Cobalt Diazo-Compounds: From Nitrilimide to Isocyanoamide via a Diazomethanediide Fleeting Intermediate

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Abstract: Lithium trimethylsilyldiazomethane and a cobalt (II) precursor with an N-anchored tris-NHC (TIMENmes) ligand provide access to the cobalt nitrilimide 1. Complex 1 was structurally characterized by single-crystal X-ray diffraction and its electronic structure was examined in detail, including EPR spectroscopy, SQUID magnetometry and computational analyses. The desilylation of the C-trimethylsilylnitrilimide reveals a transient complex with an elusive diazomethanediide ligand, which substitutes one of the mesitylene rings of the ancillary ligand through C–N bond cleavage. This transformation results in the cyclometalated cobalt(II) complex 2, featuring a rare isocyanoamido-κ-C ligand.

Single atom- or group transfer reagents provide access to intriguing chemical transformations.[1] The release of inert gaseous or aromatic compounds, such as N\textsubscript{2} or anthracene, is the driving force for many of these challenging transfer reactions.[2] For instance, the azide anion transfers N\textsubscript{2}− under release of N\textsubscript{2} (Scheme 1a); thus, giving access to metal nitrene or nitrido complexes.[3] Likewise, the isoelectronic heavier analogues, namely phosphaethynolate (P=CN\textsubscript{2}) and arsacetylnolate (As=CN\textsubscript{2}) are convenient P− and As− transfer reagents.[4] Isoelectronic with the azide anion, derivatives of diazomethane are a popular choice for carbene and carbyne transfer reactions.[3,6] Contrarily, carbon atom transfer reactions are largely elusive but are attracting increasing attention.[7] For example, Fehlhammer’s N-isocyanoiminotriphenylphosphane (Ph\textsubscript{3}P−N=−C\textsubscript{2}) and Cummins’ 7-isocyano-7-azadibenzonorbornadiene (C\textsubscript{12}H\textsubscript{8}N−N=−C\textsubscript{2}) have been proposed to transfer carbon upon four-electron oxidation; yet, their experimental realization remains challenging.[8] The diazomethanediide moiety, [C=–N=N]=, is isoelectronic and isolobal with the azide anion (Scheme 1b), could, in principle, transfer C\textsubscript{2}− in a two-electron oxidation reaction. However, this class of compounds is essentially unexplored. Solely based on IR vibrational analysis, the isolation of (explosive!) mercury and cadmium salts of diazomethanediamides have been claimed.[9] Bertrand et al. reported a series of nitrilimine derivatives, where the [CN\textsubscript{2}] entity is stabilized by two π-acidic Si, P, B, or Ge-based substituents.[10] Of further note, complexes featuring the much more stable cyanimide isomer [N=C–N]= are well known.[11,12]

The η\textsuperscript{1} metal-coordinated C-(trimethylsilyl)nitrilimide ligand [M−N=–N=−C−SiMe\textsubscript{3}] may, in principle, give access to metal-diazomethanediide complexes. In this context, we have previously reported an iron(II) nitrilimide complex [(TIMENmes)Fe(N\textsubscript{2}CSiMe\textsubscript{3})\textsuperscript{2+}]. The abstrimation of the trimethylsilylum group by fluoride led to diazo group N–N bond cleavage and the formation of the iron(IV) nitrido complex [(TIMENmes)FeN\textsubscript{2}\equivN\textsuperscript{2+}].[13] Arguably, an iron-diazomethanediide [Fe–N=–N=−C\textsubscript{2}] intermediate, which readily loses a cyanide anion, takes part in this transformation. Yet, destabilizing the N–N bond cleavage product, viz., the metal nitrido complex, may increase the stability of the intermediate η-coordinate diazomethanediide [CN\textsubscript{2}]\textsuperscript{2−} and, potentially, lead to its distinguished reactivity. Considering the higher electronegativity of cobalt in comparison to iron, we sought to...
probe the reactivity of diazomethanediide at a cobalt center. Herein, we present a cobalt(II) complex featuring a terminal nitrilimide and report its transformation to an unprecedented terminal isocyanamide upon abstraction of its trimethylsilyl group. Further, we show that the intermediate diazomethanediide ligand is highly reactive and engages in radical, aromatic C–N bond substitution of the ancillary ligand (Scheme 1c).

Treatment of a cold THF solution of [(TIMENmes)CoCl](BPh₄) with one equivalent of Li[Me₃SiNCN] resulted in an instantaneous color change from blue to dark green that—upon warming to room temperature—turned to intense red. After workup, the green crystalline product, namely [(TIMENmes)Co(N₂CSiMe₃)](BPh₄) (1), was obtained that regenerated dark red solutions upon re-dissolution (Scheme 2). The ¹H NMR spectrum revealed ten paramagnetically shifted and broadened signals in the −10 to 70 ppm range; thus, substantiating a C₅-symmetric structure in solution. The IR vibrational spectrum of 1 features an intense absorption centered at 2065 cm⁻¹ (Figure S4), assigned to the stretching vibration of the C=–N-bound (trimethylsilyl)nitrilimido ligand, which was confirmed by density functional theory (DFT) calculations (S = 3/2; 2124 cm⁻¹).[iv]

Single crystal XRD analysis of green crystals of 1 revealed a cationic complex with a four-coordinate cobalt center in a pseudo-tetrahedral ligand environment of the chelate’s three NHC carbon atoms and an apical C–(trimethylsilyl)nitrilimido ligand (Figure 1).[v] The N–N and N–C bond lengths within the nitrilimido ligand are 1.184(3) and 1.197(3) Å, respectively, suggesting a predominantly allenic resonance structure.

Perpendicular mode X-band EPR measurements of the frozen THF solution of 1 at liquid He temperatures detected a high-spin S = 3/2 species with a rhombic spectrum and effective g-values of gₛ = 4.52, gₜ₁ = 3.88, and gₜ₂ = 2.14, originating from the |±1/2⟩ Kramers’ doublet and an additional transition at gₛ = 6.20 from the |±3/2⟩ Kramers’ doublet (Figure 2). The unusually high intensity signal stemming from the |±3/2⟩ Kramers’ doublet and the temperature-dependent EPR study (Figure 2 and S14) indicate that |±3/2⟩ is the zero-field ground state. The EPR spectrum was also simulated within the spin Hamiltonian formalism, thus, revealing the zero-field splitting and rhombicity parameters D = −5.00 cm⁻¹ and E/D = 0.11, respectively, with real g-values of 2.19, 2.17, and 2.17 (Figure S15). Variable-temperature and variable-field (VT-VF) SQUID measurements of mortared samples of 1 revealed a magnetic moment, µ₀, of 4.33 µ₀ at room temperature, supporting the high spin S = 3/2 Co d⁷ electronic structure assignment (Figure 2). The room-temperature magnetic moment remains essentially constant down to 30 K, and then abruptly decreases to 3.34 µ₀ at 2 K. Simulations of the VT-VF magnetization data reveal D = −5.28 cm⁻¹ and |E/D| = 0.20, with gₑ ≈ 2.24, in excellent agreement with the EPR simulations. Finally, and in agreement with the solid-state SQUID magnetization data, the room-temperature moment of 1 in solution was determined to be 4.2 µ₀ (Evans’ method). Quantum chemical calculations at the DLPNO-CCSD(T), CASSCF/NEVPT2 (Figure S35) and DFT level of theory further corroborate the electronic structure of 1. During the synthesis of 1, a minor by-product (1minor) was formed. This by-product could be isolated by fractional crystallization and identified as a square-pyramidal cobalt(II) cyan complex [(TIMENmes)Co(CN)][BPh₄], S = 1/2, based on single-crystal XRD and EPR analyses.[vi] Tentatively, this complex forms through a 1,3-trimethylsilylium shift, resulting in [Co₁⁻–C≡N–NSiMe₃], which—upon loss of [NTMS]—provides the Co₁⁻–CN complex.[vii]

Complex 1 was treated with NBu₄F in thawing THF (Scheme 3). Monitoring the reaction by ¹⁹F NMR spectroscopy confirmed the release of Me₃SiF. Single-crystal XRD analysis of orange crystals of 2 revealed a square-pyramidal five-coordinate cobalt complex with an η⁴–C₄-bound N-
The mesityl-isocyanoamido ligand (Figure 3). To the best of our knowledge, this is the first example of a crystallographically characterized terminal isocyanoamido-C complex. [17,18] Notably, the N-mesityl substituent is derived from one NHC group, which has transformed to an imidazolate ligand. The short C–N (1.1669 Å) and relatively long N–C bond length (1.3317 Å) within the isocyanoamido ligand suggest a predominant \( \text{C} = \text{N}^+ \text{–C} \) resonance structure. The IR vibrational spectrum of the product reveals a band at 2100 cm\(^{-1} \), which was assigned by calculations (2079 cm\(^{-1} \)) to the stretching mode of the isocyanoamido ligand. The formation of complex 2 suggests a cobalt-diazometheneide [Co= NC\(_2\)] intermediate. Although with some precedents for low-valent \( p \)-element compounds,[20] de-arylation of NHC ligands is very rare; yet, has been reported for highly reduced Co and Rh complexes.[20]

SQUID magnetization measurements on powdered samples of 2 revealed a temperature-independent magnetic moment of 1.93 \( \mu_B \) at room temperature, suggestive of an \( S = \frac{3}{2} \) ground state (Figure S20), which is in agreement with the magnetic moment of 2.2 \( \mu_B \) determined by Evans’ method in THF solution. The doublet ground state is further confirmed by EPR. The X-band EPR spectroscopic analysis of 2, performed in frozen CH\(_2\)Cl\(_2\); at 7 K, reveals a rhombic spectrum with \( g_{\text{eff}} \) values of 2.43, 2.15, and 2.00, hyperfine (hf) coupling to \( ^{59} \text{Co} \) and super-hf coupling to one \( ^{14} \text{N} \) nucleus (Figure S19).

Unfortunately, all attempts to trap the transient diazometheneide with various reagents remained unproductive in our hands.[21] These experiments typically resulted in formation of either Co\(_I \) complexes, such as [(TIMEN\(_{\text{mes}}\))CoF], [(TIMEN\(_{\text{mes}}\))CoCl], 2, or the Co\(_I \) complex [(TIMEN\(_{\text{mes}}\))Co].

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**Figure 2.** CW X-band EPR spectrum (top) of a frozen THF solution of \( 1 \) at 7 K (black trace), at 50 K (grey trace), and simulation (red trace). Blue and green traces show simulated spectra for the |1/2\rangle and |3/2\rangle Kramers’ doublets. Temperature-dependent SQUID magnetization measurements for \( 1 \) at 1 T (bottom). Inset: VT-VF magnetization data with the simulation parameters.

**Scheme 3.** Synthesis of 2 by desilylation of 1 (R = Mesityl).

**Figure 3.** Molecular structure of complex 2 in crystals of [(TIMEN\(_{\text{mes}}\))Co,(CN\(_2\))Mes) obtained by vapor diffusion of Et\(_2\)O into a THF solution. Analysis of another, essentially isorootuctral crystal of [(TIMEN\(_{\text{mes}}\))Co,(CN\(_2\))Mes).3MeCN, grown from an acetonitrile solution is presented in the Supporting Information (Figure S33). Selected bond lengths and angles for 2: Co–C1 1.9296(14), Co–C2 1.9192(14), Co–C3 1.9562(14), Co–N3 2.2587(12), Co–C4 1.9186(15), C4–N1 1.1669(19), N1–N2 1.3317(17), N2–C5 1.387(2), C1–Co–C2 173.28(6), C3–Co–C4 173.27(6), C4–N1–N2 119.34(13).
To probe the mechanism for the C–N bond cleavage and clarify the alleged intermediacy of a diazomethanediide, we performed calculations at the TPSSh-D3(SMD)/ZORA-def2-TZVPP//BP86-D3/ZORA-def2-SVP level of theory, modeling both the doublet and quartet potential energy hypersurfaces (Figure 4).\(^{[21]}\) In agreement with the experiment, where an immediate reaction was observed upon addition of fluoride, even at a temperature as low as –95°C (Figure S21), the desilylation to 1\(^{\text{aMesNC}}\) with a quartet ground state is predicted to proceed essentially barrierless (Figure 4; Figure S40). This complex is kinetically unstable (\(\Delta G^\ddagger = +73 \text{kJ mol}^{-1} = -31 \text{kJ mol}^{-1} + 104 \text{kJ mol}^{-1}\)) and gives transient 1\(^{\text{aMesNC}}\) via a radical pathway (\(\Delta G = -33 \text{kJ mol}^{-1}\)). Similarly, the C–N bond scission proceeds with a remarkably low overall barrier (\(\Delta G^\ddagger = +76 \text{kJ mol}^{-1} = -28 \text{kJ} + 104 \text{kJ mol}^{-1}\)) and forms 1\(^{\text{bMesNC}}\) (\(\Delta G = -149 \text{kJ mol}^{-1}\)), having a quartet ground-state as well. Following isomerization to 1\(^{\text{cMesNC}}\) (\(\Delta G = -141 \text{kJ mol}^{-1}\)), the complex crosses to the doublet potential energy hypersurface (minimum energy crossing point MECP: \(\Delta G = -128 \text{kJ mol}^{-1}\)) and \(\text{N}\)-to-\(\text{C}\) rearrangement (\(\Delta G^\ddagger = -125 \text{kJ mol}^{-1}\)) gives 2 (\(\Delta G^\ddagger = -290 \text{kJ mol}^{-1}\)). The calculations corroborate accumulation of considerable spin density (0.2 a.u.) at the carbon atom of 1; likewise, spin density is located at this carbon atom in intermediate 1\(^{\text{NNC}}\) (0.4 a.u.; Figure S36). Consequently, we suggest that the deprotection of the trimethylsilyl group “exposes” the unpaired electron within the \(\text{CN}_2\) ligand and, thus, leads to C–N bond cleavage of one mesityl group through a radical mechanism.

In closing, we have presented the synthesis of the cobalt-(II) nitrilimido complex [(TIMEN\(^{\text{N,N,N,N}}\))Co(N(C(SiMe\(_3\)))\)](BPh\(_4\)) (1) through a salt metathesis reaction of the Co chlorido precursor with lithium trimethylsilyldiazomethane. Subsequent desilylation of 1 gives access to complex 2 with an unprecedented C-bound isocyanamido ligand. The reaction proceeds via a transient cobalt-diazomethanediide intermediate, [Co–N=N=C\(^+\)], which readily dearylates the NHC chelate and isomerizes to the \(\text{N}\)-(mesityl)-isocyanamido-\(\kappa\)-C ligand in 2.

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**Conflict of interest**

The authors declare no conflict of interest.

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Details of the EPR (Figure S16 and S17) and single-crystal XRD (Figure S26) study of the cyano complex 1\textsuperscript{red}, a thorough electrochemical analysis of 1 suggesting the existence of the Co\textsuperscript{II}/Co\textsuperscript{redox pair (Figure S6 and S7), and the independent synthesis and isolation of the reduced Co\textsuperscript{II} complex [[TIMEN\textsuperscript{II}Co(N\textsubscript{3})]] (pp. S8–S10, Figure S11 and S18) can be found in the Supporting Information file.

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For a description of trapping experiments and for a discussion of the computational methods see the Supporting Information file.

Deposition Number(s) 2048841 and 2048842 (for 1 and 2) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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