



HAL
open science

Metallacyclic actinide catalysts for dinitrogen conversion to ammonia and secondary amines

Polly Arnold, Tatsumi Ochiai, Francis Lam, Rory Kelly, Megan Seymour, Laurent Maron

► **To cite this version:**

Polly Arnold, Tatsumi Ochiai, Francis Lam, Rory Kelly, Megan Seymour, et al.. Metallacyclic actinide catalysts for dinitrogen conversion to ammonia and secondary amines. *Nature Chemistry*, 2020, 12 (7), pp.654-659. <10.1038/s41557-020-0457-9>. <hal-03885963>

HAL Id: hal-03885963

<https://hal.science/hal-03885963v1>

Submitted on 24 Sep 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

UC Berkeley

UC Berkeley Previously Published Works

Title

Metallacyclic actinide catalysts for dinitrogen conversion to ammonia and secondary amines

Permalink

<https://escholarship.org/uc/item/98h4k4mw>

Journal

Nature Chemistry, 12(7)

ISSN

1755-4330

Authors

Arnold, Polly L
Ochiai, Tatsumi
Lam, Francis YT
[et al.](#)

Publication Date

2020-07-01

DOI

10.1038/s41557-020-0457-9

Peer reviewed

Metallacyclic actinide catalysts for dinitrogen conversion to ammonia and secondary amines

Polly L. Arnold,^{1,2} Tatsumi Ochiai,^{2,†} Francis Y. T. Lam,^{2,†} Rory P. Kelly,^{2,†} Megan L. Seymour,^{2,†} Laurent Maron³

Chemists have spent over a hundred years trying to make ambient temperature/pressure catalytic systems that could convert atmospheric dinitrogen to ammonia, or to directly to amines. A handful of successful d-block metal catalysts have been developed in recent years, but even binding of dinitrogen to an f-block metal cation is extremely rare. Here we report the first f-block complexes that can catalyse the reduction and functionalisation of molecular dinitrogen, and the first catalytic conversion of molecular dinitrogen to a secondary silylamine. Simple bridging ligands assemble two actinide metal cations into narrow dinuclear metallacycles that can trap the diatom while electrons from an externally-bound group 1 metal, and protons or silanes, are added enabling N₂ to be functionalised with modest but catalytic yields of six equivalents of secondary silylamine per molecule at ambient temperature and pressure.

Many complexes of the d-block metals can bind the abundant dinitrogen molecule, but the conversion to products is very difficult, and only a few are capable of catalytic conversion. The most successful catalysts are based on Mo or Fe^{1,2,3,4,5,6,7,8}, and convert the bound dinitrogen to NH₃ or N(SiMe₃)₃, using compatible sources of reducing equivalents and protons or silyl electrophiles (e.g. KC₈ powder and lutidinium borates or Me₃SiCl)^{9,10}. The use of soluble metal catalysts offers direct routes to other functionalised organo-nitrogen molecules and further insight into the workings of the exceptional heterogeneous Haber-Bosch catalyst or the low-energy nitrogenase enzymes that directly make ammonia.^{11,12,13,14,15,16,17}

An emerging key feature of some of the most successful homogeneous systems is the ability of the complex to incorporate alkali metal cations that bring the reducing electrons to the nitrogen centres, providing additional coulombic interactions, and the capacity of the resulting multi-metallic framework to flex sufficiently to enable the N₂ coordination mode to change during reduction.^{18,19,20,21,22}

Binding of dinitrogen by any f-block metal ion is extremely rare.^{23,24} The eight known actinide-dinitrogen complexes were all made by exploiting the strongly reducing

¹ pla@berkeley.edu

² EaStCHEM School of Chemistry, The University of Edinburgh, Joseph Black Building, The King's Buildings, Edinburgh, EH9 3FJ, UK. Current address: Department of Chemistry, University of California, Berkeley, CA 94720, US.

³ Université de Toulouse and CNRS, INSA, UPS, CNRS, UMR 5215, LPCNO, 135 Avenue de Rangueil, F-31077 Toulouse, France.

capacity of the U^{III} ion.^{25,26,27,28,29,30} Interestingly, in the development of the exceptionally successful, heterogeneous Haber-Bosch catalyst that comprises supported iron with a potassium promoter, uranium was found to be equally active.³¹ No thorium dinitrogen complexes have been reported, and only the recently reported cluster $K_4U^V_2(OR)_6(\mu-E)(\mu-\eta^2:\eta^2-N_2)$ ($R = OSi(O^tBu)_3$, $E = N, O$) has achieved the six-electron reduction necessary to convert N_2 to ammonia,^{32,33} giving a 77 % yield when treated with excess H^+ . The only other actinide complex to achieve a N_2 reduction of more than two electrons is $[K(dme)_4][\{K(dme)(calix[4]tetrapyrrole)U\}_2(\mu-NK)_2]$, formed as part of a mixture of μ -oxo products, and disordered in the solid-state, but also characterised as a U^V/U^{IV} nitride by near-infrared spectroscopy.³⁴ The An^{IV} oxidation state dominates early actinide chemistry, and reduced thorium complexes are extremely difficult to stabilise.³⁵ A Th- NH_2 group was reported in the complex $K(dme)_4[Th(NH_2)\{(OC_6H_2^tBu_2,Me_4)_2CH_2\}_2(\kappa^1-dme)]$, formed from storing a mixture of a Th^{IV} aryloxide and the reductant potassium naphthalenide for two days under N_2 ; the source of the H atoms was not determined.³⁶

Here we present robust, dinuclear f-block complexes that can bind dinitrogen and mediate its reduction and functionalisation to ammonia, and the first homogeneous catalytic conversion of dinitrogen to a secondary silylamine.

Results and Discussion

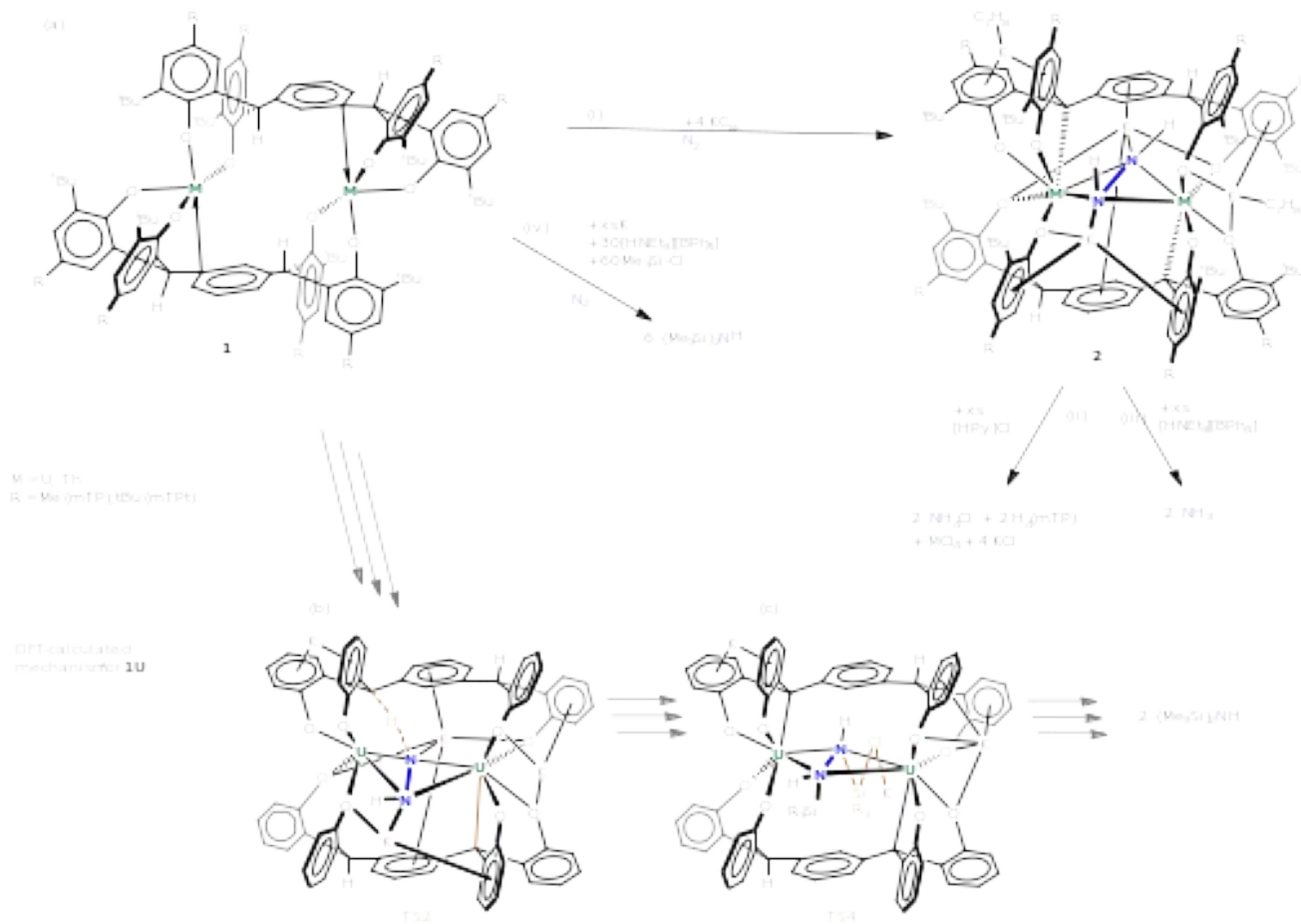


Figure 1 The activation, protonation, and silylation of dinitrogen by $M_2(mTP)_2$ complexes **1** and **2**. (a) The reactions are successful for two different actinide (An) metal cations, thorium (**1Th**) or uranium (**1U**) and different ligand alkyl (R) substitution patterns (R = Me, ^tBu). Key steps are: (i) reduction by potassium under a dinitrogen atmosphere with concomitant insertion of the 4-electron reduced N_2 into two ligand benzyl C-H bonds, and formation of two new M-C ligand bonds; (ii) release of ammonia (as its ammonium salt) and destruction of **1/2** by addition of a strong acid (pK_a of $[HPy]^+ = 5.25$); (iii) release of ammonia by addition of a weak acid (pK_a of $[HNEt_3]^+ = 10.75$); (iv) addition of a trimethylsilyl-containing electrophile and weak acid to reform the ligand C-H bond allows the catalytic formation of hexamethyldisilazane, HN^H . Solvent = benzene. Selected pictures of the computed transition states for (b) the second NH bond forming step (to form intermediate at $-51.5 \text{ kcal mol}^{-1}$ below starting materials energy, and (c) the second N-Si bond forming step (to form the final intermediate F at $-92.6 \text{ kcal mol}^{-1}$ below starting energy. Hydrocarbyl groups omitted for clarity.

The anion of the *meta*-tetraphenol-arene $H_4(mTP)$ binds Lewis acidic metal cations *via* strong M-O bonds;³⁷ 1:1 reactions with U^{IV} or Th^{IV} form rectangular metallacyclic $M_2(mTP)_2$ (**1**) (M = U, Th), which are notable by the narrow cavity (**Figure 1**). In the solid-state (see below), the coordinatively unsaturated metal cations in **1U** are positioned in the space formed by the two bridging arenes; additional electrostatic interactions with the arenes are suggested by spectroscopies.

When the strong reductant potassium (4 equivs or more) is added to a solution of **1** (either U or Th) under a dinitrogen atmosphere, the dissolved N_2 is bound, reduced, and

protonated to afford the multimetallic hydrazine adduct $K_4[M_2(\mu-N_2H_2)(mTP^{R-})_2]$ (**2**) (M = U **2U**, Th **2Th**), **Figure 1(ii)**. The bound dinitrogen forms one central hydrazido $[N_2H_2]^{2-}$ ligand with each N-H bond formed from the formal deprotonation of the (*mTP*) ligand at the benzylic position, which also generates a new M-C bond to (*mTP*). Charge balance is achieved by the inclusion of four K^+ counter-cations. The molecular structures showing the slot in **1U** and the tetra-reduced and doubly-protonated N_2 in the slot in **2U** are shown in **Figure 2a** and **b** respectively and discussed below.

It is highly unusual to be able to isolate the four-electron reduced- N_2 intermediate **2**;³² either **1** or **2** can reduce the N_2 all the way to ammonia, **Figure 1(ii)** and **(iii)**. **Table 1** (entries 1-3) contains a variety of conditions under which **1** generates ammonia from N_2 . Surprisingly, either **1U** or **1Th** congeners can reduce N_2 to ammonia (entries 1, 2) in spite of their remarkably different $M^{IV/III}$ redox potentials, but the use of sodium instead of potassium as a reductant does not yield any ammonia, (**supplementary Table 1**, entry 6). As with other previously reported metal- N_2 complexes and catalysts, the addition of acids such as pyridinium chloride, or the weaker $[HNEt_3][BPh_4]$, form up to 1.1 equivalents of NH_3 per mole of **1M**, and deuterated acids afford mixed H/D products (**supplementary Figures 5-8**) supporting the role of the ligand C-H in the functionalisation.

The addition of an excess of reductant and electrophile provides the first, albeit modest, catalytic conversions of N_2 by an f-block compound, and when a mixture of weak acid and chlorosilane are used, the first catalytic conversion of molecular N_2 to a secondary amine, hexamethyldisilazane, $HN(SiMe_3)_2$. Up to 6.4 equivalents of the silylamine can be made starting from **1U** (**Figure 1(iv)** and **Table 1**, entry 4). Complexes **1** are very poorly soluble; the addition of potassium to the start the reduction of **1** that brings it into solution prior to the addition of the other reagents results yields fewer side products such as coupled SiR_3 radical products. There is a very small amount of the tris silylamine $N(SiMe_3)_3$ formed in the catalysed reactions, a by-product which could arise from a secondary reaction of the $HN(SiMe_3)_2$ with potassium and the excess Me_3SiCl . Ammonia or silylamine can be made from **1** or **2**, so it is apparent that **1** is a pre-catalyst but we cannot unambiguously determine the nature of the reduced species formed from **1** that may be the catalytically active complex.

Table 1 Conversion of dinitrogen to ammonia or a secondary amine by the $M_2(mTP)_2$ complexes **1 ($M = U, Th$).**

entry	Complex	H/SiMe ₃ source (equiv.)	Electron source (equiv.)	Reaction conditions ^(a)	Equivalents of desired product (NH ₃ or HN(SiMe ₃) ₂)	Observation
1	1U	[HNEt ₃][BPh ₄] (20)	K (79)	Mixture stirred for 44 h in total, then volatiles vacuum distilled onto 2 M HCl in Et ₂ O. NaO ^t Bu (100 eq.) and THF added to the residues in the reaction flask and stirred for 1 h, then volatiles vacuum distilled into 2 M HCl in Et ₂ O.	0.78	
2	1Th	[HPy]Cl (13)	KC ₈ (4)	Mixture stirred for 16 h before quenching with strong acid.	0.90	1Th is also competent for NH ₃ synthesis
3	1Th^t	[HPy]Cl (56)	KC ₈ (4)	Mixture stirred for 16 h in toluene rather than benzene.	1.1	
4	1U	Me ₃ SiCl (60) [HNEt ₃][BPh ₄] (30)	K (85)	Mixture stirred for 48 h in total; volatiles vacuum distilled into an empty ampoule for analysis.	6.4	A combination of excess weak acid and SiR ₃ electrophile in benzene affords the best yields, as determined by GC-MS

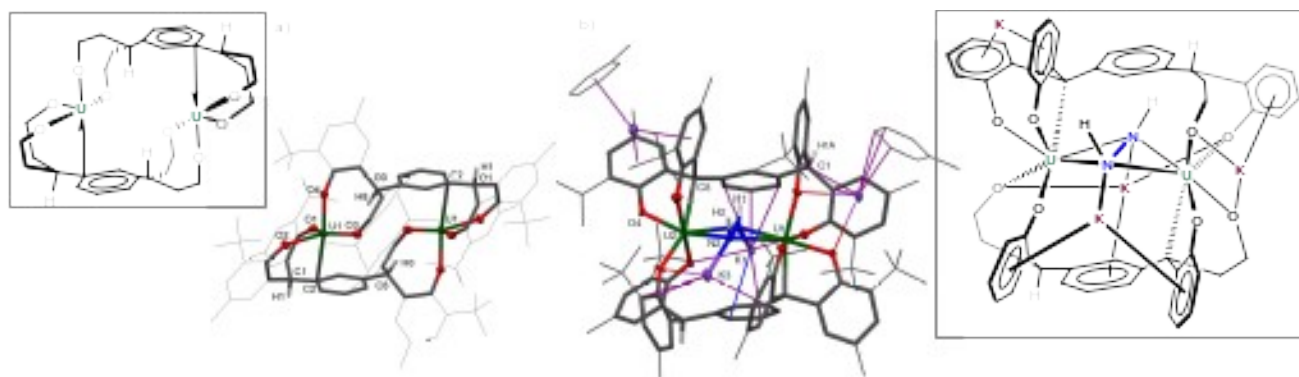


Figure 2 Solid-state structures of (a) **1U and (b) **2U**, determined by single crystal X-ray diffraction studies.** The inset in each contains a drawing of the core of the molecular structure. The structures of **1U-diox**, **1U^t-thf**, **1Th-diox**, **1Th-py**, and **3U** are discussed in the SI. Displacement ellipsoids where shown are at 50 % probability, peripheral groups are drawn as stick and wireframe. Lattice solvent and peripheral hydrogen atoms omitted for clarity. Selected distances (Å) and angles (°) For **1U**: U-U 6.573 Å, U-O_{ave.} 2.13; U1-C2 2.857(3); O3-U1-O4 84.76(8); O1-U1-O2 87.15(9). For **2U**: U1-U2 4.642; N1-N2 1.491(5); U-O_{ave.} 2.30; U1-C58 2.557(4); O3-U2-O4 80.19(13).

The reactions produce ammonia in the presence of a weak acid and reductant that only react slowly with each other. When a different electrophile is added, here SiR₃⁺, the secondary silylamine HN(SiMe₃)₂ is formed in yields of up to 6.4 equiv. per molecule of **1**. All three reagents, reductant K, weak acid [HNEt₃][BPh₄] and silane Me₃SiCl are sufficiently mutually unreactive in arene solutions over the timescale of the reaction with **1**. Comments for each entry explain the effect of different conditions. Comparisons of NMR spectroscopic and GC-MS spectrometric analysis of the N-containing products confirm the high selectivity for the product HN(SiMe₃)₂. Additional entries in supplementary Table 1 show the effect of different reagents, as well as control reactions. The N₂ silylation by **1U**, K, and ClSiMe₃ was identified as the most promising catalytic system and datapoints have been repeated up to eight times. A small amount of N(SiMe₃)₃ by-product is observed in the

catalytic reactions. It is never more than 0.5 equiv. and could form from secondary reactions of the $\text{HN}(\text{SiMe}_3)_2$ product with K metal, then ClSiMe_3 or from a reduced An-N_2 adduct that has not yet been protonated. Solvent = benzene, temperature = 298 K. (a) Suspension of **1** and K stirred for between 30 mins and 24 h, then either acid or both acid and electrophile added and the mixture stirred for an additional 20–24 h.

Both **1U** and the key intermediate that demonstrates the formation of the first N-H bond arising from ligand deprotonation have been crystallographically characterised. In **1U**, **Figure 2a**, each uranium(IV) cation is approximately trigonal bipyramidal in the solid-state, with four M-aryloxo bonds to two **mTP** ligands; the coordinatively unsaturated U^{IV} cations are positioned inside the metallacycle, at either end of the slot-shaped cavity. The U-U separation is 6.573 Å. A further U-C close contact to the π -electron system of the central arene ring is suggested; the distance to the closest carbon is 2.857(3) Å. Arene-interactions with U^{IV} centres are very rare.³⁸ The solvates **1M-sol** (supplementary section 4C) show a similar narrow cavity, but the octahedrally-coordinated metals face away from the slot. In **2U**, **Figure 2b**, the slot contains a side-on bound diazenido $[\text{N}_2\text{H}_2]^{2-}$ ligand with pseudo-pyramidal nitrogens and an N-N distance 1.491(5) Å, which is similar, within s.u.s, as in hydrazine (1.46 Å). Four incorporated potassium cations form electrostatic interactions with ligand arenes, and the N-deprotonated benzylic carbon of each ligand form new, long U-C bonds (average 2.645 Å).

The ^{15}N NMR chemical shift of $\text{K}_4[\text{U}_2(\mu\text{-}^{15}\text{N}_2\text{H}_2)(\text{mTP}^-)_2]$ **$^{15}\text{N-2U}$** (made from ^{15}N -enriched dinitrogen, supplementary Figure 12) at -4059.6 ppm is strongly shifted due to the paramagnetic uranium centres, and very different to that in $[\text{N}_2]^{2-}$ -bound $[(\text{Mes}_3\text{SiO})_3\text{U}]_2(\mu^2, \eta^2, \eta^2\text{-N}_2)$ (+4213 ppm) (Mes = $\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$).^{30,39} The absorption in FTIR spectra of **2U** at 3382 cm^{-1} is assigned as an N-H stretch, in agreement with that for $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{ZrMe}]_2(\mu^2, \eta^2, \eta^2\text{-N}_2\text{H}_2)$.¹² Raman spectra of **2U** have a weak absorption at 1138 cm^{-1} assigned as the symmetrical, singly bonded N-N stretch (supplementary Figure 21, 22), similar to the other uranium-bound $[\text{N}_2]^{4-}$ complex (1100 cm^{-1})^[33] and hydrazine (1111 cm^{-1}). The N-N stretch assigned to the ^{15}N isotopomer is shifted to 1097 cm^{-1} (expected value from reduced mass calculations cf. ^{14}NN stretch = 1092 cm^{-1}). The ^{15}N NMR spectrum shows a strongly paramagnetically shifted resonance at -4059.6 ppm. The ^1H NMR spectra of solutions of **2** and **$^{15}\text{N-2}$** that have been quenched with pyridinium chloride show the ammonium H resonance at 7.42 ppm with $^1J_{\text{NH}} = 51\text{ Hz}$, or $^1J_{\text{NH}} = 73\text{ Hz}$ due to ^{14}N ($I=1$) or ^{15}N ($I=1/2$) respectively, supplementary Figure 14.

We suggest that when dinitrogen enters the slot in $M_2(mTP)_2$ (**1**), coordination to the two Lewis acidic M activates it towards reduction by incoming alkali metals. The N-N bond length in N_2 is 1.09 Å, which would give U-N distances of 2.74 Å if N_2 was to bind end-on in **1U**. These are longer than the two known end-on U- N_2 complexes (U-N 2.492(10) Å in $(C_5Me_5)_3U(\eta^1-N_2)$;^[28] 2.24 Å in $([Ar]^tBuN)_3U-N_2-Mo(N^tBu[Ph])_3$)^[26] but close to the covalent radii of U + N (2.67 Å),⁴⁰ suggesting a Van der Waals interaction could be possible; molecular modelling studies show how it can fit, supplementary Figure 41.

Density functional theory (DFT) calculations of the reactions have been carried out and, in agreement with solution spectral analyses of **1**, find no intermediate for the N_2 binding. Two exothermic sequential steps for addition of two potassium atoms are found, with transition states showing multiple stabilising K-arene interactions. Potassium is a large, strong reductant, $E_{1/2}$ ca -3V vs ferrocene, the electrostatic interactions presumably helping multiple reductions of the bound N_2 to occur without excessive charge build-up.¹⁹

In **C** (reduced by four equiv. K, SI) an N-N single bond still remains and the two in-plane valence electron pairs of each nitrogen atom binds to either the uranium (the one orthogonal to the N-N bond inducing a three-center-two-electron interaction) or the potassium cations (the lone pair pointing in the opposite direction to the bond in stabilized by the interaction with the two potassium). The third is a lone pair orthogonal to the equatorial plane define by the two U and the two N, that π lone pair is not interacting with any potassium or uranium centers. This lone pair is oriented towards the ligand such that it can deprotonate the benzylic C-H bond. A low-lying transition state (**TS1**) was located with an associated barrier of 11.5 kcal/mol. At this transition state, there is no assistance from the uranium center and it is better described as a simple proton transfer with an almost linear geometry. The C-H bond is almost already broken and the N-H bond not yet fully formed (C-H 1.40 Å; N-H 1.41Å). Following the intrinsic reaction coordinate, it yields intermediate **D** where one nitrogen is protonated (i.e. no longer potassiated) and the carbon bonded to the uranium. Therefore, the overall bonding situation in **D** is similar to that in **C**, with one N-N bond, one N-H bond at each N, and an in-plane lone pair interacting with U and K. In both **C** and **D**, the one π lone pair on each nitrogen points in the opposite direction so that the second deprotonation will take place on the opposite side of the N-N unit. This intermediate appears to be stabilized by 13.8 kcal/mol. A similar proton reaction can occur at the second nitrogen atom. A second proton transfer transition state was located with an activation barrier of 11.5 kcal/mol (similar to the one for the first protonation). Figure 1(c) shows a transition state TS2 in the computed scheme (supplementary Figure 26) for the second of the two deprotonations of (*mTP*) at the benzylic positions that point into the cavity, by the four-electron alkali-metal reduced $[N_2]^{4-}$ unit which is now sufficiently basic.^{6,41,42}

This affords the bound hydrazine ion $\text{N}_2\text{H}_2^{2-}$ that we can fully characterise as ligand-metallated **2M**. Either **1U** or **1Th**, complexes of metals which normally have very different redox chemistry, react with excess K metal and dinitrogen in approximately the same manner, underlining the importance of the K_4M_2 combination. Reactions with added crown ethers (that abstract the K^+ from the molecule) fail to reduce N_2 , see supplementary section 6.

The addition of a weak acid such as $[\text{HNEt}_3][\text{BPh}_4]$ can then form ammonia and reprotonate the benzylic C-H groups of **1**. The reagent $[\text{HNEt}_3][\text{BPh}_4]$ is very poorly soluble in the reaction mixture, reducing undesirable side-reactions with the K reductant, and not damaging the strong M-aryloxide bonds. The resulting effective H atom transfer is also essentially the same as the coupled proton and electron-transfer (PCET) process that facilitates oxygen reduction catalysis in industrial and enzyme catalysts, and has been proposed to yield more efficient transition metal catalysts.⁴³ Pincer ligands with unsaturated backbones that can react reversibly, in concert with the metal, with H atom sources have been widely used in catalysis,⁴⁴ but these metallacycles differ in two aspects. Firstly, the metals are strongly bound by the four large O-donor aryloxides and have only very limited access to a reagent. Secondly, the ligands place the CH groups perfectly in line with the small molecule bound in the cavity, in contrast to the more distant E-H protons available to metal-coordinated small molecules in pincer systems.^{45,46}

Because the first N-H bond is formed intramolecularly, further reactions with an external chlorosilane reagent are of greater interest as this provides a new one-pot route to secondary silylamines from dinitrogen. Two stepwise routes using external reagents have recently been reported to yield differently substituted silylamines, i.e. $(\text{Me}_3\text{Si})\text{N}\{(\text{SiMe}_2\text{CH}_2)_2\}$ or $(\text{Me}_3\text{Si})_2\text{N}(\text{SiMe}_2\text{Ph})$, from the terminal N atom of Mo-bound N_2 , and also may have the potential to be developed into catalytic cycles.^{47,48,49} The silylation step was computed from complex **2M**, using SiH_3Cl as a model due to the size of the calculation. A transition state (TS3) was located for the silylation of nitrogen with a barrier of 16.2 kcal/mol. The reaction looks like a nucleophilic substitution with the transition state containing a trigonal bipyramidal silicon geometry with a long, apical Si-Cl distance of 2.20 Å and a newly forming Si-N in the equatorial position, Si-N = 1.90 Å. Interestingly, there is a potassium chlorine interaction (K-Cl distance of 2.82 Å), indicating nucleophilic assistance in the reaction. Figure 1(d) shows one of the N-Si bonds forming transition states for the silylamine synthesis. The first two silylations that form a trapped $[\text{R}_3\text{SiNNSiR}_3]^{2-}$ are computed to be exothermic, and interestingly suggest additional stabilising K-Cl interactions with the departing chloride. The second silylation has a slightly higher energy barrier of 17.0 kcal mol⁻¹. Section 13 of the SI contains a full discussion of the computed mechanism.

In summary, robust M_2L_2 metallacycles formed from two large, under-coordinated actinide M^{IV} cations and two rigid arene-bridged aryloxy ligands are capable of binding N_2 inside the cavity, enabling reducing alkali metals to reduce it by four electrons. The bridging ligands can also provide two protons to the reduced N_2 and may be key to controlling product formation. Thus, in the presence of alkali metal reductant, **1** converts dinitrogen to ammonia or secondary silylamines at ambient temperature and pressure, and when both reductant and electrophiles (H^+ and SiR_3^+) are present in excess, provides the first catalytic conversion of N_2 to a secondary silylamine. Unusually, these complexes are not reliant on the reducing power of An^{III} , which is the traditional reactivity used by all f-block systems to date for the reductive activation of N_2 and other small molecules. This now establishes thorium as another metal capable of mediating dinitrogen functionalisation, and suggests that other (and non-radioactive) electropositive M^{IV} cations might show similar chemistry. The strong actinide-aryloxy bonds and stable +4 oxidation state mean that the products can be released without decomposing the complex, enabling the catalysis to proceed at ambient temperatures and pressures. Work is in progress to identify the kinetic regime in which improved turnovers of dinitrogen to ammonia or secondary silylamines could be achieved, and whether group 4 analogues of **1** can be active catalysts.

Methods

Syntheses of the homoleptic, dinuclear metal aryloxide complexes $M_2(mTP)_2$ **1** (M = U, Th) are from combining hydrocarbon solutions of equimolar metallacyclic amide (uranium or thorium) and the arene-bridged tetraphenol $H_4(mTP)$ under an inert (dinitrogen or argon) atmosphere. The complexes can be isolated as powders by work-up from non-coordinating solvents. Reactions to form **1** in donor solvents afford solvates in which the two metals are *pseudo*-octahedral and coordinatively saturated, **1-sol**.

Reductions of complexes **1** by an alkali metal under a dinitrogen atmosphere yield the isolable reduced and protonated dinitrogen complex $K_4[M_2(\mu-N_2H_2)(mTP^{R-})_2]$ **2**, and in the presence of a source of H cation or source of trimethylsilyl cation or radical (the electrophile) generates ammonia or disilylamine respectively. Product samples were analysed by NMR spectroscopy (usually with an internal standard to allow yields to be determined) and/or gas chromatography mass spectrometry (GC-MS). The choice of actinide (U or Th) or small variations in ligand substitution patterns, have very little effect on the reactivity. Isolation of the potassium ions from the cavity in **2** stops the N_2 reductive functionalisation chemistry. Deprotonation instead of reduction of **1U** with a potassium base KCH_2Ph also deprotonates the (*mTP*) benzylic C-H groups forming $[K(THF)_6][K(THF)_2U_2(mTP^-)_2]$ **3U** with no N_2 -binding.

References

- 1 Yandulov, D. V. & Schrock, R. R. Catalytic reduction of dinitrogen to ammonia at a single molybdenum center. *Science* **301**, 76-78 (2003).
- 2 Kuriyama, S. Catalytic formation of ammonia from molecular dinitrogen by use of dinitrogen-bridged dimolybdenum-dinitrogen complexes bearing PNP-pincer ligands: remarkable effect of substituent at PNP-pincer ligand. *J. Am. Chem. Soc.* **136**, 9719-9731 (2014).
- 3 Anderson, J. S., Rittle, J. & Peters, J. C. Catalytic conversion of nitrogen to ammonia by an iron model complex. *Nature* **501**, 84 (2013).
- 4 Siedschlag, R. B. *et al.* Catalytic silylation of dinitrogen with a dicobalt complex. *J. Am. Chem. Soc.* **137**, 4638-4641 (2015).
- 5 Gao, Y., Li, G. & Deng, L. Bis(dinitrogen)cobalt(-1) Complexes with NHC Ligation: Synthesis, Characterization, and Their Dinitrogen Functionalization Reactions Affording Side-on Bound Diazene Complexes. *J. Am. Chem. Soc.* **140**, 2239-2250 (2018).
- 6 Kendall, A. J., Johnson, S. I., Bullock, R. M. & Mock, M. T. Catalytic silylation of N_2 and synthesis of NH_3 and N_2H_4 by net hydrogen atom transfer reactions using a chromium P_4 macrocycle. *J. Am. Chem. Soc.* (2018).
- 7 Doyle, L. R. *et al.* Catalytic Dinitrogen Reduction to Ammonia at a Triamidoamine-Titanium Complex. *Angew. Chem., Int. Ed. Engl.* **57**, 6314-6318 (2018).
- 8 Ashida, Y., Arashiba, K., Nakajima, K. & Nishibayashi, Y. Molybdenum-catalysed ammonia production with samarium diiodide and alcohols or water. *Nature* **568**, 536-540 (2019).
- 9 Schrock, R. R. Catalytic reduction of dinitrogen to ammonia at a single molybdenum center. *Acc. Chem. Res.* **38**, 955-962 (2005).
- 10 Nishibayashi, Y. Development of catalytic nitrogen fixation using transition metal-dinitrogen complexes under mild reaction conditions. *Dalton Trans.* **47**, 11290-11297 (2018).
- 11 Morello, L., Love, J. B., Patrick, B. O. & Fryzuk, M. D. Carbon-nitrogen bond formation via the reaction of terminal alkynes with a dinuclear side-on dinitrogen complex. *J. Am. Chem. Soc.* **126**, 9480-9481 (2004).

- 12 Bernskoetter, W. H., Pool, J. A., Lobkovsky, E. & Chirik, P. J. Dinitrogen functionalization with terminal alkynes, amines, and hydrazines promoted by $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Zr}]_2(\mu_2, \eta^2, \eta^2\text{-N}_2)$: observation of side-on and end-on diazenido complexes in the reduction of N_2 to hydrazine. *J. Am. Chem. Soc.* **127**, 7901-7911 (2005).
- 13 Akagi, F., Matsuo, T. & Kawaguchi, H. Dinitrogen cleavage by a dinobium tetrahydride complex: Formation of a nitride and its conversion into imide species. *Angew. Chem., Int. Ed.* **46**, 8778-8781 (2007).
- 14 Knobloch, D. J., Lobkovsky, E. & Chirik, P. J. Dinitrogen cleavage and functionalization by carbon monoxide promoted by a hafnium complex. *Nature Chem.* **2**, 30-35 (2010).
- 15 Ballmann, J., Yeo, A., Patrick, B. O. & Fryzuk, M. D. Carbon-Nitrogen Bond Formation by the Reaction of 1,2-Cumulenes with a Ditantalum Complex Containing Side-On- and End-On-Bound Dinitrogen. *Angew. Chem., Int. Ed.* **50**, 507-510 (2011).
- 16 Ishida, Y. & Kawaguchi, H. Nitrogen Atom Transfer from a Dinitrogen-Derived Vanadium Nitride Complex to Carbon Monoxide and Isocyanide. *J. Am. Chem. Soc.* **136**, 16990-16993 (2014).
- 17 Nakanishi, Y., Ishida, Y. & Kawaguchi, H. Nitrogen-Carbon Bond Formation by Reactions of a Titanium-Potassium Dinitrogen Complex with Carbon Dioxide, tert-Butyl Isocyanate, and Phenylallene. *Angew. Chem., Int. Ed. Engl.* **56**, 9193-9197 (2017).
- 18 Rodriguez, M. M., Bill, E., Brennessel, W. W. & Holland, P. L. N_2 reduction and hydrogenation to ammonia by a molecular iron-potassium complex. *Science* **334**, 780-783 (2011).
- 19 McWilliams, S. F. & Holland, P. L. Dinitrogen binding and cleavage by multinuclear iron complexes. *Acc. Chem. Res.* **48**, 2059-2065 (2015).
- 20 MacLeod, K. C. *et al.* Alkali-Controlled C-H Cleavage or N-C Bond Formation by N_2 -Derived Iron Nitrides and Imides. *J. Am. Chem. Soc.* **138**, 11185-11191 (2016).
- 21 Burford, R. J. & Fryzuk, M. D. Examining the relationship between coordination mode and reactivity of dinitrogen. *Nature Reviews Chem.* **1**, 0026 (2017).
- 22 Ferreira, R. B. *et al.* Catalytic Silylation of Dinitrogen by a Family of Triiron Complexes. *ACS Catalysis* **8**, 7208-7212 (2018).
- 23 Turner, Z. Molecular pnictogen activation by rare earth and actinide complexes. *Inorganics* **3**, 597 (2015).
- 24 LaPierre, H. S. & Meyer, K. Activation of small molecules by molecular uranium complexes. *Progr. Inorg. Chem.* **58**, 303-416 (2014).
- 25 Roussel, P. & Scott, P. Complex of Dinitrogen with Trivalent Uranium. *J. Am. Chem. Soc.* **120**, 1070-1071 (1998).
- 26 Odom, A. L., Arnold, P. L. & Cummins, C. C. Heterodinuclear uranium/molybdenum dinitrogen complexes. *J. Am. Chem. Soc.* **120**, 5836-5837 (1998).
- 27 Cloke, F. G. N. & Hitchcock, P. B. Reversible binding and reduction of dinitrogen by a uranium(III) pentalene complex. *J. Am. Chem. Soc.* **124**, 9352-9353 (2002).
- 28 Evans, W. J., Kozimor, S. A. & Ziller, J. W. A monometallic f element complex of dinitrogen: $(\text{C}_5\text{Me}_5)_3\text{U}(\eta\text{-N}_2)$. *J. Am. Chem. Soc.* **125**, 14264-14265 (2003).
- 29 Mansell, S. M., Kaltsoyannis, N. & Arnold, P. L. Small molecule activation by uranium tris(aryloxides): Experimental and computational studies of binding of N_2 , coupling of CO, and deoxygenation insertion of CO_2 under ambient conditions. *J. Am. Chem. Soc.* **133**, 9036-9051 (2011).
- 30 Mansell, S. M., Farnaby, J. H., Germeroth, A. I. & Arnold, P. L. Thermally stable uranium dinitrogen complex with siloxide supporting ligands *Organometallics* **32**, 4214 (2013).
- 31 Mittasch, A. *Geschichte der Ammoniaksynthese*. (Verlag Chemie, 1951).
- 32 Falcone, M. *et al.* The role of bridging ligands in dinitrogen reduction and functionalization by uranium multimetallic complexes. *Nature Chem.* (2018).

- 33 Falcone, M., Chatelain, L., Scopelliti, R., Živković, I. & Mazzanti, M. Nitrogen reduction and functionalization by a multimetallic uranium nitride complex. *Nature* **547**, 332 (2017).
- 34 Korobkov, I., Gambarotta, S. & Yap, G. P. A. A highly reactive uranium complex supported by the calix[4]tetrapyrrole tetraanion affording dinitrogen cleavage, solvent deoxygenation, and polysilanol depolymerization. *Angew. Chem., Int. Ed.* **41**, 3433-3436 (2002).
- 35 Langeslay, R. R., Fieser, M. E., Ziller, J. W., Furche, F. & Evans, W. J. Synthesis, structure, and reactivity of crystalline molecular complexes of the $\{[C_5H_3(SiMe_3)_2]_3Th\}^{1-}$ anion containing thorium in the formal +2 oxidation state. *Chem. Sci.* **6**, 517-521 (2015).
- 36 Korobkov, I., Gambarotta, S. & Yap, G. P. A. Amide from dinitrogen by in situ cleavage and partial hydrogenation promoted by a transient zero-valent thorium synthon. *Angew. Chem., Int. Ed. Engl.* **42**, 4958-4961 (2003).
- 37 Wells, J. A. L., Seymour, M. L., Suvova, M. & Arnold, P. L. Dinuclear uranium complexation and manipulation using robust tetraaryloxides. *Dalton Trans.* **45**, 16026-16032 (2016).
- 38 Halter, D. P., Heinemann, F. W., Maron, L. & Meyer, K. The role of uranium-arene bonding in H₂O reduction catalysis. *Nature Chem.* **10**, 259 (2017).
- 39 Evans, W. J., Rego, D. B. & Ziller, J. W. Synthesis, structure, and 15N NMR studies of paramagnetic lanthanide complexes obtained by reduction of dinitrogen. *Inorg. Chem.* **45**, 10790-10798 (2006).
- 40 Cordero, B. *et al.* Covalent radii revisited. *Dalton Trans.*, 2832-2838 (2008).
- 41 MacLeod, K. C., McWilliams, S. F., Mercado, B. Q. & Holland, P. L. Stepwise N-H bond formation from N₂-derived iron nitride, imide and amide intermediates to ammonia. *Chem. Sci.* **7**, 5736-5746 (2016).
- 42 Markus, R., Oliver, S., Dieter, S. & Artur, H. B. Dinuclear Diazene Iron and Ruthenium Complexes as Models for Studying Nitrogenase Activity. *Chem. Eur. J.* **7**, 5195-5202 (2001).
- 43 Chalkley, M. J., Del Castillo, T. J., Matson, B. D., Roddy, J. P. & Peters, J. C. Catalytic N₂-to-NH₃ conversion by Fe at lower driving force: A proposed role for metallocene-mediated PCET. *ACS Central Science* **3**, 217-223 (2017).
- 44 Zell, T. & Milstein, D. Hydrogenation and dehydrogenation iron pincer catalysts capable of metal-ligand cooperation by aromatization/dearomatization. *Acc. Chem. Res.* **48**, 1979-1994 (2015).
- 45 Al-Khafaji, Y., Sun, X., Prior, T. J., Elsegood, M. R. J. & Redshaw, C. Tetraphenolate niobium and tantalum complexes for the ring opening polymerization of ϵ -caprolactone. *Dalton Trans.* **44**, 12349-12356 (2015).
- 46 Tang, L. *et al.* Highly active catalysts for the ring-opening polymerization of ethylene oxide and propylene oxide based on products of alkylaluminum compounds with bulky tetraphenol ligands. *Macromolecules* **41**, 7306-7315 (2008).
- 47 Keane, A. J., Farrell, W. S., Yonke, B. L., Zavalij, P. Y. & Sita, L. R. Metal-mediated production of isocyanates, R₃EN=C=O from dinitrogen, carbon dioxide, and R₃ECl. *Angew. Chem. Int. Ed.* **54**, 10220-10224 (2015).
- 48 Liao, Q., Saffon-Merceron, N. & Mézailles, N. Catalytic dinitrogen reduction at the molybdenum center promoted by a bulky tetradentate phosphine ligand. *Angew. Chem. Int. Ed.* **53**, 14206-14210 (2014).
- 49 Liao, Q., Saffon-Merceron, N. & Mézailles, N. N₂ reduction into silylamine at tridentate phosphine/Mo center: catalysis and mechanistic study. *ACS Catal.* **5**, 6902-6906 (2015).

Acknowledgments We thank the University of Edinburgh, the EPSRC, the JSPS and the ERC for funding.

Author Contributions TO, FL, RPK, and MLS carried out the experiments. LM carried out and analysed the DFT calculations. PLA conceived and supervised the project. All authors analysed the data and contributed to the writing of the manuscript.

Competing Interests The authors declare no competing interests.

Data availability statement The crystallographic datasets for the structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre, under deposition numbers CCDC 1829624 (**1U**), 1829625 (**1U^t-thf**), 1829626 (**1U-diox**), 1829627 (**1Th-diox**), 1829628 (**1Th-py**), 1829629 (**2U**), 1829630 (**3U**). Copies of the data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>. All other data supporting the findings of this study and detailed experimental procedures and characterization of compounds are available in the Supplementary Information files, and in the depository doi:10.17632/nm46kr3cnd.1.

Reprints and permissions information is available at www.nature.com/reprints.

Correspondence and requests for materials should be addressed to PLA pla@berkeley.edu.