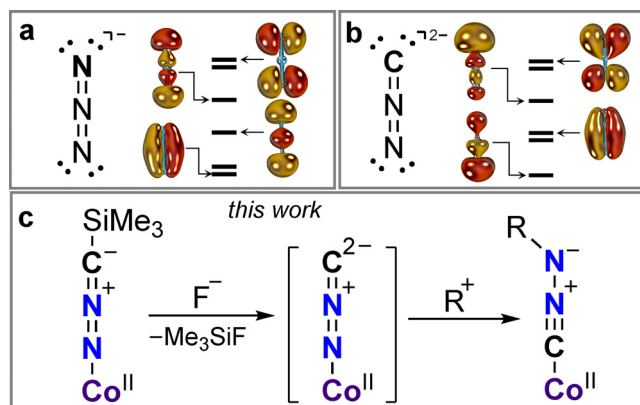**Coordination Chemistry**

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

*Sadig Aghazada, Dominik Fehn, Frank W. Heinemann, Dominik Munz,\* and Karsten Meyer\**

*Dedicated to Professor Wolfgang Kaim on the occasion of his 70th birthday*

***Abstract:*** *Lithium trimethylsilyldiazomethanide and a cobalt (II) precursor with an N-anchored tris-NHC (TIMEN^{mes}) ligand provide access to the cobalt nitrilimide* **1**. *Complex* **1** *was structurally characterized by single-crystal X-ray diffractometry (SC-XRD) and its electronic structure was examined in detail, including EPR spectroscopy, SQUID magnetometry and computational analyses. The desilylation of the C-(trimethylsilyl)nitrilimide 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.*

$\mathbf{S}$ingle atom- or group transfer reagents provide access to intriguing chemical transformations.[1] The release of inert gaseous or aromatic compounds, such as $N_2$ or anthracene, is the driving force for many of these challenging transfer reactions.[2] For instance, the azide anion transfers $N^-$ under release of $N_2$ (Scheme 1a); thus, giving access to metal nitrene or nitrido complexes.[3] Likewise, the isoelectronic heavier analogues, namely phosphaethynolate ($PCO^-$) and arsaethynolate ($AsCO^-$) 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.[5,6] Contrarily, carbon atom transfer reactions are largely elusive but are attracting increasing attention.[7] For example, Fehlhammer's *N*-isocyanoiminotriphe-



**Scheme 1.** Isoelectronic analogy between a) an azide and b) a diazomethanediide with their representative occupied frontier molecular orbitals; c) transformation reported herein.

nylphosphane ($Ph_3PN−N^+≡C^-$) and Cummins' 7-isocyano-7-azadibenzonorbornadiene ($C_{14}H_{10}N−N^+≡C^-$) have been proposed to transfer carbon upon four-electron oxidation; yet, their experimental realization remains challenging.[8] The diazomethanediide moiety, $[C=N=N]^{2-}$, which is isoelectronic and isolobal with the azide anion (Scheme 1b), could, in principle, transfer $C^{2-}$ 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 diazomethanediide have been claimed.[9] Bertrand et al. reported a series of nitrilimine derivatives, where the $[CN_2]$ 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 $[N=C=N]^{2-}$ are well known.[11,12]

The $\eta^1$ metal-coordinated *C*-(trimethylsilyl)nitrilimide ligand $[M−N=N^+=C^-−SiMe_3]$ may, in principle, give access to metal-diazomethanediide complexes. In this context, we have previously reported an iron(II) nitrilimide complex $[(TIMEN^{mes})Fe(N_2CSiMe_3)]^+$. The abstraction of the trimethylsilylium group by fluoride led to diazo group N−N bond cleavage and the formation of the iron(IV) nitrido complex $[(TIMEN^{mes})Fe^{IV}≡N]^+$.[13] Arguably, an iron-diazomethanediide $[Fe−N=N^+=C^{2-}]$ 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 *N*-coordinate diazomethanediide $[CN_2]^{2-}$ and, potentially, lead to its distinguished reactivity. Considering the higher electronegativity of cobalt in comparison to iron, we sought to

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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 isocyanoamide upon abstraction of its trimethylsily-lilium group. Further, we show that the intermediate diazo-methanediide 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 $[(TIMEN^{mes})CoCl]$-$(BPh_4)$ with one equivalent of $Li[Me_3SiCN_2]$ resulted in the 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 $[(TIMEN^{mes})Co(N_2CSiMe_3)](BPh_4)$ (**1**), was obtained that regenerated dark red solutions upon re-dissolution (Scheme 2). The $^1H$ NMR spectrum revealed ten paramag-netically shifted and broadened signals in the −10 to 70 ppm range; thus, substantiating a $C_3$-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 $\kappa^1$-$N$-bound $C$-(trimethylsilyl)ni-trilimido ligand, which was confirmed by density functional theory (DFT) calculations ($S = 3/2$: $2124\ cm^{-1}$).[14]

Single crystal XRD analysis of green crystals of **1**·3.5 THF 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 $C$-(trime-thylsilyl)nitrilimido ligand ($\tau_4 = 0.94$) (Figure 1).[15] The N−N and N−C bond lengths within the nitrilimido ligand are 1.184(3) and 1.197(3) Å, respectively, suggesting a predom-inant 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 $g_{eff,1} = 4.52$, $g_{eff,2} = 3.88$, and $g_{eff,3} = 2.14$, originating from the $|\pm 1/2\rangle$ Kramers' doublet, and an addi-tional transition at $g_{eff,1} = 6.20$ from the $|\pm 3/2\rangle$ Kramers' doublet (Figure 2). The unusually high intensity signal stem-ming from the $|\pm 3/2\rangle$ Kramers' doublet and the temperature-
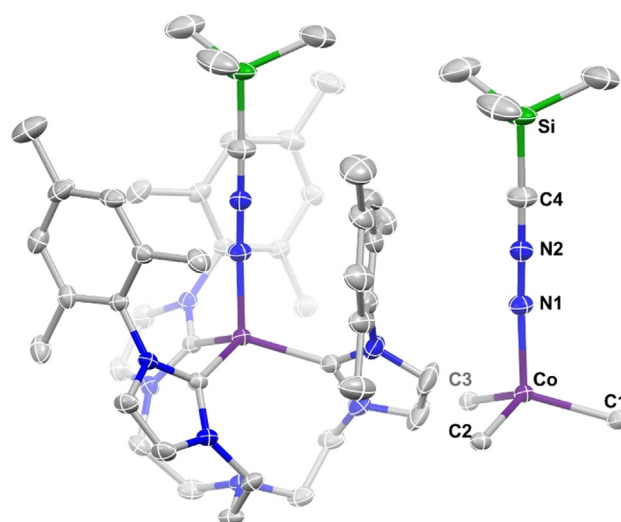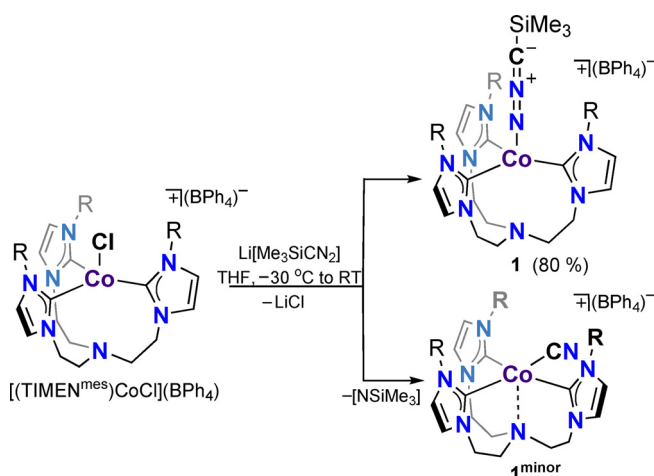


***Figure 1.*** Molecular structure of the complex cation of **1** in crystals of $[(TIMEN^{mes})Co(N_2CSiMe_3)](BPh_4)\cdot3.5\,THF$, obtained by vapor diffusion of pentane into THF solution.[22] Tetraphenylborate, solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for the complex cation of **1**: *avg*(Co-C1,2,3) 2.044, Co–N1 1.914(2), Co···$N_{anchor}$ 3.304, N1–N2 1.184(3), N2–C4 1.197(3), C4–Si 1.781(3); Co-N1-N2 174.87(19), N1-N2-C1 179.4(3), N2-C4-Si 178.5-(3).

dependent EPR study (Figure 2 and S14) indicate that $|\pm 3/2\rangle$ 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-temper-ature and variable-field (VT-VF) SQUID measurements of mortared samples of **1** revealed a magnetic moment, $\mu_{eff}$, of $4.33\ \mu_B$ at room temperature, supporting the high spin $S = 3/2$ Co $d^7$ electronic structure assignment (Figure 2). The room-temperature magnetic moment remains essentially constant down to 30 K, and then abruptly decreases to $3.34\ \mu_B$ at 2 K. Simulations of the VT-VF magnetization data reveal $D = -5.28\ cm^{-1}$ and $|E/D| = 0.20$, with $g_{avg} = 2.24$, in excellent agreement with the EPR simulations. Finally, and in agree-ment with the solid-state SQUID magnetization data, the room temperature moment of **1** in solution was determined to be $4.2\ \mu_B$ (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 (**1$^{minor}$**) formed. This by-product could be isolated by frac-tional crystallization and identified as a square-pyramidal cobalt(II) cyano complex $[(TIMEN^{mes})CoCN](BPh_4)$, $S = 1/2$, based on single-crystal XRD and EPR analyses.[16] Tenta-tively, this complex forms through a 1,3-trimethylsilylium shift, resulting in $[Co^{II}-C\equiv N-NSiMe_3]$, which—upon loss of [NTMS]—provides the $Co^{II}$-CN complex.[17]

Complex **1** was treated with $NBu_4F$ in thawing THF (Scheme 3). Monitoring the reaction by $^{19}F$ NMR spectros-copy confirmed the release of $Me_3SiF$. Single-crystal XRD analysis of orange crystals of **2** revealed a square-pyramidal five-coordinate cobalt complex with an $\eta^1$-$C4$-bound $N$-



***Scheme 2.*** Synthesis of the cobalt nitrilimide complex **1** proceeding with formation of the minor by-product **1$^{minor}$** (R = Mesityl); for **1$^{minor}$** see Supporting Information.
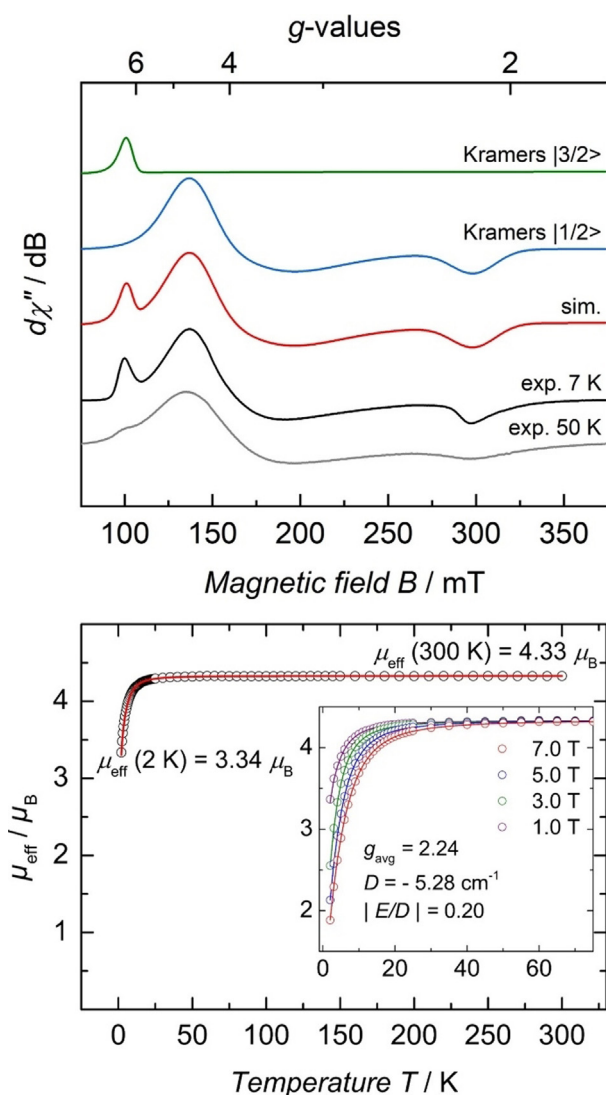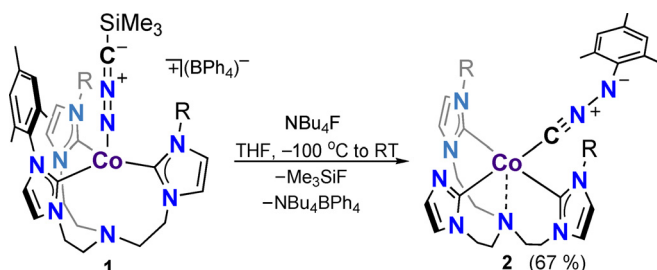
**Figure 2.** CW X-band EPR spectrum (top) of a frozen THF solution of **1** at 7 K (black trace), at 50 K (grey trace), and simulation (red trace). Blue and green traces show simulated spectra for the $|\pm1/2\rangle$ and $|\pm3/2\rangle$ Kramers' doublets. Temperature-dependent SQUID magnetization 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).

(mesityl)-isocyanoamido ligand (Figure 3). To the best of our knowledge, this is the first example of a crystallographically characterized terminal isocyanoamido-κ-C complex.[17,18] Notably, the *N*-mesityl substituent is derived from one NHC
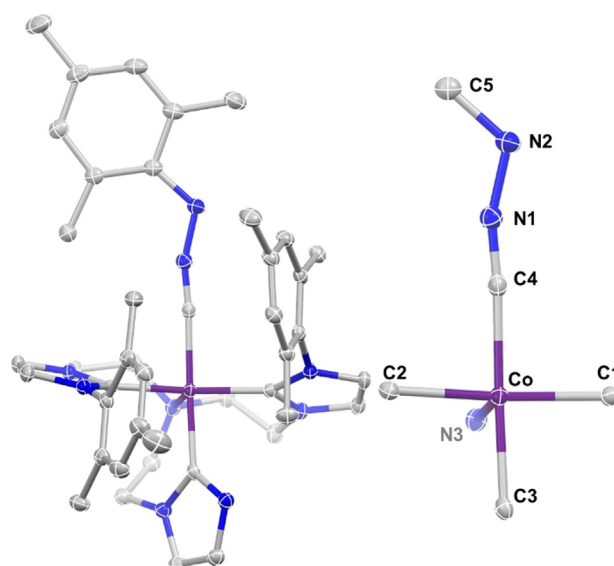


**Figure 3.** Molecular structure of complex **2** in crystals of [(TIMEN*)Co-(CN₂Mes)] obtained by vapor diffusion of Et₂O into a THF solution.[22] Analysis of another, essentially isostructural crystal of [(TIMEN*)Co-(CN₂Mes)]·3 MeCN, grown from an acetonitrile solution is presented in the Supporting Information (Figure S33). Selected bond lengths [Å] 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), Co-C4-N1 175.37(13), C4-N1-N2 162.18(14), N1-N2-C5 119.34(13).

group, which has transformed to an imidazolate ligand. The short C–N (1.1669 Å), and relatively long N–N bond length (1.3317 Å) within the isocyanoamido ligand suggest a predominant $^-C\equiv N^+-N^--R$ 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-diazomethanediide [Co−N= N$^+$=C$^{2-}$] intermediate. Although with some precedents for low-valent *p*-element compounds,[19] 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 μ$_B$ at room temperature, suggestive of an $S = \frac{1}{2}$ ground state (Figure S20), which is in agreement with the magnetic moment of 2.2 μ$_B$ 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 CH₂Cl₂ at 7 K, reveals a rhombic spectrum with $g_{\text{eff},1} = 2.43$, $g_{\text{eff},2} = 2.15$ and $g_{\text{eff},3} = 2.00$, hyperfine (hf) coupling to $^{59}$Co and super-hf coupling to one $^{14}$N nucleus (Figure S19).

Unfortunately, all attempts to trap the transient diazomethanediide with various reagents remained unproductive in our hands.[21] These experiments typically resulted in formation of either Co$^{II}$ complexes, such as [(TIME-N$^{\text{mes}}$)CoF]$^+$, [(TIMEN$^{\text{mes}}$)CoCl]$^+$, **2**, or the Co$^I$ complex [(TIMEN$^{\text{mes}}$)Co]$^+$.
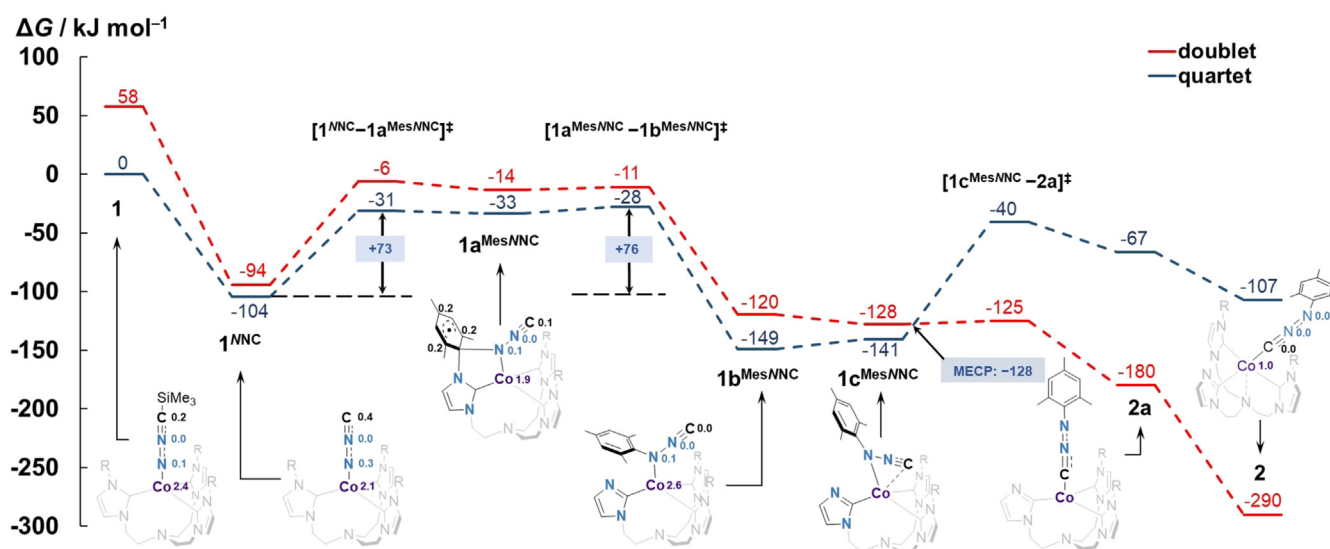
**Figure 4.** Mechanism for the conversion of **1** to **2** and electronic structures of all compounds with Löwdin spin densities in [a.u.]. MECP: minimum energy crossing point. See the Supporting Information for further transition states and isomers.

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 $\mathbf{1^{NNC}}$ with a quartet ground state is predicted to proceed essentially barrierless (Figure 4; Figure S40). This complex is kinetically unstable ($\Delta\Delta G^{\ddagger} = +73$ kJ mol$^{-1}$ = −31 kJ mol$^{-1}$ + 104 kJ mol$^{-1}$) and gives transient $\mathbf{1a^{MesNNC}}$ via a radical pathway ($\Delta G = -33$ kJ mol$^{-1}$). Similarly, the C−N bond scission proceeds with a remarkably low overall barrier ($\Delta\Delta G^{\ddagger} = +76$ kJ = −28 kJ + 104 kJ mol$^{-1}$) and forms $\mathbf{1b^{MesNNC}}$ ($\Delta G = -149$ kJ mol$^{-1}$), having a quartet ground-state as well. Following isomerization to $\mathbf{1c^{MesNNC}}$ ($\Delta G = -141$ kJ mol$^{-1}$), the complex crosses to the doublet potential energy hypersurface (minimum energy crossing point MECP: $\Delta G = -128$ kJ mol$^{-1}$) and $N$-to-$C$ rearrangement ($\Delta G^{\ddagger} = -125$ kJ mol$^{-1}$) gives **2** ($\Delta G^{\ddagger} = -290$ 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 $\mathbf{1^{NNC}}$ (0.4 a.u.; Figure S36). Consequently, we suggest that the deprotection of the trimethylsilyl group "exposes" the unpaired electron within the 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$^{mes}$)Co(N$_2$CSiMe$_3$)](BPh$_4$) (**1**) through a salt metathesis reaction of the Co chlorido precursor with lithium trimethylsilyldiazomethanide. Subsequent desilylation of **1** gives access to complex **2** with an unprecedented $C$-bound isocyanoamido ligand. The reaction proceeds via a transient cobalt-diazomethanediide intermediate, [Co−N=N$^+$=C$^{2-}$], which readily dearylates the NHC chelate and isomerizes to the $N$-(mesityl)-isocyanoamido-κ-$C$ ligand in **2**.

## Acknowledgements

## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** bond activation · cobalt · density functional theory · diazo compounds · nitrilimines

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[16] Details of the EPR (Figure S16 and S17) and single-crystal XRD (Figure S26) study of the cyano complex **1**^minor, a thorough electrochemical analysis of **1** suggesting the existence of the Co^I/Co^0 redox pair (Figure S6 and S7), and the independent synthesis and isolation of the reduced Co^0 complex [(TIMEN^mes)Co(N₂)] (*pp.* S8–S10, Figure S11 and S18) can be found in the Supporting Information file.

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

[22] Deposition Number(s) 2048841 and 2048842 (for **1** and **2**) contain(s) 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.