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Scandium-Promoted Direct Conversion of Dinitrogen into Hydrazine Derivatives via N−C Bond Formation

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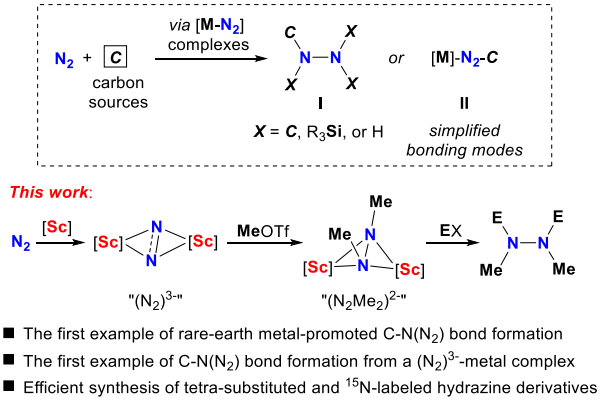
Supporting Information

ABSTRACT: Direct conversion of dinitrogen (N_2) into organic compounds, not through ammonia (NH_3), is of great significance both fundamentally and practically. Here we report a highly efficient scandium-mediated synthetic cycle affording hydrazine derivatives (RMeN−NMeR′) directly from N_2 and carbon-based electrophiles. The cycle includes three main steps: (i) reduction of a halogen-bridged discandium complex under N_2 leading to a $(N_2)^{3-}$-bridged discandium complex via a $(N_2)^{2-}$ intermediate; (ii) treatment of the $(N_2)^{3-}$ complex with methyl triflate (MeOTf), affording a $(N_2Me_2)^{2-}$-bridged discandium complex; and (iii) further reaction of the $(N_2Me_2)^{2-}$ complex with the carbon-based electrophile, producing the hydrazine derivative and regenerating the halide precursor. Furthermore, insertion of a CO molecule into one Sc−N bond in the $(N_2Me_2)^{2-}$−scandium complex was observed. Most notably, this is the first example of rare-earth metal-promoted direct conversion of N_2 to organic compounds; the formation of C−N bonds by the reaction of these $(N_2)^{3-}$ and $(N_2Me_2)^{2-}$ complexes with electrophiles represents the first case among all N_2−metal complexes reported.

Most N-containing organic compounds are currently synthesized through ammonia (NH_3), the product of the Haber−Bosch process that converts N_2 and H_2 to NH_3 using metal catalysts under high temperature and pressure. Direct conversion of N_2 into high-value N-containing organic compounds, not through NH_3, is of great significance and challenging both fundamentally and practically.[1] Although some progress in making C−N bonds through N_2−transition metal[2−4] or N_2−actinide[5] complexes and carbon-based reagents have been reported in the literature, such an approach is still in its infancy. As a class of important synthetic intermediates, hydrazine derivatives,[6] which may contain up to four C−N bonds on the N−N single-bond skeleton, are primary targets for direct conversion of N_2 (Scheme 1).[7] However, as far as we are aware, there are only a few of examples of the direct use of N_2 as the nitrogen source for the construction of C−N bonds of hydrazine derivatives, affording either pure organic compounds (**I**)[7] or hydrazido−metal complexes (**II**)[8] as the final products (Scheme 1). Type **I** compounds have been realized via N_2−metal complexes of Ti,[7g] Zr,[7e] Hf,[7d,f] Mo,[7a] and W,[7b,c] while type **II** compounds have been made and structurally characterized via N_2−metal complexes of Ti,[7g] Zr,[8b] Hf,[8c,d] Ta,[8a,e] Mo,[7a,b] and W.[7b,c] Despite these advances, the efficiency of the transformation from N_2 to **I** or **II** and the diversity of transformation strategies in terms of metals used are still very limited.

Scheme 1. Metal-Promoted Synthesis of Hydrazine Derivatives Directly from N_2 via C−N Bond Formation



In contrast to transition metals mentioned above, rare-earth metal-mediated conversion of N_2 to N-containing organic compounds has not yet been reported, even though more than 40 N_2−rare-earth metal complexes have been documented by Evans and others.[9,10] The absence of this chemistry is mainly due to the weakly activated N_2 ligand.[11,12] Herein we report a highly efficient scandium-mediated route that affords hydrazine derivatives (RMeN−NMeR′) directly from N_2 and carbon-based electrophiles (Scheme 1). In this process, the $(N_2)^{2-}$-, $(N_2)^{3-}$-, and $(N_2Me_2)^{2-}$-bridged discandium intermediates were isolated and structurally characterized. Furthermore, insertion of one CO molecule into a Sc−N bond of the $(N_2Me_2)^{2-}$−scandium complex was achieved. To our knowledge, this is the first conversion of a $(N_2)^{3-}$−metal complex to N-containing organic compounds among all metals over the periodic table. In addition, the formation of four C−N bonds on the N−N single-bond skeleton and ^{15}N-labeled hydrazine derivatives directly using N_2 or $^{15}N_2$ as the nitrogen source is also unprecedented.

The chloride-bridged discandium complex **1** could be easily prepared in a one-pot reaction from $ScCl_3$, Cp*Li (Cp* = C_5Me_5), and Li[^{n}BuC(N^iPr)$_2$] in 87% yield (Scheme 2a). When **1** was treated with 2.2 equiv of potassium under N_2 in

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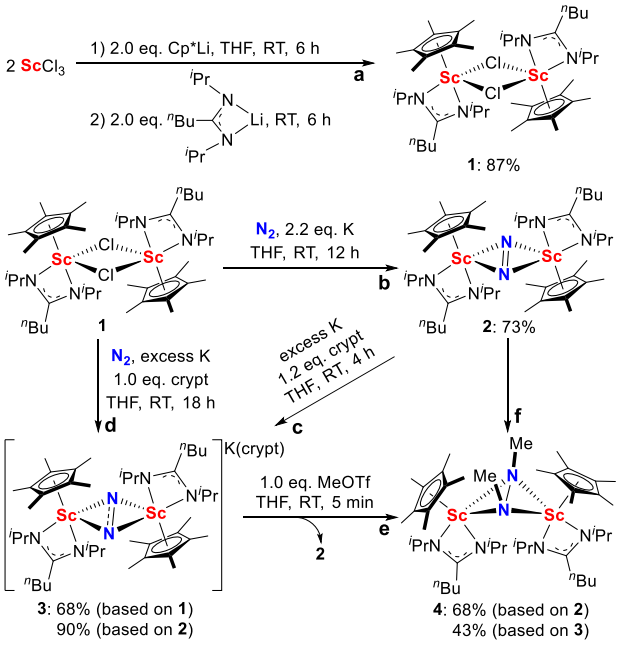
Scheme 2. Synthesis of Complexes 1−4



THF, the $(N_2)^{2-}$-bridged discandium complex **2** was obtained in 73% yield (Scheme 2b). The ^{15}N analogue ^{15}**N-2** was prepared from $^{15}N_2$ by a similar procedure. X-ray analysis of **2** revealed a dinuclear structure with a side-on bridging $(N_2)^{2-}$ ligand (Figure S27). The Sc_2N_2 skeleton of **2** is similar to the $(N_2)^{2-}$−Sc complex $[(C_5Me_4H)_2Sc]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$[9f] with a comparable N−N bond length. The Raman spectrum of **2** exhibits a strong absorption at 1420 cm^{-1} assignable to the N−N stretch.[13] On the basis of the $^{15}N/^{14}N$ mass ratio, the absorption in the ^{15}**N-2** Raman spectrum shifts to 1371 cm^{-1}. In the ^{15}N NMR spectrum of ^{15}**N-2**, the $(^{15}N_2)^{2-}$ ligand displays a chemical shift at 455.90 ppm, higher than that observed for $[(C_5Me_4H)_2Sc]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (385 ppm).[9f]

Sc-mediated N_2 activation is experimentally more challenging than with other rare-earth metals because of the small size and electropositive nature of scandium.[9] The first side-on-bridged $(N_2)^{2-}$−Sc complex was prepared by reduction of the cationic precursor $[(C_5Me_4H)_2Sc][(\mu\text{-Ph})BPh_3]$ with KC_8 under N_2[9f] or by the direct reaction of $[(C_5Me_4H)_3Sc]$ with N_2.[9g] Recently, an end-on-bridged $(N_2)^{2-}$−Sc complex was prepared via the reduction of $Sc[N(SiMe_3)_2]_3$ under N_2.[14] The transformation from **1** to **2** provides for the first time a convenient route to obtain rare-earth metal−N_2 complexes directly from the chloride precursors.

When **2** was treated with potassium in the presence of [2.2.2]cryptand (crypt) at room temperature, the paramagnetic $(N_2)^{3-}$-bridged discandium complex **3** was isolated in 90% yield (Scheme 2c). **3** could also be prepared directly in 68% yield via in situ generation of **2** from **1** (Scheme 2d). X-ray analysis revealed that **3** is a separated ion pair in which the whole $(Sc_2N_2)^-$ anion is balanced by a potassium crypt ion (Figure 1). The Sc_2N_2 unit in **3** is planar, and the dinitrogen ligand adopts a side-on $\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2$ mode. The N−N bond length is 1.3963(16) Å, which is between the lengths of a N=N double bond (1.25 Å for PhNNPh) and a N−N single bond (1.46 Å for H_2NNH_2) and consistent with the reported N−N bond lengths in $(N_2)^{3-}$−rare-earth metal complexes (1.36−1.41 Å).[10b,d] Because of the more negative charge on the

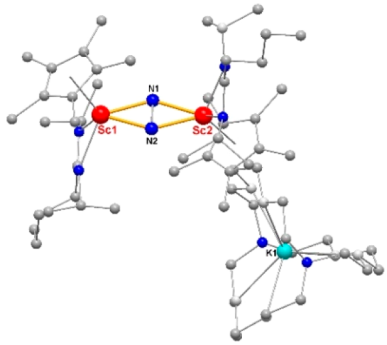


Figure 1. Molecular structure of **3** (ball-and-stick representation). Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: N1−N2 1.3963(16), Sc1−N1 2.0680(12), Sc1−N2 2.0415(12), Sc2−N1 2.0673(12), Sc2−N2 2.0475(12); N1−Sc1−N2 39.72(4), N1−Sc2−N2 39.67(4).

dinitrogen ligand, the average Sc−N(N_2) distance (2.056 Å) in **3** is significantly shorter than that in **2** (2.134 Å). In the Raman spectrum of **3**, an absorption at 975 cm^{-1} indicative of a $(N_2)^{3-}$ radical was found.[f2] Furthermore, **3** has an EPR signal with a g value of 2.0051 (Figure S6), which is in line with the reported values (2.0038 for Y[10b] and 2.0025 for La[10d]). The multiline pattern of this spectrum is consistent with the simulated spectrum, which is split by two ^{45}Sc ($I = {}^7/_2$) atoms and two ^{14}N ($I = 1$) atoms. To the best of our knowledge, **3** represents the first scandium complex with a $(N_2)^{3-}$ ligand. Density functional theory (DFT) studies further confirmed the structure of **3**. The singly occupied molecular orbital (SOMO) of **3** (Figure S35) is the essentially unperturbed π^* orbital of N_2 perpendicular to the Sc_2N_2 plane (see the Supporting Information (SI) for details).

The reaction of **3** with carbon-based electrophiles was explored. When MeOTf was added, functionalization of the $(N_2)^{3-}$ unit occurred smoothly to give complex **4** in 43% isolated yield along with the regeneration of **2** in 55% yield (Scheme 2e). The yield of **4** could be improved by adding potassium and MeOTf several times to the reaction mixture (Scheme 2f; see the SI for details). The molecular structure of **4** reveals a $(N_2Me_2)^{2-}$-bridged discandium complex (Figure 2). The dihedral angle between the Sc1−N1−N2 and Sc2−N1−N2 planes is 41.09(4)°, which indicates that the Sc_2N_2 unit is not coplanar. The length of the N1−N2 bond in **4**

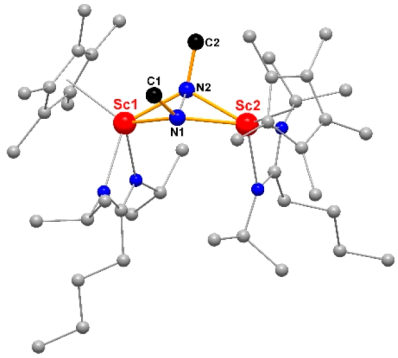


Figure 2. Molecular structure of **4** (ball-and-stick representation). Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: N1−N2 1.5044(16), C1−N1 1.4718(18), C2−N2 1.4744(18), Sc1−N1 2.2131(11), Sc1−N2 2.1292(11); N1−Sc1−N2 40.48(4), N1−Sc2−N2 40.38(4).

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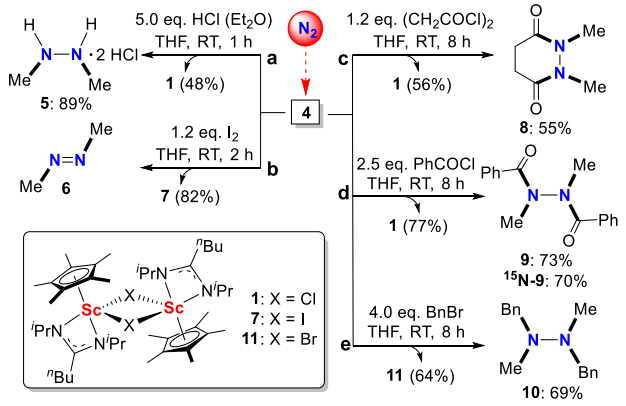
(1.5044(16) Å) is obviously longer than the corresponding N1−N2 bond in **3** (1.3963(16) Å) and is similar to the N−N distances observed in $(N_2H_2)^{2-}$ complexes derived from N_2.[10e,15] In the ^{15}N NMR spectrum of **^{15}N-4**, a δ value of −231.04 ppm is observed for the $(^{15}N_2Me_2)^{2-}$ group, which is shifted significantly upfield in comparison with that of **2**. As far as we are aware, this methylation represents the first example of the use of a $(N_2)^{3-}$−metal complex to construct C−N bonds using N_2 as the nitrogen source, and **4** is also the first $(N_2Me_2)^{2-}$ complex derived from the N_2 molecule. In contrast to **3**, complex **2** was stable toward MeOTf.

Further transformation of the $(N_2Me_2)^{2-}$-bridged discandium complex **4**, whose $(N_2Me_2)^{2-}$ unit was directly derived from N_2, was investigated (Scheme 3). Protonolysis of **4** with

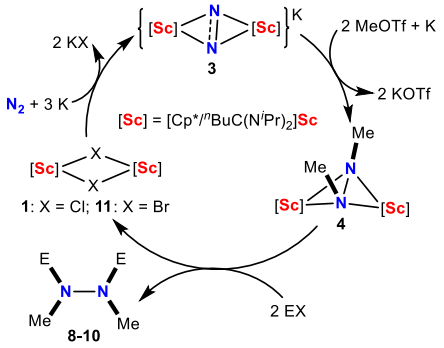
Scheme 3. Representative Reactions of 4 with HCl, I_2, $(CH_2COCl)_2$, PhCOCl, and BnBr



an Et_2O solution of anhydrous HCl was carried out, affording 1,2-dimethylhydrazine (**5**) in 89% yield (Scheme 3a). When **4** was treated with iodine, the $(N_2Me_2)^{2-}$ unit was oxidized to generate azomethane **6** accompanied by the formation of **7** (Scheme 3b). More remarkably, the $(N_2Me_2)^{2-}$ unit could be functionalized by reaction with electrophiles via further formation of C−N bonds. Thus, treatment of **4** with acyl chlorides and benzyl bromide led to the formation of the corresponding tetrasubstituted hydrazine derivatives **8**−**10** (Scheme 3c−e) with the regeneration of **1** or **11**. Besides, ^{15}N-labeled **^{15}N-9** (^{15}N NMR: δ = −240.63 ppm) was obtained in 70% isolated yield from **^{15}N-4** (Scheme 3d), providing an efficient route to access ^{15}N-labeled hydrazine derivatives. The generation of four C−N bonds on the N−N skeleton and ^{15}N-labeled hydrazine derivatives directly from N_2 or $^{15}N_2$ is unprecedented (Scheme 3c−e).

As analogues of **1**, complexes **7** and **11** (Scheme 3) could react with potassium under N_2 to provide **3**. Thus, as shown in Scheme 4, a synthetic cycle could be realized for scandium-mediated conversion of N_2, MeOTf, and electrophiles to hydrazine derivatives. The cycle includes three main steps: (i) reduction of the halogen-bridged discandium complex under N_2, leading to the formation of the $(N_2)^{3-}$-bridged discandium complex; (ii) treatment of the $(N_2)^{3-}$ complex with MeOTf, affording the $(N_2Me_2)^{2-}$-bridged discandium complex; and (iii) further reaction of the $(N_2Me_2)^{2-}$ complex with a carbon-based electrophile (EX) to produce a hydrazine derivative and regenerate the halogen-bridged discandium complex. To test the efficiency of this cycle, a one-pot reaction via sequential addition of potassium, MeOTf, and PhCOCl to a THF

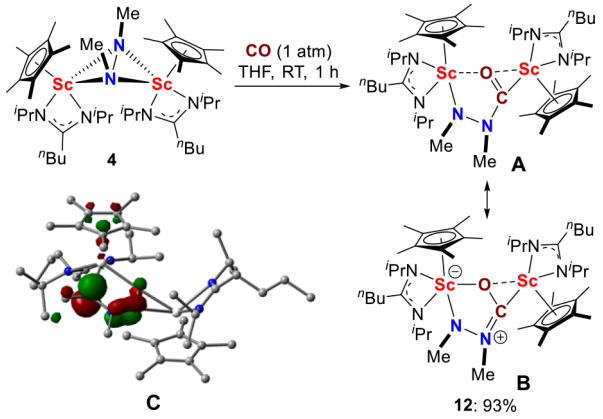
Scheme 4. Synthetic Cycle Affording Hydrazine Derivatives Using N_2 as the Nitrogen Source



solution of **1** was carried out, providing the N-containing compound **9** in 47% isolated yield along with regeneration of **1** in 57% yield (see the SI for details).

Because of the abundance of carbon monoxide (CO), the direct combination of N_2 and CO should be an attractive way to construct C−N bonds.[2c,5] When CO was bubbled into a THF solution of **4** (Scheme 5), the new dinuclear scandium

Scheme 5. Reaction of 4 with CO



complex **12**, formed via 1,1-insertion of one CO molecule into a Sc−N bond in **4**, was obtained in 93% isolated yield. The structure of **12** was confirmed by X-ray diffraction analysis (Figure 3). The CO unit is bonded with a scandium atom in an

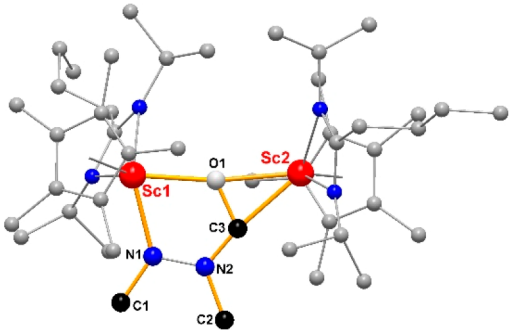


Figure 3. Molecular structure of **12** (ball-and-stick representation). Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: N1−N2 1.399(3), C3−N2 1.303(3), C3−O1 1.367(3), Sc1−O1 2.1633(17), Sc2−O1 2.1998(17), Sc2−C3 2.166(3); N2−C3−O1 114.3(2), O1−Sc1−N1 72.65(7).

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η^2 fashion, which is analogous to the previous reports of CO insertion into An−N (An = Th, U)[16] and Sc−B[17] bonds. In **12**, the C3−N2 and C3−O1 distances are 1.303(3) and 1.367(3) Å, which are outside the ranges of standard lengths of C−N single bonds (1.366−1.380 Å) and C═O double bonds (1.212−1.225 Å) in organic amides, respectively.[16] In order to understand the bonding mode in **12**, DFT calculations were carried out, and the optimized structural parameters agree well with the solid-state structure (see the SI for details). The HOMO (Scheme 5C) is mainly composed of p orbitals of the N1, N2, and C3 atoms. The Wiberg bond indexes of the C3−N2 and C3−O1 bonds are 1.41 and 1.11, in line with double-bond character of the C3−N2 bond and single-bond character of the C3−O1 bond, respectively. Hence, **12** is best described as two resonance forms (**A** and **B** in Scheme 5) with a greater contribution from **B**.

In summary, we have demonstrated a synthetic cycle of scandium-mediated conversion of N_2 and $^{15}N_2$ to hydrazine derivatives via the formation of C−N bonds in $(N_2)^{3-}$− and $(N_2Me_2)^{2-}$−scandium intermediates. This process represents the first rare-earth metal-promoted incorporation of N_2 into organic compounds and provides a useful method for the preparation of ^{15}N-labeled hydrazine derivatives. Moreover, upon addition of CO to this $(N_2Me_2)^{2-}$−scandium complex, the assembly of a C−N bond from CO and N_2 was observed.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b04293.

Experimental details; X-ray data for **1**−**4**, **7**, **11**, and **12**; NMR spectra of new compounds; EPR spectra of **3**; and Raman spectra of **2**, ^{15}**N-2**, **3**, ^{15}**N-3**, **4**, and ^{15}**N-4** (PDF)

Crystallographic data for **1**−**4**, **7**, **11**, and **12** (CIF)

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Notes

The authors declare no competing financial interest.

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