C	9.291804	3.575885	5.189861
52.C	9.877443	5.008047	5.245161
53.H	9.066316	5.747267	5.314351
54.H	10.488509	5.252786	4.366764
55.H	10.517142	5.117867	6.138489
56.C	8.616321	3.310278	6.549577
57.H	8.194281	2.297628	6.589701
58.H	7.791287	4.008497	6.726191
59.H	9.360308	3.412843	7.357515
60.C	10.444937	2.554564	5.065446
61.H	11.125678	2.665988	5.926898
62.H	11.047175	2.681490	4.157007
63.H	10.062635	1.522895	5.078650
64.N	5.081855	5.271721	3.576489
65.C	5.026481	6.513702	3.807372
66.C	6.436864	8.031690	2.294157
67.H	7.145812	7.196967	2.202015
68.H	6.794127	8.698267	3.089690
69.H	6.452661	8.601077	1.348388
70.C	4.565747	6.719776	1.309209
71.H	3.539805	6.344065	1.417935
72.H	5.214024	5.855129	1.128982
73.H	4.600209	7.385495	0.430645
74.C	4.045339	8.699038	2.703101
75.H	4.078901	9.299522	1.777947
76.H	4.304526	9.367608	3.533811
77.H	3.006657	8.365764	2.842920
78.C	3.540683	7.452526	5.683475
79.H	2.870534	6.595902	5.527254
80.H	3.150152	8.308656	5.117401
81.H	3.507195	7.718597	6.755117
82.C	5.206000	0.498479	3.756887
83.C	5.539921	-0.093896	5.189814
84.C	7.041590	-0.460620	5.274208
85.H	7.656132	0.407198	4.998060
86.H	7.317526	-1.302022	4.624909
87.H	7.295116	-0.741090	6.311523
88.C	4.692562	-1.325707	5.583910
89.H	4.831436	-2.190458	4.922237
90.H	3.620760	-1.079650	5.607624
91.H	4.979849	-1.644775	6.600199
92.C	5.274538	0.979550	6.259961
93.H	5.484509	0.559523	7.258253
94.H	4.234084	1.325832	6.227754

95.H	5.907784	1.861095	6.106221
96.C	4.952966	-0.456131	2.515492
97.C	3.496902	-0.982001	2.541957
98.H	2.789710	-0.144165	2.614896
99.H	3.307486	-1.661629	3.383037
100.H	3.279729	-1.533615	1.610520
101.C	5.123909	0.355553	1.216240
102.H	4.926208	-0.294325	0.347490
103.H	6.143092	0.752969	1.128845
104.H	4.438082	1.209486	1.186103
105.C	5.925160	-1.653319	2.416696
106.H	5.859979	-2.340672	3.269239
107.H	6.968114	-1.313102	2.332611
108.H	5.692336	-2.235255	1.508724
109.C	5.919737	8.277840	5.536883
110.H	6.947551	8.063527	5.210750
111.H	5.957648	8.486695	6.618902
112.H	5.585746	9.199020	5.040713
113.C	4.988820	7.071362	5.291138

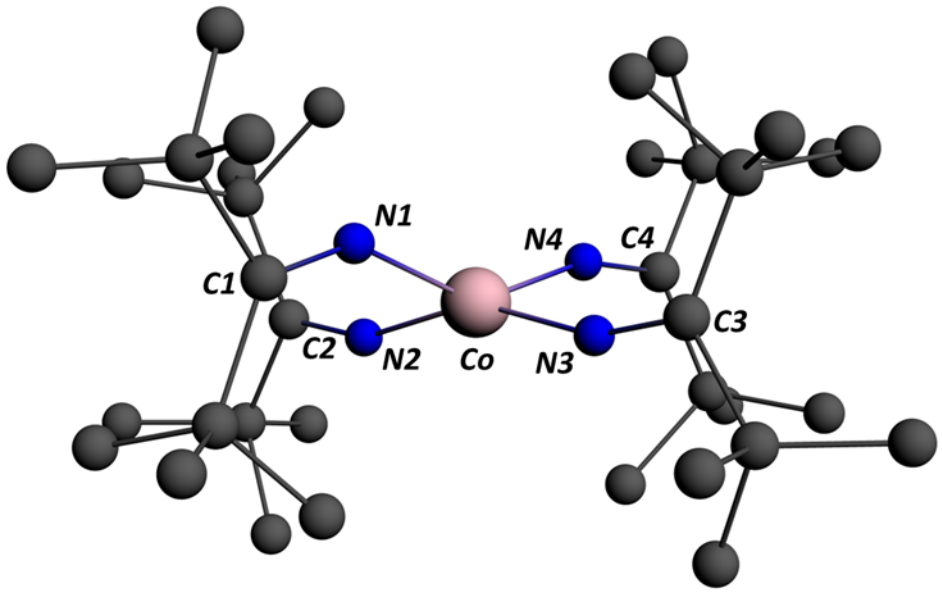

Figure S1.12. Optimized molecular structure of D_{2d} unconstrained $[Co(NC^tBu_2)_4]^-$ (S = 1). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Co-N1, 1.993; Co-N2, 1.822; Co-N3, 1.821; Co-N4, 1.828; N1-Co-N4, 146.4; N2-Co-N3, 156.1; Co-N1-C1, 144.1; Co-N2-C2, 157.8; Co-N3-C3, 159.9; Co-N4-C4, 159.9.

Table S1.5. Comparison of Calculated vs. Experimental Structures for $[Co(NC^tBu_2)_4]^-$ (S = 1) and $[Li(12\text{-crown-}4)_2][Co(NC^tBu_2)_4]$ (X-ray).

Parameter/Complex	**$[Co(NC^tBu_2)_4]^-$ (S = 1, Calc)**	**$[Li(12\text{-crown-}4)_2][Co(NC^tBu_2)_4]$ (Exp)**	**% Difference**
Co-N1	1.933 Å	1.8722(18) Å	3.2
Co-N2	1.822 Å	1.8407(19) Å	1.0
Co-N3	1.821 Å	1.8201(18) Å	0.0
Co-N4	1.828 Å	1.8332(18) Å	0.2
N1-Co-N4	146.4°	148.70(9)°	1.5
N2-Co-N3	156.1°	150.32(9)°	3.8
Co-N1-C1	144.1°	147.75(17)°	2.5
Co-N2-C2	157.8°	153.71(18)°	2.7
Co-N3-C3	159.9°	158.31(18)°	1.0
Co-N4-C4	159.9°	156.16(18)°	2.4

S1.5.3. Optimized Cartesian Coordinates for D_{2d} Unconstrained $[Co(NC^tBu_2)_4]^-$ (S = 1).

1.Co	5.182671	3.514743	4.002464
2.N	3.452112	3.476834	4.862819
3.N	5.125258	1.724013	3.640249
4.C	7.552264	3.743364	1.514871
5.H	7.281408	4.793784	1.684466
6.H	6.647808	3.149291	1.688300
7.H	7.870826	3.623173	0.465859
8.C	4.987255	7.515052	2.600816
9.C	5.447045	5.993226	6.298284
10.H	5.425585	6.377473	7.331708
11.H	6.467558	5.664731	6.063456
12.H	4.797926	5.111428	6.227916
13.C	2.205232	3.510658	4.657329
14.C	1.292867	3.351287	5.967333
15.C	2.139133	3.691006	7.210578
16.H	2.463861	4.740152	7.193911
17.H	3.043574	3.075701	7.250864
18.H	1.538032	3.525673	8.121423
19.C	0.855351	1.873215	6.110416
20.H	0.347669	1.720573	7.079369
21.H	1.735559	1.215400	6.079946
22.H	0.164817	1.553345	5.319427
23.C	0.043817	4.259587	6.032572
24.H	-0.482309	4.085424	6.987362
25.H	-0.679838	4.075520	5.228839
26.H	0.323085	5.323385	6.002056
27.C	1.506236	3.682298	3.240460
28.C	0.298650	2.746073	2.998455
29.H	-0.096568	2.922923	1.982930

30.H	-0.531268	2.902400	3.699041
31.H	0.597898	1.688926	3.054987
32.C	1.050335	5.150305	3.049876
33.H	1.893905	5.833771	3.218456
34.H	0.233937	5.439040	3.724612
35.H	0.693799	5.296980	2.014810
36.C	2.518650	3.375040	2.125818
37.H	2.025606	3.470384	1.143118
38.H	2.919229	2.359074	2.226706
39.H	3.372076	4.062413	2.158876
40.N	6.989450	3.532714	4.230771
41.C	8.218351	3.476816	3.955101
42.C	8.693427	3.307636	2.452541
43.C	8.975328	1.811489	2.173192
44.H	9.162547	1.660519	1.095894
45.H	8.103112	1.207039	2.457143
46.H	9.849135	1.432904	2.720003
47.C	9.934238	4.141704	2.063561
48.H	10.836494	3.878722	2.630651
49.H	9.748748	5.218161	2.193470
50.H	10.160142	3.972712	0.997028
51.C	9.264541	3.563850	5.145586
52.C	9.858092	4.992184	5.226439
53.H	9.052240	5.737724	5.284047
54.H	10.491489	5.239351	4.364842
55.H	10.477444	5.088395	6.135208
56.C	8.534578	3.301138	6.476577
57.H	8.113569	2.288360	6.506214
58.H	7.704934	4.001342	6.620818
59.H	9.245197	3.408600	7.312952
60.C	10.415687	2.536886	5.059381
61.H	11.065943	2.644345	5.944513
62.H	11.049307	2.664819	4.172631
63.H	10.029453	1.507029	5.057203
64.N	5.062807	5.294484	3.628797
65.C	5.016641	6.534934	3.853324
66.C	6.418188	8.040291	2.325183
67.H	7.122454	7.201498	2.233574
68.H	6.782243	8.708573	3.116149
69.H	6.433735	8.605438	1.376952
70.C	4.544523	6.727176	1.353011
71.H	3.516568	6.357242	1.460427
72.H	5.189357	5.857314	1.185716
73.H	4.586519	7.384127	0.468136
74.C	4.029910	8.719987	2.733435
75.H	4.067671	9.317254	1.806064
76.H	4.291228	9.390816	3.561719
77.H	2.989476	8.392252	2.872451

78.C	3.541215	7.474838	5.721278
79.H	2.878698	6.611888	5.567726
80.H	3.145879	8.322941	5.147887
81.H	3.503483	7.747193	6.790309
82.C	5.200371	0.478504	3.814921
83.C	5.523486	-0.131379	5.242109
84.C	7.025925	-0.494542	5.328832
85.H	7.638698	0.373652	5.049207
86.H	7.303144	-1.335054	4.678764
87.H	7.282722	-0.774201	6.365372
88.C	4.677528	-1.368563	5.619712
89.H	4.825512	-2.226045	4.950448
90.H	3.604773	-1.126754	5.634841
91.H	4.956079	-1.697636	6.635365
92.C	5.246125	0.939235	6.311884
93.H	5.447890	0.522024	7.312852
94.H	4.205890	1.285604	6.267544
95.H	5.874007	1.823954	6.159648
96.C	4.958300	-0.464922	2.557243
97.C	3.499608	-0.982989	2.563243
98.H	2.796584	-0.141872	2.640434
99.H	3.298848	-1.671613	3.394149
100.H	3.287334	-1.521578	1.622978
101.C	5.147733	0.361340	1.270153
102.H	4.956052	-0.275649	0.390489
103.H	6.170319	0.753660	1.198834
104.H	4.469157	1.220589	1.243888
105.C	5.924739	-1.666612	2.453102
106.H	5.848116	-2.364196	3.296491
107.H	6.970435	-1.332429	2.381686
108.H	5.696683	-2.236702	1.536249
109.C	5.918714	8.316911	5.571566
110.H	6.945419	8.109140	5.238059
111.H	5.960224	8.529465	6.652955
112.H	5.575112	9.233682	5.072485
113.C	4.992299	7.100583	5.331551

S1.5.4. Computational Variation of the Ground-State Electronic Configuration in $[Co(NC^tBu)_4]^-$. A series of calculations were performed to rationalize the $S = 1$ ground-state configuration of $[Co(NC^tBu)_4]^-$ as a function of ketimide-to-Co π-bonding. For these calculations, $[Co(NC^tBu)_4]^-$ was constrained to molecular D_{2d} symmetry and the N-Co-N angles along the molecular two-fold axis were fixed at values ranging from 148˚ – 155˚ (with both angles being equal to preserve D_{2d} symmetry). Notably, The value of 149˚ represents the average N-Co-N angle from the crystallographic structure determination of $[Li(12\text{-crown-}4)_2][Co(NC^tBu_2)_4]$ (see text).

The computational results revealed a systematic variation in the d-orbital ordering for the $S = 1$ ground state of D_{2d}-symmetric $[Co(NC^tBu_2)_4]^-$ as a function of N-Co-N angle. Specifically,

as the two N-Co-N angles along the molecular two-fold axis are increased from 148˚ to 155˚, the energy of the a_1-symmetry dz^2 orbital lowers in energy. At a value of 155˚, the $a_1(dz^2)$ orbital falls below the energy of the e-symmetry dxz/dyz orbital pair (Figure S1.12). The energetic lowering of the $a_1(z^2)$ orbital relative to the e(xz, yz) with increasing N-Co-N angle is consistent with less ketimide-to-cobalt π-donation. As the two N-Co-N angles along the molecular two-fold axis increase, the ketimide nitrogen lone pairs overlap less efficiently with the dz^2 orbital. Accordingly, an $S = 1$ ground state with an $b_1(x^2\text{-}y^2)^2a_1(z^2)^2e(xz, yz)^2b_2(xy)^0$ overall configuration is achieved.

It is important to note that the $S = 1$, freely optimized (unconstrained) calculation of $[Co(NC^tBu_2)_4]^-$ (Section S1.5.3; Figure S1.11) was performed without application of molecular symmetry. Accordingly, an unrealistic $b_1(x^2\text{-}y^2)^2e(xz, yz)^3a_1(z^2)^1b_2(xy)^0$ orbital configuration resulted. This electronic configuration would undoubtedly be subject to Jahn-Teller instability in a perfect D_{2d} ligand field and is an artifact of the computational method applied. We recognize that the computationally determined N-Co-N angle leading to the "e over a_1" configuration for $S = 1$ $[Co(NC^tBu_2)_4]^-$ occurs at a value of 155˚, whereas the crystallographic average is 149˚. However, we believe this 6˚ discrepancy within reasonable error of the small orbital energy differences (Figure S1.12) and the experimental structural variation in $[M(NCR_2)_4]^n$ complexes.

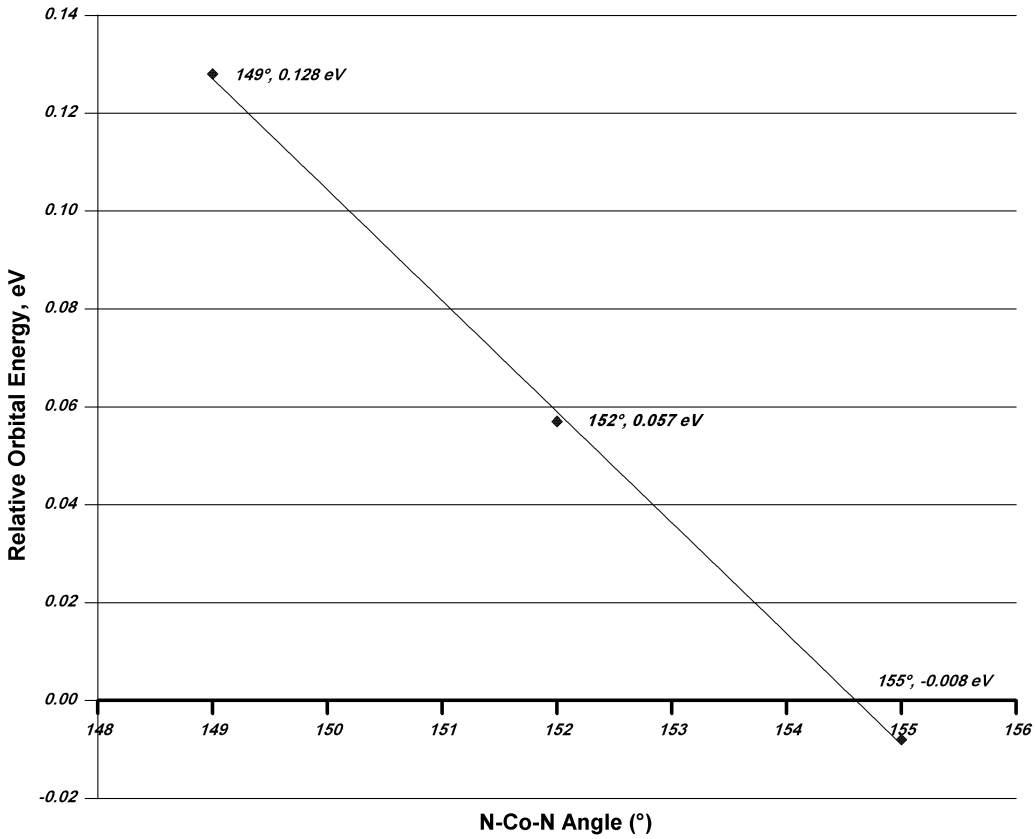

Figure S1.13. Relative orbital energy ($a_1(z^2)$ – e(xz, yz)) vs. N-Co-N angle for $[Co(NC^tBu_2)_4]^-$ with enforced D_{2d} symmetry. The angle corresponds to the two N-Co-N angles bisecting the primary molecular two-fold (C_2) axis in D_{2d} symmetry.

S1.5.5. Results for T_d Constrained $[Co(NC^tBu_2)_4]^-$ ($S = 0$ and $S = 1$).

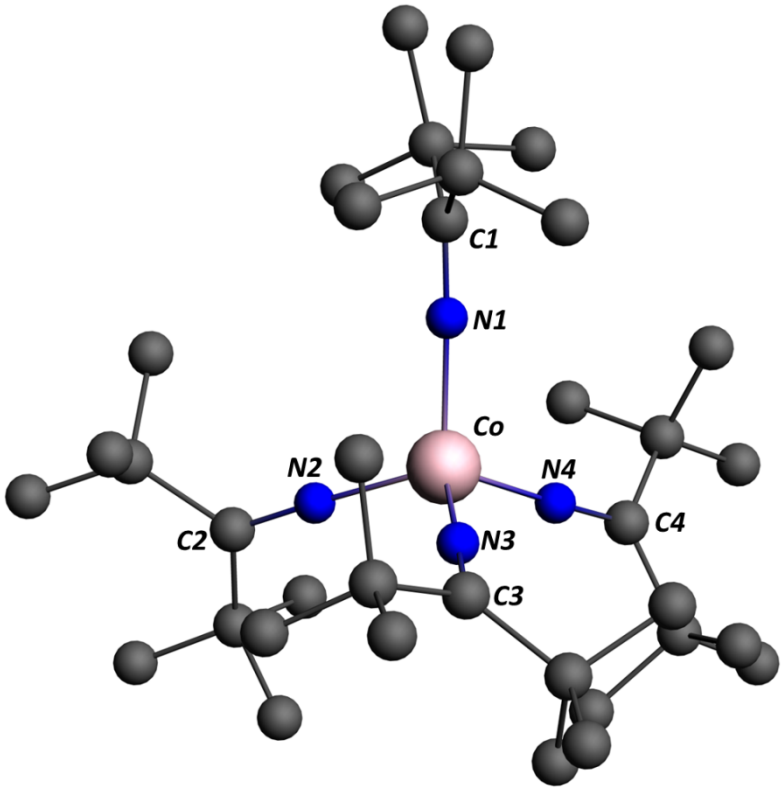

Figure S1.14. Optimized molecular structure of T_d constrained $[Co(NC^tBu_2)_4]^-$ ($S = 0$). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Co-N1, 1.926; Co-N2, 1.921; Co-N3, 1.918; Co-N4, 1.917; N1-Co-N3, 109.5; N2-Co-N4, 109.5; Co-N1-C1, 177.7; Co-N2-C2, 177.9; Co-N3-C3, 179.1; Co-N4-C4, 177.6.

S1.5.6 Optimized Cartesian Coordinates for T_d Constrained $[Co(NC^tBu_2)_4]^-$ ($S = 0$).

1.Co	-0.000787	0.026190	0.020303
2.N	-0.183951	0.511960	1.872933
3.N	-1.065109	-1.547256	-0.341731
4.N	-0.619126	1.509112	-1.109636
5.N	1.849460	-0.347191	-0.365850
6.C	-0.281388	0.822050	3.095760
7.C	-1.727821	-2.604508	-0.548225
8.C	-1.036214	2.401799	-1.900531
9.C	3.066385	-0.582343	-0.616624
10.C	-0.897693	3.923600	-1.397838
11.C	-1.696863	1.986225	-3.289208
12.C	3.981789	0.653711	-1.078476
13.C	3.618376	-2.087396	-0.501791
14.C	-0.879046	2.267845	3.454227

15.C	0.229397	-0.184076	4.226985
16.C	-2.590689	-3.250618	0.641246
17.C	-1.726416	-3.259375	-2.020789
18.C	3.456556	1.141414	-2.464826
19.H	2.731465	1.957764	-2.352725
20.H	4.285787	1.502494	-3.096713
21.H	2.947869	0.335019	-3.009233
22.C	5.507841	0.450145	-1.240028
23.H	5.944537	1.425898	-1.511379
24.H	6.003068	0.122339	-0.316536
25.H	5.770277	-0.247966	-2.044407
26.C	3.813945	1.765916	-0.013658
27.H	2.842331	2.261698	-0.106744
28.H	3.873430	1.346874	1.000849
29.H	4.612593	2.520947	-0.117083
30.C	5.128521	-2.380454	-0.675133
31.H	5.488541	-2.162746	-1.688803
32.H	5.773174	-1.865150	0.047470
33.H	5.265787	-3.464093	-0.520019
34.C	2.907629	-2.951222	-1.579991
35.H	2.039771	-3.460101	-1.153335
36.H	2.541217	-2.343354	-2.415896
37.H	3.580765	-3.722072	-1.989429
38.C	3.237024	-2.586924	0.913868
39.H	3.485687	-1.833656	1.674841
40.H	2.161146	-2.783718	0.985165
41.H	3.788103	-3.511671	1.159535
42.C	-3.531254	-4.449096	0.368613
43.H	-4.042824	-4.675786	1.319507
44.H	-4.308764	-4.250066	-0.380672
45.H	-2.986985	-5.357668	0.084145
46.C	-1.578196	-3.766472	1.692969
47.H	-0.682304	-4.193103	1.218613
48.H	-1.246884	-2.949231	2.326944
49.H	-2.024139	-4.542091	2.338582
50.C	-3.484120	-2.126456	1.227837
51.H	-2.915419	-1.445204	1.870997
52.H	-3.920034	-1.518499	0.422015
53.H	-4.314926	-2.558271	1.812128
54.C	1.774480	-0.324555	4.096882
55.H	2.034699	-1.171897	3.449071
56.H	2.227778	0.568761	3.648716
57.H	2.240496	-0.491067	5.081781
58.C	-0.442790	-1.532332	3.923568
59.H	-1.501470	-1.385511	3.666718
60.H	0.048151	-2.005661	3.070605
61.H	-0.397535	-2.214165	4.789309
62.C	-0.098243	0.100854	5.711096

63.H	0.252665	-0.766873	6.294320
64.H	0.400585	0.985396	6.121962
65.H	-1.178100	0.190932	5.893408
66.C	-1.060352	2.710976	4.924585
67.H	-1.764438	2.087372	5.488521
68.H	-0.114771	2.771342	5.478073
69.H	-1.479730	3.731364	4.901687
70.C	0.104646	3.296009	2.838971
71.H	1.145192	2.988655	3.018722
72.H	-0.019154	3.371106	1.756871
73.H	-0.030184	4.295652	3.287681
74.C	-2.286861	2.336581	2.819658
75.H	-2.227929	2.373441	1.730847
76.H	-2.870313	1.440924	3.081282
77.H	-2.843424	3.218422	3.182571
78.C	-0.273590	-3.306452	-2.514333
79.H	0.143689	-2.304311	-2.655568
80.H	0.348504	-3.821362	-1.773789
81.H	-0.200091	-3.872671	-3.458853
82.C	-2.264176	-4.697253	-2.218729
83.H	-1.765796	-5.435360	-1.574504
84.H	-3.346910	-4.782519	-2.078895
85.H	-2.055423	-4.984880	-3.263193
86.C	-2.564038	-2.330873	-2.937463
87.H	-3.359882	-1.820455	-2.378242
88.H	-1.925432	-1.553734	-3.373374
89.H	-3.032529	-2.890568	-3.764041
90.C	-0.666892	1.084357	-4.011391
91.H	0.325759	1.557809	-4.022091
92.H	-0.560386	0.115948	-3.510771
93.H	-0.975270	0.920280	-5.058493
94.C	-3.018406	1.206999	-2.992165
95.H	-2.981213	0.194243	-3.407297
96.H	-3.197847	1.104517	-1.915865
97.H	-3.885959	1.715111	-3.441600
98.C	-2.072716	3.096888	-4.294223
99.H	-2.483747	2.605791	-5.192007
100.H	-2.855972	3.762923	-3.912450
101.H	-1.217507	3.704672	-4.617227
102.C	-1.242537	5.101468	-2.337490
103.H	-0.646964	5.140508	-3.257806
104.H	-2.307588	5.126794	-2.598729
105.H	-1.038159	6.026347	-1.771782
106.C	-1.838311	4.103802	-0.169016
107.H	-2.408214	3.191906	0.030571
108.H	-1.275369	4.341001	0.740683
109.H	-2.556364	4.922270	-0.327802
110.C	0.586160	4.102953	-1.006473

111.H	0.865984	3.424481	-0.193764
112.H	1.238668	3.877033	-1.863707
113.H	0.783094	5.143307	-0.697151

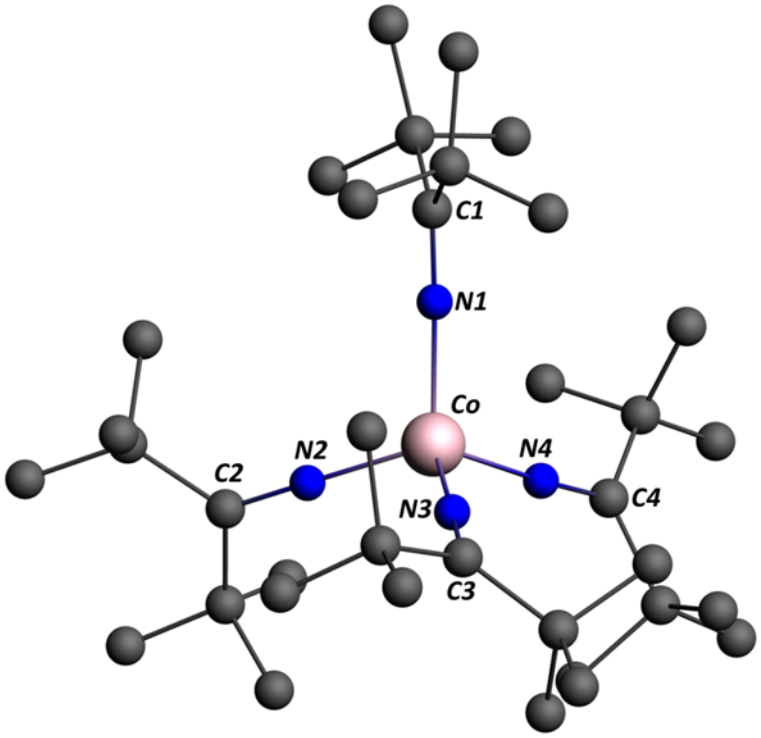

Figure S1.15. Optimized molecular structure of T_d constrained $[Co(NC^tBu_2)_4]^-$ ($S = 1$). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Co-N1, 1.934; Co-N2, 1.927; Co-N3, 1.924; Co-N4, 1.964; N1-Co-N3, 109.5; N2-Co-N4, 109.5; Co-N1-C1, 177.6; Co-N2-C2, 179.5; Co-N3-C3, 178.9; Co-N4-C4, 175.9.

S1.5.7. Optimized Cartesian Coordinates for T_d Constrained $[Co(NC^tBu_2)_4]^-$ ($S = 1$).

1.Co	-0.000787	0.026190	0.020303
2.N	-0.183951	0.511960	1.872933
3.N	-1.065109	-1.547256	-0.341731
4.N	-0.619126	1.509112	-1.109636
5.N	1.849460	-0.347191	-0.365850
6.C	-0.281388	0.822050	3.095760
7.C	-1.727821	-2.604508	-0.548225
8.C	-1.036214	2.401799	-1.900531
9.C	3.066385	-0.582343	-0.616624
10.C	-0.897693	3.923600	-1.397838
11.C	-1.696863	1.986225	-3.289208
12.C	3.981789	0.653711	-1.078476
13.C	3.618376	-2.087396	-0.501791
14.C	-0.879046	2.267845	3.454227

15.C	0.229397	-0.184076	4.226985
16.C	-2.590689	-3.250618	0.641246
17.C	-1.726416	-3.259375	-2.020789
18.C	3.456556	1.141414	-2.464826
19.H	2.731465	1.957764	-2.352725
20.H	4.285787	1.502494	-3.096713
21.H	2.947869	0.335019	-3.009233
22.C	5.507841	0.450145	-1.240028
23.H	5.944537	1.425898	-1.511379
24.H	6.003068	0.122339	-0.316536
25.H	5.770277	-0.247966	-2.044407
26.C	3.813945	1.765916	-0.013658
27.H	2.842331	2.261698	-0.106744
28.H	3.873430	1.346874	1.000849
29.H	4.612593	2.520947	-0.117083
30.C	5.128521	-2.380454	-0.675133
31.H	5.488541	-2.162746	-1.688803
32.H	5.773174	-1.865150	0.047470
33.H	5.265787	-3.464093	-0.520019
34.C	2.907629	-2.951222	-1.579991
35.H	2.039771	-3.460101	-1.153335
36.H	2.541217	-2.343354	-2.415896
37.H	3.580765	-3.722072	-1.989429
38.C	3.237024	-2.586924	0.913868
39.H	3.485687	-1.833656	1.674841
40.H	2.161146	-2.783718	0.985165
41.H	3.788103	-3.511671	1.159535
42.C	-3.531254	-4.449096	0.368613
43.H	-4.042824	-4.675786	1.319507
44.H	-4.308764	-4.250066	-0.380672
45.H	-2.986985	-5.357668	0.084145
46.C	-1.578196	-3.766472	1.692969
47.H	-0.682304	-4.193103	1.218613
48.H	-1.246884	-2.949231	2.326944
49.H	-2.024139	-4.542091	2.338582
50.C	-3.484120	-2.126456	1.227837
51.H	-2.915419	-1.445204	1.870997
52.H	-3.920034	-1.518499	0.422015
53.H	-4.314926	-2.558271	1.812128
54.C	1.774480	-0.324555	4.096882
55.H	2.034699	-1.171897	3.449071
56.H	2.227778	0.568761	3.648716
57.H	2.240496	-0.491067	5.081781
58.C	-0.442790	-1.532332	3.923568
59.H	-1.501470	-1.385511	3.666718
60.H	0.048151	-2.005661	3.070605
61.H	-0.397535	-2.214165	4.789309
62.C	-0.098243	0.100854	5.711096

63.H	0.252665	-0.766873	6.294320
64.H	0.400585	0.985396	6.121962
65.H	-1.178100	0.190932	5.893408
66.C	-1.060352	2.710976	4.924585
67.H	-1.764438	2.087372	5.488521
68.H	-0.114771	2.771342	5.478073
69.H	-1.479730	3.731364	4.901687
70.C	0.104646	3.296009	2.838971
71.H	1.145192	2.988655	3.018722
72.H	-0.019154	3.371106	1.756871
73.H	-0.030184	4.295652	3.287681
74.C	-2.286861	2.336581	2.819658
75.H	-2.227929	2.373441	1.730847
76.H	-2.870313	1.440924	3.081282
77.H	-2.843424	3.218422	3.182571
78.C	-0.273590	-3.306452	-2.514333
79.H	0.143689	-2.304311	-2.655568
80.H	0.348504	-3.821362	-1.773789
81.H	-0.200091	-3.872671	-3.458853
82.C	-2.264176	-4.697253	-2.218729
83.H	-1.765796	-5.435360	-1.574504
84.H	-3.346910	-4.782519	-2.078895
85.H	-2.055423	-4.984880	-3.263193
86.C	-2.564038	-2.330873	-2.937463
87.H	-3.359882	-1.820455	-2.378242
88.H	-1.925432	-1.553734	-3.373374
89.H	-3.032529	-2.890568	-3.764041
90.C	-0.666892	1.084357	-4.011391
91.H	0.325759	1.557809	-4.022091
92.H	-0.560386	0.115948	-3.510771
93.H	-0.975270	0.920280	-5.058493
94.C	-3.018406	1.206999	-2.992165
95.H	-2.981213	0.194243	-3.407297
96.H	-3.197847	1.104517	-1.915865
97.H	-3.885959	1.715111	-3.441600
98.C	-2.072716	3.096888	-4.294223
99.H	-2.483747	2.605791	-5.192007
100.H	-2.855972	3.762923	-3.912450
101.H	-1.217507	3.704672	-4.617227
102.C	-1.242537	5.101468	-2.337490
103.H	-0.646964	5.140508	-3.257806
104.H	-2.307588	5.126794	-2.598729
105.H	-1.038159	6.026347	-1.771782
106.C	-1.838311	4.103802	-0.169016
107.H	-2.408214	3.191906	0.030571
108.H	-1.275369	4.341001	0.740683
109.H	-2.556364	4.922270	-0.327802
110.C	0.586160	4.102953	-1.006473

111.H	0.865984	3.424481	-0.193764
112.H	1.238668	3.877033	-1.863707
113.H	0.783094	5.143307	-0.697151

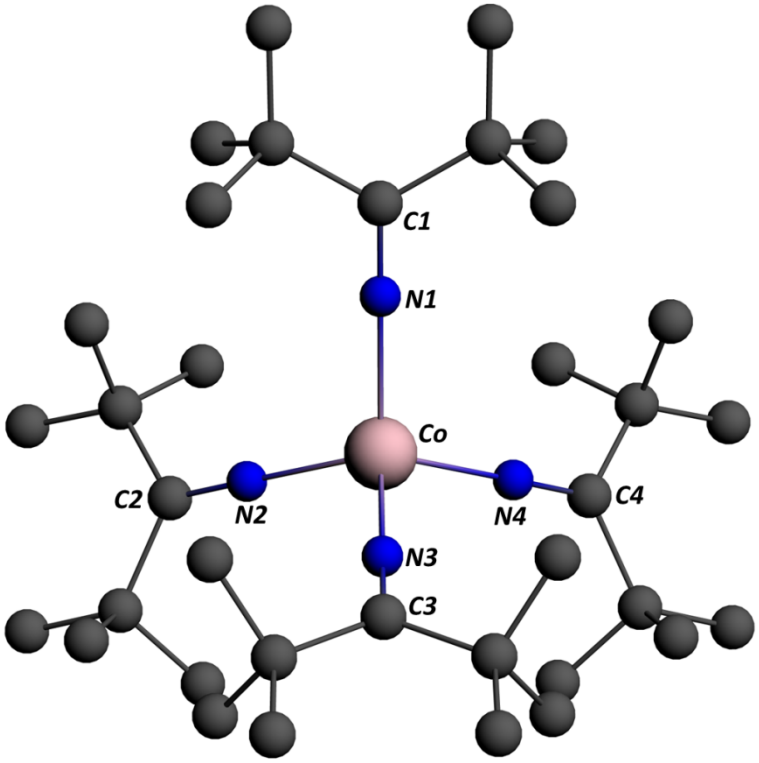

Figure S1.16. Optimized molecular structure of T_d constrained (symmetry constrained) $[Co(NC^tBu_2)_4]^-$ ($S = 0$). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Co-N1, 2.145; Co-N2, 2.145; Co-N3, 2.145; Co-N4, 2.145; N1-Co-N3, 109.5; N2-Co-N4, 109.5; Co-N1-C1, 178.9; Co-N2-C2, 178.9; Co-N3-C3, 178.9; Co-N4-C4, 178.9.

S1.5.8. Optimized Cartesian Coordinates for T_d Constrained (symmetry constrained) $[Co(NC^tBu_2)_4]^-$ ($S = 0$).

1.N	1.238272	-1.238272	-1.238355
2.Co	0.000000	0.000000	0.000000
3.N	1.238272	1.238272	1.238355
4.N	-1.238272	1.238272	-1.238355
5.N	-1.238272	-1.238272	1.238355
6.C	1.959622	-1.959622	-1.990080
7.C	1.959622	1.959622	1.990080
8.C	-1.959622	1.959622	-1.990080
9.C	-1.959622	-1.959622	1.990080
10.C	2.311979	-4.324784	-3.374561
11.C	-3.222382	0.107481	-3.225623
12.C	-4.253884	1.200319	-1.215588
13.C	3.222382	-0.107481	-3.225623

14.C	4.324784	2.311979	3.374561
15.C	3.222382	0.107481	3.225623
16.C	-3.222382	-0.107481	3.225623
17.C	-2.311979	4.324784	-3.374561
18.C	3.419291	1.439815	2.474318
19.C	-0.107481	-3.222382	3.225623
20.C	-4.324784	-2.311979	3.374561
21.C	1.439815	3.419291	2.474318
22.C	1.200319	4.253884	1.215588
23.C	-0.107481	3.222382	-3.225623
24.C	-1.439815	3.419291	-2.474318
25.C	-1.200319	-4.253884	1.215588
26.C	4.253884	1.200319	1.215588
27.C	-3.419291	1.439815	-2.474318
28.C	-4.253884	-1.200319	1.215588
29.C	-2.311979	-4.324784	3.374561
30.C	-1.439815	-3.419291	2.474318
31.C	-1.200319	4.253884	-1.215588
32.C	2.311979	4.324784	3.374561
33.C	-3.419291	-1.439815	2.474318
34.C	-4.324784	2.311979	-3.374561
35.C	0.107481	3.222382	3.225623
36.C	1.439815	-3.419291	-2.474318
37.C	0.107481	-3.222382	-3.225623
38.C	4.253884	-1.200319	-1.215588
39.C	3.419291	-1.439815	-2.474318
40.C	1.200319	-4.253884	-1.215588
41.C	4.324784	-2.311979	-3.374561
42.H	4.623328	3.251009	2.892111
43.H	3.909070	2.536558	4.362660
44.H	5.247482	1.730733	3.530622
45.H	1.730733	5.247482	3.530622
46.H	3.251009	4.623328	2.892111
47.H	2.536558	3.909070	4.362660
48.H	2.536558	-3.909070	-4.362660
49.H	1.730733	-5.247482	-3.530622
50.H	3.251009	-4.623328	-2.892111
51.H	5.247482	-1.730733	-3.530622
52.H	3.909070	-2.536558	-4.362660
53.H	4.623328	-3.251009	-2.892111
54.H	-1.730733	5.247482	-3.530622
55.H	-3.251009	4.623328	-2.892111
56.H	-2.536558	3.909070	-4.362660
57.H	-4.623328	3.251009	-2.892111
58.H	-5.247482	1.730733	-3.530622
59.H	-3.909070	2.536558	-4.362660
60.H	-4.623328	-3.251009	2.892111
61.H	-5.247482	-1.730733	3.530622

62.H	-3.909070	-2.536558	4.362660
63.H	-1.730733	-5.247482	3.530622
64.H	-3.251009	-4.623328	2.892111
65.H	-2.536558	-3.909070	4.362660
66.H	-0.795693	5.247505	-1.479283
67.H	-0.485753	3.738143	-0.581463
68.H	-2.125271	4.404135	-0.638091
69.H	-3.738143	0.485753	-0.581463
70.H	-5.247505	0.795693	-1.479283
71.H	-4.404135	2.125271	-0.638091
72.H	-2.623726	0.260135	-4.136534
73.H	-4.205427	-0.290151	-3.535471
74.H	-2.715354	-0.639525	-2.601638
75.H	0.290151	4.205427	-3.535471
76.H	-0.260135	2.623726	-4.136534
77.H	0.639525	2.715354	-2.601638
78.H	2.125271	-4.404135	-0.638091
79.H	0.795693	-5.247505	-1.479283
80.H	0.485753	-3.738143	-0.581463
81.H	-0.290151	-4.205427	-3.535471
82.H	0.260135	-2.623726	-4.136534
83.H	-0.639525	-2.715354	-2.601638
84.H	5.247505	-0.795693	-1.479283
85.H	4.404135	-2.125271	-0.638091
86.H	3.738143	-0.485753	-0.581463
87.H	4.205427	-0.290151	3.535471
88.H	2.715354	-0.639525	2.601638
89.H	2.623726	0.260135	4.136534
90.H	5.247505	0.795693	1.479283
91.H	4.404135	2.125271	0.638091
92.H	3.738143	0.485753	0.581463
93.H	4.205427	0.290151	-3.535471
94.H	2.715354	0.639525	-2.601638
95.H	2.623726	-0.260135	-4.136534
96.H	0.260135	2.623726	4.136534
97.H	-0.639525	2.715354	2.601638
98.H	-0.290151	4.205427	3.535471
99.H	0.485753	3.738143	0.581463
100.H	2.125271	4.404135	0.638091
101.H	0.795693	5.247505	1.479283
102.H	-2.623726	-0.260135	4.136534
103.H	-4.205427	0.290151	3.535471
104.H	-2.715354	0.639525	2.601638
105.H	-4.404135	-2.125271	0.638091
106.H	-3.738143	-0.485753	0.581463
107.H	-5.247505	-0.795693	1.479283
108.H	0.639525	-2.715354	2.601638
109.H	0.290151	-4.205427	3.535471

110.H	-0.260135	-2.623726	4.136534
111.H	-2.125271	-4.404135	0.638091
112.H	-0.795693	-5.247505	1.479283
113.H	-0.485753	-3.738143	0.581463

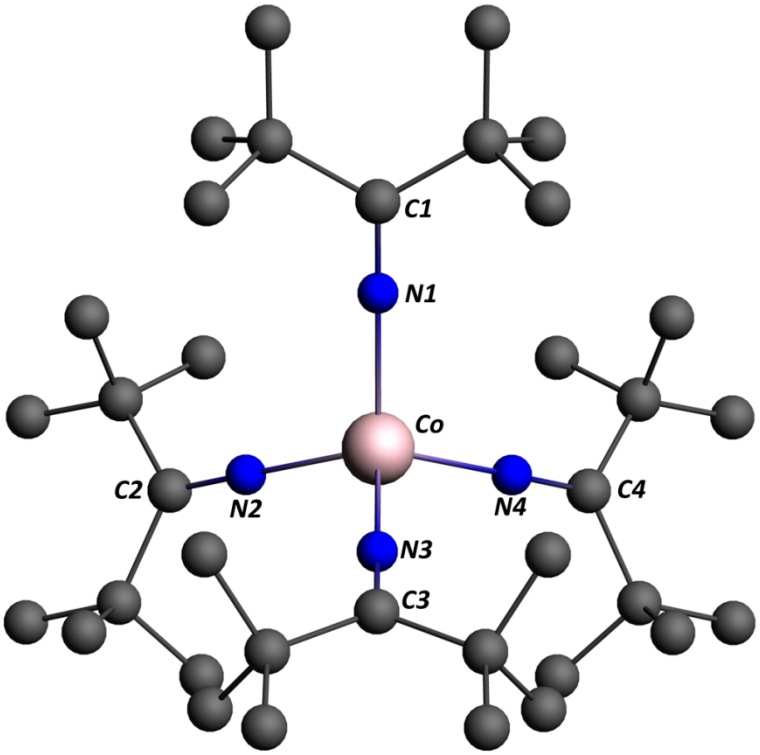

Figure S1.17. Optimized molecular structure of T_d constrained (symmetry constrained) $[Co(NC^tBu_2)_4]^-$ ($S = 1$). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Co-N1, 2.142; Co-N2, 2.142; Co-N3, 2.142; Co-N4, 2.142; N1-Co-N3, 109.5; N2-Co-N4, 109.5; Co-N1-C1, 178.8; Co-N2-C2, 178.8; Co-N3-C3, 178.8; Co-N4-C4, 178.8.

S1.5.9. Optimized Cartesian Coordinates for T_d Constrained (symmetry constrained) $[Co(NC^tBu_2)_4]^-$ ($S = 1$).

1.N	1.236919	-1.236919	-1.236881
2.Co	0.000000	0.000000	0.000000
3.N	1.236919	1.236919	1.236881
4.N	-1.236919	1.236919	-1.236881
5.N	-1.236919	-1.236919	1.236881
6.C	1.955641	-1.955641	-1.988168
7.C	1.955641	1.955641	1.988168
8.C	-1.955641	1.955641	-1.988168
9.C	-1.955641	-1.955641	1.988168
10.C	2.312417	-4.321171	-3.379100
11.C	-3.221498	0.108184	-3.224672
12.C	-4.252747	1.204470	-1.216227

13.C	3.221498	-0.108184	-3.224672
14.C	4.321171	2.312417	3.379100
15.C	3.221498	0.108184	3.224672
16.C	-3.221498	-0.108184	3.224672
17.C	-2.312417	4.321171	-3.379100
18.C	3.419963	1.439588	2.475842
19.C	-0.108184	-3.221498	3.224672
20.C	-4.321171	-2.312417	3.379100
21.C	1.439588	3.419963	2.475842
22.C	1.204470	4.252747	1.216227
23.C	-0.108184	3.221498	-3.224672
24.C	-1.439588	3.419963	-2.475842
25.C	-1.204470	-4.252747	1.216227
26.C	4.252747	1.204470	1.216227
27.C	-3.419963	1.439588	-2.475842
28.C	-4.252747	-1.204470	1.216227
29.C	-2.312417	-4.321171	3.379100
30.C	-1.439588	-3.419963	2.475842
31.C	-1.204470	4.252747	-1.216227
32.C	2.312417	4.321171	3.379100
33.C	-3.419963	-1.439588	2.475842
34.C	-4.321171	2.312417	-3.379100
35.C	0.108184	3.221498	3.224672
36.C	1.439588	-3.419963	-2.475842
37.C	0.108184	-3.221498	-3.224672
38.C	4.252747	-1.204470	-1.216227
39.C	3.419963	-1.439588	-2.475842
40.C	1.204470	-4.252747	-1.216227
41.C	4.321171	-2.312417	-3.379100
42.H	4.614617	3.253595	2.898987
43.H	3.896502	2.534362	4.364026
44.H	5.251480	1.745282	3.547720
45.H	1.745282	5.251480	3.547720
46.H	3.253595	4.614617	2.898987
47.H	2.534362	3.896502	4.364026
48.H	2.534362	-3.896502	-4.364026
49.H	1.745282	-5.251480	-3.547720
50.H	3.253595	-4.614617	-2.898987
51.H	5.251480	-1.745282	-3.547720
52.H	3.896502	-2.534362	-4.364026
53.H	4.614617	-3.253595	-2.898987
54.H	-1.745282	5.251480	-3.547720
55.H	-3.253595	4.614617	-2.898987
56.H	-2.534362	3.896502	-4.364026
57.H	-4.614617	3.253595	-2.898987
58.H	-5.251480	1.745282	-3.547720
59.H	-3.896502	2.534362	-4.364026
60.H	-4.614617	-3.253595	2.898987

61.H	-5.251480	-1.745282	3.547720
62.H	-3.896502	-2.534362	4.364026
63.H	-1.745282	-5.251480	3.547720
64.H	-3.253595	-4.614617	2.898987
65.H	-2.534362	-3.896502	4.364026
66.H	-0.794669	5.245174	-1.476031
67.H	-0.497542	3.731723	-0.578080
68.H	-2.132264	4.406559	-0.643946
69.H	-3.731723	0.497542	-0.578080
70.H	-5.245174	0.794669	-1.476031
71.H	-4.406559	2.132264	-0.643946
72.H	-2.625438	0.260075	-4.138089
73.H	-4.203954	-0.293571	-3.530996
74.H	-2.709365	-0.631921	-2.598842
75.H	0.293571	4.203954	-3.530996
76.H	-0.260075	2.625438	-4.138089
77.H	0.631921	2.709365	-2.598842
78.H	2.132264	-4.406559	-0.643946
79.H	0.794669	-5.245174	-1.476031
80.H	0.497542	-3.731723	-0.578080
81.H	-0.293571	-4.203954	-3.530996
82.H	0.260075	-2.625438	-4.138089
83.H	-0.631921	-2.709365	-2.598842
84.H	5.245174	-0.794669	-1.476031
85.H	4.406559	-2.132264	-0.643946
86.H	3.731723	-0.497542	-0.578080
87.H	4.203954	-0.293571	3.530996
88.H	2.709365	-0.631921	2.598842
89.H	2.625438	0.260075	4.138089
90.H	5.245174	0.794669	1.476031
91.H	4.406559	2.132264	0.643946
92.H	3.731723	0.497542	0.578080
93.H	4.203954	0.293571	-3.530996
94.H	2.709365	0.631921	-2.598842
95.H	2.625438	-0.260075	-4.138089
96.H	0.260075	2.625438	4.138089
97.H	-0.631921	2.709365	2.598842
98.H	-0.293571	4.203954	3.530996
99.H	0.497542	3.731723	0.578080
100.H	2.132264	4.406559	0.643946
101.H	0.794669	5.245174	1.476031
102.H	-2.625438	-0.260075	4.138089
103.H	-4.203954	0.293571	3.530996
104.H	-2.709365	0.631921	2.598842
105.H	-4.406559	-2.132264	0.643946
106.H	-3.731723	-0.497542	0.578080
107.H	-5.245174	-0.794669	1.476031
108.H	0.631921	-2.709365	2.598842

109.H	0.293571	-4.203954	3.530996
110.H	-0.260075	-2.625438	4.138089
111.H	-2.132264	-4.406559	0.643946
112.H	-0.794669	-5.245174	1.476031
113.H	-0.497542	-3.731723	0.578080

S1.5.10. Results for D_{4h} Constrained $[Co(NC^tBu_2)_4]^-$ ($S = 0$ and $S = 1$).

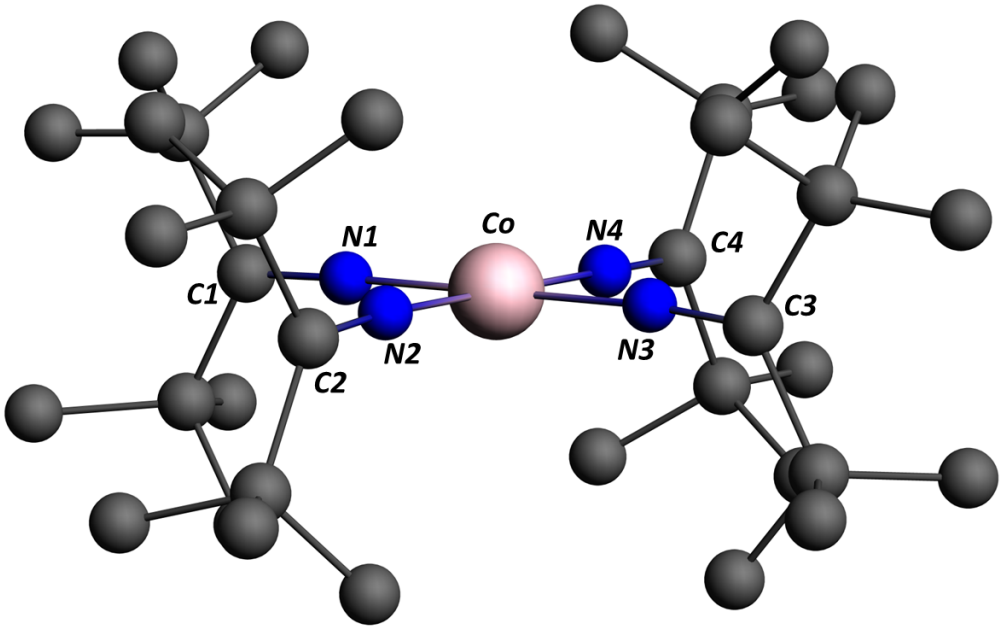

Figure S1.18. Optimized molecular structure of D_{4h} constrained $[Co(NC^tBu_2)_4]^-$ ($S = 0$). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Co-N1, 1.857; Co-N2, 1.867; Co-N3, 1.852; Co-N4, 1.881; N1-Co-N3, 180.0; N2-Co-N4, 179.8; Co-N1-C1, 178.1; Co-N2-C2, 175.0; Co-N3-C3, 175.0; Co-N4-C4, 178.8.

S1.5.11. Optimized Cartesian Coordinates for D_{4h} Constrained $[Co(NC^tBu_2)_4]^-$ ($S = 0$).

1.Co	-0.010529	-0.006237	-0.071862
2.N	1.855911	-0.030571	-0.105009
3.N	-0.035170	-1.858379	-0.094645
4.N	-1.890720	0.018352	-0.033198
5.N	0.014141	1.850317	-0.047497
6.C	-0.010219	-3.112230	-0.007926
7.C	3.109932	-0.040556	-0.018470
8.C	-3.147607	0.009288	-0.008969
9.C	0.027883	3.105403	0.011029
10.C	-3.970220	0.009596	-1.411187
11.C	-3.915534	-0.003441	1.415769
12.C	-0.020883	3.977080	-1.350363
13.C	0.030806	3.892473	1.400171

14.C	3.975017	0.030570	-1.385599
15.C	3.889336	-0.041773	1.387644
16.C	-0.002280	-3.994661	-1.362296
17.C	-0.007001	-3.890346	1.380098
18.C	0.125625	5.512206	-1.246585
19.H	-0.021527	5.928834	-2.257561
20.H	-0.626114	5.975235	-0.592108
21.H	1.121465	5.827676	-0.915011
22.C	-1.357502	3.719383	-2.071163
23.H	-1.361105	2.728113	-2.533180
24.H	-2.211280	3.767114	-1.382913
25.H	-1.521590	4.470500	-2.864218
26.C	1.121281	3.476501	-2.245700
27.H	2.071831	3.478969	-1.698865
28.H	0.927351	2.444289	-2.561982
29.H	1.236513	4.112144	-3.141581
30.C	1.090603	5.033232	1.481754
31.H	0.695753	6.006640	1.167221
32.H	1.428793	5.149800	2.524636
33.H	1.981743	4.816791	0.874548
34.C	0.389612	2.902271	2.518974
35.H	-0.327528	2.076707	2.579391
36.H	1.379206	2.464510	2.333412
37.H	0.416686	3.434991	3.484887
38.C	-1.398533	4.469969	1.654164
39.H	-1.935059	3.866376	2.399626
40.H	-1.368641	5.509197	2.022604
41.H	-2.013107	4.464922	0.742926
42.C	-3.549602	1.270711	-2.180472
43.H	-3.615454	2.161318	-1.542337
44.H	-2.512152	1.179056	-2.516787
45.H	-4.197695	1.434049	-3.059504
46.C	-3.534391	-1.235082	-2.201323
47.H	-2.507136	-1.121784	-2.562488
48.H	-3.568619	-2.132622	-1.570885
49.H	-4.198105	-1.404319	-3.067627
50.C	-5.517629	-0.002926	-1.434646
51.H	-5.817157	0.001140	-2.496912
52.H	-5.957976	-0.901992	-0.986401
53.H	-5.973799	0.880543	-0.972343
54.C	-5.462284	0.032294	1.458090
55.H	-5.890696	0.936414	1.008313
56.H	-5.931817	-0.844660	0.996254
57.H	-5.762683	0.030316	2.519182
58.C	-3.505529	-1.291142	2.166766
59.H	-3.496878	-2.161736	1.495877
60.H	-2.502200	-1.193303	2.594526
61.H	-4.212705	-1.505761	2.987416

62.C	-3.449684	1.237743	2.205610
63.H	-2.400524	1.143904	2.509823
64.H	-3.538608	2.146741	1.593349
65.H	-4.073465	1.377701	3.106793
66.C	-1.282734	-4.784637	1.518054
67.H	-1.051264	-5.860370	1.481042
68.H	-1.785925	-4.591480	2.477332
69.H	-2.015852	-4.575992	0.726278
70.C	-0.020595	-2.877875	2.532939
71.H	0.864399	-2.236621	2.514319
72.H	-0.897061	-2.226810	2.473706
73.H	-0.044133	-3.426200	3.490124
74.C	1.280917	-4.736178	1.556395
75.H	1.359883	-5.084468	2.601000
76.H	1.309202	-5.628123	0.921654
77.H	2.175971	-4.133908	1.339438
78.C	-0.016864	-5.538052	-1.250147
79.H	-0.149594	-5.943006	-2.267262
80.H	0.929689	-5.946498	-0.875517
81.H	-0.834818	-5.932003	-0.636482
82.C	1.259527	-3.627294	-2.163545
83.H	1.160840	-2.629607	-2.604818
84.H	2.147651	-3.616376	-1.517013
85.H	1.438236	-4.356548	-2.973280
86.C	-1.240475	-3.595659	-2.179336
87.H	-2.154978	-3.666373	-1.575304
88.H	-1.146722	-2.558827	-2.516281
89.H	-1.363771	-4.249162	-3.060504
90.C	3.481405	-1.116321	-2.279116
91.H	3.527960	-2.072474	-1.741102
92.H	2.436056	-0.948330	-2.561461
93.H	4.097268	-1.205693	-3.190783
94.C	5.515196	-0.081838	-1.321941
95.H	5.895844	0.052214	-2.348327
96.H	5.979079	0.698422	-0.702055
97.H	5.865581	-1.061747	-0.977604
98.C	3.682569	1.371436	-2.084053
99.H	2.673513	1.378182	-2.504506
100.H	3.759799	2.215326	-1.384792
101.H	4.404999	1.547228	-2.900586
102.C	5.192539	-0.890517	1.447838
103.H	6.074856	-0.358936	1.075321
104.H	5.400682	-1.144295	2.500545
105.H	5.104198	-1.837542	0.896625
106.C	2.971713	-0.655919	2.453395
107.H	2.025278	-0.113037	2.547737
108.H	2.741302	-1.695108	2.183596
109.H	3.489525	-0.667728	3.428154

110.C	4.230099	1.430294	1.777345
111.H	4.204089	2.106752	0.912065
112.H	3.506941	1.818475	2.508812
113.H	5.233336	1.510962	2.230505

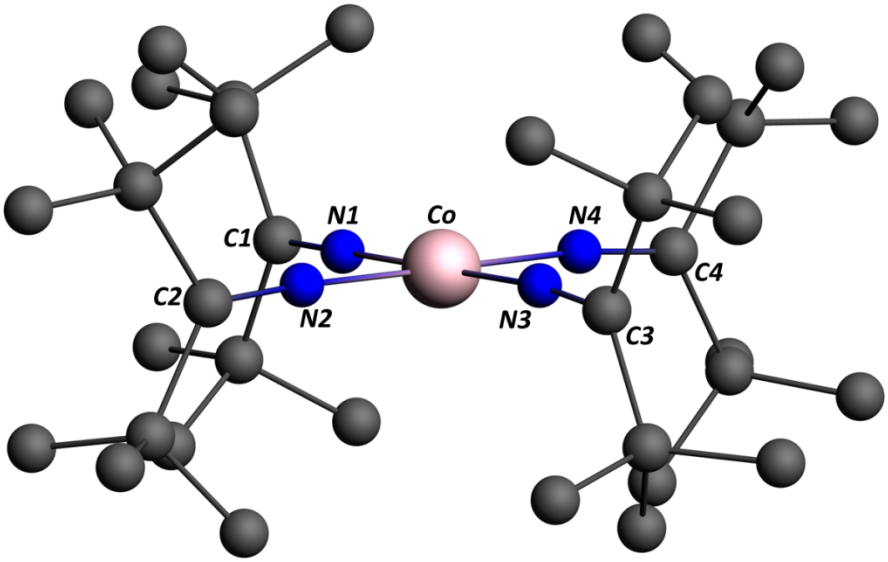

Figure S1.19. Optimized molecular structure of D_{4h} constrained $[Co(NC^tBu_2)_4]^-$ (S = 1). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Co-N1, 1.883; Co-N2, 1.858; Co-N3, 1.862; Co-N4, 1.849; N1-Co-N3, 179.9; N2-Co-N4, 179.7; Co-N1-C1, 179.9; Co-N2-C2, 176.6; Co-N3-C3, 173.3; Co-N4-C4, 174.2.

S1.5.12. Optimized Cartesian Coordinates for D_{4h} Constrained $[Co(NC^tBu_2)_4]^-$ (S = 1).

1.Co	-0.007200	-0.012534	-0.093554
2.N	1.854436	-0.023373	-0.144580
3.N	-0.018861	-1.861256	-0.117717
4.N	-1.889214	-0.001426	-0.044185
5.N	0.003923	1.845719	-0.078775
6.C	-0.004308	-3.113978	-0.010006
7.C	3.108996	-0.037070	-0.031074
8.C	-3.148326	-0.001019	-0.011699
9.C	0.024145	3.099777	0.003919
10.C	-3.972132	0.003927	-1.409094
11.C	-3.901199	-0.005415	1.415108
12.C	-0.025249	3.987642	-1.346133
13.C	0.034231	3.866205	1.399707
14.C	3.983975	0.037730	-1.389823
15.C	3.864371	-0.041953	1.378655
16.C	0.001871	-4.008042	-1.356110
17.C	-0.009985	-3.870073	1.384905
18.C	0.118780	5.522853	-1.237187

19.H	-0.036137	5.944095	-2.245223
20.H	-0.627797	5.984497	-0.575699
21.H	1.117993	5.835779	-0.912126
22.C	-1.357586	3.723024	-2.066277
23.H	-1.377832	2.701590	-2.453034
24.H	-2.220556	3.843212	-1.397174
25.H	-1.485030	4.419496	-2.913493
26.C	1.109048	3.497121	-2.255273
27.H	2.079331	3.573955	-1.748419
28.H	0.946103	2.443581	-2.509403
29.H	1.157640	4.090014	-3.184820
30.C	1.104504	4.994130	1.496478
31.H	0.730663	5.965721	1.153603
32.H	1.404344	5.122688	2.549463
33.H	2.012978	4.757283	0.923650
34.C	0.370483	2.861938	2.511650
35.H	-0.335269	2.024727	2.526870
36.H	1.373088	2.442607	2.357047
37.H	0.351924	3.376080	3.487404
38.C	-1.384690	4.465503	1.662103
39.H	-1.946636	3.837479	2.367468
40.H	-1.328030	5.481898	2.087442
41.H	-1.984667	4.527723	0.743117
42.C	-3.539108	1.259443	-2.178087
43.H	-3.676895	2.165007	-1.571895
44.H	-2.478348	1.184002	-2.434106
45.H	-4.125444	1.377098	-3.106306
46.C	-3.529723	-1.231810	-2.205160
47.H	-2.474961	-1.141252	-2.481869
48.H	-3.643161	-2.148733	-1.611151
49.H	-4.132803	-1.342010	-3.123626
50.C	-5.517494	-0.002831	-1.431395
51.H	-5.824849	0.006526	-2.491735
52.H	-5.959931	-0.901324	-0.982767
53.H	-5.967467	0.881602	-0.963849
54.C	-5.445482	0.033967	1.469922
55.H	-5.873769	0.939458	1.021694
56.H	-5.918729	-0.841199	1.007849
57.H	-5.742927	0.032507	2.532885
58.C	-3.479489	-1.285668	2.166633
59.H	-3.538087	-2.171789	1.517458
60.H	-2.446224	-1.200220	2.518658
61.H	-4.133288	-1.459206	3.039478
62.C	-3.415119	1.231557	2.196426
63.H	-2.343560	1.155806	2.415213
64.H	-3.575022	2.149930	1.612939
65.H	-3.971649	1.330600	3.145529
66.C	-1.283140	-4.767018	1.531049

67.H	-1.050235	-5.840775	1.472913
68.H	-1.767917	-4.590361	2.503292
69.H	-2.031245	-4.546364	0.757024
70.C	-0.027481	-2.844881	2.525827
71.H	0.856378	-2.203360	2.502774
72.H	-0.902686	-2.194409	2.455657
73.H	-0.055666	-3.380687	3.489558
74.C	1.273937	-4.717303	1.576315
75.H	1.336780	-5.068231	2.620748
76.H	1.305508	-5.605696	0.936272
77.H	2.172130	-4.115658	1.372421
78.C	-0.019560	-5.550917	-1.242501
79.H	-0.148862	-5.956914	-2.260161
80.H	0.922464	-5.965490	-0.860667
81.H	-0.844168	-5.939029	-0.634235
82.C	1.261065	-3.641899	-2.159563
83.H	1.191274	-2.612833	-2.527308
84.H	2.163707	-3.712624	-1.536998
85.H	1.384869	-4.321146	-3.021408
86.C	-1.228926	-3.606908	-2.180356
87.H	-2.157348	-3.745276	-1.608482
88.H	-1.159020	-2.550079	-2.450897
89.H	-1.301930	-4.210510	-3.101095
90.C	3.496623	-1.101917	-2.295674
91.H	3.604014	-2.073723	-1.795379
92.H	2.434717	-0.962310	-2.524810
93.H	4.072188	-1.133646	-3.236395
94.C	5.523582	-0.068595	-1.320723
95.H	5.911748	0.070160	-2.344287
96.H	5.982700	0.709686	-0.694281
97.H	5.873377	-1.049778	-0.977502
98.C	3.678822	1.376135	-2.082145
99.H	2.641768	1.396445	-2.424613
100.H	3.825992	2.226853	-1.401117
101.H	4.343277	1.522411	-2.951806
102.C	5.155349	-0.905652	1.454403
103.H	6.041075	-0.395736	1.061292
104.H	5.366321	-1.131660	2.513385
105.H	5.049559	-1.866508	0.929707
106.C	2.925057	-0.632066	2.437777
107.H	1.963888	-0.107689	2.468101
108.H	2.727872	-1.687805	2.208122
109.H	3.404933	-0.585980	3.429995
110.C	4.225184	1.424317	1.769386
111.H	4.280756	2.088549	0.894628
112.H	3.465915	1.843865	2.445849
113.H	5.198340	1.473567	2.288428

S1.6. Energy Decomposition Analysis (EDA) on $Co(CNCH_2)_4$ and $[Co(CNCH_2)_4]^-$.

S1.6.1. EDA Parameters for $Co(CNCH_2)_4$ in D_{2d} Symmetry.

Term	Energy (kcal/mol)
ΔE_{int}	-3365.34
ΔE_{Pauli}	335.93
ΔE_{elstat} (36.6%)[a]	-1356.19
ΔE_{orb} (63.4%)[a]	-2345.08
A_1 (20.3%)[b]	-477.0
A_2 (2.0%)[b]	-46.6
B_1 (25.2%)[b]	-590.4
B_2 (8.3%)[b]	-194.3
E (44.2%)[b]	-1036.8
ΔE(π-donation A_1+E) (64.5%)[b]	1513.8
ΔE(π-back bonding B_1) (25.2%)[b]	-590.4

a Values in parenthesis give percent contribution to total attractive interactions ($\Delta E_{elstat} + \Delta E_{orb}$).
b Values in parenthesis give percent contribution to total orbital interactions.

S1.6.2. Optimized Coordinates for $Co(CNCH_2)_4$ used for Energy Decomposition Analysis.

Co	0.00000000	0.00000000	0.00000000
N	1.23824000	-1.23824000	-0.40617000
N	1.23824000	1.23824000	0.40617000
N	-1.23824000	1.23824000	-0.40617000
N	-1.23824000	-1.23824000	0.40617000
C	2.10379000	-2.10379000	-0.14721000
C	2.10379000	2.10379000	0.14721000
C	-2.10379000	2.10379000	-0.14721000
C	-2.10379000	-2.10379000	0.14721000
H	2.63654000	2.63654000	0.95427000
H	-2.37945000	-2.37945000	-0.88771000
H	2.37945000	-2.37945000	0.88771000
H	2.37945000	2.37945000	-0.88771000
H	2.63654000	-2.63654000	-0.95427000
H	-2.37945000	2.37945000	0.88771000
H	-2.63654000	-2.63654000	0.95427000
H	-2.63654000	2.63654000	-0.95427000

S1.6.2. EDA Parameters for $[Co(CNCH_2)_4]^-$ in D_{2d} Symmetry.

Term	Energy (kcal/mol)
ΔE_{int}	-2140.12
ΔE_{Pauli}	317.49
ΔE_{elstat} (46.4%)[a]	-1140.96
ΔE_{orb} (53.6%)[a]	-1316.65
A_1 (13.8%)[b]	-181.46
A_2 (1.8%)[b]	-23.85
B_1 (18.3%)[b]	-240.95
B_2 (18.3%)[b]	-241.31
E (47.8%)[b]	-629.08
ΔE(π-donation A_1+E) (61.6%)[b]	-810.54
ΔE(π-back bonding B_1) (18.3%)[b]	-240.95

a Values in parenthesis give percentage contribution to total attractive interactions
b Values in parenthesis give percentage contribution to total orbital interactions

S1.6.2. Optimized Coordinates for $[Co(CNCH_2)_4]^-$ used for Energy Decomposition Analysis.

Co	0.00000000	0.00000000	0.00000000
N	1.23102670	-1.23102670	-0.57377171
N	1.23102670	1.23102670	0.57377171
N	-1.23102670	1.23102670	-0.57377171
H	-2.68432863	-2.68432863	0.84034676
C	2.06908733	-2.06908733	-0.14567907
C	2.06908733	2.06908733	0.14567907
C	-2.06908733	2.06908733	-0.14567907
C	-2.06908733	-2.06908733	0.14567907
H	2.25840730	2.25840730	-0.93557875
H	2.68432863	-2.68432863	-0.84034676
H	-2.25840730	2.25840730	0.93557875
H	2.25840730	-2.25840730	0.93557875
H	-2.68432863	2.68432863	-0.84034676
N	-1.23102670	-1.23102670	0.57377171
H	-2.25840730	-2.25840730	-0.93557875
H	2.68432863	2.68432863	0.84034676

S1.7 ***References***

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