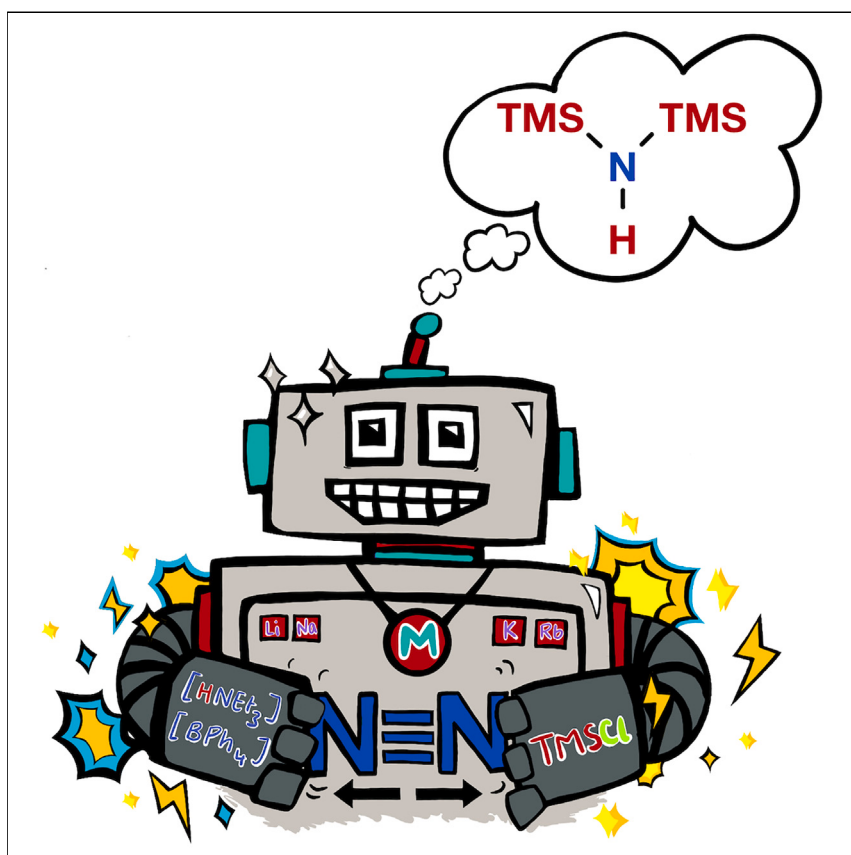


Article

Catalytic reduction of dinitrogen to silylamines by earth-abundant lanthanide and group 4 complexes



The low-energy conversion of atmospheric dinitrogen to amines is a grand challenge and could bring food and energy justice to many. For decades, chemists targeting homogeneous catalysts for this, citing biology as inspiration, have focused on electron-rich d-block complexes. Now, metallacycles formed from cheap, earth-abundant f-block and group-4 complexes with bridging phenolates can trap dinitrogen and moderate its reduction and functionalization. Studies demonstrate the importance of the metal-ligand architecture and cooperativity in controlling for unusual bis(substituted) nitrogen reduction products.

Anthony Wong, Francis Y.T. Lam, Matthew Hernandez, ..., R. David Britt, Nikolas Kaltsoyannis, Polly L. Arnold

pla@berkeley.edu

Highlights

Ambient conversion of N_2 to bis(silyl)amines (N_2RR) by electropositive metal aryloxides

First rare-earth-metal-complex-mediated N_2RR catalysts

First zirconium-complex-mediated N_2RR catalyst

Robust, recyclable Ti-based N_2RR catalyst with highest TON to date

Article

Catalytic reduction of dinitrogen to silylamines by earth-abundant lanthanide and group 4 complexes

Anthony Wong,¹ Francis Y.T. Lam,¹ Matthew Hernandez,¹ Jaden Lara,¹ T. Michael Trinh,¹ Rory P. Kelly,¹ Tatsumi Ochiai,¹ Guodong Rao,² R. David Britt,² Nikolas Kaltsoyannis,³ and Polly L. Arnold^{1,4,*}

SUMMARY

Dinitrogen is a challenging molecule to reduce to useful products under ambient conditions. The range of d-block metal complexes that can catalyze dinitrogen reduction to ammonia or tris(silyl) amines under ambient conditions has increased recently but lacks electropositive metal complexes, such as those of the f-block, which lack filled d-orbitals that would support classical binding modes of N₂. Here, metallacyclic phenolate structures with lanthanide or group 4 cations can bind dinitrogen and catalyze its conversion to bis(silyl)amines under ambient conditions. The formation of this unusual product is controlled by metallacycle sterics. The group 4 complexes featuring small cavities are most selective for bis(silyl)amine, while lanthanide complexes and the solvated uranium(IV) congener, with larger cavities, can also make a conventional tris(silyl)amine product. These results offer new catalytic applications for plentiful titanium and more earth-abundant members of the lanthanides that are also less toxic than many base metals used in catalysis.

INTRODUCTION

One of the most interesting challenges in homogeneous bond activation chemistry is dinitrogen (N₂). The strong N≡N bond (bond dissociation free energy [BDFE] = 945 kJ mol⁻¹) and large highest occupied molecular orbital-lowest unoccupied molecular orbital gap (10.82 eV) result in a high activation energy barrier and significant energy input requirement for the nitrogen reduction reaction (N₂RR).¹ Taking inspiration from nature, electron-rich, mid-d-block complexes^{2–7} have been widely studied for the reductive functionalization of N₂ to ammonia or its protected equivalent tris(trimethylsilyl)amine N(SiMe₃)₃ (Scheme 1A). The number of complexes showing turnover has recently started to increase rapidly. For example, one of the most successful studies to date has focused on developing a family of Mo-based PXP (X = C, N, P) pincer complexes that convert N₂ to NH₃. Through extensive catalyst optimization involving tuning of both the ligand and the reaction conditions, yields have improved with each generation from 12 equiv of ammonia per Mo atom to thousands, although the most effective catalysis is stoichiometric in Sm^{II} reductants.^{8–14}

N₂RR catalysts with Lewis acidic early d-block metals are significantly rarer. A small number of titanium complexes have been reported to effect catalytic reductive functionalization of dinitrogen.¹⁵ In the 1990s, Mori and co-workers reported that the reaction of Ti(OⁱPr)₄ with lithium, 45 equiv of Me₃SiCl, and dinitrogen (1 atm) gave a mixture assumed to contain [ClTi=NSiMe₃], [Cl₂Ti–N(SiMe₃)₂], and N(SiMe₃)₃ which could subsequently be converted into benzamide by treatment with HCl.¹ The other previously reported homogeneous titanium N₂RR catalysts, both supported by the

THE BIGGER PICTURE

Small-cavity metallacycles containing two earth-abundant lanthanide, actinide, or group 4 cations catalyze the conversion of ambient, atmospheric N₂ to bis(silyl)amines. The reduction of dinitrogen is challenging and has, for a century, been studied with electron-rich d-block metal compounds since conventional f-block metal complexes do not have filled d-orbitals that would enable binding of N₂. The metal cations, reductant, and ligand architecture work cooperatively, providing new fundamental information on this important transformation and showing how the nitrogen-binding cavity can be used to control the selective formation of bis(substituted) amines. The development of a new catalyzed reaction using f-block ions teaches us more about these less commonly studied metals. Because this system works in a polar solvent, opportunities to use a green source of electrons, e.g., from solar power, could enable smaller-scale amine production from atmospheric nitrogen wherever the sun shines.



chelating, more electron-donating, substituted tris(ethylenediamino)amine (tren) ligand, showed catalytic N_2 RR forming up to 9 equiv of NH_3 or 16.5 equiv of $N(SiMe_3)_3$ per Ti.^{16–18}

Homogeneous N_2 RR catalysts remain limited to d-block metals with the sole exception of our f-block metallacyclic uranium catalyst $U_2(L)_2$, **1U**,¹⁹ where L = the O-donor tetraphenolate $\{[2-(OC_6H_2-2-^tBu,4-Me)_2CH]-1,3-C_6H_4\}$,²⁰ which was able to catalyze the conversion of ambient N_2 to secondary silylamines in the presence of reductant, weak acid, and Me_3SiCl electrophile, generating 6.4 equiv of amine per complex (Scheme 1B). Calculations and the characterization of an intermediate containing the $[N_2H_2]^{2-}$ fragment suggested that the reactive ligand C–H in L facilitates delivery of a proton to the activated N_2 ligand.¹⁹ Prior to this, we had shown dinitrogen reduction by U^{III} centers with monodentate aryloxo or siloxido ligands, but reactions to target the further N_2 reduction needed for N-element bond formation usually results in O-ligand scrambling.^{21–23}

The $U_2(L)_2$ complex **1U** was also the first catalyst to selectively make a secondary amine from catalytic N_2 RR.¹⁹ Our discovery of the uranium catalysis was unexpected since the valence electrons that electron-rich d-block cations use to stabilize N_2 adducts, via back bonding from metal to the unoccupied nitrogen π -orbitals,²⁴ are not readily accessible to f-block metal cations, whose valence f-orbitals are contracted. The first evidence for N_2 binding in f-block chemistry came from the Sm^{II} organometallic complex Cp^*_2Sm , which exists in a dynamic equilibrium with the formally Sm^{III} , reduced dinitrogen adduct $\{Cp^*_2Sm\}_2(\mu-N_2)$ ($Cp^* = \eta-C_5Me_5$) in toluene solution under an N_2 atmosphere, demonstrating a minimally activated N_2 group.²⁵ More recently, combining simple Ln^{III} complexes with potassium metal or KC_8 under a dinitrogen atmosphere forms complexes containing the N_2 dianion in the form $\{X_2Ln(sol)_n\}_2(\mu-N_2)$ ($Ln = Sc, Y, La-Nd, Gd-Tm, Lu$; $X =$ bulky monodentate anionic O-, N-, or C-donor ligand, $M = K$, $n = 0-2$) and, in some cases, triply reduced N_2 complexes $[K(sol')][X_2Ln(sol)_n]_2(\mu-N_2)$ ($Ln = Y, Er$, and $La, Gd-Er, Lu$; $sol =$ monodentate- or crown-ether or cryptand).^{26–33} This new family of complexes upturned 90 years of accepted wisdom by proving that rare earths can bind and reduce dinitrogen, thus transforming conceptualizations of d- and f-orbital participation in bonding.^{34,35} Indeed, some of the complexes display remarkable magnetic properties as a result of their unusual electronic structures.³⁶ However, the only rare-earth complexes that have shown N-element bond formation to date are the methylation of the N_2 trianion in $\{[X_2Sc]_2(\mu-N_2)\}^-$, which forms a $(N_2Me_2)^{2-}$ unit,³⁷ and protonation of the side-on, reduced $(N_2)^{3-}$ yttrium analog with $[HNEt_3][BPh_4]$, which forms a crystallographically characterized bridging $(N_2H_2)^{2-}$ unit.³⁸

We considered the most significant discovery of our work in N_2 RR catalysis to be the formation of a secondary amine $HN(SiMe_3)_2$ as opposed to the usually observed product $N(SiMe_3)_3$. Here, we show that earth-abundant 4f and group 4 metal congeners of **1U** can form metallacyclic catalysts for the conversion of N_2 to bis(silyl)amines at ambient conditions. The THF-solvated f-block complexes, which have larger metallacyclic cavities, can also catalyze the transformation of N_2 to tris(silyl)amines, highlighting the increased flexibility of f-block catalysts compared to the d-block.³⁹

RESULTS

Synthesis and structures of the group 4 and lanthanide catalysts

The colorless bis- Ln^{III} metallacycles $[K_2Ln_2(L)_2(THF)_n]$ **1Ln-THF** ($Ln = Ce$, $n = 4$; $Ln = Sm$, $n = 3$) and bis- M^{IV} metallacycles $[M_2(L)_2]$ **1M**, $M = Ti$ yellow, Zr colorless) are

¹University of California, Berkeley, and Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

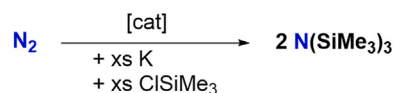
²University of California, Davis, Davis, CA 95616, USA

³Department of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK

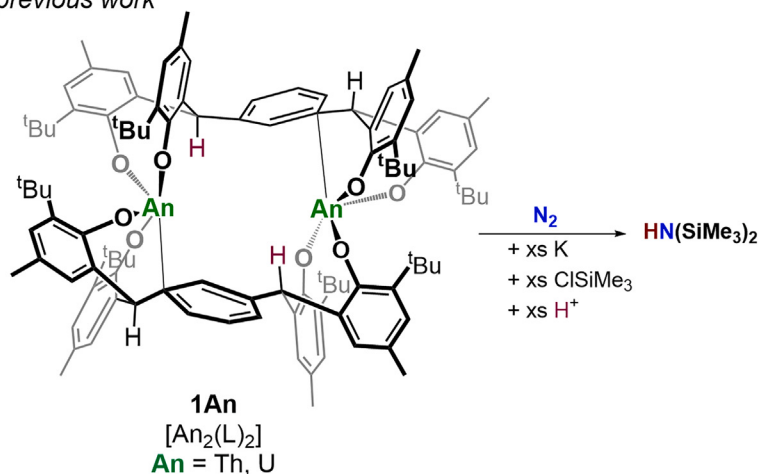
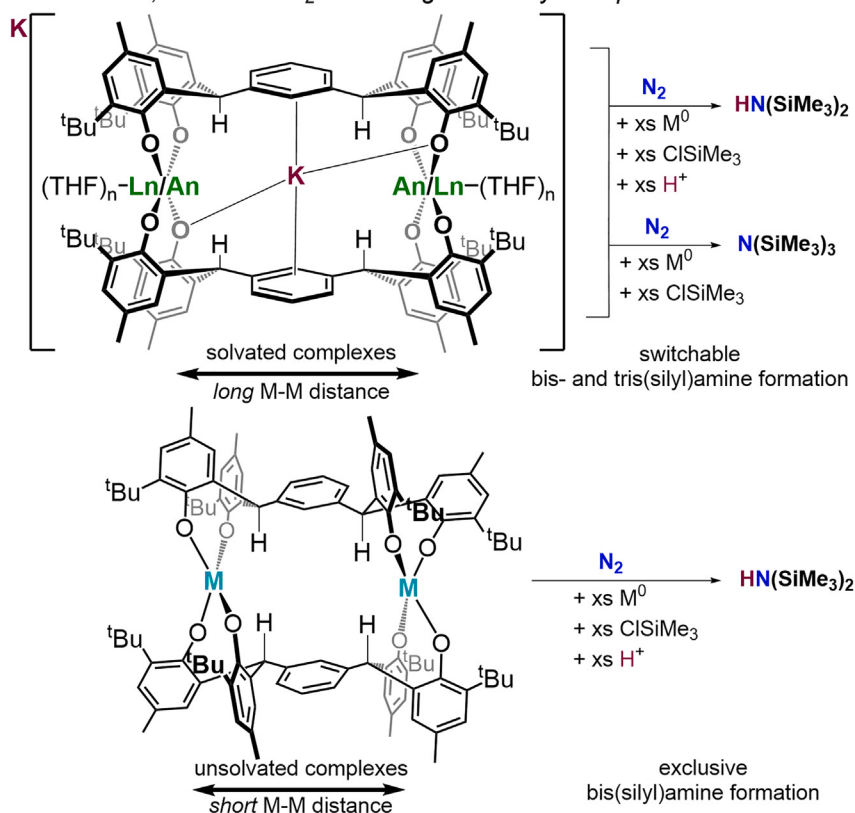
⁴Lead contact

*Correspondence: pla@berkeley.edu

<https://doi.org/10.1016/j.checat.2024.100964>

A Nitrogen Reduction Reaction (N_2 RR) to silylamines

B previous work

C this work; controlled N_2 RR and ligand cavity manipulation**Scheme 1. The N_2 RR catalysts 1Ln-THF, 1An, 1U-THF, and 1Ti/Zr**

(A) Generic catalyzed reaction for the conversion of N_2 to tris(silyl)amine.

(B) Previous work on the unsolvated tetravalent 1U, which has a small metallacyclic cavity, as a catalyst for N_2 RR.

(C) This work on lanthanide 1Ln-THF and solvated uranium 1U-THF catalysts with larger metallacyclic cavities (top) and unsolvated group 4 complexes 1Ti and 1Zr with smaller cavities

Scheme 1. Continued

(bottom). All catalyze the ambient conversion of N_2 to secondary silylamines, and the larger-cavity complexes (**1Ln-THF**, **1U-THF**) also catalyze the ambient conversion of N_2 to tertiary silylamines. Ln = Ce, n = 4; Sm, n = 3; U, n = 4; M = Ti, Zr; xs., excess.

prepared via protonolysis reactions between metal precursors and the tetraphenol H_4L in THF or arene solvent. The molecules (Scheme 1C) have been fully characterized, including by single-crystal X-ray diffraction (XRD) (see Figures S77–S83 and 1). Complex **1Ti** is air stable. Cyclic voltammetry data for THF solutions of **1Ln-THF**, **1U-THF**, **1Ti**, and **1Zr** with supporting alkyl ammonium-based electrolytes are shown in Figures S1–S5. The cyclic voltammogram of **1Ti** contains two reversible reductions at $E_{1/2} = -1.91$ V and -2.11 V vs. Fc/Fc^+ assigned as metal-based events.⁴⁰ No reduction event that could be assigned to a metal reduction was measurable for the other precatalysts within the electrochemical solvent window, i.e., as far as -3.2 V vs. Fc/Fc^+ .^{41,42}

The relationship between the geometry of the metallacycle pocket and the potential for reactivity within it is of greatest interest. The solid-state structure of **1Sm-THF** shows two octahedral Sm centers that form a rectangular cavity through coordination of two anionic aryloxy donors of each tetraanionic L (Figure 1A). The Sm–Sm distance in **1Sm-THF** is 9.3830(7) Å, significantly longer than the U–U distances in both the unsolvated **1U** (6.5732(5) Å) and the hydrazido adduct $[K_4U_2(\mu-\eta^2:\eta^2-N_2H_2)(L^-)_2]$ (4.6422(7) Å), which contains the four-electron reduced $(N_2H_2)^{2-}$.¹⁹ However, it is similar to the U–U distance in the solvated **1U-THF**, 9.3069(7) Å,¹⁹ since the two additional THF ligands on each metal displace the weak U–C close contacts formed with the meta-arene in **1U**.¹⁹ In addition, there is one potassium counter cation located in the **1Ln-THF** cavity with bonds to Ln through two phenolate O atoms and an η^1 interaction with the central carbon in the bridging arene of each L; the arenes are co-planar but offset. A second K^+ counter cation is solvated outside the cavity by six THF molecules. The structure of the cerium congener **1Ce-THF** is very similar to that of **1Sm-THF** (see Figure S80) except for slightly longer Ln–O bonds ($r_{cov, 6-coord}$: Ce(III) = 1.15, Sm(III) = 1.098 Å, U(IV) = 1.03 Å).

In contrast, both **1Ti** and **1Zr** display two tetrahedral metal centers (Figure 1B for Ti) and shorter M–M distances (7.8902(4) Å for **1Ti** and 7.8240(9) Å for **1Zr**), likely due to their smaller ionic radii of Ti and Zr compared to those of the lanthanides (Figure S83; $r_{cov, 4-coord}$: Ti(IV) = 0.56, Zr(IV) = 0.73 Å).

A common feature between **1Ln-THF** and **1M** (Ln = Ce, Sm; M = Ti, Zr) is that all four benzylic C–H bonds point into the metallacyclic cavity, whereas in **1U** and **1U-THF**, only two (one from each L) point inwards; the benzylic CH, assigned C7 and C30, in the structure of **1Sm-THF** are further from the center of the cavity than they are in **1U** by an average of 1.31 Å. The distances between the closest benzylic C–H and the midpoint between the two Sm in **1Sm-THF** or two Ti in **1Ti** are 3.72 Å in **1Sm-THF** and 3.70 Å in **1Ti**.

Catalytic N_2 RR

The metallacyclic complexes **1Ln-THF**, **1U-THF**, and **1M** are catalysts for the conversion of N_2 to bis(silyl)amine $HN(SiMe_3)_2$; the general reaction involves stirring a THF solution of the catalyst with an excess of potassium metal to provide electrons, excess chlorotrimethylsilane Me_3SiCl (electrophile), and excess weak acid $[HNEt_3][BPh_4]$ together under an ambient N_2 atmosphere for 24 h (Scheme 2A). Reactions of **1Ln-THF**, **1U-THF**, and **1M** were also carried out in the absence of acid to target formation

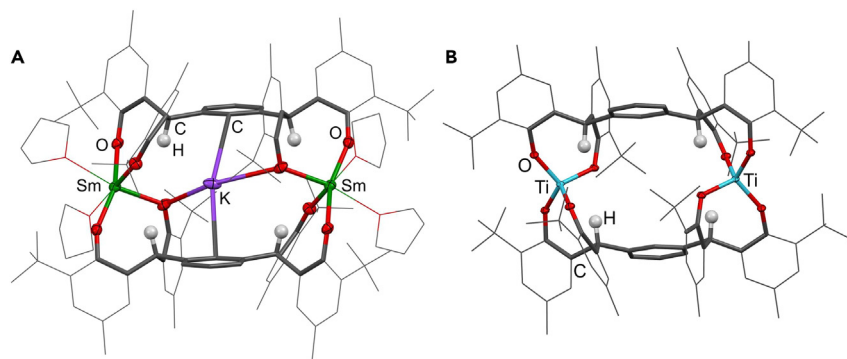


Figure 1. Structure of the N_2 RR catalysts **1Sm-THF and **1Ti****

(A) Anion of **1Sm-THF** and (B) **1Ti**. Hydrogen atoms, lattice solvent, and the $[K(THF)_6]$ counter cation for **1Sm-THF** are omitted for clarity. The inter-lanthanide/group 4 metal cation distances are Sm1–Sm2 = 9.3830(7) Å, Ce1–Ce2 = 9.3706(5) Å, Ti1–Ti2 = 7.8902(4) Å, and Zr1–Zr2 = 7.8241(7) Å (see [supplemental information](#)).

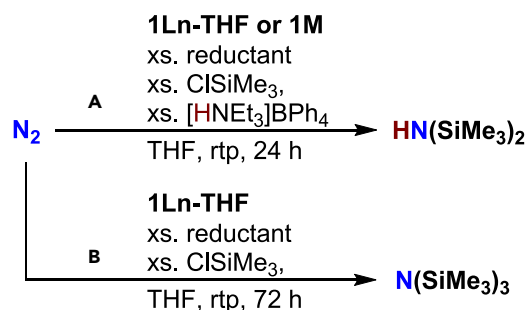
of the tris(silyl)amine ([Scheme 2B](#)). In THF, **1U** is converted to **1U-THF**, which is much more catalytically active compared to the unsolvated **1U** was in arene solvent. A range of control reactions and reactions under different conditions and with alternative reagents and isotopomers are described in the [supplemental information](#).

The most informative reactions are outlined in [Table 1](#). Nitrogen reduction products are identified and quantified by ^{29}Si nuclear magnetic resonance (NMR) spectroscopy and gas chromatography (GC) ([Figures S9–S11](#) and [S37–S50](#)), and yields are reported as an average of three runs.

Under an atmosphere of N_2 at room temperature, the complex **1Sm-THF** catalytically converts dinitrogen to the bis(silyl)amine $\text{HN}(\text{SiMe}_3)_2$, forming 3.71 ± 0.62 equiv of amine per binuclear **1Sm-THF** complex ([Table 1](#), entry 2). This is the second instance of catalytic N_2 reduction providing a selective route to secondary amine product formation, following **1U**.¹⁹ Under the same conditions, **1Ce-THF** produces silylamines in close to stoichiometric quantities ([Table 1](#), entry 1), affording a combined 2.1 equiv of bis(silyl)amine and tris(silyl)amine by-product (see below) per molecule of **1Ce-THF**. Lastly, **1U-THF** generates 20.5 ± 1.7 combined equiv of amine and is a better catalyst than **1U** (6.4 equiv of amines in our initial report).¹⁹

In the absence of weak acid, **1Sm-THF** is an even better catalyst for the conversion of N_2 to tris(silyl)amine, making 5.44 ± 0.81 equiv per **1Sm-THF**. Yields for **1Ce-THF** are substoichiometric ([Table 1](#), entries 6 and 7) unless Rb is used as the reductant partner instead of K ([Table 1](#), entry 4), yielding 2.80 ± 0.48 equiv of tris(silyl)amine. For **1Sm-THF**, K is the most effective group 1 metal reductant ([Tables 1](#); [Table S1](#), entries 1–18). **1U-THF** also catalyzes the formation of $\text{N}(\text{SiMe}_3)_3$, yielding 10.1 ± 1.5 equiv of the tris(silyl)amine; this contrasts with the inability of **1U** to produce the tris(silyl)amine in arene solvent, which we attribute to the larger cavity of solvated **1U-THF**. The precatalyst **1Sm-THF** is more active for the synthesis of tris(silyl)amine than bis(silyl)amine because a side reaction with the weak acid takes the active catalyst out of the solution. The reaction of **1Sm-THF** with $[\text{HNEt}_3][\text{BPh}_4]$ (8 equiv) in THF shows the release of some H_4L after 1 h ([Figure S55](#)). The group 4 complexes do not release H_4L , even after prolonged reaction times.

Compound **1Ti** gives the highest turnovers for N_2 RR yet reported for any molecular Ti catalyst with combined 35.1 ± 1.4 equiv of amine being produced ([Table 1](#),



Scheme 2. N_2RR catalyzed by the lanthanide, uranium, and group 4 complexes **1Ln-THF**, **1U-THF**, and **1M** (Ln = Ce, Sm; M = Ti, Zr)

(A) Ambient temperature and pressure formation of $\text{HN(SiMe}_3\text{)}_2$ from N_2 catalyzed by the lanthanide metallacycles **1Ln-THF**, **1U-THF**, or **1M** using a group 1 metal reductant, trimethylchlorosilane electrophile, and a weak acid.

(B) The conventional product $\text{N(SiMe}_3\text{)}_3$ can be made by **1Ln-THF** or **1U-THF** if acid is omitted. rtp, room temperature and pressure; xs., excess.

entry 9; Table S2, entry 2). Furthermore, the catalyst longevity of **1Ti** was tested by adding further reagent to the post-run catalytic mixture, yielding a combined 84.1 equiv of amine for the four collected runs (Table 1, entry 12; Table S2, entry 11). The two reported homogeneous titanium N_2RR catalysts gave up to 9 equiv of NH_3 or 16.5 equiv of $\text{N(SiMe}_3\text{)}_3$ per Ti.^{16–18} The heavier Zr metallacycle **1Zr** is the first Zr-based N_2RR catalyst, though it is poorer and less selective than **1Ti**, forming $\text{HN(SiMe}_3\text{)}_2$ (5.46 ± 0.45 equiv) and $\text{N(SiMe}_3\text{)}_3$ (2.74 ± 1.56 equiv) (Table 1, entry 11). Even Ti(OAr)_4 (OAr = $\text{OC}_6\text{H}_3\text{-2-}^t\text{Bu-4-Me}$) supported by monodentate aryloxides can catalyze the formation of bis(silyl)amine in the presence of a 2:1 ratio of silyl electrophile to acid, albeit in poorer yields than **1Ti** (see Table 1, entry 13). We considered if the ratio of acid to electrophile might dominate the product selectivity, but others have not seen this selectivity.³⁹ Therefore, we suggest that the combination of Ti(OAr)_4 and potassium counter cations in the reaction mixture can also form a protected space around the Ti-N_2 species that gives some selectivity for the bis(silyl)amine. Further, decreasing the fraction of acid below the 2:1 ratio of $\text{R}_3\text{Si}^+:\text{H}^+$ decreases both yield and selectivity for bis(silyl)amine with **1Ti** (Table S2, entry 4).

Interestingly, both **1M** and **1U** are inactive for the catalytic formation of $\text{N(SiMe}_3\text{)}_3$ (Table 1, entry 10; Table S2, entry 20).¹⁹ We suggest that this is due to insufficient space in the metallacycle for product turnover. For **1Sm-THF**, **1Ti**, and **1Zr**, K is also the most effective group 1 metal reductant (Table S2, entries 1–24). In all cases studied, sodium as reductant gives little or no turnover for N_2RR . Replacement of the reductant K with Na for **1** results in substoichiometric yields of the silylamines (e.g., 0.42 equiv of $\text{HN(SiMe}_3\text{)}_2$ and 0.43 equiv of $\text{N(SiMe}_3\text{)}_3$ for **1Sm-THF**). The replacement of $[\text{HNEt}_3]^+$ salts with other weak acids including $[\text{HPCy}_3][\text{Cl}]$ and phenol are described in Figure S41 and Table S2 (entries 6 and 8–10).

In the catalytic reactions to form $\text{HN(SiMe}_3\text{)}_2$, $\text{N(SiMe}_3\text{)}_3$ is a by-product of a secondary reaction between the newly formed $\text{HN(SiMe}_3\text{)}_2$ and K metal to form $\text{KN(SiMe}_3\text{)}_2$, which reacts with ClSiMe_3 . To demonstrate this, aliquots were removed over the course of different runs, using **1Ti**, **1U-THF**, or Ti(OAr)_4 , and analyzed by GC. In the **1Ti**-catalyzed reaction, the amount of $\text{HN(SiMe}_3\text{)}_2$ increases over the first 9 h (Figure S12) and then plateaus and starts to decrease as the $\text{N(SiMe}_3\text{)}_3$ by-product starts to form (Figure S14). We repeated the kinetic study using the standard conditions, except we replaced $[\text{HNEt}_3][\text{BPh}_4]$ with $[\text{DNEt}_3][\text{BPh}_4]$, and observed a decrease in

Table 1. Catalytic conversion of N₂ to silylamines by metallacycles 1Ln-THF, 1U-THF, and 1M under ambient conditions

Entry	Precatalyst	Reductant (300 equiv) ^a	CiSiMe ₃ equiv	[HNEt ₃][BPh ₄] equiv ^b	HN(SiMe ₃) ₂ equiv ^c	N(SiMe ₃) ₃ equiv
1	1Ce-THF	K	225	131	1.84	0.26
2	1Sm-THF	K	225	131	3.71 ± 0.62	0
3	1U-THF	K	225	131	17.5 ± 1.4	2.91 ± 1.71
4	1Ce-THF	Rb	300	0	0	2.80 ± 0.48
5	1Sm-THF	Rb	300	0	0	3.29 ± 0.22
6	1Ce-THF	K	300	0	0	1.21
7	1Sm-THF	K	300	0	0	5.44 ± 0.81
8	1U-THF	K	300	0	0	10.1 ± 1.5
9	1Ti	K	225	131	29.7 ± 0.9	5.35 ± 0.51
10	1Ti	K	300	0	0	1.44
11	1Zr	K	225	131	5.46 ± 0.45	2.74 ± 1.56
12 ^d	1Ti	K	225 (4x)	131 (4x)	75.9	8.16
13	Ti(OAr) ₄	K	225	131	16.3 ± 1.0	2.43 ± 0.79

^aReductant.^bCatalysis results with other weak acids are in the [supplemental information](#).^cYields quoted for all these complexes are per molecule rather than per Ln/M; average of 3 or more runs.^dAdditional reagent added to recycled, post-run 1Ti catalyst showing catalyst longevity; product yield reported for the four collected runs.

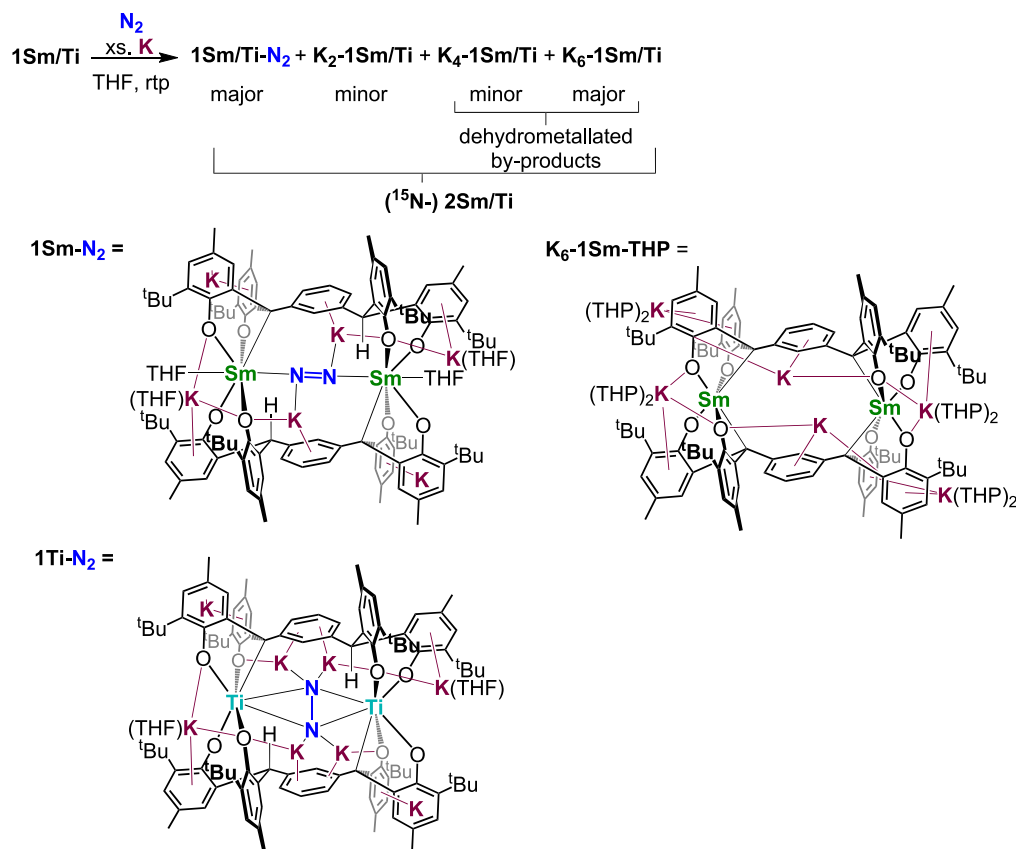
the overall rate of formation of H/DN(SiMe₃)₂, which may suggest that N–H bond formation/cleavage is involved in the rate-determining step ([Figure S13](#)). Analogous kinetic studies with both 1U-THF and Ti(OAr)₄ show the same trend as 1Ti: the bis(silyl)amine product is made early in the reaction, while the tris(silyl)amine product is only produced during later time points ([Figures S15 and S16](#)).

Studies of potential intermediates arising from N₂ reduction and reductive dehydrometallation

In the 1U N₂RR system, we characterized an intermediate containing a doubly reduced and doubly protonated, side-on-bound dinitrogen and demonstrated that the NH in HN(SiMe₃)₂ derives from the benzylic CH group within the metallacycle. We targeted a reduced N₂-containing complex from the reactions between 1Sm-THF or 1Ti and excess potassium under N₂ ([Scheme 3](#)).

In each case, we isolate a dark red powder that contains a mixture of complexes, denoted 2Sm and 2Ti, respectively, containing a reduced N₂ species and products containing M–C_{benzylic} bonds arising from the deprotonation of one or more ligand benzylic CH groups, i.e., dehydrometallated congeners of 1Sm/Ti. We were unable to isolate pure compounds from the mixture 2Sm due to similar solubilities and extreme air sensitivity but have used isotopomer substitutions and spectroscopies to confirm that around half of the material in each case is a reduced dinitrogen adduct. Analysis (electron-spray ionization mass spectrometry and NMR spectroscopies) of the reduced mixtures 2Sm and 2Ti after quenching with the weak acid [DNEt₃][BPh₄] reveals the overall level of dehydrometallation to be around one-quarter of the total ligand benzylic CH groups in each case ([Figures S6, S7, S29, S30, and S34–S36](#)).

Complete deprotonation of the benzylic carbons forms [K₆(THF)₄M^{III}₂(L^{2−})₂] (K₆-1 Sm/Ti) as red-orange K₆-1Sm or olive green K₆-1Ti, which we can make independently and have structurally characterized for both M = Sm (as the THP solvate [K₆(THP)₈M^{III}₂(L^{2−})₂]) and Ti ([supplemental information](#)). L^{2−} is the hexaanionic



Scheme 3. Reduction of 1Sm-THF or 1Ti under dinitrogen in the absence of electrophile and acid

The products are reduced, N_2 -containing and dehydrometallated mixtures denoted **2Sm** or **2Ti**, and line drawings of proposed structures of **1Sm-N₂**, **1Ti-N₂**, and the structurally characterized THP solvate of **K₆-1Sm**, **K₆-1Sm-THP**. The solid-state structures of **K₆-1Sm-THP**, **K₄-1Zr**, and the three **K_n-1Ti** ($n = 2, 4, 6$) are shown in the [supplemental information](#). THP, tetrahydropyran.

ligand $[\{2-(\text{OC}_6\text{H}_2-2\text{-}^t\text{Bu-4-Me})_2\text{C}\}-1,3\text{-C}_6\text{H}_4]$. The respective M–M distances in **1 Sm/Ti** vs. **K₆-1 Sm/Ti** are 9.3830(7) vs. 6.8395(7) Å for Sm and 7.8902(4) vs. 6.9919(12) Å for Ti. We expect that these metallations that reduce the cavity size disfavor N_2 binding since the M–C_{benzylic} bonds reduce the void volume: only the complexes without Ti–C_{benzylic} bonds (**1Ti** and **K₂-1Ti**) are capable of binding N_2 upon further reduction (see [Scheme S1](#)). The stoichiometric reduction of **1Ti** with 2 equiv of reductant generates yellow $[\text{K}_2(\text{THF})_4\text{Ti}^{\text{III}}_2\text{L}_2]$ (**K₂-1Ti**), while dark brown $[\text{K}_4(\text{THF})_4\text{Ti}^{\text{IV}}_2(\text{L}^{2-})_2]$ **K₄-1Ti** can be made from careful reoxidation of **K₆-1Ti** (see the [supplemental information](#)). The solid-state structure of $[\text{K}_4(\text{THF})_4\text{Zr}^{\text{IV}}_2(\text{L}^{2-})_2]$ **K₄-1Zr** is also shown in the [supplemental information](#).

The reduced mixtures are active precatalysts for the N_2RR reactions and give similar product yields ([Table S3](#), entries 1–4), although they may not be on-cycle intermediates according to the calculations described below. However, the metallated complexes **K_n-1Ti** ($n = 4, 6$) can become catalytically active upon the addition of weak acid, which reprotonates the benzylic C in **K_n-1Ti** ($n = 4, 6$).

The N–N bond orders of the two reduced N_2 complexes were determined by Raman spectroscopy. Spectra of the **2Sm** mixture contain an absorption at $1,337\text{ cm}^{-1}$, which is shifted to a lower energy ($1,306\text{ cm}^{-1}$) for $^{15}\text{N-}2\text{Sm}$, consistent with a doubly reduced N_2 with a double-bond character ([Figures S61–S63](#)). Raman spectroscopy of **2Ti** shows

the presence of an N–N single bond. The absorption at $\nu(^{15}\text{N}_2) = 796\text{ cm}^{-1}$ in the Raman spectrum of the mixture reduced under $^{15}\text{N}_2$, ^{15}N -2Ti, shows a bathochromic shift compared to 2Ti ($\nu(^{14}\text{N}_2) = 846\text{ cm}^{-1}$) (Figures S65–S67). The shift is larger than predicted by the reduced mass calculation for the two N isotopes, which would be consistent with the involvement of the adjacent heavy atoms in this stretching mode. No N–H bonds were identified in 2Sm or 2Ti by Fourier transform infrared spectroscopy. Addition of weak acid to either ^{15}N -2Sm or ^{15}N -2Ti also generates a doublet in the ^1H NMR spectrum at 7.35 ppm ($J_{\text{NH}} = 71.3\text{ Hz}$) indicative of $^{15}\text{NH}_4\text{Cl}$, confirming that the amine N is derived from N_2 (Figures S28 and S33).

We were able to separate the other paramagnetic Ti complexes, K_2 -1Ti and K_6 -1Ti, from the 2Ti mixture by fractional crystallization. We then used pulsed electron paramagnetic resonance (EPR) spectroscopy to probe the remaining N_2 -bonded titanium species, denoted 1Ti- N_2 , and its isotopomer 1Ti- $^{15}\text{N}_2$. Q-band electron spin-echo modulation (ESEEM) spectra are shown in Figure 2. Very interestingly, while the majority of the modulation patterns in the 3-pulse ESEEM spectra arise from coupling to ^{39}K , a comparison between the frequency domain spectra of 1Ti- N_2 and 1Ti- $^{15}\text{N}_2$ shows a sharp difference peak at 5.36 MHz, exactly at the Larmor frequency of ^{15}N at the Q-band (1,241 mT). The coupling to ^{15}N is corroborated by the two-dimensional hyperfine sublevel correlation spectroscopy, which clearly reveals a ^{15}N coupling peak with a very small hyperfine interaction of $\sim 0.2\text{ MHz}$, which likely arises from pure through-space electron nuclear dipole interactions, the magnitude of which implies very little, if any, orbital overlap between Ti^{III} and ^{15}N . Assuming a small T of 0.1–0.2 MHz corresponds to a Ti–N distance of 3–4 Å, which suggests that there is little or no covalency in the Ti- N_2 bonding in 1Ti- N_2 .⁴³ Given the Ti^{III} – Ti^{III} distance of 6.36 Å calculated from the EPR spectra (see supplemental information section 13) and the estimated N–N bond length of 1.2–1.4 Å, the Ti–N distance suggested by EPR for 1Ti- N_2 is estimated to be $\sim 3.3\text{ Å}$. Together, these data are consistent with a reduced N_2 unit positioned in the center of the ligand cavity oriented in a side-on fashion relative to the two Ti centers.

EPR spectra of frozen 2-Me-THF solutions of several independently synthesized samples of 2Sm at 15 K show only a resonance assigned to an organic radical impurity at $g = 2.005$ without any discernable hyperfine features (Figure S73).

Because isolation of a highly reduced N_2 -containing compound proved difficult, we carried out reactions targeted to trap the reduced N_2 anion in 2Sm and 2Ti with various electrophiles (e.g., alkyl halides, phenyl isocyanate, and stoichiometric Me_3SiCl) (see supplemental information section 6). Comparison of ^1H NMR spectra between reactants and products showed subtle shifts in complex ligand resonances, but structural characterization of these products by XRD failed under numerous crystallization conditions.

DISCUSSION

Selectivity for secondary amine

This is the second report of catalytic N_2 reduction providing a selective route to secondary amine product formation, following our identification of the $\text{U}_2(\text{L})_2$ catalyst 1U. To the best of our knowledge, all other systems reported to date make tri-substituted amines in the presence of ClSiMe_3 except for Hidai's *cis*- $\text{Mo}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4$ complex, which catalytically converts N_2 into mixtures of silylamines in up to 25.5 combined equiv per Mo; the best selectivity they could achieve for the bis(silyl)amine was at lower conversions, with excess Na metal and BrSiMe_3 ,

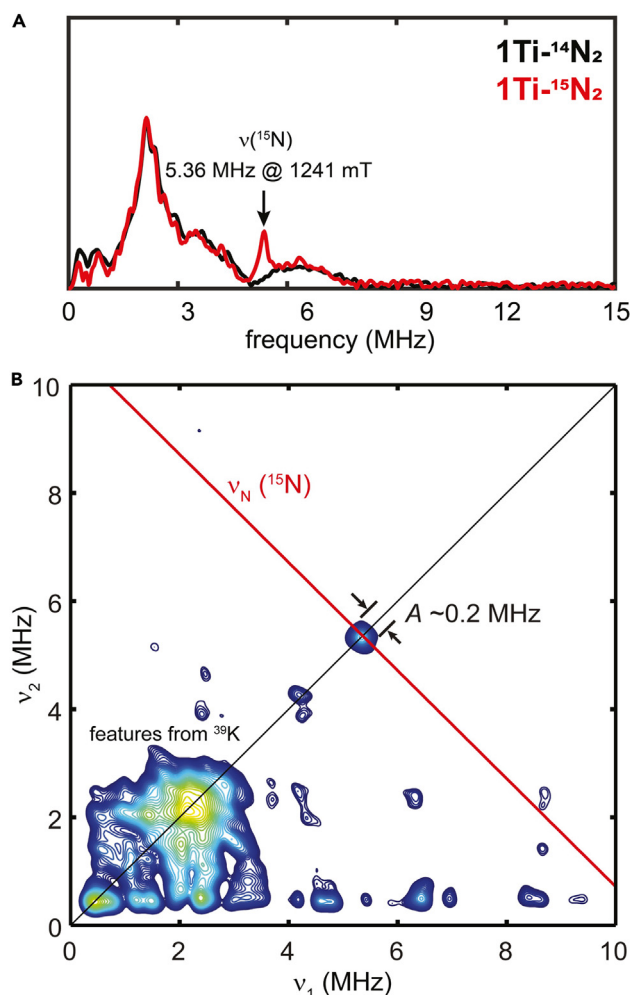


Figure 2. Pulsed EPR spectra of the isolated product of reduction of 1Ti under dinitrogen

Q-band frequency domain 3-pulse ESEEM spectra of the isolated product of reduction of 1Ti under dinitrogen of (A) 1Ti- N_2 (black trace) and 1Ti- $^{15}N_2$ (red trace) reveal a difference peak at 5.36 MHz, exactly at the Larmor frequency for ^{15}N at Q-band (1,241 mT). Q-band hyperfine sublevel correlation spectroscopy (HYSCORE) spectrum (B) of 1Ti- $^{15}N_2$ reveals the magnitude of the hyperfine coupling interaction of ^{15}N and Ti^{III} to be ~ 0.2 MHz. $T = 20$ K, $\pi/2 = 12$ ns, $\tau = 300$ ns.

converting N_2 to a mixture of $HN(SiMe_3)_2$ (1.8 mol/Mo atom) and $N(SiMe_3)_3$ (3.2 mol/Mo atom).⁴⁴ The protons were suggested to derive from THF or trace water. Relatedly, Sita devised a stoichiometric route to $HN(SiMe_3)_2$ by functionalizing a terminal Mo imido with sequential additions of acid, electrophile, and reductant.⁴⁵ Here, the pseudo-tetrahedrally coordinated 1Ti/Zr, like the unsolvated $U_2(L)_2$ catalyst we previously reported, catalyze the synthesis of bis(silyl)amine but are inactive for the catalyzed formation of tris(silyl)amine. All these unsolvated complexes have smaller metallacyclic cavities than 1-Ln-THF, suggesting that the selective formation of bis(silyl)amine is most effectively controlled by the size of the metallacyclic pocket.

The 1Ln-THF precatalysts have pseudo-octahedral, THF-solvated metal cations (as does 1U-THF), large metallacyclic cavities, and presumably relatively flexible coordination geometries. They can catalyze the formation of bis(silyl)amine in the presence of silyl electrophile and acid but, in the absence of acid, can also catalyze the formation of tris(silyl)amine.

Above, we noted that all four benzylic H point into the cavity for **1Ln-THF** and **1M** (Ln = Ce, Sm; M = Ti, Zr); tetra-dehydrometallation takes the complex off cycle as **K₆-1M**. The geometries of **1U** and **1U-THF** only allow for double dehydrometallation, leaving space for N₂ binding in the cavity. Reprotonation of the tetra-dehydrometallated **K₆-1M** complexes brings them back on cycle, corroborating the calculations that find that the reaction takes place inside the cavity for Ti and U.

The kinetic studies of **1Ti**, **1U-THF**, and **Ti(OAr)₄** all confirm that **HN(SiMe₃)₂** is the dominant initial product of these aryloxide-supported electropositive-metal-mediated N₂RRs, and secondary reactions lead to tris(silyl)amine. Combined with the fact that neither **1Ti** nor unsolvated **1U** is able to produce the larger **N(SiMe₃)₃** catalytically, we reason that the small cavity space dominates the control of selectivity for the formation of the bis(silyl)amine product, while the **R₃Si⁺:H⁺** ratio influences the final product distribution. We have probed the latter by allowing a catalytic reaction involving **1Ti** to stir for a longer time period (3 days) and observed higher yields of tris(silyl)amine at the expense of bis(silyl)amine (Table S2, entry 3).

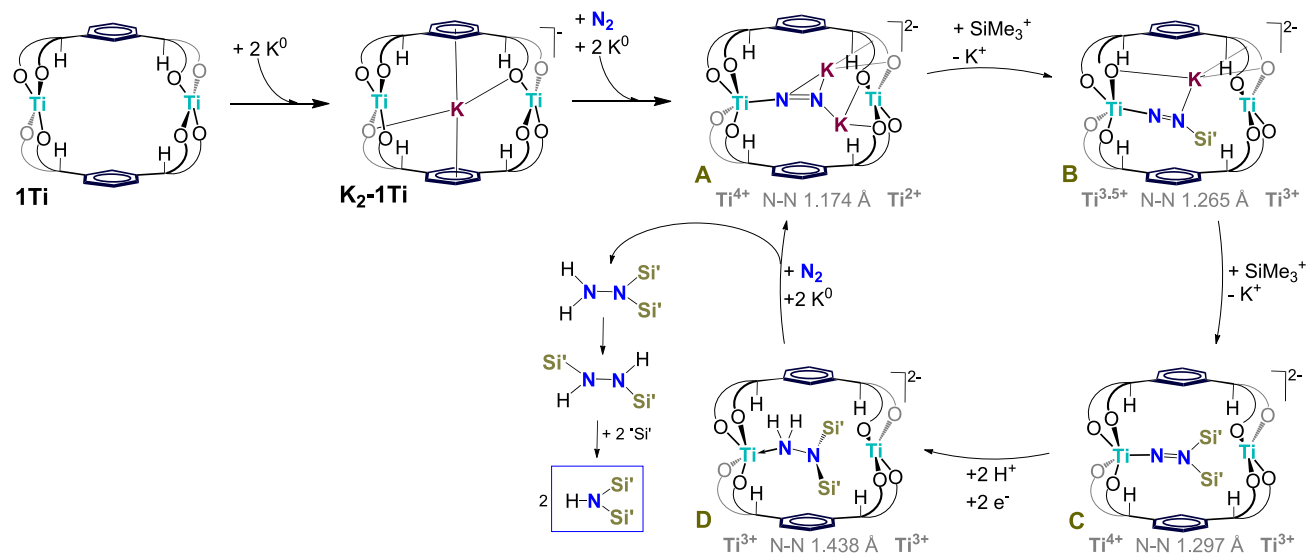
Identity of the Ln or group 4 metal and cooperativity with the group 1 metal reductant

The Ln^{III} and M^{IV} metallacycles **1** all feature the stable metal oxidation state and strong Ln/M–O bonding that characterized **1U**, and again, there is no evidence of N₂ binding until the reductant is added.

The group 4 complexes that do not bind donor solvents (*r*_{cov, 4-coord}: Ti(IV) = 0.56, Zr(IV) = 0.73 Å) and the unsolvated **1U** can only form the smaller bis(silyl)amine product. The solvated **1Ln-THF** and **1U-THF** have a larger and likely more flexible metallacyclic cavity (*r*_{cov, 6-coord}: Ce(III) = 1.15 Å, Sm(III) = 1.098, U(IV) = 1.03 Å) and can catalyze the formation of either bis- or tris(silyl)amine.

Complex **1Ti** can be reversibly reduced twice at *E*_{1/2} = –1.91 V and –2.11 V vs. **Fc/Fc⁺**, whereas no reduction event for **1Ln-THF**, **1U-THF**, and **1Zr** that could be assigned to a metal reduction was measurable as far as –3.2 V vs. **Fc/Fc⁺**. The values measured for **1Ti** are very negative for a Ti^{IV/III} couple, in line with the strongly electron-donating nature of the ligand set. In line with this observation, group 4 metallocene complexes that reductively functionalize N₂^{46–48} did not show catalytic turnover, perhaps because the cyclopentadienyl ligands do not support a sufficiently reducing metal center.⁴⁹ The higher reactivities for the Ti, Sm, and U catalysts, compared to their Zr, Ce, and Th¹⁹ congeners, respectively, suggest that access to the reducing Ti^{IV/III}, Sm^{III/II}, and U^{IV/III}^{50,51} redox states, respectively, may be advantageous in N₂RR even if the binding mode of the reduced N₂ intermediates is different in these different metal catalysts.⁵²

Finally, the identity of the group 1 reductant is very important. Incorporation of the reductant counter cations is found to be essential in the calculated mechanism, providing electrostatic stabilization to intermediates, and was also shown to be essential for **1U**.¹⁹ Various groups have noted the importance of group 1 counter cation choice when stabilizing reduced N₂ complexes,^{53–55} If the first reduction potential of the Lewis acidic metal Ln^{III/II} or M^{IV/III} in the metallacycle is less negative than the M^{0/I} potential of the reductant, then catalytic N₂ reduction is better. The M^{0/I} potential for Na is –2.56 V and for K and Rb is –2.88 V vs. **Fc^{0/+}** in MeCN.⁵⁶ It is not clear why K is a better reductant partner for **1Sm-THF** while Rb is a better partner for **1Ce-THF**, but this could be due to a better fit of the s-block cations within the cavity that helps stabilize the reduced intermediates. The inability of the smaller,



Scheme 4. DFT-calculated structures of catalytic intermediates in the 1Ti cycle

The intermediates found by theory are shown as simplified cartoon line drawings, with the charges and redox states drawn underneath as found from the calculations. $Si' = SiMe_3$.

harder sodium to function as an effective reductant supports this, although there may be more of a redox potential difference between K and Rb in THF.

The most highly reduced, metalated complexes such as N_2 -containing **1Sm-N₂** and **1Ti-N₂** are off cycle, while dehydrometalated **K₄-1M** and **K₆-1M**, which are formed from overreduction prior to N_2 binding and have the smallest cavities, are not involved in the catalysis. Nevertheless, **2Ln** and **2Ti** are active precatalysts, and **K₄-1Ti** and **K₆-1Ti** can both reform **K₂-1Ti** and re-enter the N_2 RR cycle.

Proposed mechanism for 1Ti and comparison with possible mechanisms for 1Ln and 1An

Density functional theory (DFT) calculations were undertaken to identify possible reaction intermediates for an N_2 RR catalytic cycle mediated by **1Ti**, and the structures of theoretical catalytic intermediates are shown in Scheme 4. The methods used mirrored those for the **1U** system, but we have found that, computationally, the 3d and 5f compounds behave differently. The lack of formation of any bis(silylamine) by **1Ln-THF** catalysts in the absence of weak acid also implies mechanistic differences between **1Ln-THF** and **1U**. The side-on N_2 arrangement from the U modeling was initially used for the Ti calculations, but numerous attempts at getting N_2 reduction in this configuration were unsuccessful (*vide infra*). End-on-bound N_2 is more reactive toward further functionalization than side-on-bound N_2 in reported d-block chemistry.⁵⁷ Further, reduced U pathways were not previously considered for U, as it was not necessary to do so. The U mechanism calculations focused on transformations between intermediates in which K cations were replaced by silyl cations and did not consider the potential role of $SiMe_3$ radicals. While others suggest that the $Me_3Si\cdot$ radical may be involved in solution-phase catalytic N_2 RR at low temperatures (150–200 K), the $Me_3Si\cdot$ radical has a half-life of 0.005–0.01 s.⁵⁸

We begin with **1Ti** modeled as a neutral singlet with two Ti(IV) centers. Calculation gives Ti–Ti = 7.813 Å and average Ti–O = 1.808 Å, which compare well with the experimental values of 7.890 and 1.812 Å, respectively. From **1Ti**, we move to **K₂-**

1Ti, here modeled as a monoanionic triplet with only the internal K cation present and the external counter cation excluded from the calculation. The structural agreement with experiment is once again very good: calculated Ti–Ti = 7.728 Å, Ti–K = 3.864 Å, and average Ti–O = 1.913 Å vs. 7.676, 3.838, and 1.914 Å from XRD. The Mulliken spin density is 1.029 on each Ti(III) center. At this stage, we introduce an additional K and an N₂ molecule. The latter was initially placed in a variety of starting orientations, midway between the two Ti centers, and with overall C_i symmetry. Subsequent symmetry-constrained geometry optimizations of systems with different spin multiplicities yielded little evidence of N₂ reduction, with N–N distances close to those in free dinitrogen. Harmonic vibrational frequency analysis indicated that one of the converged geometries—a quintet in which the N₂ unit is oriented approximately along the Ti–Ti vector—is a transition state, with an imaginary mode of 69.2i cm^{−1} corresponding to translation of the N₂ unit between the Ti centers. Relaxed geometry optimization yielded a structure that is 67.3 kJ/mol more stable in energy than the transition state, in which the N₂ unit bonds to only one of the Ti centers and the N–N distance lengthens to 1.172 Å.

Subsequent reoptimization of this system in different spin states established that the most stable structure is a triplet, 46.5 kJ/mol more stable than the quintet, and with a very similar geometry (N–N = 1.174 Å, Ti–N = 1.901 Å) (intermediate **A** in Scheme 4). The spin-density data suggest that the N₂-bound Ti is Ti(IV), with minimal spin density on the N₂ unit. The other Ti center has spin density = 1.929. We were surprised to find that one Ti center plays the dominant role because almost all electropositive metal complexes containing reductively functionalized N₂ reported to date contain the reduced N₂ anion bound to two metals, and all of these are symmetrical.²¹ However, we note that only 1Ti and the two tren-supported complexes cited above^{16,17} have shown N₂RR catalysis. Moreover, the distal mechanism, which invokes end-on binding and would seem most reasonable for Ti(OAr)₄, is more common for those catalysts whose mechanisms have been studied so far.⁵⁷ Note also that while the computed mechanism for N₂ reduction by our uranium-based catalyst¹⁹ featured side-on-bound N₂ coordinated by both metals, the U–U distance in the precatalyst 1U is ~1.3 Å shorter than the Ti–Ti distance in 1Ti (which also features significantly smaller metal ions). Upon reductive activation of dinitrogen by 1U, the U–U distance decreases by 1.931 Å.¹⁹ A molecule of N₂ placed centrally in an end-on geometry in the cavity of the Sm^{III} starting material 1Sm-THF would have an Sm–N distance of 4.13 Å, which is too long for any significant orbital overlap, but the mechanism calculated for 1Ti shows N₂ binding to only one Ti during catalysis, and group 1 metal cations fill the remaining space before being replaced by electrophiles. There appears to be only a minimal energy difference between the side-on- and end-on-bound (N₂)^{2−} isomers in the instances where both have been reported for {X₂Ln(sol)}₂(μ-N₂).^{26–34}

From **A** we move to species **B**, in which one of the K ions bound to the distal N is replaced by SiMe₃⁺. This system, as with all the others shown in Scheme 4 except 1Ti and K₂-1Ti, is a dianionic triplet. The spin density is distributed such that the N₂-free Ti is Ti(III), with the residual spin spread over the other Ti (0.363) and the N₂ unit (0.538). The buildup of spin density on the latter is consistent with the lengthening of the N–N distance to 1.265 Å in a formal [KSiMe₃N₂]^{−0.5} group. Replacement of the second N-bound K⁺ with SiMe₃⁺ leads to species **C**, in which there is greater spin-density buildup on the N₂ (0.702) and an even longer N–N (1.297 Å). The N₂-free Ti remains Ti(III), and the Ti–N₂ distance remains short at 1.770 Å.

The final structure we have located is **D**. Two hydrogen atoms are added to the proximal N, leading to substantial changes in the spin-density distribution and key distances. Both Ti centers are now Ti(III), and the N₂ unit now carries almost no net spin density. This is consistent with further lengthening of the N–N distance to 1.438 Å and an N–N single bond. The Ti–N₂ distance also lengthens substantially and at 2.116 Å is now 0.346 Å longer than in **C**. The overall structure of **D** is essentially a doubly reduced version of **1Ti** with an H₂N₂(SiMe₃)₂ molecule sitting in the cavity, and while intermediates with one silyl group on each nitrogen were also investigated computationally, the Ti cavity limits silylation to two per N₂.

Release of the disilylhydrazine bound inside the Ti₂L₂ cavity (Scheme 4) is easy, and the 1,2 rearrangement of silylalkyl groups in disilylhydrazine is known to be rapid, so upon release from the cavity, HNNSi'₂ rapidly forms the more stable 1,2-disilylhydrazine (**Z**),⁵⁹ which can react with the excess ·SiMe₃ radicals^{60,61} to form the HN(SiMe₃)₂ product.

We have combined the DFT-calculated proposed mechanism for **1Ti** with the observations made for **1Ln-THF** and **1U(-THF)** in Scheme S1.

Conclusions

Metallacyclic group 4 and f-block complexes of tetradentate, bridging aryloxides, are capable of binding dinitrogen in the cavity formed by the chelating aryloxide ligands upon reduction. The complexes demonstrate selective catalytic functionalization of dinitrogen to secondary amines by the rare earths and zirconium, a product yet to be made catalytically by all the other d-block catalysts to date. The group 4 complexes selectively make the secondary amine in yields of up to 84.1 equiv per complex, while the more coordinatively flexible f-block complexes can catalyze the N₂RR to make either HN(SiMe₃)₂ or N(SiMe₃)₃ amines from atmospheric dinitrogen in yields of up to 6.4 and 7.8 equiv per complex, respectively.

Kinetic and computational studies show that the bis(silyl)amine is the favored product when weak acid and trimethylsilyl electrophile are present. The ligand framework also helps to accommodate the group 1 counter cations needed to stabilize the reduced N₂-containing intermediates. DFT calculations on the titanium-catalyzed reaction find that the major functionalization steps are associated with N₂ adopting an end-on binding to just one of the metal centers, with the reducing group 1 alkali cations, rather than the second metal, stabilizing the distal N. This mechanism, involving the reduction of at least one metal in all the located intermediates, differs from the side-on mechanism reported by Arnold et al.¹⁹ in which reduction to U(III) was not considered or required. Further work is in progress to determine the nature of N₂ binding in the intermediates in the lanthanide-catalyzed reactions and if reduced f-block metal centers can play a role in the catalysis.

The N₂RR catalysis by **1Zr** is the first example of N₂RR for a zirconium complex to our knowledge. Differences in the reactivity of the group 4, lanthanide, and actinide metallacycles, coupled with theory, suggest that the N₂ coordination to electropositive metal cations that are easier to reduce enables sufficient activation of the bound N₂ in the cavity such that it can be functionalized. Furthermore, the metallacycles with smaller cavities, **1Ti**, **1Zr**, and unsolvated **1U**, make secondary silylamines, while the solvated Ln and U systems with larger cavities, **1Ln-THF** and **1U-THF**, make secondary or tertiary amines depending on the reagents. The differences between Na, K, and Rb as reductants show the importance of the choice of group 1 metal in dinitrogen reduction chemistry.

In addition to demonstrating N₂RR catalysis with the most abundant lanthanides, the formation of secondary amines using plentiful titanium under ambient conditions is notable. The ability to function in polar solvents suggests that the chemical reductant in these reactions could be replaced by a greener electrochemical source of electrons in the future.^{62,63}

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Requests for further information and resources should be directed to and will be fulfilled by the lead contact, Polly L. Arnold (pla@berkeley.edu).

Materials availability

The catalysts described are available upon request, but we might require a payment because of their need to be synthesized by researchers with suitable expertise in an appropriate facility.

Data and code availability

Crystallographic data in CIF format are available at <https://ccdc.cam.ac.uk/> under accession codes CCDC: 2181896–2181898, 2195247 and 2204194, 2210077–2210079, 2210081–2210083, and 2307225. Raw datasets for all other processed data in this paper are available at <https://doi.org/10.5061/dryad.3r2280gpz>. Full synthetic and characterization data for the compounds and catalysts described are available in the [supplemental information](#). Computational details and xyz coordinates of the computed intermediates are provided in [Scheme 4](#).

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.checat.2024.100964>.

ACKNOWLEDGMENTS

The synthetic work was supported by the National Science Foundation (CHE-2154369 to A.W. and P.L.A.) and the US Department of Energy (DOE) Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division in the Catalysis Program (J.L., M.H., and A.W.) and the Rare Earth Project in the Separations Program at the Lawrence Berkeley National Laboratory (F.Y.T.L., T.M.T., and P.L.A.). The Catalysis Laboratory in the DOE Catalysis Program also provided resources and instrumentation used in this work, and some diffraction data were collected at Beamline 12.2.1 of the Advanced Light Source, which is a DOE Office of Science User Facility. All of these DOE programs and facilities operate under contract no. DE-AC02-05CH11231. EPR spectroscopic studies were funded by the National Institutes of Health (NIH) (R35 grant 1R35GM126961 to R.D.B.). Raman spectra were acquired on instrumentation provided by the Liquid Sunlight Alliance, which is supported by the US DOE Office of Science, Office of Basic Energy Sciences, Fuels from Sunlight Hub, under award no. DE-SC0021266. Funding for CheXray comes from an NIH Shared Instrument Grant (S10-RR027172). We thank Hasan Celik for NMR spectroscopic support and discussions and the NIH for funding the UC Berkeley College of Chemistry NMR facility under grant no. 1S10RR016634-01. We thank The University of Manchester for its Computational Shared Facility (CSF3 and CSF4) and associated support services. We also thank the UK EPSRC for financial support through grant number EP/X042049/1. This project also received funding for some of the early synthetic work from the European Research

Council under the European Union's Horizon 2020 Research and Innovation Programme (grant agreement no. 740311 to P.L.A. and R.P.K.). We thank Amy Kynman for the graphical abstract artwork.

AUTHOR CONTRIBUTIONS

A.W., F.Y.T.L., M.H., J.L., T.M.T., R.P.K., and T.O. made and characterized the compounds and reactions and, with P.L.A., analyzed the data and wrote the manuscript. G.R. and R.D.B. collected and interpreted the EPR spectra. N.K. carried out and analyzed the mechanistic calculations and wrote the DFT part of the manuscript. P.L.A. raised the funding and conceptualized the project with contributions from A.W., F.Y.T.L., R.D.B., and N.K., and all authors reviewed and edited the manuscript. F.Y.T.L., M.H., and J.L. contributed equally.

DECLARATION OF INTERESTS

An international patent application (PCT/US23/74839) has been filed with the US receiving office.

Received: November 16, 2023

Revised: February 11, 2024

Accepted: March 13, 2024

Published: April 8, 2024

REFERENCES

- Kuriyama, S., and Nishibayashi, Y. (2021). Development of catalytic nitrogen fixation using transition metal complexes not relevant to nitrogenases. *Tetrahedron* 83, 131986. <https://doi.org/10.1016/j.tet.2021.131986>.
- Yandulov, D.V., and Schrock, R.R. (2003). Catalytic reduction of dinitrogen to ammonia at a single molybdenum center. *Science* 301, 76–78. <https://doi.org/10.1126/science.1085326>.
- Sekiguchi, Y., Arashiba, K., Tanaka, H., Eizawa, A., Nakajima, K., Yoshizawa, K., and Nishibayashi, Y. (2018). Catalytic Reduction of Molecular Dinitrogen to Ammonia and Hydrazine Using Vanadium Complexes. *Angew. Chem. Int. Ed.* 57, 9064–9068. <https://doi.org/10.1002/anie.201802310>.
- Yin, J., Li, J., Wang, G.-X., Yin, Z.-B., Zhang, W.-X., and Xi, Z. (2019). Dinitrogen Functionalization Affording Chromium Hydrazido Complex. *J. Am. Chem. Soc.* 141, 4241–4247. <https://doi.org/10.1021/jacs.9b00822>.
- Anderson, J.S., Rittle, J., and Peters, J.C. (2013). Catalytic conversion of nitrogen to ammonia by an iron model complex. *Nature* 501, 84–87. <https://doi.org/10.1038/nature12435>.
- Piascik, A.D., Li, R., Wilkinson, H.J., Green, J.C., and Ashley, A.E. (2018). Fe-Catalyzed Conversion of N₂ to N(SiMe₃)₃ via an Fe-Hydrazido Resting State. *J. Am. Chem. Soc.* 140, 10691–10694. <https://doi.org/10.1021/jacs.8b06999>.
- Fajardo, J., Jr., and Peters, J.C. (2017). Catalytic Nitrogen-to-Ammonia Conversion by Osmium and Ruthenium Complexes. *J. Am. Chem. Soc.* 139, 16105–16108. <https://doi.org/10.1021/jacs.7b10204>.
- Ashida, Y., Mizushima, T., Arashiba, K., Egi, A., Tanaka, H., Yoshizawa, K., and Nishibayashi, Y. (2023). Catalytic production of ammonia from dinitrogen employing molybdenum complexes bearing N-heterocyclic carbene-based PCP-type pincer ligands. *Nat. Synth.* 2, 635–644. <https://doi.org/10.1038/s44160-023-00292-9>.
- Arashiba, K., Miyake, Y., and Nishibayashi, Y. (2011). A molybdenum complex bearing PNP-type pincer ligands leads to the catalytic reduction of dinitrogen into ammonia. *Nat. Chem.* 3, 120–125. <https://doi.org/10.1038/nchem.906>.
- Tanaka, H., Arashiba, K., Kuriyama, S., Sasada, A., Nakajima, K., Yoshizawa, K., and Nishibayashi, Y. (2014). Unique behaviour of dinitrogen-bridged dimolybdenum complexes bearing pincer ligand towards catalytic formation of ammonia. *Nat. Commun.* 5, 3737. <https://doi.org/10.1038/ncomms4737>.
- Arashiba, K., Kinoshita, E., Kuriyama, S., Eizawa, A., Nakajima, K., Tanaka, H., Yoshizawa, K., and Nishibayashi, Y. (2015). Catalytic Reduction of Dinitrogen to Ammonia by Use of Molybdenum–Nitride Complexes Bearing a Tridentate Triphosphine as Catalysts. *J. Am. Chem. Soc.* 137, 5666–5669. <https://doi.org/10.1021/jacs.5b02579>.
- Eizawa, A., Arashiba, K., Tanaka, H., Kuriyama, S., Matsuo, Y., Nakajima, K., Yoshizawa, K., and Nishibayashi, Y. (2017). Remarkable catalytic activity of dinitrogen-bridged dimolybdenum complexes bearing NHC-based PCP-pincer ligands toward nitrogen fixation. *Nat. Commun.* 8, 14874. <https://doi.org/10.1038/ncomms14874>.
- Ashida, Y., Arashiba, K., Nakajima, K., and Nishibayashi, Y. (2019). Molybdenum-catalysed ammonia production with samarium diiodide and alcohols or water. *Nature* 568, 536–540. <https://doi.org/10.1038/s41586-019-1134-2>.
- Bora, D., Gayen, F.R., and Saha, B. (2022). Ammonia from dinitrogen at ambient conditions by organometallic catalysts. *RSC Adv.* 12, 33567–33583. <https://doi.org/10.1039/D2RA06156B>.
- Huang, W., Peng, L.-Y., Zhang, J., Liu, C., Song, G., Su, J.-H., Fang, W.-H., Cui, G., and Hu, S. (2023). Vanadium-Catalyzed Dinitrogen Reduction to Ammonia via a [V] NNH₂ Intermediate. *J. Am. Chem. Soc.* 145, 811–821. <https://doi.org/10.1021/jacs.2c08000>.
- Doyle, L.R., Wooles, A.J., Jenkins, L.C., Tuna, F., McInnes, E.J.L., and Liddle, S.T. (2018). Catalytic Dinitrogen Reduction to Ammonia at a Triamidoamine–Titanium Complex. *Angew. Chem. Int. Ed.* 57, 6314–6318. <https://doi.org/10.1002/anie.201802576>.
- Ghana, P., van Kruchten, F.D., Spaniol, T.P., van Leusen, J., Kögerler, P., and Okuda, J. (2019). Conversion of dinitrogen to tris(trimethylsilyl) amine catalyzed by titanium triamido-amine complexes. *Chem. Commun.* 55, 3231–3234. <https://doi.org/10.1039/C8CC09742A>.
- Sekiguchi, Y., Meng, F., Tanaka, H., Eizawa, A., Arashiba, K., Nakajima, K., Yoshizawa, K., and Nishibayashi, Y. (2018). Synthesis and reactivity of titanium- and zirconium-dinitrogen complexes bearing anionic pyrrole-based PNP-type pincer ligands. *Dalton Trans.* 47, 11322–11326. <https://doi.org/10.1039/C8DT02739K>.
- Arnold, P.L., Ochiai, T., Lam, F.Y.T., Kelly, R.P., Seymour, M.L., and Maron, L. (2020).

- Metallacyclic actinide catalysts for dinitrogen conversion to ammonia and secondary amines. *Nat. Chem.* 12, 654–659. <https://doi.org/10.1038/s41557-020-0457-9>.
20. Wells, J.A.L., Seymour, M.L., Suvova, M., and Arnold, P.L. (2016). Dinuclear uranium complexation and manipulation using robust tetraaryloxides. *Dalton Trans.* 45, 16026–16032. <https://doi.org/10.1039/C6DT02630C>.
21. Mansell, S.M., Kaltsoyannis, N., and Arnold, P.L. (2011). Small Molecule Activation by Uranium Tris(aryloxides): Experimental and Computational Studies of Binding of N₂, Coupling of CO, and Deoxygenation Insertion of CO₂ under Ambient Conditions. *J. Am. Chem. Soc.* 133, 9036–9051. <https://doi.org/10.1021/ja2019492>.
22. Mansell, S.M., Farnaby, J.H., Germeroth, A.I., and Arnold, P.L. (2013). Thermally stable uranium dinitrogen complex with siloxide supporting ligands. *Organometallics* 32, 4214–4222. <https://doi.org/10.1021/om4003957>.
23. Batov, M.S., del Rosal, I., Scopelliti, R., Fadaei-Tirani, F., Zivkovic, I., Maron, L., and Mazzanti, M. (2023). Multimetallic Uranium Nitride Cubane Clusters from Dinitrogen Cleavage. *J. Am. Chem. Soc.* 145, 26435–26443. <https://doi.org/10.1021/jacs.3c10617>.
24. Hasanayn, F., Holland, P.L., Goldman, A.S., and Miller, A.J.M. (2023). Lewis Structures and the Bonding Classification of End-on Bridging Dinitrogen Transition Metal Complexes. *J. Am. Chem. Soc.* 145, 4326–4342. <https://doi.org/10.1021/jacs.2c12243>.
25. Evans, W.J., Ulibarri, T.A., and Ziller, J.W. (1988). Isolation and x-ray crystal structure of the first dinitrogen complex of an f-element metal, [(C₅Me₅)₂Sm]₂N₂. *J. Am. Chem. Soc.* 110, 6877–6879. <https://doi.org/10.1021/ja00228a043>.
26. Turner, Z. (2015). Molecular pnictogen activation by rare earth and actinide complexes. *Inorganics* 3, 597–635.
27. Evans, W.J., and Lee, D.S. (2005). Early developments in lanthanide-based dinitrogen reduction chemistry. *Can. J. Chem.* 83, 375–384. <https://doi.org/10.1139/v05-014>.
28. Evans, W.J., Rego, D.B., and Ziller, J.W. (2006). Synthesis, structure, and ¹⁵N NMR studies of paramagnetic lanthanide complexes obtained by reduction of dinitrogen. *Inorg. Chem.* 45, 10790–10798. <https://doi.org/10.1021/ic061485g>.
29. Evans, W.J., Lorenz, S.E., and Ziller, J.W. (2009). Investigating metal size effects in the Ln₂(μ-η²-N₂) reduction system: Reductive reactivity with complexes of the largest and smallest trivalent lanthanide ions, La³⁺ and Lu³⁺. *Inorg. Chem.* 48, 2001–2009. <https://doi.org/10.1021/ic801853d>.
30. Rinehart, J.D., Fang, M., Evans, W.J., and Long, J.R. (2011). A N₂³⁻ Radical-Bridged Terbium Complex Exhibiting Magnetic Hysteresis at 14 K. *J. Am. Chem. Soc.* 133, 14236–14239. <https://doi.org/10.1021/ja206286h>.
31. MacDonald, M.R., Bates, J.E., Fieser, M.E., Ziller, J.W., Furche, F., and Evans, W.J. (2012). Expanding Rare-Earth Oxidation State Chemistry to Molecular Complexes of Holmium(II) and Erbium(II). *J. Am. Chem. Soc.* 134, 8420–8423. <https://doi.org/10.1021/ja303357w>.
32. Woen, D.H., Chen, G.P., Ziller, J.W., Boyle, T.J., Furche, F., and Evans, W.J. (2017). End-On Bridging Dinitrogen Complex of Scandium. *J. Am. Chem. Soc.* 139, 14861–14864. <https://doi.org/10.1021/jacs.7b08456>.
33. Ryan, A.J., Balasubramani, S.G., Ziller, J.W., Furche, F., and Evans, W.J. (2020). Formation of the end-on bound lanthanide dinitrogen complexes [(R₂N)₃Ln–N=N–Ln(NR₂)₃]²⁻ from divalent [(RN)₃Ln]¹⁻ salts (R = SiMe₃). *J. Am. Chem. Soc.* 142, 9302–9313. <https://doi.org/10.1021/jacs.0c01021>.
34. Mondal, A., Price, C.G.T., Tang, J., and Layfield, R.A. (2023). Targeted Synthesis of End-On Dinitrogen-Bridged Lanthanide Metallocenes and Their Reactivity as Divalent Synthons. *J. Am. Chem. Soc.* 145, 20121–20131. <https://doi.org/10.1021/jacs.3c07600>.
35. Fang, M., Bates, J.E., Lorenz, S.E., Lee, D.S., Rego, D.B., Ziller, J.W., Furche, F., and Evans, W.J. (2011). (N₂)₃⁻ Radical Chemistry via Trivalent Lanthanide Salt/Alkali Metal Reduction of Dinitrogen: New Syntheses and Examples of (N₂)²⁻ and (N₂)³⁻ Complexes and Density Functional Theory Comparisons of Closed Shell Sc³⁺, Y³⁺, and Lu³⁺ versus 4f⁹ Dy³⁺. *Inorg. Chem.* 50, 1459–1469. <https://doi.org/10.1021/ic102016k>.
36. Demir, S., Gonzalez, M.I., Darago, L.E., Evans, W.J., and Long, J.R. (2017). Giant coercivity and high magnetic blocking temperatures for N₂³⁻ radical-bridged dilanthanide complexes upon ligand dissociation. *Nat. Commun.* 8, 2144. <https://doi.org/10.1038/s41467-017-01553-w>.
37. Lv, Z.-J., Huang, Z., Zhang, W.-X., and Xi, Z. (2019). Scandium-Promoted Direct Conversion of Dinitrogen into Hydrazine Derivatives via N–C Bond Formation. *J. Am. Chem. Soc.* 141, 8773–8777. <https://doi.org/10.1021/jacs.9b04293>.
38. Fang, M., Lee, D.S., Ziller, J.W., Doedens, R.J., Bates, J.E., Furche, F., and Evans, W.J. (2011). Synthesis of the (N₂)³⁻ Radical from Y²⁺ and Its Protonolysis Reactivity To Form (N₂H₂)²⁻ via the [Y(N(SiMe₃)₂)₃/KC₈ Reduction System. *J. Am. Chem. Soc.* 133, 3784–3787. <https://doi.org/10.1021/ja1116827>.
39. Shephard, J.J., Berryman, V.E.J., Ochiai, T., Walter, O., Price, A.N., Warren, M.R., Arnold, P.L., Kaltsoyannis, N., and Parsons, S. (2022). Covalent bond shortening and distortion induced by pressurization of thorium, uranium, and neptunium tetrakis aryloxides. *Nat. Commun.* 13, 5923. <https://doi.org/10.1038/s41467-022-33459-7>.
40. Lateskey, S., Keddington, J., McMullen, A.K., Rothwell, I.P., and Huffman, J.C. (1985). Chemistry of sterically crowded aryloxide ligands. 5. Synthesis, structure, spectroscopic properties, and electrochemical behavior of group 4 metal derivatives containing bulky aryloxide ligands. *Inorg. Chem.* 24, 995–1001. <https://doi.org/10.1021/ic00201a007>.
41. David, F.H. (2008). About low oxidation states, hydration and covalence properties of f elements. *Radiochim. Acta* 96, 135–144. <https://doi.org/10.1524/ract.2008.1470>.
42. Evans, W.J. (2016). Tutorial on the role of cyclopentadienyl ligands in the discovery of molecular complexes of the rare-earth and actinide metals in new oxidation states. *Organometallics* 35, 3088–3100. <https://doi.org/10.1021/acs.organomet.6b00466>.
43. Bae, D.Y., Lee, G., and Lee, E. (2021). Fixation of Dinitrogen at an Asymmetric Binuclear Titanium Complex. *Inorg. Chem.* 60, 12813–12822. <https://doi.org/10.1021/acs.inorgchem.1c01050>.
44. Komori, K., Oshita, H., Mizobe, Y., and Hidai, M. (1989). Preparation and properties of molybdenum and tungsten dinitrogen complexes. 25. Catalytic conversion of molecular nitrogen into silylamines using molybdenum and tungsten dinitrogen complexes. *J. Am. Chem. Soc.* 111, 1939–1940. <https://doi.org/10.1021/ja00187a092>.
45. Duman, L.M., and Sita, L.R. (2017). Closing the Loop on Transition-Metal-Mediated Nitrogen Fixation: Chemoselective Production of HN(SiMe₃)₂ from N₂, Me₃SiCl, and X–OH (X = R, R₃Si, or Silica Gel). *J. Am. Chem. Soc.* 139, 17241–17244. <https://doi.org/10.1021/jacs.7b08859>.
46. Manriquez, J.M., and Bercaw, J.E. (1974). Preparation of a dinitrogen complex of bis(pentamethylcyclopentadienyl)zirconium(II). Isolation and protonation leading to stoichiometric reduction of dinitrogen to hydrazine. *J. Am. Chem. Soc.* 96, 6229–6230. <https://doi.org/10.1021/ja00826a071>.
47. Knobloch, D.J., Lobkovsky, E., and Chirik, P.J. (2010). Dinitrogen cleavage and functionalization by carbon monoxide promoted by a hafnium complex. *Nat. Chem.* 2, 30–35. <https://doi.org/10.1038/nchem.477>.
48. Kim, S., Loose, F., and Chirik, P.J. (2020). Beyond Ammonia: Nitrogen–Element Bond Forming Reactions with Coordinated Dinitrogen. *Chem. Rev.* 120, 5637–5681. <https://doi.org/10.1021/acs.chemrev.9b00705>.
49. Hanna, T.E., Lobkovsky, E., and Chirik, P.J. (2009). Dinitrogen Complexes of Bis(cyclopentadienyl) Titanium Derivatives: Structural Diversity Arising from Substituent Manipulation. *Organometallics* 28, 4079–4088. <https://doi.org/10.1021/om900282u>.
50. Bratsch, S.G., and Lagowski, J.J. (1985). Lanthanide thermodynamic predictions. 7. Thermodynamics of 2+, 3+, and 4+ aquo ions and standard electrode potentials at 298.15 K. *J. Phys. Chem.* 89, 3317–3319. <https://doi.org/10.1021/j100261a031>.
51. Bratsch, S.G., and Lagowski, J.J. (1986). Actinide thermodynamic predictions. 3. Thermodynamics of compounds and aquo-ions of the 2+, 3+, and 4+ oxidation states and standard electrode potentials at 298.15 K. *J. Phys. Chem.* 90, 307–312. <https://doi.org/10.1021/j100274a021>.
52. Kawaguchi, H., and Matsuo, T. (2004). Aryloxide-based multidentate ligands for early transition metals and f-element metals. *J. Organomet. Chem.* 689, 4228–4243. <https://doi.org/10.1016/j.jorganchem.2004.08.004>.
53. Falcone, M., Chatelain, L., Scopelliti, R., Zivković, I., and Mazzanti, M. (2017). Nitrogen reduction and functionalization by a

- multimetallc uranium nitride complex. *Nature* 547, 332–335. <https://doi.org/10.1038/nature23279>.
54. Suzuki, S., Ishida, Y., Kameo, H., Sakaki, S., and Kawaguchi, H. (2020). Counterion Dependence of Dinitrogen Activation and Functionalization by a Diniobium Hydride Anion. *Angew. Chem. Int. Ed.* 59, 13444–13450. <https://doi.org/10.1002/anie.202006039>.
55. Grubel, K., Brennessel, W.W., Mercado, B.Q., and Holland, P.L. (2014). Alkali Metal Control over N–N Cleavage in Iron Complexes. *J. Am. Chem. Soc.* 136, 16807–16816. <https://doi.org/10.1021/ja507442b>.
56. Marcus, Y. (1985). Thermodynamic functions of transfer of single ions from water to nonaqueous and mixed solvents: Part 3 - Standard potentials of selected electrodes. *Pure Appl. Chem.* 57, 1129–1132. <https://doi.org/10.1351/pac198557081129>.
57. Lv, Z.-J., Wei, J., Zhang, W.-X., Chen, P., Deng, D., Shi, Z.-J., and Xi, Z. (2020). Direct transformation of dinitrogen: synthesis of N-containing organic compounds via N–C bond formation. *Natl. Sci. Rev.* 7, 1564–1583. <https://doi.org/10.1093/nsr/nwaa142>.
58. Tumanskii, B., Karni, M., and Apeloig, Y. (2012). Persistent and Stable Silyl Radicals. In *Encyclopedia of Radicals in Chemistry, Biology and Materials*. <https://doi.org/10.1002/9781119953678.rad066>.
59. West, R., Ishikawa, M., and Bailey, R.B. (1966). Anionic Rearrangement of Hydrazines. II.1 Isomers of Bis(organosilyl)hydrazines. *J. Am. Chem. Soc.* 88, 4648–4652. <https://doi.org/10.1021/ja00972a022>.
60. Siedschlag, R.B., Bernales, V., Vogiatzis, K.D., Planas, N., Clouston, L.J., Bill, E., Gagliardi, L., and Lu, C.C. (2015). Catalytic silylation of dinitrogen with a dicobalt complex. *J. Am. Chem. Soc.* 137, 4638–4641. <https://doi.org/10.1021/jacs.5b01445>.
61. Chalkley, M.J., Drover, M.W., and Peters, J.C. (2020). Catalytic N₂-to-NH₃ (or -N₂H₄) Conversion by Well-Defined Molecular Coordination Complexes. *Chem. Rev.* 120, 5582–5636. <https://doi.org/10.1021/acs.chemrev.9b00638>.
62. Qing, G., Ghazfar, R., Jackowski, S.T., Habibzadeh, F., Ashtiani, M.M., Chen, C.-P., Smith, M.R., and Hamann, T.W. (2020). Recent Advances and Challenges of Electrocatalytic N₂ Reduction to Ammonia. *Chem. Rev.* 120, 5437–5516. <https://doi.org/10.1021/acs.chemrev.9b00659>.
63. Garrido-Barros, P., Derosa, J., Chalkley, M.J., and Peters, J.C. (2022). Tandem electrocatalytic N₂ fixation via proton-coupled electron transfer. *Nature* 609, 71–76. <https://doi.org/10.1038/s41586-022-05011-6>.