

Cobalt–Magnesium and Cobalt–Calcium Heterotrimetallic Dinitrogen Complexes

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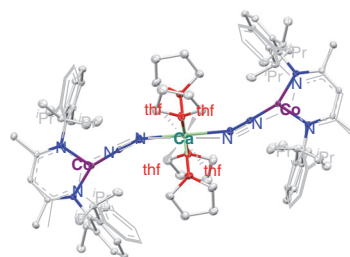
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In memory of Davood Amiri (Feb 1974–Apr 2022)



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Abstract We report the use of alkaline earth metals magnesium and calcium for the reduction of the cobalt(II) complex $[\text{Pr}_2\text{NN}]\text{Co}(\mu\text{-Cl})_2\text{Li}(\text{thf})_2$ [Pr_2NN = 2,4-bis(2,6-diisopropylphenylimido)pentyl] that resulted in heterotrimetallic dinitrogen complexes with a rare example of a $[\text{Co}-\text{N}_2-\text{M}-\text{N}_2-\text{Co}]$ core where $\text{M} = \text{Mg}$ and Ca . The dinitrogen ligands in these new complexes showed weakened N–N bonds, as judged by infrared spectroscopy, and the crystal structures of the complexes were illustrated by X-ray crystallography. These cobalt complexes can be isolated as pure solids that are stable in solutions of non-coordinating solvents such as *n*-pentane or cyclohexane, as well as tetrahydrofuran. These results demonstrate the correlation between the binding mode of the Lewis acid and N–N weakening in heterotrimetallic dinitrogen complexes.

Key words cobalt, dinitrogen activation, β -diketimines, alkaline earth metals, X-ray crystallography

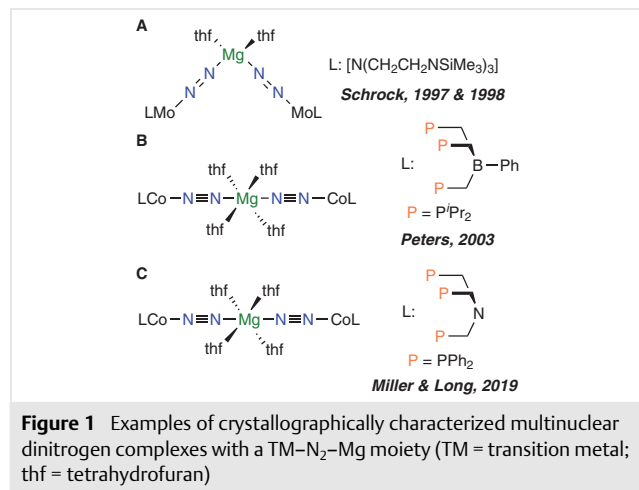
Transition-metal-mediated activation and reduction of dinitrogen is of great interest to inorganic and organometallic chemists.^{1–5} This has encouraged chemists to study transition-metal complexes of dinitrogen as catalysts in the hope of finding alternative routes to produce ammonia. Ammonia is currently being produced through the Haber–Bosch process that consumes approximately 1–2% of the world's total primary energy sources, resulting in more than 1% of total CO₂ emissions globally.^{6,7} Thus, the coordination, activation, and full dissociation of the strong $\text{N}\equiv\text{N}$

bond of the dinitrogen molecule have become a significant challenge for synthetic chemists.

So far, several transition-metal well-defined molecular catalysts containing early to mid-transition metals such as Ti, V, Cr, Mo, W, Re, Fe, Ru, and Os, as well as late transition metals like Co, have been developed for the catalytic conversion of dinitrogen into ammonia under mild reaction conditions.⁸ While Mo and Fe complexes are the most prominent catalysts amongst the studied systems in the literature,^{9–11} there is great interest in systems based on other base metals such as cobalt.^{12–18} In the past two decades, an increasing number of Co dinitrogen complexes has been explored. In most cases, the Co precursor complexes are reduced via strong reductants such as potassium graphite (KC_8)^{17,19,20} or sodium amalgam (Na/Hg),¹³ to reduce both the Co center as well as the dinitrogen ligand. Other reducing agents such as cobaltocene (CoCp_2) and its derivatives, including decamethylcobaltocene (CoCp^*_2), Sm^{2+} , or triethylhydridoborate ($[\text{BHEt}_3]^-$) have also found use in nitrogen activation/reduction reactions.^{21–24} On the other hand, alkaline earth metals such as Mg and Ca have been far less studied in the context of dinitrogen activation and only a few studies have been carried out where Mg was used to activate dinitrogen,^{25–28} while far fewer studies have been done with Ca as a reductant.^{29–32}

One example of such dinitrogen reduction with Mg is the work done by Schrock and co-workers where a trimetallic Mo–Mg–Mo system (Figure 1A) supported by triamidoamine ligands was reported for the synthesis of diazenide (N_2^{2-}) directly from N_2 .²⁶ In another example, Betley and Peters observed dinitrogen functionalization of a formally Co^0 species in which methyl- and silyl-diazenido $\text{Co}(\text{II})$ complexes were synthesized through reduction with

Mg (Figure 1B).²⁵ In their work, the Co center was supported by an anionic B-triphos ligand with a linear LCo–N₂–Mg–N₂–CoL core (L = anionic B-triphos ligand). Later, Miller and Long reported the synthesis of a cobaltate congener N₂ complex supported by a triphos ligand (Figure 1C).²⁸ In 2013, Holland and co-workers synthesized a trimetallic system with a linear LCo–N₂–Mg–N₂–CoL core (L = bulky β -diketiminato) in minimal yields (~6%).²⁷ Their attempts to obtain X-ray quality crystals were unsuccessful.



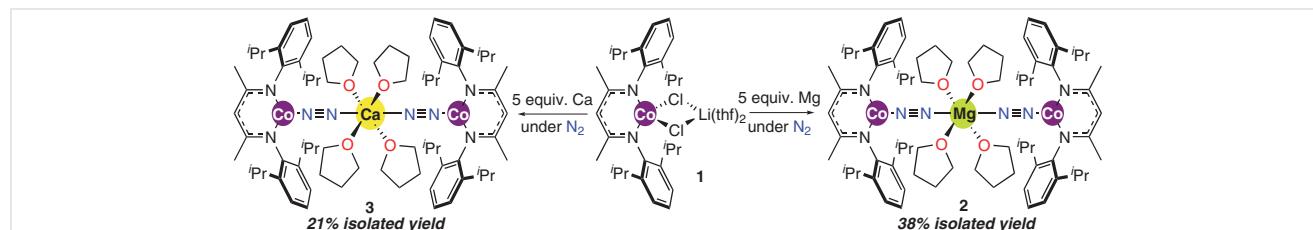
We sought to study the reduction of β -diketiminato Co(II) complex $[^i\text{Pr}_2\text{NN}]\text{Co}(\mu\text{-Cl})_2\text{Li}(\text{thf})_2$ [$^i\text{Pr}_2\text{NN}$ = 2,4-bis(2,6-diisopropylphenylimido)pentyl] (**1**) with alkaline earth metals Mg and Ca to investigate the reduction and activation of the N≡N bond in dinitrogen at the Co center. Herein, we present the synthesis and characterization of rare examples of Co dinitrogen complexes bridged with alkaline metals Mg (complex **2**) and Ca (complex **3**). In both cases, we observed heterotrimetallic Co–N₂–M–N₂–Co (M = Mg and Ca) cores, corroborated by solid-state structure determination via X-ray crystallography (Scheme 1).

The reduction of $[^i\text{Pr}_2\text{NN}]\text{Co}(\mu\text{-Cl})_2\text{Li}(\text{thf})_2$ (**1**)³³ with 5 equivalents of magnesium turnings in anhydrous THF under a N₂ atmosphere over 2 hours resulted in a dark red mixture. This reaction mixture led to the isolation of $\{^i\text{Pr}_2\text{NNCo}(\mu\text{-N}_2)\}_2\text{Mg}(\text{thf})_4$ (**2**) in 38% yield as dark red crystals after purification and crystallization from a concentrat-

ed solution in *n*-pentane. Complex **2** is highly soluble in THF, less soluble in Et₂O, and sparingly soluble in nonpolar hydrocarbon solvents such as *n*-pentane or cyclohexane. The elemental analysis of crystals of **2** showed that they had a N content corresponding to the presence of one N₂ ligand per cobalt center. Overall, the elemental analysis was consistent with the formulation $\{^i\text{Pr}_2\text{NNCo}(\mu\text{-N}_2)\}_2\text{Mg}(\text{thf})_4$. X-ray crystallographic analysis on single crystals of **2** displayed a central $[\text{Mg}(\text{thf})_4]^{2+}$ fragment bound to two cobaltate fragments $[^i\text{Pr}_2\text{NNCo}(\mu\text{-N}_2)]^-$.

The cobaltate moieties $[^i\text{Pr}_2\text{NNCo}(\mu\text{-N}_2)]^-$ are presumably comprised of formally Co⁰ centers which is fully consistent with the CHN analysis results. The IR spectrum of compound **2** in solid state (KBr pellet) revealed an intense band at 1882 cm^{−1} that is attributed to the N–N stretching vibration (compare ν_{NN} = 2331 cm^{−1} for free N₂).³⁴ The observed value for ν_{NN} in the IR spectrum of **2** is in excellent agreement with the previously reported $\{^i\text{Pr}_2\text{NNCo}(\mu\text{-N}_2)\}_2\text{Mg}(\text{thf})_4$ complex by the group of Holland in 2013.²⁷ Complex $\{^i\text{Pr}_2\text{NNCo}(\mu\text{-N}_2)\}_2\text{Mg}(\text{thf})_4$ could not be analyzed crystallographically, and its crystals were only suitable for revealing the connectivity of $\{^i\text{Pr}_2\text{NNCo}(\mu\text{-N}_2)\}_2\text{Mg}(\text{thf})_4$ with a very high *R* of approximately 20%. The X-ray crystal structure of **2** is presented in Figure 2. Single crystals of **2** were grown from *n*-pentane at −35 °C inside a glovebox freezer. Complex **2** exhibits a sigmoid-like structure via an assembly of linear Co–N≡N and bent Mg–N≡N fragments (Figure 2). The stabilizing central Mg cation bridges between two $[^i\text{Pr}_2\text{NNCo}(\mu\text{-N}_2)]^-$ and has an octahedral geometry with two axial $[^i\text{Pr}_2\text{NNCo}(\mu\text{-N}_2)]^-$ anions *trans* to one another and four equatorial thf ligands. The Co–N≡N–Mg–N≡N–Co core shows almost linear Co–N–N bonds with a Co1–N1–N2 angle of 168.7(5)° and N1–N2–Mg1 bond angle of 156.1(18)°. The Co–N_{N2} bond distance was determined to be 1.685(3) Å and the Mg–N_{N2} bond lengths were measured at 2.07(7) Å. The N–N distance in compound **2** was determined to be 1.158(6) Å that shows an elongated N–N bond compared to that of free N₂ (N–N bond distance in free N₂ = 1.11 Å).³⁵

To our delight, we were able to reduce **1** with 5 equivalents of calcium turnings and successfully obtained the calcium analogue of complex **2**, namely $\{^i\text{Pr}_2\text{NNCo}(\mu\text{-N}_2)\}_2\text{Ca}(\text{thf})_4$ (**3**), in 21% yield as dark red crystals (Scheme 1, Figure 2). Freshly prepared complex **3** showed a band at 1868 cm^{−1} in



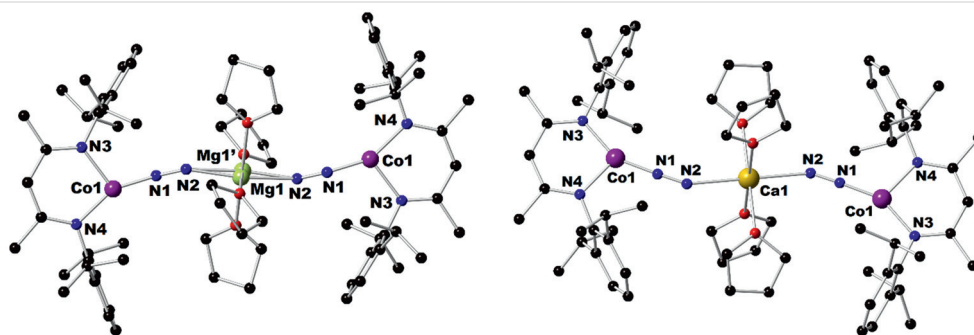


Figure 2 POV-Ray depiction of complexes **2** (CCDC 2309166, left) and **3** (CCDC 2309167, right). The hydrogen atoms (for both complexes) and *n*-pentane solvent (in complex **3**) molecule are omitted for clarity.³⁶

the IR spectrum (KBr pellet) that was assigned as the N–N bond stretch. In the solid state of complex **3**, the Co–N≡N–Ca–N≡N–Co core adopts a slight sigmoid-like structure with almost linear Co(1)–N(1)–N(2) bonds [bond angle of 177.7(2)°] and bent N(1)–N(2)–Ca(1) bonds [154.3(2)°]. The Co–N_{N2} bond distance was observed at 1.683(3) Å, while the Ca–N_{N2} bond length was determined to be 2.343(3) Å. The X-ray analysis of **3** also revealed that the N–N bond length is 1.149(3) Å that is elongated compared to free N₂ (N–N = 1.11 Å).³⁵ This indicates an activated N₂ ligand and is in accordance with the low ν_{NN} band in the IR spectrum (1868 cm^{−1}). Similar to the crystal structure of compound **2**, compound **3** is composed of a calcium cation as a Lewis acid in an octahedral environment with two axial [iPr₂NN–Co(μ–N₂)][−] fragments that are *trans* to one another, along with four equatorial thf ligands. It is worthy to note that both complexes **2** and **3** are highly temperature- and air-sensitive and all manipulations must be carried out under an atmosphere of dry dinitrogen inside a nitrogen-filled glovebox or using standard Schlenk techniques.

Comparing the IR stretch of the dinitrogen ligand in the present report (Figure 3) with that in [L^{tBu}Co–N₂–Mg–N₂–CoL^{tBu}] complex reported by Holland and co-workers,²⁷ it can be

concluded that the degrees of dinitrogen activation are mostly identical (ν_{NN} of 1882 cm^{−1} for **2** vs 1878 cm^{−1} in [L^{tBu}Co–N₂–Mg–N₂–CoL^{tBu}] complex²⁷). Replacing the Lewis acid Mg by Ca does not show a significant difference in dinitrogen activation, judged by the ν_{NN} value of 1868 cm^{−1} in complex **3**. This observation is reminiscent of the results observed for a similar systematic investigation by Holland and co-workers.³⁷ They prepared a series of cobalt–dinitrogen complexes with the general formula M₂[L^{tBu}CoN=NCOL^{tBu}] (M = Na and K) and observed that the alkali metal cations coordinated to the N₂ units do not significantly contribute to the extent of N₂ activation (ν_{NN} of 1598 cm^{−1} for M = Na and ν_{NN} of 1599 cm^{−1} for M = K).³⁷ The effects of reductant and their coordination mode (end-on coordination in the current report vs side-on coordination for alkali metals) are illustrated in Table 1.

Table 1 Metrical Parameters and ν_{NN} for Formally Zero-Valent Co–N₂ Complexes Supported by β-Diketiminato Ligands

Compound	ν_{NN} (cm ^{−1})	N–N (Å)	Ref.
2	1882	1.158(6)	this work
3	1868	1.149(3)	this work
Na ₂ L ^{tBu} ₂ Co ₂ N ₂ ^a	1598	1.211(3)	37
K ₂ L ^{tBu} ₂ Co ₂ N ₂ ^a	1599	1.220(2)	37

^a L^{tBu} = 2,2,6,6-tetramethyl-3,5-bis(2,6-triisopropylphenylimido)hept-4-yl

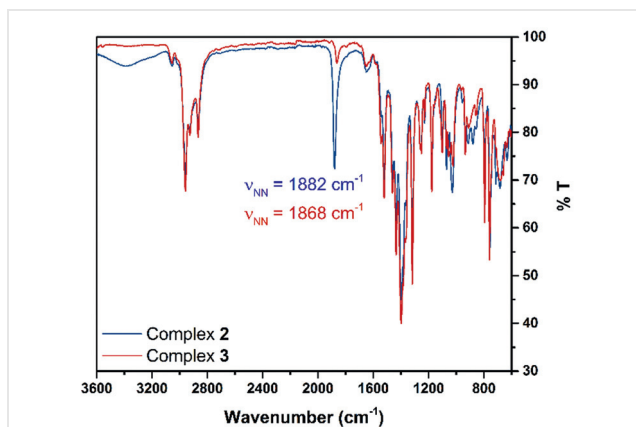


Figure 3 Overlaid IR spectra (KBr pellets) of compounds **2** and **3**

In situ reactivity studies of the activated dinitrogen complexes **2** and **3** were carried out for the functionalization at the Lewis acid capped dinitrogen ligands. We turned our attention to the protonolysis of Co–N₂ complexes **2** and **3** to see if we can generate ammonia. Therefore, we reacted complexes **2** and **3** with Brookhart's acid {[H(OEt)₂]₂BAR^F₄ [Ar^F = 3,5-(CF₃)₂C₆H₃]} in diethyl ether and we observed *reproducible* low yields of ammonia (1.9–2.6% for compound **2** and 3.2–3.8% for complex **3**). Details of the protonolysis of compounds **2** and **3** are given in the Supporting Information. While these yields look minimal, they are greater than

zero, which means that the dinitrogen ligands are activated in compounds **2** and **3**. We attribute these low yields of electrophilic protonolysis to the steric protection of the bulky β -diketiminato ligand that hampers access to the N_2 unit. We also believe that the higher yield of NH_3 formation for complex **3** could be due to more access to the dinitrogen unit since the Ca– N_{N_2} bond is slightly longer [2.343(3) Å] than that of complex **2** with Mg– N_{N_2} of 2.07(7) Å.

In short, the results presented herein demonstrated that alkaline earth metals can be used to activate dinitrogen at transition metal centers such as cobalt however, it must be noted that the reduction of N_2 by alkaline earth metals e.g. Mg and Ca can have a lower impact on the reduction level of the coordinated N_2 compared to alkali metals such as Na or K.

Details of the experiments, spectroscopic studies, and crystal structure determination can be found in the Supporting Information. 1H NMR spectra were collected on a JEOL 400 SS spectrometer at 400 MHz and are calibrated to the residual protio solvent peak (cyclohexane- d_{12} : 1.38 ppm). IR spectra for both solids were recorded on a Thermo Scientific Nicolet iS10 spectrometer. Elemental analyses were performed on a PerkinElmer PE4200 microanalyzer. For details on preparing [iPr_2NN]Co(μ -Cl) $_2$ Li(thf) $_2$ [iPr_2NN = 2,4-bis(2,6-diisopropylphenylimido)pentyl] (**1**) precursors, see the Supporting Information. Elemental magnesium and calcium were purchased from MilliporeSigma and used without further purification.

Synthesis of Complex 2

Inside a dry box filled with dry dinitrogen, [iPr_2NN]Co(μ -Cl) $_2$ Li(thf) $_2$ (**1**; 490 mg, 0.700 mmol) was dissolved in anhydrous THF (10 mL) to give a dark green solution. To this solution was added Mg turnings (97.9 mg, 3.5 mmol, 5 equiv.) and the mixture was stirred at room temperature. A dark red color was observed after 1–2 h. The stirring was continued for another 16 h and then the dark red mixture was filtered through a pad of Celite. The dark red solution was dried under reduced pressure to yield the crude product. As much of the crude product as possible was dissolved in anhydrous *n*-pentane (~15 mL), and the mixture was filtered through a syringe filter to remove any small amount of insoluble brownish material. The dark red solution was then stored at –35 °C in a freezer inside a dry box to give dark red crystals that were suitable for X-ray crystallography (176 mg, 0.133 mmol, 38% per Co).

IR (KBr pellet): 1882 (N–N) cm^{-1} .

1H NMR (400 MHz, cyclohexane- d_{12}): δ = 17.14–11.05 (m, 9 H), 8.13 (s, 4 H), 2.40 (s, 17 H), 1.43 (d, J = 3.4 Hz, 7 H), 0.88 (td, J = 6.7, 2.7 Hz, 4 H), –0.69 to –1.68 (m, 24 H), –5.82 (s, 16 H), –7.22 (s, 1 H), –9.13 (s, 2 H), –15.94 (s, 4 H).

Anal. Calcd for $C_{79}H_{126}Co_2MgN_8O_4$ (1392.84): C, 68.06; H, 9.11; N, 8.04. Found: C, 68.24; H, 9.20; N, 8.16.

Synthesis of Complex 3

Inside a dry box filled with dry dinitrogen, [iPr_2NN]Co(μ -Cl) $_2$ Li(thf) $_2$ (**1**; 490 mg, 0.700 mmol) was dissolved in anhydrous THF (10 mL) to give a dark green solution. To this solution was added Ca turnings (140 mg, 3.5 mmol, 5 equiv.) and the mixture was stirred at room temperature. A dark red color was observed after 2 h. The stirring was

continued for another 16 h and then the dark red mixture was filtered through a pad of Celite. The dark red solution was dried under reduced pressure to yield the crude product. As much of the crude product as possible was dissolved in anhydrous *n*-pentane (~15 mL), and the mixture was filtered through a syringe filter to remove any small amount of insoluble brownish material. The dark red solution was then stored at –35 °C in a freezer inside a dry box to give dark red crystals that were suitable for X-ray crystallography (99 mg, 0.074 mmol, 21% per Co).

IR (KBr pellet): 1868 (N–N) cm^{-1} .

1H NMR (400 MHz, cyclohexane- d_{12}): δ = 9.11 (s), 3.74 (s), 2.18 (s), 1.44 (s), 1.30–1.20 (m), 0.92–0.83 (m), –0.85 (s), –4.55 (s), –17.93 (s); due to the paramagnetic properties of **3**, satisfactory integrations could not be obtained.

Anal. Calcd for $C_{79}H_{126}CaCo_2N_8O_4$ (1408.82): C, 67.30; H, 9.01; N, 7.95. Found: C, 67.39; H, 9.12; N, 8.12.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/a-2263-8235>.

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