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Stabilization of a Cobalt–Cobalt Bond by Two Cyclic Alkyl Amino Carbenes

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Supporting Information

ABSTRACT: $(Me_2\text{-cAAC:})_2Co_2$ (**2**, where Me_2-cAAC: = cyclic alkyl amino carbene, $:C(CH_2)(CMe_2)_2N\text{-}2,6\text{-}i\text{Pr}_2C_6H_3$)) was synthesized via the reduction of precursor $(Me_2\text{-cAAC:}Co^{II}(\mu\text{-Cl})Cl)_2$ (**1**) with KC_8. **2** contains two cobalt atoms in the formal oxidation state zero. Magnetic measurement revealed that **2** has a singlet spin ground state $S = 0$. The cyclic voltammogram of **2** exhibits both one-electron oxidation and reduction, indicating the possible synthesis of stable species containing $\mathbf{2}^{\bullet-}$ and $\mathbf{2}^{\bullet+}$ ions. The latter was synthesized via reduction of **1** with required equivalents of KC_8 and characterized as $[(Me_2\text{-cAAC:})_2Co_2]^{\bullet+}OTf^-$ ($\mathbf{2}^{\bullet+}\mathbf{OTf}^-$). Electron paramagnetic resonance spectroscopy of $\mathbf{2}^{\bullet+}$ reveals the coupling of the electron spin with 2 equiv ^{59}Co isotopes, leading to a $(Co^{0.5})_2$ state. The experimental Co1–Co2 bond distances are 2.6550(6) and 2.4610(6) Å for **2** and $\mathbf{2}^{\bullet+}\mathbf{OTf}^-$, respectively. Theoretical investigation revealed that both **2** and $\mathbf{2}^{\bullet+}\mathbf{OTf}^-$ possess a Co–Co bond with an average value of 2.585 Å. A slight increase of the Co–Co bond length in **2** is more likely to be caused by the strong π-accepting property of cAAC. $\mathbf{2}^{\bullet+}$ is only 0.8 kcal/mol higher in energy than the energy minimum. The shortening of the Co–Co bond of $\mathbf{2}^{\bullet+}$ is caused by intermolecular interactions.

Cobalt compounds are often used as efficient catalysts for organic transformations,[1] C–F bond activations,[2] and initiators for polymerization reactions.[3] The N-heterocyclic carbene (NHC: = $:C[N(2,6\text{-}i\text{Pr}_2C_6H_3)CH]_2$)) was found to be very advantageous toward the stabilization of several metal-containing species that show a broad range of important catalytic properties.[1] They were utilized to stabilize monoatomic metals such as Ni[4a,b] and Pd[4c] in their formal zero oxidation state. Besides transition metals, molecular species (Si_2, Ge_2, Sn_2, P_2, As_2, and B_2)[5] have also been prepared in the presence of various NHCs.

To date, several NHC-stabilized cobalt compounds have been reported. $(NHC{:}Co^{II}(\mu\text{-Cl})Cl)_2$ and $(NHC{:})_2Co^{II}Cl_2$ are formed when NHC is reacted with $CoCl_2$ in 1:1 and 2:1 molar ratio, respectively.[6] $(NHC{:})_2Co^{I}Cl$ with three-coordinated Co(I) was synthesized by reacting $(Ph_3P{:})_2Co^{I}Cl$ with 2 equiv of NHC:.[6b] Further reduction of $(NHC{:})_2Co^{I}Cl$ with metallic sodium or sodium amalgam leads to the C–H bond activation of NHCs, which finally results in the formation of $(NHC{:})_2Co^{II}R_2$.[6e] To our surprise, so far, two-valent Co(0) species have not been stabilized by NHC:. A compound containing one Co(0) atom should have one unpaired[6c] electron, which might be why it initiates C–H bond activation.[6a,b] However, $[(NHC{:})_2Co]^+BPh_4^-$, which contains a two-coordinated Co(I), can be synthesized from $(NHC{:})_2Co^{I}Cl$ with three-coordinated Co(I).[6a] Recently, square planar $[(NHC{:})_4Co]^+BPh_4^-$ [6d] was prepared by reacting $(Ph_3P{:})_2Co^{I}Cl$ with a less bulky NHC in a 1:4 molar ratio in the presence of $NaBPh_4$.

It is well known that NHCs have an enormous impact on the production of compounds with low-valent elements through the formation of donor–acceptor coordinate bonds.[7] The carbene carbon atom of NHC: is bound to two σ-withdrawing and two π-donating N-atoms. When the cyclic alkyl amino carbene (cAAC:) is used instead of the NHC:, one σ-withdrawing and π-donating N-atom is replaced by one σ-donating quarternary C-atom. The cAAC: is becoming more nucleophilic but also more electrophilic when compared with NHC:.[8−10] Hence, several radical species of main-group elements were stabilized by cAAC:.[9]

Keeping such crucial differences in mind, we explored the synthesis, structure, and theoretical analysis of $(Me_2\text{-cAAC:})_2Co_2$ (**2**, where Me_2-cAAC: = $:C(CH_2)(CMe_2)_2N\text{-}2,6\text{-}i\text{Pr}_2C_6H_3$), with two cobalt atoms in the formal oxidation state zero, and its radical cationic analogue, $[(Me_2\text{-cAAC:})_2Co_2]^{\bullet+}\text{-}OTf^-$ ($\mathbf{2}^{\bullet+}\mathbf{OTf}^-$) (Scheme 1). Furthermore, the nature of the Co–Co bond[11−13] is discussed, which is still an interesting topic in terms of the existence of metal–metal bonds.

$(Me_2\text{-cAAC:}Co^{II}(\mu\text{-Cl})Cl)_2$ (**1**), an analogue of $(NHC{:}Co^{II}(\mu\text{-Cl})Cl)_2$,[6a,b] was synthesized in 80% yield when Me_2-cAAC: and $CoCl_2$ were reacted in a 1:1 molar ratio in THF. The product was isolated as a light violet-blue crystalline powder. **1** is insoluble in toluene and benzene; when we attempted to crystallize it from THF, initially a dark blue solution was formed, which slowly turned to a green-blue color, indicating

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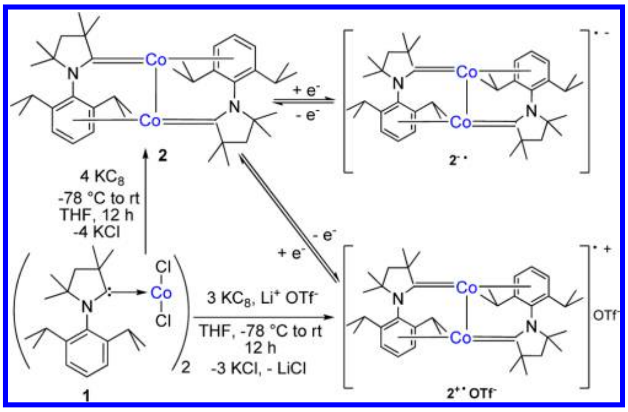
Scheme 1. Syntheses of the Chemical Species 2 and $2^{\bullet +}$ from 1 under KC_8 Reduction



decomposition. A comparable decomposition was reported for $(NHC{:}Co^{II}(\mu\text{-}Cl)Cl)_2$.[6a]

The dark blue THF solution of **1** was further reduced to **2** utilizing 4 equiv of KC_8 (Scheme 1). Compound **2** crystallizes as large black shiny needles in 65% yield from the dark brown solution stored at −32 °C. **2** is soluble in THF, toluene, and benzene. Precursor **1** decomposes above 293 °C, while **2** melts in the range of 249−250 °C. The ^1H and ^{13}C resonances recorded in C_6D_6 show line broadening; in contrast, the reported $Co_2(CO)_6(HC{\equiv}CC_6H_{10}{-}OH)$ exhibits no line broadening in the NMR spectra.[11] All resonances of **2** are upfield shifted when compared with those of free Me_2-cAAC:. Compound **2** was also characterized by ESI-MS (m/z $[M^+]$ (%): 688 (100)) (Supporting Information (SI)).

Compound **2·toluene** crystallizes in the orthorhombic space group $Pna2_1$. **2** contains two Co(0) atoms, each coordinated by one Me_2-cAAC: carbene carbon and additionally η^6-bound to the carbon perimeter of the diisopropylaniline part of another carbene molecule (Figure 1). Each of the Co(0) atoms adopts the coordination environment of a half-sandwich complex. The Co1−Co2 bond distance of **2** (2.6550(6) Å) is close to the values quoted in the literature for weak Co−Co closed-shell interactions.[12] For comparison, the Co−Co single bond length in $(CO)_4Co{-}Co(CO)_4$ is 2.52 Å.[13] The $Co{-}C_{aromatic}$ bond distances are in the range of 2.075(2)−2.187(2) Å, close to the values reported for cobalt half-sandwich complexes. The Co1−C1 and Co2−C21 bond lengths of **2** are 1.854(2) and 1.853(2) Å, which are shortened by ∼0.2 Å when compared with those of **1a** (2.038(4)−2.042(4) Å). The reported $Co{-}C_{NHC}$ bond lengths range from 1.87 to 2.09 Å.[6,14]

It has been found that few carbenes can stabilize the radical center on carbene carbon atoms and form M−C single bonds.[15] On one hand, the $C_{cAAC}{-}N$ bond length becomes longer due to the stabilization of the radical electron on the carbene carbon.[16] On the other hand, when the cAAC: carbene forms a coordinate bond, the $C_{cAAC}{-}N$ bond becomes shorter (1.298(5)−1.301(5) Å in **1a**, see SI).[17] The $C_{carbene}{-}N$ bond lengths in **2** are comparably short (1.369(3) Å for C1−N1 and 1.367(3) Å for C21−N2), which might be due to strong electronic back-donation from cobalt to the carbene carbon atom.[10]

The magnetic susceptibility measurement on **2** confirms the diamagnetic spin ground state (S = 0), similar to that of $Co_2(CO)_6(HC{\equiv}CC_6H_{10}{-}OH)$ with a Co−Co bond length of 2.46482(13) Å.[11] On the basis of theoretical charge density studies and DFT calculation, it has been concluded that $Co_2(CO)_6(HC{\equiv}CC_6H_{10}{-}OH)$ does not possess a direct Co−Co bond, as expected on the basis of obeying the conventional 18-electron rule rather a singlet diradical character as predicted by DFT calculation.[11a]

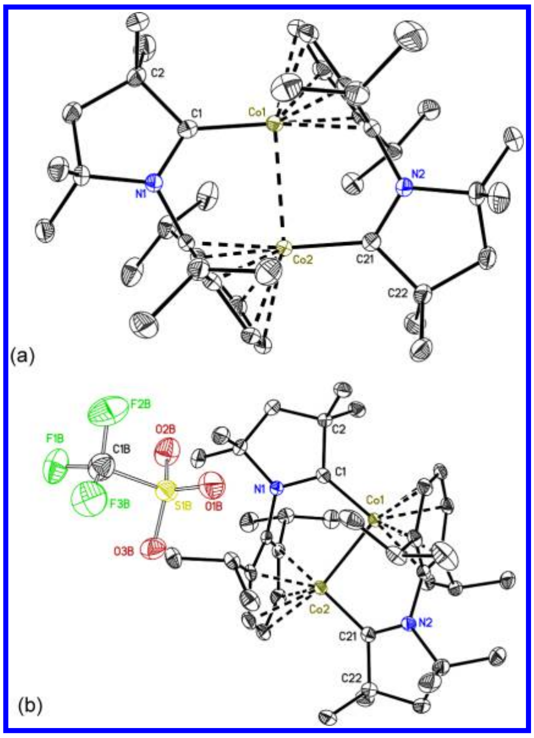


Figure 1. Molecular structures of (a) **2** and (b) $\mathbf{2^{\bullet +}}$. H-atoms are omitted for clarity. Selected experimental [calculated at B3LYP/def2-SVP for the ground state] bond lengths [Å] and angles [°] of $2/2^{\bullet +}$: Co1−C1 1.854(2)/1.891(2) [1.854/1.975], Co2−C21 1.853(2)/ 1.920(2) [1.853/1.891], Co1−Co2 2.6550(6)/2.4610(6) [2.586/2.596], C1−N1 1.369(3)/1.338(3) [1.364/1.326], C21−N2 1.367(3)/1.328(3) [1.364/1.367]; N1−C1−Co1 125.52(17)/123.59(18) [124.9/122.5], C2−C1−Co1 129.38(17)/129.87(17) [129.2/129.2], N1−C1−C2 104.9(19)/ 106.4(2) [105.7/108.4], N2−C21−Co2 124.92(17)/ 123.22(18) [124.9/126.2], C22−C21−Co2 129.45(16)/129.96(18) [129.2/126.9], N2−C21−C22 105.50(19)/106.47(2) [105.7/106.6].

The cyclic voltammogram of a dichloromethane solution of **2**, containing 0.1 M n-Bu_4NPF_6 as an electrolyte, shows a one-electron reversible reduction of $E_{1/2}$ = −0.80 V and a one-electron reversible oxidation at $E_{1/2}$ = +0.45 V versus $(Cp_2Fe)/(Cp_2Fe)^+$, indicating the formation of both radical anion $\mathbf{2^{\bullet -}}$ and radical cation $\mathbf{2^{\bullet +}}$ (Figure 2). Indeed, the radical cation $\mathbf{2^{\bullet +}}$ can be synthesized as $\mathbf{2^{\bullet +}OTf^-}$ in 90% yield when **1** is reduced with 3 equiv of KC_8 in the presence of LiOTf (Scheme 1). Black blocks of $\mathbf{2^{\bullet +}OTf^-}$ are formed when a THF/toluene solution (5:2) is stored at −32 °C for 1 week in a refrigerator. The dark blocks of $\mathbf{2^{\bullet +}OTf^-}$ do not change or decompose when they are heated to 325 °C.

Compound $\mathbf{2^{\bullet +}OTf^-}$ crystallizes in the monoclinic space group $P2_1/n$. The molecular unit of $\mathbf{2^{\bullet +}OTf^-}$ is similar (Figure 1) to that of **2**. To balance the charge, it contains one disordered triflate anion (OTf^-). The Co−Co distance is decreased to 2.4610(6) Å in $\mathbf{2^{\bullet +}OTf^-}$ when compared with that of **2** (2.6550(6) Å). The C−N bond lengths slightly decrease (1.328(3)−1.338(3) Å), while the $Co{-}C_{cAAC}$ bond distances increase (1.891(2)−1.920(2) Å), compared with those of **2**. This is in line with the decrease of back-bonding from dicobalt to both

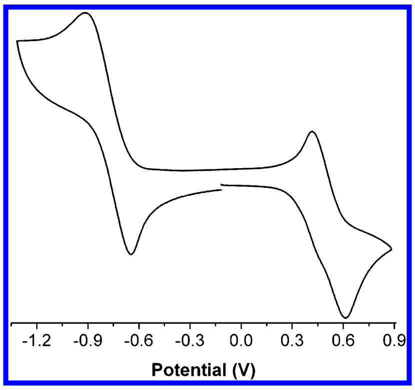


Figure 2. Cyclic voltammogram of a dichloromethane solution of **2**, containing 0.1 M *n*-Bu_4NPF_6 as an electrolyte.

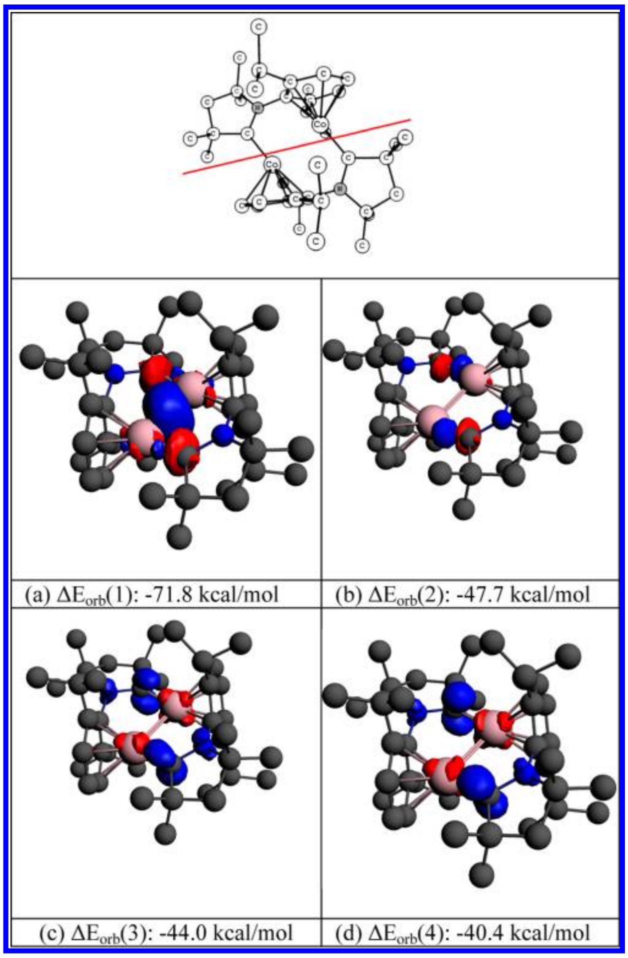
of the carbenes due to the decrease of electron density on the dicobalt unit of $\mathbf{2}^{\bullet+}\mathbf{OTf}^{-}$. A superposition image and tables of bond lengths and angles of **2** and $\mathbf{2}^{\bullet+}\mathbf{OTf}^{-}$ are given in the SI.

At room temperature, the paramagnetic THF solutions of $\mathbf{2}^{\bullet+}\mathbf{OTf}^{-}$ exhibit an unresolved EPR signal, about 1200 G wide. At 115 K in frozen solution, the spectrum revealed separate **g** tensor components at $g_1 = 2.346$, $g_2 = 2.07$, and $g_3 = 2.008$. The most revealing feature is the g_1 component, which shows a clear splitting by 2 equiv ^{59}Co ($I = 7/2$) nuclei with the proper intensity distribution 1:2:3:4:5:6:7:8:7:6:5:4:3:2:1 for coupling of one electron spin with two Co nuclei (Figure S4). The coupling constant of only 54 G is also compatible with metal—metal spin delocalization and thus with valence averaging to a new $(Co^{0.5})_2$ species (class III mixed-valency according to the Robin and Day definition). Hyperfine structure for g_2 is not resolved at X band frequency, and g_3 shows an 8-line splitting from ^{59}Co with a coupling constant of 33 G.

We optimized the geometry of **2** using density functional theory (DFT) at the B3LYP/def2-SVP level.[18] The calculated structure is in good agreement with the experimental values (see Figure 1 and SI). We analyzed the bonding situation in the molecule with the Energy Decomposition Analysis using Natural Orbitals for Chemical Valency method (EDA-NOCV)[19] at the BP86/TZVP$^+$ level using the B3LYP/def2-SVP optimized geometry. The full set of numerical results is shown in Table S13. The most important question concerns the nature of the Co—Co and Me_2-cAAC—Co interactions; it can be answered by inspection of the deformation densities, which come from the EDA-NOCV calculations, and the associated stabilization energies, which come from the pairwise orbital interactions between the two fragments that are shown at the top of Figure 3.

There are four pairs of orbital interactions that dominate the total ΔE_{orb} term. The largest contribution, $\Delta E_{orb}(1) = -71.8$ kcal/mol, comes from the σ donation of the Me_2-cAAC donor orbitals into a Co—Co bonding orbital. The second largest contribution, $\Delta E_{orb}(2) = -47.7$ kcal/mol, comes also from σ donation $Me_2\text{-cAAC}\rightarrow\text{CoCo}\leftarrow\text{cAAC-}Me_2$, but the shape of the deformation density, $\Delta\rho(2)$, shows that the acceptor orbital of the Co_2 fragment has antibonding character (Figure 3b). Since $\Delta E_{orb}(1)$ is significantly larger than $\Delta E_{orb}(2)$, it can be concluded that there is a Co—Co bond in **2**.

This is supported by a Quantum Theory of Atoms in Molecules (QTAIM)[20] calculation, which shows a Co—Co bond path. Even more conclusive is the shape of the Laplacian distribution in the Me_2-cAAC—Co—Co plane (Figure 4). There is clearly a small area of charge concentration at the bond critical point of the Co—Co bond. The other two orbital contributions, $\Delta E_{orb}(3) = -44.0$ kcal/mol and $\Delta E_{orb}(4) = -40.4$ kcal/mol, are easily identified as components of the $Me_2\text{-cAAC}\leftarrow\text{CoCo}\rightarrow\text{cAAC-}Me_2$ π back-donation. Thus, **2** has a Co—Co bond, and it possesses donor—acceptor bonds between the Me_2-cAAC ligands and the Co_2 moiety, which has significant π back-donation.


(a) $\Delta E_{orb}(1)$: -71.8 kcal/mol

(b) $\Delta E_{orb}(2)$: -47.7 kcal/mol

(c) $\Delta E_{orb}(3)$: -44.0 kcal/mol

(d) $\Delta E_{orb}(4)$: -40.4 kcal/mol

Figure 3. Results of the EDA-NOCV calculations of **2**: deformation densities $\Delta\rho$ of the four most important pairs of interacting orbitals of the two fragments, which are shown at the top of the figure, and associated stabilization energies ΔE_{orb}. The charge flow of the deformation densities is red→blue.

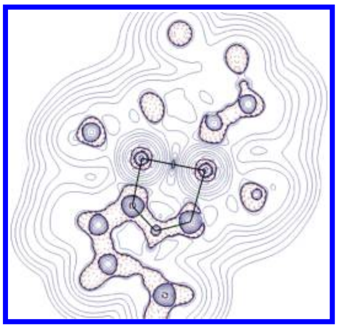


Figure 4. Laplacian distribution of **2** in the Me_2-cAAC—Co—Co plane.

We also optimized the geometry of the radical cation $\mathbf{2}^{\bullet+}$ without the counterion. The calculated bond lengths and angles are in good agreement with experiment (Figure 1), except for the Co−Co distance. X-ray structure analysis shows that the Co−Co bond in the cation is significantly shorter (2.4610 Å) than that in the neutral species (2.6551 Å), while the calculations give nearly the same distances for **2** and $\mathbf{2}^{\bullet+}$. We optimized the geometry of the cation with a frozen Co−Co bond length of 2.4610 Å, which gave a structure that is only 0.8 kcal/mol higher in energy than the energy minimum. It is conceivable that the Co−Co bond shortening in $\mathbf{2}^{\bullet+}$ comes from intermolecular interactions.

One cobalt atom has nine valence electrons. Since **2** has a singlet ground state, the cobalt atoms should have at least one electron-sharing bond. Molecular orbital analysis shows that the HOMO−1 (Figure S8) is clearly a Co−Co bond which comes from a hybridization of d(z^2), s, and p(z). The NBO calculations also give a Co−Co bond with an occupation of 1.93e that has 15% s, 6% p, and 75% d character and a Wiberg bond order of 0.87. This leads to a straightforward explanation of the bonding situation where each Co atom has an 18-electron configuration. This means that the Co−Co bond is not just a weak, closed-shell interaction but a real Co−Co single bond, which has a bond length of 2.66 Å. This is somewhat longer than a typical single bond (2.52 Å),[13,21] which could be caused by the strong π-accepting property of cAAC.[10] The phenyl groups and the cAAC ligands donate altogether eight electrons to each Co atom of the Co_2 fragment, which therefore attains an 18e configuration. The ionization takes place from the HOMO, which is a Co−ligand orbital. The large stabilization which comes from the orbital interactions, $\Delta E_{orb}(1)$ (Figure 3a), is, according to this, formation of the Co−Co bond between the unpaired electrons of the fragments.

In conclusion, we have synthesized (Me$_2$-cAAC:)$_2$Co$_2$(0) (**2**) with two cobalt atoms in the formal oxidation state zero, stabilized by two cyclic alkyl amino carbenes. **2** possesses a diamagnetic spin ground state. Cyclic voltammetry shows that **2** can be reversibly reduced or oxidized by one electron to generate the radical anion $\mathbf{2}^{\bullet-}$ or cation $\mathbf{2}^{\bullet+}$. The Co−Co bond length is shortened by ~0.2 Å in $\mathbf{2}^{\bullet+}\mathbf{OTf}^-$ when **2** undergoes one-electron oxidation to produce $\mathbf{2}^{\bullet+}$. Low-temperature electron paramagnetic resonance spectroscopy of $\mathbf{2}^{\bullet+}$ reveals the coupling of the electron spin with 2 equiv ^{59}Co isotopes, leading to a $(Co^{0.5})_2$ state. Both **2** and $\mathbf{2}^{\bullet+}\mathbf{OTf}^-$ can be synthesized from their precursor, (Me$_2$-cAAC:Co^{II}(μ-Cl)Cl)$_2$ (**1**), under KC$_8$ reduction. Moreover, (Me$_2$-cAAC:)$_2$Co^{I}Cl (**3**), with three-coordinate Co(I), was prepared by the reaction of **1**, Me$_2$-cAAC:, and KC$_8$ in a molar ratio of 1:2:2 (SI).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis of **1**, **1a**, **1b**, **1c**, $\mathbf{2}^{\bullet+}\mathbf{OTf}^-$, and **3**; UV, EPR, magnetism, crystal structure determination, and theoretical details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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