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EPR Spectroscopy

Stabilization of a Two-Coordinate Mononuclear Cobalt(0) Compound

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In memory of Mike Lappert

Abstract: Compound (Me_2-cAAC:)$_2$Co^0 (**2**; Me_2-cAAC:= cyclic (alkyl) amino carbene; :C(CH_2)(CMe_2)$_2$N-2,6-*i*$Pr_2C_6H_3$) was synthesized by the reduction of the precursor (Me_2-cAAC:)$_2$Co^{I}Cl (**1**) with KC_8 in THF. The cyclic voltammogram of **1** exhibited one-electron reduction, which suggests that synthesis of a bent 2-metallaallene (**2**) from **1** should be possible. Compound **2** contains one cobalt atom in the formal oxidation state zero, which is stabilized by two Me_2-cAAC: ligands. Bond lengths from X-ray diffraction are 1.871(2) and 1.877(2) Å with a C-Co-C bond angle of 170.12(8)°. The EPR spectrum of **2** exhibited a broad resonance attributed to the unique quasi-linear structure, which favors near degeneracy and gives rise to very rapid relaxation conditions. The cAAC–Co bond in **2** can be considered as a typical Dewar–Chatt–Duncanson type of bonding, which in turn retains 2.5 electron pairs on the Co atom as nonbonding electrons.

Over the last few decades, several fascinating Co^0 species were reported.[1] They can mediate several unusual unusual transformations in organic chemistry and have received great importance as active catalysts. Carbon monoxide stabilizes [$Co_2(CO)_8$] species, which mainly exists in a CO-bridged dimeric [$(CO)_3$Co(μ-CO)$_2$Co$(CO)_3$] form, but can be cocrystallized as [$(CO)_4$Co–Co$(CO)_4$] along with C_{60}.[2] Substituted phosphine ligands can stabilize mononuclear Co^0 species with the general formula [Co^0(:PR_3)$_4$] (R = Me, Ph), which have a d^9 electronic configuration with tetrahedral symmetry.[3] *N*-Heterocyclic carbene (NHC:) can form stable mono (NHC:Co^{II}(μ-Cl)Cl)$_2$ or bis adducts (NHC:)$_2$Co$^{II}Cl_2$ when it reacts with $CoCl_2$ in 1:1 or 2:1 molar ratio, respectively.[4] (NHC:)$_2$Co^{I}Cl with three-coordinate cobalt(I) was prepared by reacting (Ph_3P:)$_2$Co^{I}Cl with two equivalents of NHC:.[4b] Two-coordinate stable and isolable cobalt(0) species have not been characterized neither with phosphine nor with NHC: as ligands. The synthesis of (NHC:)$_2$Co^0 from (NHC:)$_2$Co^{I}Cl was not successful.[4d] The reduction of (NHC:)$_2$Co^{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:)$_2$Co$^{II}R_2$.[4d] A two-coordinate Co^0 compound should have an unpaired[3,4c] electron, which might be the reason why it initiates C–H bond activation.[4e] [(NHC:)$_2$Co]$^+$BPh$_4^-$ with a two-coordinate cobalt(I) was synthesized from a three-coordinate cobalt(I) species (NHC:)$_2$Co^{I}Cl by removing the chloride ion and replacing it by BPh$_4^-$.[4a] Recently, square-planar [(NHC:)$_4$Co]$^+$[BPh$_4^-$][4e] was synthesized by reacting (Ph_3P:)$_2$Co^{I}Cl with a less bulky NHC: in a 1:4 molar ratio in the presence of $NaBPh_4$. Herein, we report the synthesis, characterization, EPR, and theoretical calculations of two-coordinate mononuclear (Me_2-cAAC:)$_2$Co^0 (**2**).

Since the cAAC carbene is a better σ donor and π acceptor,[5] we choose the (Me_2-cAAC:)$_2$Co^{I}Cl (**1**)[6] as a precursor for the synthesis of **2**. The cyclic voltammogram of a dimethylfor-

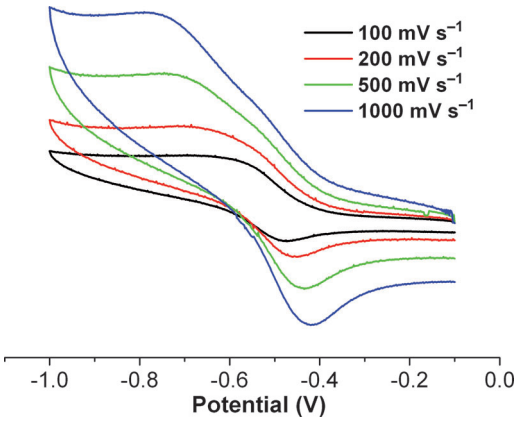

Figure 1. Cyclic voltammogram of a dimethylformamide solution of **1**, containing 0.1 M nBu_4NPF_6 as an electrolyte. The potentials refer to the decamethylferrocene/ferrocenium system as a standard.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201403525. It contains the synthesis, X-ray single-crystal diffraction, UV/Vis, catalysis, and theoretical calculations data.

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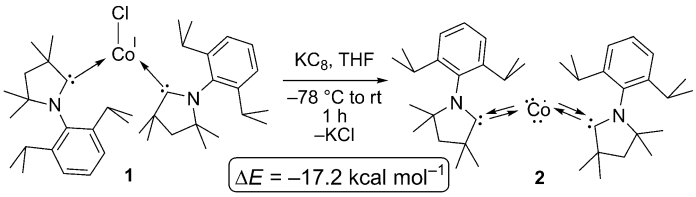

Scheme 1. Syntheses of $(Me_2\text{-cAAC:})_2Co^0$ (**2**) from $(cAAC:)_2Co^ICl$ (**1**).

mamide solution of **1**, containing 0.1 M nBu_4NPF_6 as electrolyte, showed a one-electron quasi-reversible reduction at $E_{1/2} = -0.57$ V versus $(Cp^*_2Fe)/(Cp^*_2Fe)^+$ indicating the possible formation of **2** (Figure 1). Indeed, compound **2** was chemically synthesized from **1** (Scheme 1).

The 1:1 molar mixture of $(Me_2\text{-cAAC:})_2Co^ICl$ (**1**) and KC_8 reacted in THF to give a dark blue solution, which was filtered (Scheme 1). This solution was slowly concentrated under vacuum to form dark shiny needles of $(Me_2\text{-cAAC:})_2Co^0$ (**2**), which are separated by filtration and dried in vacuum, giving 98% yield. The volume of the solvent should be maintained to carry out a cleaner reaction to obtain such high yields (see the Supporting Information). However, it is important to mention that the yield of **2** dropped upon decreasing the volume of the solvent. Compound **2** can also be synthesized within fifteen minutes by the reduction of precursor **1** at room temperature in a similar yield when 2.2 equivalents of $LiNiPr_2$ (LDA) were employed as a reducing agent, instead of one equivalent of KC_8 (see the Supporting Information). The detailed synthesis, purification, and characterization of compound **2** are given in the Supporting Information. Compound **2** is stable in an inert atmosphere and decomposes above 134 °C. It produces a blue color when dissolved in organic solvents, such as THF, toluene, and benzene. ^{1}H NMR spectrum of **2** showed broad resonances ranging from $\delta = -2.5$ to 10 ppm indicating the paramagnetic[7–9] nature of the solution, as was expected. Compound **2** can be further characterized by MS (EI) spectrometry (*m/z* (100%): 629.4; see the Supporting Information). The reaction energy for the formation of **2** from **1** was calculated (at the M06/def2-TZVPP//BP86/def2-SVP level of theory) to be exothermic by -17.2 kcal mol^{-1} (KC_8 as a reducing agent), which also indicates the feasibility of the reaction (Scheme 1).

Compound **2** crystallizes in the triclinic space group $P\bar{1}$. The central cobalt atom is bound to two carbene carbon atoms adopting a two-coordinate bent geometry (Figure 2). The C-Co-C bond angle is 170.12(8)°, which is far wider when compared with that of precursor **1** (122.33(10)°). The Co–C_{cAAC} and N–C_{cAAC} bond lengths of **2** are 1.871(2)/1.877(2) and 1.343(2)/1.349(2) Å, respectively, which are close to the values of 1.920(2)/1.932(2) and 1.335(3)/1.333(3) found in **1**.[6] The slight shortening of the Co–C_{cAAC} bond lengths and increasing of C_{cAAC}–N bond lengths might be due to the Co→C_{cAAC} π-back donation.

We have performed theoretical calculations at the M06/def2-TZVPP//BP86/def2-SVP level of theory for the different spin states of the two-coordinate cobalt model compound CoL_2 (L = Me_2-cAAC:) (**2**) using Gaussian 09 program package.[10] The calculated equilibrium geometries of the doublet state (**2m**) and the quartet state (**2m**) of CoL_2 suggest that the doublet state **2m** resembles more closely to the crystal structure of **2**. Note that the quartet state **2m′** is 16.9 kcal mol^{-1} higher in energy than the doublet state **2m** (Figure S3 in the Supporting Information). Thus, the geometrical data and relative energy indicate the doublet **2m** as the ground state. The Co center in **2m** exists in a bent geometry with the bending angle of 168.2°. The dihedral angle between the planes of the two cAAC: ligands in **2m** (78.8°) indicates that the two cAAC: ligands are almost perpendicular to each other. The Co–C_{cAAC} bond length is slightly longer, and the C_{cAAC}–N bond lengths are slightly shorter in **2m** than the corresponding bond lengths in the previously reported $(Me_2\text{–cAAC:})_2Co_2$.[11] Note also that the C_{cAAC}–N bond length is significantly longer than the C_{cAAC}–N bond length in free cAAC:, which signifies Co→C–N π*-back donation. Hence, these geometrical data suggest that **2m** can be considered as a bent 2-metallaallene.[12]

The natural bond orbital (NBO) charge analysis revealed that the Co center in **2m** is positively charged (0.122 e), and hence the C_{cAAC}→Co σ donation can be considered as being weaker than the C_{cAAC}←Co π-back donation.[10] This is reflected in the smaller Wiberg bond index of the C–N bond (1.31) compared with the corresponding value in free cAAC: (1.50). On the one hand, the NBO spin density in **2m** showed significant accumulation of α spin on the Co atom (1.526). On the other hand, the β-spin density is delocalized over the cAAC: ligand with major coefficient on the carbene C and the N atoms (0.253; Figure 3a). This results in one unpaired electron of **2m**. The Mulliken charge and spin density analysis also give similar results (Table S3 in the Supporting Information). Such accumulation of excess α-spin density at the metal center and delocalization of the β-spin over the cAAC: ligands was also observed for the recently reported $(cAAC:)_2Mn$ complex.[13] The bonding

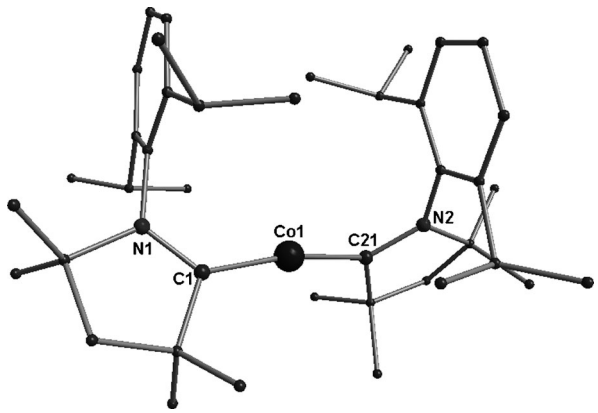

Figure 2. Molecular structure of compound **2**. Hydrogen atoms are omitted for clarity. Selected experimental [calculated ones at the BP86/def2-SVP level for the ground state] bond lengths [Å] and angles [°] from single-crystal X-ray diffraction: Co1–C1 1.871(2) [1.883], Co1–C21 1.877(2) [1.884], C1–N1 1.343(2) [1.362], C21–N2 1.349(2) [1.362]; C1-Co1-C21 170.12(8) [168.2], C2-C1-N1 106.67(16) [106.3], N2-C21-C22 106.81(15)[106.3], C2-C1-Co1 122.51(14) [121.9], N1-C1-Co1 130.69(13) [131.4].

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in the two-coordinate **2m** is described by the following molecular orbital (MO) and the EDA-NOCV analysis (see the Supporting Information).[10]

The L–Co–L bonding in CoL_2 (**2m**) (L = Me_2-cAAC:) can be explained as follows (Figure S4 in the Supporting Information). Thirteen valence electrons are available for the C_{cAAC}-Co-C_{cAAC} bond formation, which are comprised of nine valence electrons from Co ($4s^2 3d^7$) and one σ lone pair from each of the cAAC: ligands. The molecular orbital (MO) analysis revealed that four of the 3d orbitals on Co are doubly occupied and the fifth d orbital is singly occupied. This fifth d orbital is significantly mixed with the 4s orbital on the Co center. This leads to two hybrid orbitals on the Co atom, namely, one empty and another with an unpaired electron (Figure 3b). Thus, the vacant orbital on Co can accept electrons from the bonding combination of the σ-lone pairs of electrons of the two cAAC: ligands (Figure 3c). However, there is no proper symmetric d orbital on the Co that can interact with the antibonding combination of the two σ-lone pairs of the two cAAC: ligands (Figure 3d). Bending of the C_{cAAC}-Co-C_{cAAC} results in the mixing of the σ-lone pair and the C–N π*-MO of the cAAC: ligand. The resultant orbitals in turn could overlap more effectively with the 3d orbital on the Co atom (Figure 3e, f). This interaction can be considered as the donation of the 3d electrons from Co to the vacant C–N π*-MO, which leads to the C–N bond elongation, as well as reduction of the C–N Wiberg bond indices. The remaining four electrons on Co atom are retained as two lone pairs (Figure S4 in the Supporting Information). The molecular orbitals analysis suggests that the bonding in bent 2-metallaallene (**2m**) can be best described as a slightly modified bonding situation similar to that of carbones.[14] Herein, the Co–C_{cAAC} bonding can be considered as that of typical Dewar–Chatt–Duncanson type of bonding.[15] This results in two Co–C_{cAAC} partial double bonds and 2.5 electron pairs on Co as nonbonding electrons. This bonding interaction can be further analyzed in a quantitative manner by EDA-NOCV approach implemented in ADF 2013.01.[10]

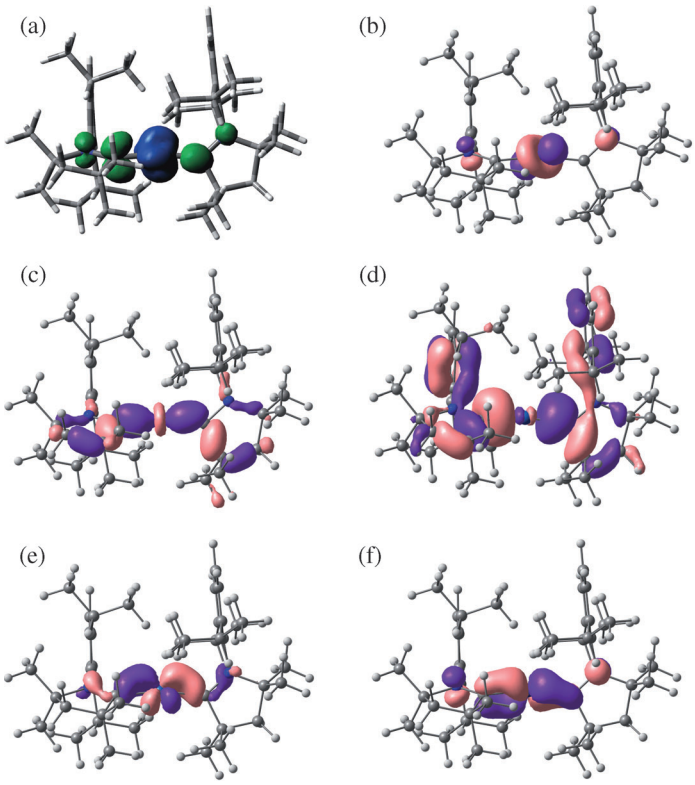

Figure 3. Plot of a) NBO spin density, where the blue color corresponds to α-spin density and the green color corresponds to β-spin density b)–f) important occupied molecular orbitals of CoL_2, L = Me_2-cAAC (**2m**) at the M06/def2-TZVPP//BP86/def2-SVP level of theory.

As a d^9 transition-metal compound with a calculated $d(z^2)^1$ configuration, compound **2** should exhibit EPR activity. Indeed, an extremely broad but unresolved (*g* components, ^{59}Co hyperfine coupling) resonance was observed in the X-band experiment at 4 K in the solid and in THF solution (Figure 4). However, no EPR resonance was observed at room temperature. This unusual behavior for a $S = 1/2$ species is attributed to the unique quasi-linear structure, which favors near degeneracy and gives rise to very rapid relaxation conditions.

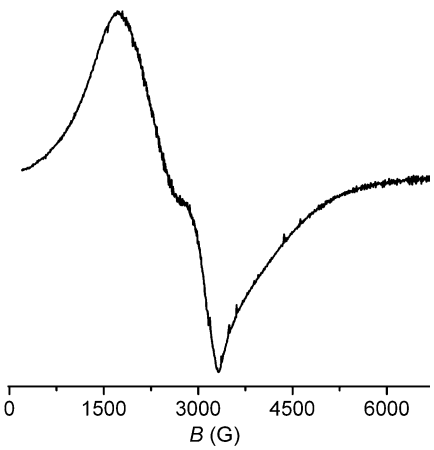

Figure 4. X-band EPR spectrum of solid sample of **2** at 4 K. The resonance is unresolved due to the ^{59}Co hyperfine coupling.

Cobalt compounds are often utilized as efficient catalysts for transformations in organic chemistry.[16–18] The successful synthesis of compound **2**, having a cobalt(0) atom with a low coordination geometry, inspired us to examine its catalytic activity. C2-Alkenylation of *N*-pyrimidylindole with diphenylacetylene and cyclotrimerization of diphenylacetylene proceeded smoothly under different conditions in the presence of **2** as catalyst (see the Supporting Information). Yoshikai and coworkers have developed a synthetic route of alkenylation of *N*-methylpyrrolidinone by using $CoBr_2$ and pyphos (pyphos = $Ph_2P(CH_2)_2$-C_5H_4N) as a ligand in the presence of 60 mol% of $tBuCH_2MgBr$ at room temperature.[18] However, the actual catalyst might be an intermediate species, which has never been isolated and characterized. Most often, cobalt-catalyzed organ-

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ic transformations (such as arylation,[18a] alkylation,[18b] and alkenylation[18c]) involve the use of Grignard reagents (RMgX) as common ingredients, where the role of RMgX is not well known. Herein, we showed that well characterized (Me_2-cAAC:)$_2$Co^0 (**2**) can catalyze an alkenylation process without using any Grignard reagent (Table S6 in the Supporting Information).

In conclusion, a mononuclear cobalt(0) species was stabilized by two cyclic alkyl(amino) carbenes, which is formulated as (Me_2-cAAC:)$_2$Co^0 (**2**). It was synthesized from the precursor (Me_2-cAAC:)$_2$Co^{I}Cl (**1**) in 98% yield. Compound **2** is stable in an inert atmosphere for three months and decomposes above 134 °C. It was characterized by X-ray single-crystal diffraction and further studied by EPR and theoretical calculations. The cobalt atom of **2** adopts a two-coordinate bent geometry with a C-Co-C bond angle of 170°. A broad EPR resonance was observed, as was expected for a d^9 system ($S = {}^1/_2$) with unique quasi-linear structure favoring a near-degenerate electronic state which is undergoing very rapid relaxation. The C_{cAAC}—Co bond in **2** can be considered as a typical Dewar–Chatt–Duncanson type of bonding with the retention of 2.5 nonbonding pairs of electrons on the Co atom. The geometry and bonding analysis indicates that it can likewise be considered as 2-cobaltallene. Preliminary catalytic properties of **2** were investigated (see the Supporting Information).[19]

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Keywords: carbenes · cobalt · density functional calculations · EPR spectroscopy · synthetic methods

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