Merging Pincer Motifs and Potential Metal–Metal Cooperativity in Cobalt Dinitrogen Chemistry: Efficient Catalytic Silylation of \( \text{N}_2 \) to \( \text{N} \left( \text{SiMe}_3 \right)_3 \)

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Dedicated to Prof. Gottfried Huttner

Abstract: Using a pyrazolate-bridged dinucleating ligand that provides two proximate pincer-type PNN binding sites ("two-in-one pincer"), different synthetic routes have been developed towards its dicobalt(I) complex 2 that features a twice deprotonated ligand backbone and two weakly activated terminal \( \text{N}_2 \) substrate ligands directed into the bimetallic pocket. Protonation of 2 is shown to occur at the ligand scaffold and to trigger conversion to a tetracobalt(I) complex 4 with two end-on \( \mu_3\text{N}_2 \)-bridging \( \text{N}_2 \); in THF 4 is labile and undergoes temperature-dependent \( \text{N}_2 \)/triflate ligand exchange. These pyrazolate-based systems combine the potential of exhibiting both metal–metal and metal–ligand cooperativity, viz. two concepts that have emerged as promising design motifs for molecular \( \text{N}_2 \) fixation catalysts. Complex 2 serves as an efficient (pre)catalyst for the reductive silylation of \( \text{N}_2 \) into \( \text{N} \left( \text{SiMe}_3 \right)_3 \) (using \( \text{K}_8 \) and \( \text{Me}_3\text{SiCl} \)), yielding up to 240 equiv \( \text{N} \left( \text{SiMe}_3 \right)_3 \) per catalyst.

Introduction

More than 99% of global nitrogen exists in the form of molecular \( \text{N}_2 \) in the atmosphere,\[^{[1]}\] yet most organisms cannot metabolize the chemically inert \( \text{N}_2 \) but only nitrogenous substances such as ammonia (\( \text{NH}_3 \)) or nitrate (\( \text{NO}_3^- \)).\[^{[2]}\] Thus, the conversion of molecular \( \text{N}_2 \) into \( \text{NH}_3 \) or other useful chemical feedstocks is of fundamental importance.\[^{[3]}\] In the biosphere, \( \text{N}_2 \) can be reduced under ambient conditions to ammonia by the FeMo-cofactor of nitrogenase via a sequence of electron and proton transfers,\[^{[4]}\] while industrial nitrogen fixation is performed with \( \text{H}_2 \) at heterogenous Fe-based catalysts under high pressures and temperatures in the Haber–Bosch process.\[^{[5]}\] Recent years have seen substantial research efforts devoted to the reductive cleavage and catalytic functionalization of \( \text{N}_2 \) under homogeneous conditions using molecular transition metal complexes.\[^{[6–12]}\] While molybdenum catalysts are most prominent\[^{[13]}\] and bioinspired approaches are focusing on iron complexes,\[^{[14,15]}\] catalyst systems based on other earth abundant metals such as cobalt are also particularly attractive.

In that context an increasing number of cobalt dinitrogen complexes has been reported in recent years;\[^{[16]}\] selected examples are depicted in Figure 1. Some of them have been...
shown to mediate the catalytic formation of NH₃ from N₂ using KC₈ and a proton source, with low turnover numbers (TONs). For example, complex D[27] (E = B; using 60 equiv of KC₈) gave 2.4 equiv[27a] and complex G[28] (with 200 equiv KC₈) gave 17.9 equiv of NH₃.

Catalytic silylation of N₂ with an excess of SiMe₃Cl under reductive conditions, first reported by Shiina for simple metal halide salts using Li wire as a reducing agent,[19] is an interesting alternative for N₂ valorization; the formed silylamines can also be hydrolyzed to NH₃. This reaction is generally assumed to proceed via the in situ generation of silyl radicals, and complexes of a variety of metal ions have been shown to catalyze N₂ silylation.[20] In a systematic study evaluating the effect of 3d metal ion type on N₂ silylation by polynuclear complexes of Cr, Mn, Fe, Co, and Ni, Murray et al. recently demonstrated the superiority of Co for this reaction (≈ 200 equiv N(SiMe₃)₃/Co₃Cl₃).[21] In most reported cases, however, TONS (i.e., equiv of N(SiMe₃)₃ formed per equiv of catalyst) are still <100.[12,20] The Nishibayashi group developed an efficient catalytic system, trans-[Mo(N₂)(dpf)][dpf] (dpf = 1,1′-bis(diethylphosphino)ferrocene) which mediated the conversion of N₂ to N(SiMe₃)₃ with a TON of 226 when using 8000 equiv of Na and SiMe₃Cl.[22] In the case of Co, the best performing systems so far are the anionic dicobalt complex C based on a trisphosphino(triamido)amine scaffold developed by Lu et al. (using 2000 equiv KC₈ and SiMe₃Cl,[23] and the iminophosphorane-cobalt derivative H reported by Fryzuk, Masuda et al. (1500 equiv KC₈ and 2000 equiv SiMe₃Cl,[24] both systems catalyze the conversion of N₂ to N(SiMe₃)₃ with TONS of ≈ 200. Deng et al. showed that reactions of NHCl-ligated low-valent Co complexes such as [(ICy)₂Co(N₃)₂]+ (E; TON ≈ 120 for N₂ silylation with 2000 equiv KC₈ and SiMe₃Cl) with SiR₃Cl (R = Me, Et) result in the formation of diazene complexes [(ICy)₂Co(SiR₃)₂(SiNNSiR₃)₃], suggesting that they represent intermediates in the catalytic cycle.[25]

Two conceptual approaches have emerged as promising design guidelines for N₂ fixation with molecular catalysts, both in Co/N₂ chemistry and beyond: (i) the use of tridentate pincer-type ligand scaffolds[26] (see, e.g., B[27] F[28] and G[29] in Figure 1) that potentially allow for metal–ligand cooperativity (MLC)[30] and (ii) the use of bimetallic systems that synergistically achieve the overall N₂ reduction required to fully cleave N≡N (e.g., A[31] B[27,28] and C[30] in Figure 1) and that potentially exploit metal–metal cooperativity (MMC). In order to combine these two features in a single platform, we recently developed a so-called „two-in-one“ pincer ligand that provides two PNN pincer-type binding sites fused via a central pyrazolate (Figure 2).[32] A dirhodium complex LFe₃(-OTf)₄[(CH₃CN)] of the compartmental ligand [L] was shown to undergo rapid ligand exchange reactions (coupled to spin transitions)[33] within the bimetallic pocket into which the two accessible coordination sites X of the pincer subunits are directed, and we demonstrated that double backbone dearomatization in dirhodium(I) complexes of [L] is possible via sequential deprotonation at the side-arm methylene groups.[34] We have now exploited the „two-in-one“ pincer platform in Co/N₂ chemistry, and we show that some of the new dinuclear cobalt complexes serve as efficient precatalysts for the silylation of N₂ into N(SiMe₃), producing up to ≈ 240 equiv N(SiMe₃).  

Results and Discussion

As an entry into cobalt coordination chemistry of the pyrazolate-based „two-in-one“ pincer ligand [L] , the proligand HL was treated with one equivalent of KO'Bu and two equivalents of CoCl₂ in THF to generate a blue suspension from which, after workup, the dicobalt(II) complex [L-(CoCl₂)(µ-Cl)] (I) was isolated (Scheme 1). Blue rod-shaped crystals were obtained by slow diffusion of pentane into a CH₃CN solution of I, with an excellent yield of 90%. The molecular structure of complex I (Figure 3) determined by X-ray diffraction confirms that the two cobalt ions are hosted in the tridentate [PNN] binding sites of the anionic compartmental ligand scaffold, bridged by the pyrazolate and an exogenous chloride. Each metal ion has an additional terminal chlorido ligand which constitutes an overall distorted square-pyramidal coordination environment (τ = 0.31 and 0.27).[35] The comparatively long Co–Cl₂ (2.44/2.46 Å) and Co–N₁/Co–N₈ bonds (2.24/2.26 Å; compared to Co₁–N₁/ Co₂–N₂ which are 2.00/2.01 Å) indicate that the relatively wide Co–Co separation imposed by the binucleating scaffold (3.81 Å in I) leads to some strain and significant deviation of the N3/Co–Cl₂ angles from linearity (N₃-Co₁-Cl₂: 158.7°, N₄-Co₂-Cl₂: 152.8°).

Positive-ion electrospray ionization mass spectrometry (ESI(+)-MS; Figure S5) of a solution of I in MeCN shows a dominant peak at m/z = 725.1 corresponding to the cation [L-Co₂Cl₃]⁺, evidencing that the dinuclear core remains intact in solution. The ¹H NMR spectrum of complex I in CDCl₃ (Figure S1) exhibits eight resonances between –11 and 86 ppm at room temperature, in accordance with paramagnetism and C₂ symmetry. No signals were observed in the ³¹P NMR spectrum, presumably because of the vicinity of the nuclei to paramagnetic metal ions. Variable-temperature magnetic susceptibility data recorded with a SQUID magnetometer confirm the presence of two high-spin cobalt(II) ions (S = 3/2) that are antiferromagnetically coupled to give an S = 0 ground state; the best fit of the data leads to g = 2.4 and an exchange coupling J = –7.2 cm⁻¹ (Figure S7).
In literature reports, Co(N\textsubscript{2})\textsubscript{2} complexes are often obtained from the reaction of a suitable cobalt halide precursor with strong reductants such as Na/Hg, Na(C\textsubscript{10}H\textsubscript{8}) or KC\textsubscript{8} under N\textsubscript{2} atmosphere. In the present case, however, treatment of complex 1 with an excess of the above reductants proved unsuccessful but led to unidentified products. In contrast, addition of ten equivalents of KH and four equivalents of [2.2.2]cryptand to a solution of complex 1 in THF under N\textsubscript{2} atmosphere in a one-pot reaction gave rise to a dark blue solution, from which the highly air-sensitive complex [L\textsuperscript{3}@]([Co(N\textsubscript{2})\textsubscript{2}]\textsubscript{2}[K([2.2.2]cryptand)] (2) could be isolated in 55% yield ([L\textsuperscript{3}@] is the twice deprotonated derivative of [L\textsuperscript{-}]): complex 2 shows characteristic UV-Vis absorptions at \(\lambda_{\text{max}} = 335, 479, 521 \text{ and } 621 \text{ nm (Figure S17). The molecular structure of the anion of 2 determined by X-ray diffraction is shown in Figure 4; the potassium cation is encapsulated by the [2.2.2]cryptand and is thus separated from the anion. Selected bond lengths and angles are listed in Table 1.}

The two cobalt ions in 2 are found in roughly square-planar coordination environment, nested in the [PNN] compartments of the dinucleating ligand scaffold and spanned by the pyrazolato bridge. The planarity of the peripheral chelate rings and inspection of bond lengths reveals that the two methylene groups of the „two-in-one“ pincer are deprotonated in 2, which is accompanied by dearomatization of the pyridine rings, giving a trianionic ligand [L\textsuperscript{3}@].

Most
indicative is the shortening of the exocyclic C–C bonds in the side arms from 1.506(3)/1.507(3) Å in complex 1 to 1.372(3)/1.384(3) Å in complex 2. The coordination sphere of each cobalt ion in 2 is completed by an end-on bound N₂ that is oriented into the bimetallic pocket. The N≡N bond lengths of the coordinated N₂ molecules are 1.124(3) and 1.125(3) Å, which is consistent with those in previously reported Co(II) complexes such as D[15] (E = Si, 1.123(3) Å), F[28] (1.122–(2) Å), and H[30] (1.12(6) Å) in Figure 1 and not much longer than in free N₂ (1.098 Å)[30] this corroborates that 2 is best described as having two Co(I) (d⁸, S = 0) ions and weakly activated N₂. The Co···Co separation in 4 of 3.40 Å is distinctly longer by 0.49 Å than in complex 1, and the Co-N-N-Co torsion angle is quite large (34.2°). This reflects the congestion caused by the two N₂ ligands coming into steric clash within the bimetallic pocket, forcing them to point below or above the equatorial plane defined by the pyrazolate heterocycle. The results in (non-crystallographic) C₂ symmetry of the anion of 2, with both enantiomers present in the crystal.

The ¹H NMR spectrum of 2 in [D₂]THF shows that complex 2 is a diamagnetic species, in accordance with the presence of two Co(I) (d⁸, S = 0) ions (Figure S8). Apparent C₈ symmetry in solution indicates that interconversion of the two enantiomeric forms is rapid on the NMR time scale, even at 203 K (Figure S11). The ³¹P NMR spectrum reveals a peak at 81.3 ppm (Figure S12), and the ¹⁵N NMR spectrum of the isotopically labeled complex 2-¹⁵N₂ shows two resonances at δ = −28.6 and −58.1 ppm (Figure S16); the latter signal at higher field is assigned to N₂ (N₂ is the atom bound to the metal and N₃ is the terminal atom). Complex 2-¹⁵N₂ can be readily prepared from 2 via ligand exchange under ¹⁵N₂ atmosphere at room temperature, indicating that the N₂ ligands are rather labile.

The IR spectrum of solid 2 show two intense N₂ isotope sensitive bands at 2032 and 2009 cm⁻¹ that shift to 1973 and 1950 cm⁻¹ upon ¹³N₂ labelling (Δ(¹³N₂–¹⁵N₂) = −59 cm⁻¹, ¹³N (¹⁴N,¹⁵N) ¹⁴N (¹³N,¹⁵N) = 1.03, calculated 1.035 for an isolated harmonic N–N oscillator) (Figure 5). Based on the DFT calculated IR spectrum (Figure S82) the two bands are assigned to the antisymmetric and symmetric N–N stretches, respectively, indicating substantial vibrational coupling. The frequencies for 2 are similar to those of other pincer ligated Co(I) complexes with end-on bound N₂ (cf. 2021 cm⁻¹ for F, 2071 cm⁻¹ for H; Figure 1) and reflect weak activation of the N₂ ligand (N-N stretch of free N₂ at 2331 cm⁻¹).[37]

In the absence of cryptand, the reaction of complex 1 with excess KH in THF generates a brown solution that contains both diamagnetic and paramagnetic species according to NMR spectroscopy; however, these species could not be identified. The cryptand obviously plays a crucial role in the reaction of KH with complex 1 to give complex 2, likely improving the solubility and/or increasing the reactivity of KH in THF. Since KH serves both as a base and a reductant in this transformation, a stepwise synthetic route was developed (Scheme 1). To that end, complex 1 was first reacted with three equivalents of the base KH(SiMe₃)₃ in THF at room temperature, leading to an immediate color change of the solution to red. The new dicobalt(II) complex [L(Co-N(SiMe₃))₂(CoCl)(K(THF))][3] (Figure 6) could be isolated, and crystals suitable for X-ray diffraction were grown by layering a concentrated THF solution with hexanes at −40°C.

3 features the twice deprotonated ligand [L]⁻ with deamidated pyridines (the exocyclic C–C bonds in the side arms are 1.366(3) and 1.381(3) Å), a large Co···Co separation of 4.54 Å (0.24 Å longer than in 2) and a wide Co-N-Co torsion angle of 62.0°. One equivalent of the formed KCl is still retained in the structure of 3. The ¹H NMR spectrum of 3 in [D₂]THF displays paramagnetically shifted resonances (Figure S18). Magnetic susceptibility data (SQUID) indeed revealed weakly antiferromagnetically coupled S = 3/2 and S = 1/2 cobalt(II) ions (J = −1.0 cm⁻¹); the former is tentatively assigned to the distorted tetrahedral Co1 (τ₁ = 0.71)[38] and the latter to the roughly square-planar Co2 (τ₂ = 0.21) (Figure S20).

Subsequent reduction of dicobalt(II) complex 3 was achieved by either KHBEt₃ or KC₈ (2 equiv) in THF solution under N₂ atmosphere. The resulting complex 2' could be isolated by precipitation from a mixture of THF and hexanes.
Two different views of the molecular structure of the cation of 4 (30% probability thermal ellipsoids); hydrogen atoms omitted for clarity.

As N₂ reduction is commonly assumed to proceed through coupled H⁺/e⁻ transfer pathways, protonation of complexes 2 and 2' was studied individually. Treatment of complexes 2 or 2' in THF with two equivalents of triflic acid (HOTf) under N₂ atmosphere at −40 °C resulted in an immediate color change of the solution from dark blue to red-brown. Block-shaped crystals suitable for X-ray diffraction were grown from the concentrated red-brown THF solution at −40 °C and revealed the formation of a tetracobalt complex with two bridging N₂ ligands ([LCo₂(N₂)₂]⁺OTf (1; Figure 7). Complex 4 features two [LCo₂] subunits, and metric parameters of the aromatic pyridine rings as well as the lengths of the exocyclic C–C bonds (1.490(8)–1.511(7) Å) confirm that the protonation has occurred at the ligand side arms. The cobalt ions are found in distorted square-planar environment with Co–Co distances of 4.35/4.44 Å within the [LCo₂] subunits (Table 1). The protonated ligand scaffold appears to be quite flexible as the [LCo₂] strands are twisted to minimize deviation from the square-planar metal coordination sphere, leading to large Co-N-N-Co torsion angles of 68.2° and 70.0°.

The two [LCo₂] fragments in 4 are linked by two end-on bridging N₂ ligands with N–N bond lengths (1.140(5)/1.142(6) Å) that are slightly longer than in 2 because of charge transfer to the N₂-ligand from two metal ions, but in the range typical for previously reported Co²⁺(µ₂-N₂)-Co²⁺ systems. The Co–N⁻(N₂) bonds in 1 (1.764(4)–1.783(4) Å) are slightly longer than in 2 (1.742(2) Å), reflecting diminished π-back donation for the individual Co–N⁻ interactions and likely weakened Co–N₂ bonding; the latter is evidenced in solution by facile temperature-dependent replacement of the N₂ ligands by triflate (see below).

The N–N stretching vibrations of 4 could not be observed by IR spectroscopy (Figure S45), but a Raman spectrum of solid 4 shows a weak absorption at 2000 cm⁻¹ that shifts to 1935 cm⁻¹ for 4-[¹⁵N₂] (Δv(¹⁵N₂–¹⁴N₂) = −65 cm⁻¹; 重塑N–N/重塑(¹⁵N–¹⁴N)/重塑(¹⁴N–¹⁴N) = 1.034, calculated 1.035 for an isolated harmonic N–N oscillator; Figure 8). Comparison of the N–N bond lengths and the N–N stretching frequencies indicates that the bridging N₂ in complex 4 is more reduced than the end-on bound N₂ in complex 2, but still rather weakly activated (cf. 2024 cm⁻¹ in 2).

The UV-Vis spectrum of solid 4 shows a broad band at ∼670 nm and further bands at 517 and 323 nm (Figure S47). However, variable temperature (VT) UV-Vis spectra of 4 in THF in the range from 298 K to 233 K indicate some complex solution equilibria (Figure 9). The UV-Vis spectrum of 4 in THF at 298 K shows that the band at 670 nm is absent, but the spectrum indicates the presence of a new species 5 with λ_max at 313, 510 and 774 nm. After cooling the THF solution to 233 K under Ar the spectrum remains essentially unchanged (Figure S58). Under N₂ at 233 K, however, the spectrum gradually changes as the band at 774 nm disappears over the course of...
The reversibility of \( \text{N}_2 \) binding in solution and the conclusions drawn from VT UV-Vis spectroscopy.

Temperature-dependent equilibria involving 4 and 5 in solution are also evidenced by VT NMR spectroscopy (Figure S32 and S48). Complex 5 at 238 K under Ar exhibits the spectral pattern expected for a \( \text{Co}_2 \) symmetrical complex (six resonances in the \(^1\text{H} \) NMR spectrum, Figure S49; \( \delta^{(31)\text{P}} = 219.0 \) ppm, Figure S56) and the \(^{19}\text{F} \)-NMR spectrum at 213 K shows a single peak at \(-77.7 \) ppm for bound triflate (Figure S57). Upon warming the signals shift and broaden, suggesting paramagnetic contributions at higher temperatures possibly caused by fast equilibration arising from triflate/THF ligand exchange. Under \( \text{N}_2 \) atmosphere the VT NMR spectra of 4 and 5 are identical, and at high temperatures they are essentially identical to the ones of 5 recorded under Ar atmosphere. In [D\(_4\)]THF under \( \text{N}_2 \) at 238 K and below, the signal pattern reflects the reduced symmetry of diamagnetic 4 with two resonances each for the diastereotopic tBu groups and for the protons of the CH\(_2\) group in Figure S33 (and \( \delta^{(31)\text{P}} 218.0 \) ppm at 298 K (Figure S43). The sharp \(^{31}\text{F} \) NMR signal at \(-78.8 \) ppm for 4 at 213 K broadens and shifts to \(-75.5 \) ppm at 298 K (Figure S43), \(^1\text{H} \) DOSY spectra (using the solvent signal as an internal standard)\(^{[39]} \) recorded in [D\(_8\)]THF at 238 K for 4 under \( \text{N}_2 \) and for 5 under Ar confirm their different nuclearity (Figure S34, S44 and S50): the dicobalt complex 4 has a diffusion coefficient \( D = 1.293 \times 10^{-10} \) m\(^2\) s\(^{-1}\) corresponding to a hydrodynamic radius \( r = 13.81 \) Å (derived from the Stokes–Einstein equation)\(^{[40]} \) while dicyclobutyl complex 5 has \( D = 2.507 \times 10^{-10} \) m\(^2\) s\(^{-1}\) \( (r = 7.12 \) Å) which is similar to the values for the free ligand HL at 238 K \( (D = 2.306 \times 10^{-10} \) m\(^2\) s\(^{-1}\), \( r = 7.74 \) Å)\(^{[41]} \).

Having established the identity of the Co/N\(_2\) complexes of the two-in-one pincer scaffold in the solid state and in solution, their ability to mediate the catalytic silylation of N\(_2\) in the presence of an excess of KC\(_8\) (2000 equiv) and SiMe\(_3\)-Cl (2000 equiv) in THF has been studied (Table 2). The product N(SiMe\(_3\))(P), was identified by GC/MS and quantified by GC using cycloodocane as the internal standard. Complex 2 is a very efficient catalyst that generates N(SiMe\(_3\))(P) in 22.4 % yield (150 equiv N(SiMe\(_3\))(P) per catalyst or 75 equiv N(SiMe\(_3\)) per Co atom) at room temperature. The yield rises to 36.0 % (240 equiv N(SiMe\(_3\))(P)/catalyst) when the reaction is first conducted at \(-40^\circ\text{C} \) for 2 h before warming to room temperature; when carried out at \(-90^\circ\text{C} \) for 2 h the yield is 32.9 % (219 equiv N(SiMe\(_3\))(P)/catalyst; see entries 4–6 in Table 2). These values compare favorably with the most active...
Table 2: Reductive silylation of N₂ to N(SiMe₃), using complexes 1, 2, 2’, 3 and 5 as catalysts.

| Entry | Catalyst | Conditions | N(SiMe₃)₂ (mmol) | N(SiMe₃)₃ / catalyst (%) | Yield [%] |
|-------|----------|------------|------------------|--------------------------|----------|
| 1     | 5        | −40°C 2 h; r.t. 22 h | 1.04 | 208 (104) | 31.2 |
| 2     | 2’       | −40°C 2 h; r.t. 22 h | 1.17 | 234 (117) | 35.1 |
| 3     | 3        | −40°C 2 h; r.t. 22 h | 1.14 | 228 (114) | 34.2 |
| 4     | 2        | −40°C 2 h; r.t. 22 h | 1.20 | 240 (120) | 36.0 |
| 5     | 2        | −90°C 2 h; r.t. 22 h | 1.19 | 219 (109.5) | 32.9 |
| 6     | 2        | r.t. 24 h | 0.75 | 150 (75) | 22.4 |
| 7     | 1        | −40°C 2 h; r.t. 22 h | 0.95 | 190 (95) | 28.5 |
| 8     | 2.0 equiv CoCl₂ | −40°C 2 h; r.t. 22 h | 0.58 | 58 (58) | 17.4 |
| 9     | 2.0 equiv CoCl₂ | r.t. 24 h | 0.1 | 10 (10) | 3.0 |
| 10    | none     | −40°C 2 h; r.t. 22 h | 0 | 0 (0) | 0 |

[a] N(SiMe₃)₃ was identified by GC/MS and quantified by GC with cyclododecane as the internal standard. All values are the average of at least three trials. [b] Calculated as the molar ratio of N(SiMe₃)₂ to catalyst. [c] The yields of N(SiMe₃)₃ are based on starting material SiMe₃Cl [d] per Co. [e] Acid hydrolysis of N(SiMe₃)₃ and quantification of the formed NH₃⁺ by ¹H NMR spectroscopy using an internal standard (average of three trials, see Supporting Information for details) yielded 230 equiv NH₃⁺/catalyst (115 equiv NH₃⁺/Co atom).

Conclusion

This work commences the exploration of dinuclear complexes of the pyrazolato-based „two-in-one pincer“ ligand, which features two pyridyl-centered PNN compartments, in dinitrogen fixation chemistry. Such systems bear the potential of combining in a single platform two cooperativity concepts that have emerged as promising approaches for molecular N₂ fixation catalysis, viz., functional tridentate pincer sites that may undergo reversible ligand-centered (de)protonation associated with pyridyl (de)aromatization, and bimetallic scaffolds that provide a multi-electron reservoir for challenging substrate reductions. Cobalt(I) dinitrogen complexes of the bis(PNN) pincer ligand have been isolated, and it is demonstrated that protonation at the ligand backbone leads to release of terminal N₂ to give a labile tetracobalt(I) complex with two central Co₉−(μ₃−N₃)−Co entities. Using SiMe₃Cl in the presence of the reducing agent KC₈, the new dinuclear cobalt complexes have been shown to mediate the silylation of N₂ to N(SiMe₃)₃, producing up to 240 equiv N(SiMe₃)₃ per catalyst (or 120 equiv N(SiMe₃)₃ per Co atom), which are among the highest reported so far for this reaction. Future work will focus on mechanistic insight and on the possible role of metal–ligand and metal–metal cooperativity for this and related N₂ transformations catalyzed by the highly preorganized „two-in-one pincer“ based bimetallic complexes.

Experimental Section

General experimental details and characterization data for all of the reported compounds are included in the Supporting Information. Deposition Numbers 2054109, 2054110, 2054111, 2054112, and 2054113 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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Conflict of interest

The authors declare no conflict of interest.

Stichwörter: cobalt · dinitrogen complexes · dinuclear complexes · nitrogen fixation · pincer ligands