EDGE ARTICLE
Marinella Mazzanti et al.
Nitrogen activation and cleavage by a multimetallic uranium complex
Nitrogen activation and cleavage by a multimetallic uranium complex†

Megan Keener, ‡ a Farzaneh Fadaei-Tirani, a Rosario Scopelliti, a Ivica Zivkovic b and Marinella Mazzanti c, *a

Multimetallic-multielectron cooperativity plays a key role in the metal-mediated cleavage of N2 to nitrides (N3−). In particular, low-valent uranium complexes coupled with strong alkali metal reducing agents can lead to N2 cleavage, but often, it is ambiguous how many electrons are transferred from the uranium centers to cleave N2. Herein, we design new dinuclear uranium nitride complexes presenting a combination of electronically diverse ancillary ligands to promote the multimetallic transformation of N2. Two heteroleptic diuranium nitride complexes, [K(UV(OSi(O-Bu)3)3(N(SiMe3)2)2)]2(μ-N)] (1) and [Cs(U(IV)(OSi(O-Bu)3)3(N(SiMe3)2)2(μ-N)] (3-Cs), containing different combinations of Os(O′Bu)3 and N(SiMe3)2 ancillary ligands, were synthesized. We found that both complexes could be reduced to their U(II)/U(IV) analogues, and the complex, [K2(U(IV)(OSi(O-Bu)3)3(N(SiMe3)2)2(μ-N)] (6-K), could be further reduced to a putative U(II)/U(II) species that is capable of promoting the 4e− reduction of N2, yielding the N2+ complex [K2(U(III)(OSi(O-Bu)3)3(N(SiMe3)2)2(μ-N)](μ-η2:η2-N2)]. Parallel N2 reduction pathways were also identified, leading to the isolation of N2 cleavage products, [K3(U(IV)(OSi(O-Bu)3)3(N(SiMe3)2)2(μ-N)](μ-η2:η2-N2)] (7-K), and [K4((OSi(O′Bu)3)2(U(IV)](μ-N)](μ-η2:η2-C,N-CH2SiMe2NSiMe3)-[(U(IV)(OSi(O-Bu)3)3(N(SiMe3)2)2)[K(N(SiMe3)2)2]] (9). These complexes provide the first example of N2 cleavage to nitride by a uranium complex in the absence of reducing alkali metals.

Introduction

The search for catalysts capable of converting dinitrogen into ammonia, or higher-value organic products under mild low-energy conditions, continues to attract intensive research on dinitrogen binding and cleavage by molecular compounds of d and f block elements.1 Uranium nitrides were shown to be highly active catalysts in the conversion of dinitrogen (N2) to ammonia (NH3), before equally active iron oxides were adopted and f block elements.2 This has generated significant interest towards the N2 chemistry of uranium,3a,b,d,3e−f leading to the discovery of complexes capable of stoichiometrically converting N2 to NH3.3b,d,y and in one system, catalytically converting N2 to amine (6.4 equiv.).4d However, the reaction of dinitrogen with well characterized molecular U(n) complexes, in most cases resulted in reversible binding,3b,f or in the 2e− reduction to N2−, with electrons being provided by two 1e− transfers from two mononuclear complexes.3b,e In contrast, the few reported cases of 4e− reduction of N214 or N2 cleavage to nitride,4a,b,h,i,j usually required a combination of U(n) or U(iv) complexes and highly reducing alkali ions (K or Cs), leaving ambiguity on the number of electrons transferred by the uranium centers.

Recently, we identified a molecular dinuclear nitride U(n) complex (complex C prepared from the reduction of the U(iv)/U(iv) analogue A, Scheme 1) that effects the 4e− reduction of N2 to N2+ (complex D), which can be further functionalized by protons (H+) or CO, without addition of highly reducing alkali ions. In this dinuclear system, each uranium center is capable of transferring two electrons to N2−.15

Although multielectron transfer reactions are not common in uranium chemistry, reports of metal based two-electron transfer reactions have been rapidly increasing.4,5 In contrast, redox reactivity involving more than two electrons has been so far limited to complexes of uranium with redox-active ligands.6 However, our recent report of the first unambiguous example of metal-based 4e− transfer by a U(n) complex,7 suggests that 3e− transfer reactions may also be possible. Specifically, the 3e− transfer in dinuclear U(n) complexes is a pre-requisite to affect N2 cleavage without addition of reducing agents.

We reasoned that dinuclear U(n) nitride complexes presenting ligands more electron-donating than the siloxide ligand, (OSi(O′Bu)3), would be able to transfer a high number of...
electrons to dinitrogen. We recently identified the bulky silylamine ligand \(\{\text{N(SiMe}_3\}_2\}\) as well-suited for determining ligand effects on the reactivity and magnetic properties of nitride-bridged uranium complexes, due to the more electron-donating character and a slightly higher steric demand.

Inspired by the original report by Fortier and Hayton\(^8\) of the synthesis of the nitride bridged diuranium(IV) complex, \([\text{Na(dme)}_3]_2[(\text{N(SiMe}_3\}_2\}_2\text{U(IV)}\text{U(IV)NO}_3\text{C}_7\text{H}_8\text{SiMe}_2\text{NSiMe}_3\}]\), we previously identified routes to homoleptic complexes, \([\text{K}_2\text{UIV(O}3\text{Si(O}3\text{Bu})_3\text{)}_2\text{N(SiMe}_3\}_2\}_2\text{U(IV)}\text{U(IV)NO}_3\text{C}_7\text{H}_8\text{SiMe}_2\text{NSiMe}_3\}]\), \([\text{Me}_3\text{Si}N\}]\), and \([\text{Me}_3\text{Si}N\}_2\] (Scheme 1).\(^9\) However, reduction of these complexes to their U(III)/U(III) analogue \([\text{K}_2\text{UIV(O}3\text{Si(O}3\text{Bu})_3\text{)}_2\text{N(SiMe}_3\}_2\}_2\text{U(III)}\text{U(III)NO}_3\text{C}_7\text{H}_8\text{SiMe}_2\text{NSiMe}_3\}]\) was determined by X-ray diffraction studies, and shows the presence of an ion pair consisting of one K cation and the \([\text{UIV(O}3\text{Si(O}3\text{Bu})_3\text{)}_2\text{N(SiMe}_3\}_2\}_2\text{U(III)NO}_3\text{C}_7\text{H}_8\text{SiMe}_2\text{NSiMe}_3\}]\) anion. The two uranium(IV) ions in 1 are bridged by a nitride (N\(^3\)), and each are bound by one Os(O\(_3\text{Bu})\_3\) and two N(SiMe\(_3\)) ligands. Both complexes could be reduced to the U(III)/U(III) analogue and complex, \([\text{K}_2\text{UIV(O}3\text{Si(O}3\text{Bu})_3\text{)}_2\text{N(SiMe}_3\}_2\}_2\text{U(III)NO}_3\text{C}_7\text{H}_8\text{SiMe}_2\text{NSiMe}_3\}]\) (6-K), could be further reduced to a highly reactive putative U(II)/U(II) species that is able to promote the 4e\(^-\) reduction of N\(_2\). This reactivity provides the third example of 4e\(^-\) reduction of N\(_2\) by a dinuclear U(II) complex. Here, parallel N\(_2\) reduction pathways were also identified, leading to the isolation of N\(_2\) cleavage products, providing the first example of N\(_2\) cleavage to nitride by a uranium complex in the absence of reducing alkali metals.

### Results and discussion

**Synthesis of heteroleptic U(n) nitride complexes**

In order to probe ligand effects on N\(_2\) binding, we sought to synthesize a series of heteroleptic uranium complexes with Os(O\(_3\text{Bu})\_3\) and N(SiMe\(_3\)) ancillary ligands in various ratios.

First, we attempted to incorporate a higher number of Os(O\(_3\text{Bu})\_3\) ligands within the previously reported mixed-ligand nitride system, \([\text{UIV(O}3\text{Si(O}3\text{Bu})_3\text{)}_2\text{U(IV)}\text{U(IV)NO}_3\text{C}_7\text{H}_8\text{SiMe}_2\text{NSiMe}_3\}][\text{UIV(O}3\text{Si(O}3\text{Bu})_3\text{)}_2\text{U(IV)}\text{U(IV)NO}_3\text{C}_7\text{H}_8\text{SiMe}_2\text{NSiMe}_3\}]\), \([\text{K}_2\text{UIV(O}3\text{Si(O}3\text{Bu})_3\text{)}_2\text{N(SiMe}_3\}_2\}_2\text{U(III)}\text{U(III)NO}_3\text{C}_7\text{H}_8\text{SiMe}_2\text{NSiMe}_3\}]\). Addition of 2.0 equiv. of KOSi(O\(_3\text{Bu})\_3\) to a solution of E in THF at room temperature, resulted in the immediate formation of a pink-brown solution and precipitation of a white solid. Large orange crystals of complex \([\text{K}_2\text{UIV(O}3\text{Si(O}3\text{Bu})_3\text{)}_2\text{N(SiMe}_3\}_2\}_2\text{U(III)NO}_3\text{C}_7\text{H}_8\text{SiMe}_2\text{NSiMe}_3\}]\) (Scheme 2, Fig. 1a), were obtained from a concentrated hexane solution at −40 °C in 82% yield. The \(^1\)H NMR spectrum of isolated complex 1 displays two resonances at −0.10 and −3.81 ppm, corresponding to the Os(O\(_3\text{Bu})\_3\) and N(SiMe\(_3\)) ligands, respectively (Fig. S8†). The solid-state molecular structure of complex 1 was determined by X-ray diffraction studies, and shows the presence of an ion pair consisting of one K cation and the \([\text{UIV(O}3\text{Si(O}3\text{Bu})_3\text{)}_2\text{N(SiMe}_3\}_2\}_2\text{U(III)NO}_3\text{C}_7\text{H}_8\text{SiMe}_2\text{NSiMe}_3\}]\) anion. The two uranium(IV) ions in 1 are bridged by a nitride (N\(^3\)), and each are bound by one Os(O\(_3\text{Bu})\_3\) and two N(SiMe\(_3\)) ligands, resulting in a mixed-ligand framework. The K cation binds to the bridging nitride ligand (2.953(3) Å) and to four oxygens of the two Os(O\(_3\text{Bu})\_3\) ligands. The U–N–U bond angle (162.5(1)°) and distances (2.071(2), 2.077(2) Å; Table 1) are consistent with those found for the previously reported all-Os(O\(_3\text{Bu})\_3\) \([\text{UIV(O}3\text{Si(O}3\text{Bu})_3\text{)}_2\text{U(III)NO}_3\text{C}_7\text{H}_8\text{SiMe}_2\text{NSiMe}_3\}]\) (A, Scheme 1); (170.2(3)°;
2.058(5) Å,
the all-N(SiMe$_3$)$_2$ complexes, E (168.97(14°); 2.055(3) Å) and G (179.0(1°); 2.076(3) Å).

Next, we investigated the synthesis of a heteroleptic complex with a different combination of OsO$_3$(O'Bu)$_3$ (four) and N(SiMe$_3$)$_2$ (two) ligands, to probe the effect of ancillary ligands in N$_2$ binding and activation.

We pursued the synthesis of the targeted nitride complex by reacting the heteroleptic precursor “[U$^{III}$(Os(O'Bu)$_3$)($N$(SiMe$_3$)$_2$)$_2$]” with CsN$_3$, a method that had proven successful for the synthesis of all-OsO$_3$(O'Bu)$_3$ complexes, A, $^{a,b}$ and other homoleptic nitride bridged U(IV) compounds. $^{a,c}$ First, we synthesized the mononuclear heteroleptic complex, [U$^{III}$(Os(O'Bu)$_3$)$_2$(THF)$_3$]$^{+}$ by reaction of [U$_1$(THF)$_5$]$_2$ with 2.0 equiv. KOOSi(O'Bu)$_3$, and then further incorporated a N(SiMe$_3$)$_2$ ligand by salt metathesis to afford the heteroleptic complex “[U$^{III}$(Os(O'Bu)$_3$)$_2$(N(SiMe$_3$)$_2$)$_2$]” (Scheme S1†).

Isolation of the heteroleptic complex “[U$^{III}$(Os(O'Bu)$_3$)$_2$(N(SiMe$_3$)$_2$)$_2$]” in analytically pure form proved unsuccessful, leading to ligand scrambling products (see ESIF for details), and therefore further reactivity studies were carried out using the in situ generated heteroleptic U(IV) complex.

Addition of 0.5 equiv. CsN$_3$ to an Et$_2$O solution of in situ generated heteroleptic complex “[U$^{III}$(Os(O'Bu)$_3$)$_2$(N(SiMe$_3$)$_2$)$_2$]” at −40 °C for four days, resulted in the formation of a light brown–pink solution. Analysis of the reaction mixture by $^1$H NMR spectroscopy in d$_6$-toluene showed disappearance of the U(IV) precursor and appearance of new resonances (Fig. S7†). Light brown crystals of the heteroleptic complex, [Cs{U$^{IV}$(Os(O'Bu)$_3$)$_2$(N(SiMe$_3$)$_2$)$_2$(μ−N)] (Scheme 2, Fig. 1b), were obtained from a concentrated Et$_2$O solution at −40 °C in 56% yield. The solid-state molecular structure of complex 3-Cs was determined by X-ray diffraction studies, and shows the presence of an ion pair consisting of one Cs cation and the {[U$^{IV}$(Os(O'Bu)$_3$)$_2$(N(SiMe$_3$)$_2$)$_2$(μ−N)]} anion. The two uranium(IV) ions in 3-Cs are bridged by a nitride (N−), and each ion is bound by two OsO$_3$(O'Bu)$_3$ and one N(SiMe$_3$)$_2$ ligand, resulting in a mixed-ligand framework. This altogether differs from complex 1 in the Os(O'Bu)$_3$/N(SiMe$_3$)$_2$ ligand ratio (e.g. 2:4 in 1 vs. 4:2 in 3-Cs). The Cs cation binds the bridging nitride (3.063(3) Å) and four oxygens from two OsO$_3$(O'Bu)$_3$ ligands. The U−N−U bond angle (156.9(2)°) is slightly smaller than 1, but has similar U−N bond distances (2.064(3), 2.074(3) Å; Table 1).

Complex 3-Cs is stable in toluene at −40 °C for one month and in THF at −80 °C for up to 8 hours. However, the product begins to decompose in THF after 1 hour at −40 °C, and is fully consumed after 2 hours at room temperature with a solution color change from pink to yellow (Fig. S14†). From this mixture, yellow crystals were isolated at −40 °C in concentrated n-hexane.

---

**Table 1: Selected bond lengths (Å) and angles (°) of complexes.**

| Complex | 1 | 3-Cs | 3b-Cs | 4 | 5 | 6-K | 6-Cs |
|---------|---|-----|-------|---|---|-----|------|
| U−N$^{n}$tride | 2.071(2), 2.077(2) | 2.064(3), 2.074(3) | — | U2: 1.995(4), U1: — | — | U2: 2.024(11), U1: 2.187(12) | U2: 2.043(6), U1: 2.124(6) |
| N$^{n}$tride−M (M = K) | K1: 2.953(3), Csx: 3.068(3) | — | K1: 2.864(5) | — | K1: 2.967(11), K2: 3.256(11) | Csx: 3.260(6) Csx: 3.477(6) |
| U−NH$_{\text{imido}}$ | — | — | 2.167(8), 2.198(8) | — | U1: 2.184(11), U1′: 2.355(12) | — | — |
| U−N−U | 162.51(13) | 156.91(17) | — | 163.9(3) | — | 151.6(6) | 166.0(3) |
| U−NH−U | — | — | 119.7(4) | — | 119.5(6) | — | — |

© 2022 The Author(s). Published by the Royal Society of Chemistry
mixed-ligand uranium–nitrides and to investigate their ability to bind and reduce N₂.

Addition of 10.0 equiv. of KC₈ to a solution of 1 in d₄-THF at −80 °C led to the appearance of new resonances and consumption of 1 as seen by ¹H NMR spectroscopy (Fig. S31†). Dark black prism crystals of [K[U₁⁺⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻~-~-]

Fig. 2 Molecular structure of complex, [Cs{(OSi(O²Bu)₃)₂(UV)(μ-NH)(μ-x⁻²,C-N-CH₂SiMe₂NSiMe₃)-{U³⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻~-~-]

and characterized by XRD analysis as a diuranium imido cyclometallated complex, [Cs{(OSi(O²Bu)₃)₂(UV)(μ-NH)(μ-x⁻²,C-N-CH₂SiMe₂NSiMe₃)-{U³⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻~-~-]

Synthesis and characterization of heteroleptic U(m)/U(n) and U(m)/U(n) nitrides

With heteroleptic nitride complexes 1 and 3-Cs in hand, we next explored their reduction chemistry to prepare new, low-valent,
a THF/hexane mixture at -40 °C in 74% yield, and characterized by X-ray diffraction studies (see ESI†).

Next, we investigated the reduction of complex 3-Cs. Addition of 1.0 or 10.0 equiv. of KC₈ to solutions of 3-Cs in d₈-THF at -40 °C, led to significant differences in reactivity. Notably, the reaction with 1.0 equiv. of KC₈ led to a brown–red solution and the appearance of new resonances and unreacted 3-Cs (a, Fig. S35†). Crystals of [K₂[U(IV)(O'Bu)₃]₂[N(SiMe₃)₂]₂[μ-μ]] (6-K) (Scheme 3) were isolated from a concentrated n-hexane solution at -40 °C and characterized by XRD analysis. Attempts to isolate analytically pure 6-K from this pathway proved unsuccessful due to the contaminant precipitation of 3-Cs.

Instead, isolation of 6-K could be carried out by reacting 10.0 equiv. of KC₈ with 3-Cs in Et₂O at -40 °C. Analysis of the reaction mixture by ¹H NMR spectroscopy in d₈-toluene indicated full consumption of 3-Cs and formation of 6-K (Fig. S36†), which could be isolated from a concentrated hexane solution at -40 °C in 72% yield. Complex 6-K is stable in toluene at -40 °C for one month, whereas in THF, the product begins to decompose at -40 °C after 24 hours. The solid state molecular structure of complex 6-K shows the presence of an ion pair consisting of two K cations and the [U(IV)(O'Bu)₃]₂[N(SiMe₃)₂]₂[μ-μ] anion (Fig. 4a). The two uranium(μ)/μ ions are bridged by a nitride (N₃), and are bound by two OSi(O'Bu)₃ and one N(SiMe₃)₂ ligand. The K cations bind to the bridging nitride (2.967(11), 3.256(11) Å), and the four OSi(O'Bu)₃ ligands. The U–N–U bond angle (151.6(6)°) is slightly bent, but has similar U–N bond distances (U₂: 2.024(12), U₁: 2.187(12) Å; Table 1) found in complex 4 (163.9(3); 1.995(4) Å, 2.210(4) Å), indicating localized U(IV)/U(IV) centers.

Alternatively, when the reduction of 3-Cs is carried out in the presence of 10.0 equiv. of KC₈ in THF at -40 °C, a dark purple solution is obtained. Analysis of the reaction mixture by variable temperature ¹H NMR spectroscopy indicated full consumption of complex 3-Cs, and formation of new resonances. (Fig. S39 and S42†). The same species was also obtained by reduction of isolated 6-K with KC₈ in THF (Fig. S43†). This suggests that further reduction of 6-K yields a putative U(III)/U(III) nitride, [K₃[U(III)(O'Bu)₃]₂[N(SiMe₃)₂]₂[μ-μ]] [X], analogous to the one previously observed in homoleptic nitride systems (C; Scheme 1). Attempts to isolate single crystals or analytically
pure material from the reaction mixture proved unsuccessful, most likely due to the highly reactive nature of the formed species, which results in the formation of 6-K in toluene solution at −40 °C after 24 hours (Fig. S41†). These results indicate that depending on the nature of the solvent (Et₂O or THF), reduction with excess KC₈ can either lead to the formation of a U(m)/U(n) or U(m)/U(m) species, highlighting the importance in tuning the reaction conditions in order to reach low-valent species.

Next, to probe the role of the cation in the synthesis and stability of the proposed heteroleptic U(m)/U(m) species, X, we also performed the reduction of 3-Cs with 10.0 equiv. CsC₈ in THF at −40 °C. In comparison to the KC₈ reactivity, this reaction instead resulted in a red–brown solution (Fig. S37†). Light orange crystals suitable for XRD analysis were obtained from a concentrated hexane solution at −40 °C in 78% yield, and characterized as the Cs analogue of 6-K, [Cs₂[UIV/III(OSi(OBu)₃)₂₂(N(SiMe₃)₂)₂]₂(μ-N)] (6-Cs) (Scheme 3, Fig. 4b). The solid state molecular structure of complex 6-Cs shows the presence of an ion pair consisting of two Cs cations and the \([\{U^[IV/III](OSi(OBu)₃)₂₂(N(SiMe₃)₂)₂]₂(μ-N)\] anion. The two uranium(m)/n(IV) ions are bridged by a nitride \(N^3\) moiety, and are bound by two Os(OBu)₃ and one N(SiMe₃)₂ ligand.

The Cs cations bind to the bridging nitride (3.260(6), 3.477(6)Å) and the four Os(OBu)₃ ligands. The U–N–U bond angle (166.0(3)°) and distances (U2: 2.043(6), U1: 2.124(6)Å) are consistent with complex 6-K, indicating a localized U(iv)/U(n) structure, and the previously reported complex, [Cs₂[UIV/III(OSi(OBu)₃)₂₂(N(SiMe₃)₂)₂]₂(μ-N)] (B; where M = Cs, Scheme 1) (169.1(7)°; 2.081(12)–2.099(12)Å).³ These results indicate that with excess CsC₈, we cannot produce the analogous Cs₂U(m)–N–U(m) species. This contrasts the previous studies for the reduction of the all-Osi(OBu)₃ analogue, [Cs[UIV/III(OSi(OBu)₃)₂]₂(μ-N)] (A), with KC₈ and CsC₈, where in both systems, the respective K₄U(m)–N–U(m) and Cs₃U(m)–N–U(m) species were obtained. The unreactive nature of the U(m)–N–U(n) species, with excess CsC₈, can be explained by a predicted, more negative reduction potential in comparison to 6-K, due to the replacement of the K cation by Cs in the second coordination sphere. Notably, the stronger K–O bonds (vs. Cs–O bonds) in the secondary coordination sphere help drive the reaction to the U(m)/U(m) state. However, the redox potentials for these species could not be obtained due to the rapid decomposition in THF solution at room temperature (3-Cs → 3b-Cs).

Reactivity of heteroleptic nitrides

Now with the U(m)/U(n) complexes 4, 6-K, and 6-Cs in hand, we sought to probe their reactivity toward N₂ activation and cleavage. However, in all systems, the U(m)/U(n) precursors showed no reactivity with 1 atm N₂ in toluene or THF solutions, resulting in unreacted starting materials as evidenced by ¹H NMR studies (see ESI†).

In contrast, addition of 1 atm N₂ to the in situ generated U(m)/U(m) complex X, in toluene solution at −100 °C, led to an unambiguous color change from dark purple to light brown. Analysis of the reaction mixture by ¹H NMR spectroscopy at variable temperature displays new resonances and the consumption of complex X (Fig. S48†). Dark brown crystals suitable for XRD analysis were obtained from the toluene reaction mixture at −40 °C after 24 hours, and characterized as the N₂₄⁻ complex, \([K₄[UIV(OSi(OBu)₃)₂₂(N(SiMe₃)₂)₂]₂(μ-η²:η²-N₂)]\) [7] in 56% yield (Scheme 3, Fig. 5). Complex 7 shows the presence of an ion pair consisting of three K cations and the \([\{U^[IV](OSi(OBu)₃)₂₂(N(SiMe₃)₂)₂]₂(μ-N)(μ-η²:η²-N₂)\] anion. The two uranium(v) ions are bridged by a nitride \(N^3\) and a side-on-bound hydrazido \(N^4\) moiety, and each U(v) is bound by two Os(OBu)₃ and one N(SiMe₃)₂ ancillary ligand. All K cations in complex 7 are inner-sphere, bound by the nitride, \(N^4\) moiety, and the four Os(OBu)₃ ligands. One K cation, binds to the bridging nitride \(N\) and four oxygens of two Os(OBu)₃ ligands. The other two K atoms bind the \(N^4\) moiety, where K2 is bound to both nitrogen atoms, and K3 interacts with only one. Due to the mixed-ligand nature, the four Os(OBu)₃ ligands...
ligands support all three K cations. This contrasts the previously reported all-OSi(OBu)_3, U(V) nitride–hydrazido complex (D, Scheme 1), in which the three K cations are bound to six OSi(OBu)_3 ligands and one K and is bound to the N_2^+ moiety, while two K atoms are bound to the bridging nitride. The U–N_nitride bond distances (2.101(15), 2.137(13)Å) (Table 2) are consistent with the previously reported complex D (2.069(2)Å), and U<v>/U<v>v bis-nitride complexes (2.022(5), 2.101(6)Å). The U_2(μ-N:η^2-N_2+δ) moiety features U–N bond distances which range between (2.178(15)–2.318(15)Å), consistent with U–N single bonds. The value of the N=N bond length (1.54(2)Å) corresponds to a highly-activated N_2, that has undergone a 4e⁻ reduction to a hydrazido moiety (N_2^+δ), and is elongated compared to previously reported U–N(=N) (1.109(7)–1.120(14)Å) and U–(N≡N) (1.124(12)–1.232(10)Å) moieties. The homoleptic OSi(OBu)_3 analogue of X.

Next, variable-temperature magnetic and EPR data were measured on isolated complex 7 in order to confirm the presence of two U<v>(5f^) ions, consistent with the 4e⁻ reduction of N_2. The magnetic susceptibility (χ_m) of complex 7 shows a paramagnetic behaviour with two magnetically independent U ions (purple, Fig. S65a†). This is in contrast to the previously reported complex D, which displays antiferromagnetic coupling at 50 K. The solid-state magnetic moment of 7 at 250 K was found to be 1.76 μ_B per uranium, (data were collected between 2–250 K to avoid thermal decomposition of the product). This value is lower than the theoretical value expected for a free U<v> ion (2.54 μ_B; 3F/2 ground term), however it is in the range of other reported bimetallic U<v> systems (1.35–3.32 μ_B). The μ_eff for complex 7 shows a steady decrease when the temperature is lowered, reaching 1.23 μ_B at 50 K, and then more rapidly to reach a value of 0.32 μ_B at 2 K (blue, Fig. S65a†). Although this temperature profile is typical for U<v>, the value at 2 K is rather low. However, this behavior has been previously observed for the dimeric U<v> bridging bis-oxo complex, [([(^4ArO)N]U)_2(μ-O)]_2 in which they report a similar χ_m plot and absence of antiferromagnetic coupling, altogether combined with a low μ_eff value at 2 K (0.36 μ_B per U). This was attributed to a potential antiferromagnetic interaction that was not observable, leading to the unexpected low temperature value. Additionally, the X-band (9.4 GHz) EPR spectrum of complex 7 shows an intense signal at 6 K that was fit to an axial set of signals (g_1 = 2.740; g_2 = 2.008; g_3 = 1.797), further supporting the U<v> oxidation state (Fig. S64†).

Interestingly, separation and crystallization of the supernatant from four independent reactions of complex X with N_2, after removal of complex 7, led to the identification of two N_2^+δ-cleavage products, characterized by XRD analysis as a formal U<v>v/V<v>/U<v>v tris-nitride complex, [K_4(U^V)(OSi(OBu)_3)_{2}(N(SiMe_3)_2)]_2, (8), and a U<v>v/V<v>/U<v>v bis-nitride imido cyclometallated product, [K_4((OSi(OBu)_3)_{2}(N(SiMe_3)_2)]_2(N≡N)]_2, (9) (Fig. 6). Over four trials, complex 8 was isolated once, while complex 9 was isolated on three occasions. Each crystallization of the supernatant always led to a mixture of species, in which the only other product that could be crystallographically identified was the K analogue of complex 3-Cs, [K(U^IV)(OSi(OBu)_3)_{2}(N(SiMe_3)_2)]_2(μ-N)]_2 (3-K) (Fig. S62†). Overall preventing the further characterization of these N_2 cleavage products. However, these crystal structures provide important insight into N_2 cleavage and reactivity.

The solid-state molecular structure of complex 8 shows the presence of a symmetric tetrameric structure, comprising of two dimers in a diamond-shaped core, with two K atoms at the apical positions, capping the terminal and bridging nitride moieties (Fig. S63†). Due to the imposed crystal symmetry, identical bond metrics are found for each dimeric unit. U_1 is bound by two OSi(OBu)_3 and one N(SiMe_3)_2 ligands.

Table 2. Selected bond lengths (Å) of complexes, [K_4(U^V)(OSi(OBu)_3)_{2}(N(SiMe_3)_2)]_2(N≡N)]_2(μ-N)]_2, (8), and [K_4((OSi(OBu)_3)_{2}(N(SiMe_3)_2)]_2(N≡N)]_2(μ-N)]_2, (9).

| Complex          | 7                | 8                | 9                |
|------------------|------------------|------------------|------------------|
| U–N_2^+δ–U       | 1.54(2)          |                  |                  |
| U–N_nitride      | 2.101(15), 2.137(13) | 1.922(4)–2.311(4) | 1.916(13), 2.323(13) |
| U–NHimido        |                  | 2.218(14), 2.318(14) |
| U≡Nterminal      |                  | 1.784(4)         | 1.847(13)        |
Conversely, U2 is bound by one OSi(OBu)3, one N(SiMe3)2, and a terminal nitride, indicating that loss of one OSi(OBu)3 ligand has occurred, most likely as KOSi(OBu)3. The U1 and U2 ions are bridged by two nitride (N3−) ligands, where N2 is coordinated to two K atoms (K1, K2), bound through a combination of the OSi(OBu)3 and N(SiMe3)2 ancillary ligands. The bridging U–N bond distances are asymmetric, featuring a combination of short (U1–N1: 1.922(4), U2–N2: 1.927(3) Å) and elongated (U1–N2: 2.253(4), U2–N1: 2.311(4) Å) bond distances (Table 2). This is consistent with the presence of U≡N multiple bonds and singly bound U–N, respectively, as previously observed in U(ν) bis-nitride bridged complexes.22

Two nitrides (N2, N3), bind the U2 ion in a slightly bent trans configuration (167.59(17)°), with different bond distances for U2–N3 and U2–N2 (1.784(4) and 1.927(3) Å). These parameters can be compared to those of the two previously reported linear trans-bis-nitride U(ν) complexes.22 In contrast, in the complex [K2{(OSi(OBu)3)2UIV(NH3)5(ν)}(μ4-N)(μ4-κ2:C,N-CH2SiMe3NSiMe3){UIV(μ-N)(μ-κ2:C,N-CH2SiMe3NSiMe3)}2]2+, the N≡Ucen N〈94.8(8) and 1.902(8) Å〉 and the bond angle is linear (179.07(11)°).22 In the complex [[NH3]8UIV(μ-N)-U<sup>IV</sup>(NH3)<sub>3</sub>][μ-μ(μ-κ2:C,N-CH2SiMe3NSiMe3)], the N≡Ucen N〈1.963(8) and 1.902(8) Å〉 and the bond angle is linear (179.07(11)°).22 The terminal nitride has a bond distance of 1.784(4) Å, consistent with the bond distances found in the only two previously reported terminal U(ν) nitrides (1.769(2), 1.799(7) Å)24 and shorter than those found in alkali-capped (1.846(3)–1.929(6) Å)25 and borane-capped U(ν) nitrides (1.880(4), 1.916(4) Å).26

The solid-state molecular structure of complex 9 displays the presence of a dimeric imido cyclo metallated anion, where the two uranium ions are bridged by three anionic ligands, namely a nitride (N3−), an imido (NH2−), and a μ-κ3-N,C-CH2SiMe3-NSiMe3 ligand. The presence of an imido group, arising from the 1,2 addition of a C–H bond of the N(SiMe3)2 ligand across the U–N–U bond, was confirmed by 1H NMR spectroscopy of the reaction mixture, showing resonances of the imido and methylene protons at δ 627.91 ppm and δ −138.25 and −153.55 ppm, respectively. In complex 9, one U-bound N(SiMe3)2 ligand is lost, and two KN(SiMe3)2 are bound in the second coordination sphere. Two nitrides bind the U2 ion in a trans configuration (170.0(6)°) and the U(ν) bond distances for the terminal and bridging nitride are 1.847(13) Å and 1.916(13) Å, respectively. The bis-imido motif R−N═U<sup>IV</sup>═N−R, an analogue of the UO<sub>2</sub><sup>2+</sup> cation, has been previously observed by Boncella and coworkers.27 However, such an analogous bis-nitride motif, N≡U≡N, has not been previously observed for U(ν). The terminal nitride (1.847(13) Å) is elongated compared to the terminal K-capped U(ν) nitride in complex 8 (1.784(4) Å; Table 2), and is comparable to that of the previously reported alkali-capped24 and borane-capped U(ν) nitrides.28 The bridging U–N–U (U1–N1: 2.323(13), U2–N1: 1.916(13) Å) and U–NH–U (U1–N2: 2.218(14), U2–N2: 2.318(14) Å)29 bond distances are consistent with the presence of a U–N single and a short U≡N multiple bond (similar to complex 8), and a bridging imido, respectively. Complexes 8 and 9 provide the first example of N2 cleavage promoted by a low-valent U(m) complex without addition of alkali reducing agents. We recently reported N2 cleavage in the all-OSi(OBu)3 diuranium(ν) oxide bridged complex [K2{{UIV(μ-κ2:C,N-CH2SiMe3NSiMe3)}2}{(μ-κ2:C,N-CH2SiMe3NSiMe3)}2]2+, to yield a tetranitride cluster.30 However, this reactivity was only observed upon reduction with KC8.

Once isolated, the diuranium(ν)-N2<sup>2+</sup> complex 7 is stable in toluene solution at −40 °C for one month, indicating that the formation of the nitride complexes, 8 and 9, must arise from parallel redox pathways. The formal oxidation state of complex 8, indicates that its formation requires the 1e− reduction of complex 7 by an external reducing agent. This would result in

---

**Fig. 6** Molecular structures of (a) [K2{(OSi(OBu)3)2UIV(NH3)5(ν)}(μ-N)(μ-κ2:C,N-CH2SiMe3NSiMe3){UIV(μ-N)(μ-κ2:C,N-CH2SiMe3NSiMe3)}2]2+, and (b) [K2{(OSi(OBu)3)2UIV(μ-N)(μ-κ2:C,N-CH2SiMe3NSiMe3)}2]2+. The solid-state molecular structure of complex 9 (Fig. 6, top right). The bridging U–N bond distances in complex 8 are 1.847(13) Å and 1.916(13) Å, respectively. The bis-imido motif R−N═U<sup>IV</sup>═N−R, an analogue of the UO<sub>2</sub><sup>2+</sup> cation, has been previously observed by Boncella and coworkers. However, such an analogous bis-nitride motif, N≡U≡N, has not been previously observed for U(ν). The terminal nitride (1.847(13) Å) is elongated compared to the terminal K-capped U(ν) nitride in complex 8 (1.784(4) Å; Table 2), and is comparable to that of the previously reported alkali-capped and borane-capped U(ν) nitrides. The bridging U–N–U bonds in complex 8 are 2.323(13), 1.916(13) Å, and 2.318(14) Å, respectively. Complexes 8 and 9 provide the first example of N2 cleavage promoted by a low-valent U(m) complex without addition of alkali reducing agents. We recently reported N2 cleavage in the all-OSi(OBu)3 diuranium(ν) oxide bridged complex, to yield a tetranitride cluster. However, this reactivity was only observed upon reduction with KC8.

Once isolated, the diuranium(ν)-N2<sup>2+</sup> complex 7 is stable in toluene solution at −40 °C for one month, indicating that the formation of the nitride complexes, 8 and 9, must arise from parallel redox pathways. The formal oxidation state of complex 8, indicates that its formation requires the 1e− reduction of complex 7 by an external reducing agent. This would result in...
the overall 2e\textsuperscript{−} reduction and cleavage of the N\textsubscript{2}\textsuperscript{4−} single bond, where an additional 1e\textsuperscript{−} is provided by the U(v)/U(vi) oxidation.

Overall, complex 8 is the product of an unprecedented case of 3e\textsuperscript{−} transfer from a U(n) center. Whereas the formation of complex 9 most likely involves a 2e\textsuperscript{−} reduction of the N\textsubscript{4}\textsuperscript{−} moiety by an external reducing agent. Formation of these unusual species suggests a high redox flexibility of the uranium centers in the mixed-ligand environment, provided by the combination of OSi(O\textsubscript{tBu})\textsubscript{3} and N(SiMe\textsubscript{3})\textsubscript{3} ligands.

A potential source for the additional 1 and 2e\textsuperscript{−} required to form complexes 8 and 9, respectively, is the U(m)/U(n) nitride complex, X. One could envision that the reduction of complex 7, promoted by the highly reducing U(m)/U(n) complex X, occurs in parallel with the binding of N\textsubscript{2}.

To confirm such a pathway, we sought out the reduction of 7 with the U(m)/U(n) complex X. Addition of 1.0 equiv. (2e\textsuperscript{−}) of in\textit{situ} generated complex X in \textit{d}\textsubscript{5}-toluene at 7 \textdegree C, resulted in an unambiguous color change from dark purple to brown with precipitation of orange crystals. Analysis of the reaction mixture by variable temperature \textsuperscript{1}H NMR spectroscopy, led to the complete consumption of X and formation of new resonances, including the imido (NH; δ 627.91 ppm) and methylene protons (δ −138.25 and −153.55 ppm), attributed to complex 9 (Fig. S57\textsuperscript{f}). Quantitative \textsuperscript{1}H NMR studies of the reaction mixture demonstrated that complex 9 is formed in 51% yield (Fig. S21\textsuperscript{f}). Crystallization of the reaction mixture from a concentrated toluene solution at −40 \textdegree C led to a mixture of pale green, orange, and colorless crystals. The pale green and orange crystals were identifiable as complexes 9 and 3-K, respectively. This indicates that complex 7 undergoes a 2e\textsuperscript{−} reduction promoted by the oxidation of the U(m)/U(n) complex to U(n)/U(iv). Attempts to isolate analytically pure 9 from this route proved unsuccessful due to the contaminant precipitation of 3-K.

In order to probe the reactivity of the U\textsubscript{2}(N\textsubscript{2}\textsuperscript{4−}) moiety in complex 7, we next investigated the reactivity with acid (H\textsuperscript{+}). Addition of HCl in Et\textsubscript{2}O to isolated complex 7, led to the formation of a broad, ill-defined triplet at δ 7.41 ppm in the \textsuperscript{1}H NMR spectrum, possibly consistent with \textit{14}NH\textsubscript{4}Cl (Fig. S59\textsuperscript{f}). Although ammonia quantification is difficult in this system, the number of equivalents of NH\textsubscript{3} increased by about ~1.7, compared to the amount obtained from the addition of acid to isolated complex 7.

This indicates that complex 7 undergoes a 2e\textsuperscript{−} reduction and N\textsubscript{2}\textsuperscript{4−} cleavage to a tris-nitride complex, promoted \textit{via} the U(m)/U(n) reducing agent, X.

**Conclusions**

Herein, we have identified rational routes for the synthesis of heteroleptic nitride bridged diuranium(n) complexes containing OSi(O\textsubscript{tBu})\textsubscript{3} and N(SiMe\textsubscript{3})\textsubscript{3} ligands in varying ratios. The differences in the electronic and steric properties of these ligands allow for the tuning of redox properties and reactivity of these diuranium complexes. The reactivity of the heteroleptic complexes [K\textsuperscript{+}(OSi(O\textsubscript{tBu})\textsubscript{3})(N(SiMe\textsubscript{3})\textsubscript{3})\textsubscript{2}[μ-N]] (1) and [Cs\textsuperscript{+}(OSi(O\textsubscript{tBu})\textsubscript{3})(N(SiMe\textsubscript{3})\textsubscript{3})\textsubscript{2}[μ-N]] (3-Cs), differs significantly from the previously reported all-OSi(O\textsubscript{tBu})\textsubscript{3} and all-N(SiMe\textsubscript{3})\textsubscript{3} analogues. Notably, the reduction of one of the U(n) centers can be performed for 1 and 3-Cs to yield the nitride bridged U(m)/U(iv) complexes, 4, 6-K, and 6-Cs, while reduction of the anionic all-amide complex G was unattainable, probably due the higher electron-rich character of the N(SiMe\textsubscript{3})\textsubscript{3} ligand compared to OSi(O\textsubscript{tBu})\textsubscript{3}. The presence of two additional OSi(O\textsubscript{tBu})\textsubscript{3} ligands in the U(m)/U(iv) complex 4, compared to the cationic all-amide complex E, results in an increased stability towards the 1,2 addition of the C–H bond of a N(SiMe\textsubscript{3})\textsubscript{3} ligand across the uranium–nitride,\textsuperscript{26} most likely due to the siloxide-bound K cation capping the nitride. Removal of the K cation by addition of 2,2,2-cryptand, increases nitride reactivity towards C–H activation, affording the imido cyclometallated complex 5. The U(m)/U(iv) complexes 4 and 6-Cs cannot be reduced further, most likely due to the very electron-rich character of the U. However, reduction of the second U(n) center is possible for complex 6-K, but is highly dependent upon the reduction reaction conditions. The putative U(m)/U(iv) heteroleptic nitride complex X, is significantly more reactive than the only other example of the all-OSi(O\textsubscript{tBu})\textsubscript{3} U(m)/U(iv) nitride complex, A. Similar to complex A, X reacts with N\textsubscript{2} and promotes the 4e\textsuperscript{−} reduction to yield the U(v)/U(v)–N\textsubscript{2}\textsuperscript{3−} complex 7. N\textsubscript{2} cleavage products were also identified from the reaction of X and N\textsubscript{2}, and were crystallographically characterized. The tris–nitride complex 8 is generated through the overall 6e\textsuperscript{−} cleavage of the bound N\textsubscript{2} moiety, promoted by a 2e\textsuperscript{−} transfer from the two U(m) centers to form a U(v)/U(vi) complex, with an additional 1e\textsuperscript{−} arising from an external source. In complex 9, cleavage of N\textsubscript{2} has also occurred to yield a U(v)/U(v) nitride, with 2e\textsuperscript{−} arising from an external source. We found that addition of 7 to X results in the formation of complexes 9 and 3-K, indicating that the diuranium(m) precursor, X, provides 1 or 2e\textsuperscript{−} to further reduce the bound N\textsubscript{2}\textsuperscript{4−} moiety in 7. These results demonstrate that by tuning the ancillary ligands, the reducing power and the redox flexibility of the uranium center can be altered leading to the 3e\textsuperscript{−} transfer from U(m) to N\textsubscript{2}. This work has demonstrated the first example of N\textsubscript{2} cleavage by a uranium complex in the
absence of alkali metals. Further tuning of the ancillary ligands in diuranium nitride complexes, should allow better control of these transformations.

Data availability

All data associated were included in the supporting information.

Author contributions

M. K. carried out the synthetic experiments and analyzed the experimental data. F. F.-T. and R. S. carried out the X-ray single crystal structure analyses. I. V. collected the variable-temperature magnetic data. M. M. originated the central idea, coordinated the work, and analyzed the experimental data. The manuscript was written through contributions of all authors.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

We acknowledge support from the Swiss National Science Foundation grant number 200021_178793, and the Ecole Polytechnique Fédérale de Lausanne (EPFL). We thank Dr Andrzej Sienkiewicz for EPR data collection.

References

1 (a) M. D. Walter, Adv. Organomet. Chem., 2016, 65, 261–377; (b) M. Falcone, L. Chatelain, R. Scopelliti, I. Zivkovic and M. Mazzanti, Nature, 2017, 547, 332–335; (c) Y. Roux, C. Duboc and M. Gennari, Chemphyschem, 2017, 18, 2606–2617; (d) P. L. Arnold, T. Ochiai, F. Y. T. Lam, R. P. Kelly, M. L. Seymour and L. Maron, Nat. Chem., 2020, 12, 654–659; (e) M. Reiners, D. Baabe, K. Munster, K. M. Zaretzke, M. Freytag, P. G. Jones, Y. Coppel, S. Bontemps, I. del Rosal, L. Maron and M. D. Walter, Nat. Chem., 2020, 12, 740–746; (f) S. J. K. Forrest, B. Schluschass, E. Y. Yuzik-Klimanova and S. Schneider, Chem. Rev., 2021, 121, 6522–6587; (g) F. Masero, M. A. Perrin, S. Dey and V. Mougel, Chem.–Eur. J., 2021, 27, 3892–3928.

2 (a) F. Haber, Ammonia German Patent, DE 229126 Pat., 1909; (b) F. Haber, Angew. Chem., 1914, 27, 473–477.

3 (a) A. L. Odom, P. L. Arnold and C. C. Cummins, J. Am. Chem. Soc., 1998, 120, 5836–5837; (b) P. Roussel and P. Scott, J. Am. Chem. Soc., 1998, 120, 1070–1071; (c) F. G. N. Cloke and P. B. Hitchcock, J. Am. Chem. Soc., 2002, 124, 9352–9353; (d) I. Korobkov, S. Gambarotta and G. P. A. Yap, Angew. Chem., Int. Ed. Engl., 2002, 41, 3433–3436; (e) W. J. Evans, S. A. Kozimor and J. W. Ziller, J. Am. Chem. Soc., 2003, 125, 14264–14265; (f) S. M. Mansell, N. Kaltsoyannis and P. L. Arnold, J. Am. Chem. Soc., 2011, 133, 9036–9051; (g) S. M. Mansell, J. H. Farnaby, A. I. Germeroth and P. L. Arnold, Organometallics, 2013, 32, 4214–4222; (h) M. Falcone, L. Barluzzi, J. Andrez, F. F. Tirani, I. Zivkovic, A. Fabrizio, C. Corminboeuf, K. Severin and M. Mazzanti, Nat. Chem., 2019, 11, 154–160; (i) E. Lu, B. E. Atkinson, A. J. Wooles, J. T. Boronski, L. R. Doyle, F. Tuna, J. D. Cryer, P. J. Cobb, I. J. Vitorica-Yrezabal, G. F. S. Whitehead, N. Kaltsoyannis and S. T. Liddle, Nat. Chem., 2019, 11, 806–811; (j) X. Q. Xin, I. Douair, Y. Zhao, S. Wang, L. Maron and C. Q. Zhu, J. Am. Chem. Soc., 2020, 142, 15004–15011; (k) N. Jori, L. Barluzzi, I. Douair, L. Maron, F. Fadaei-Tirani, I. Zivkovic and M. Mazzanti, J. Am. Chem. Soc., 2021, 143, 11225–11234; (l) P. L. Wang, I. Douair, Y. Zhao, S. Wang, J. Zhu, L. Maron and C. Q. Zhu, Angew. Chem., Int. Ed. Engl., 2021, 60, 473–479.

4 (a) S. Fortier, N. Kaltsoyannis, G. Wu and T. W. Hayton, J. Am. Chem. Soc., 2011, 133, 14224–14227; (b) D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, Science, 2012, 337, 717–720; (c) C. Camp, J. Pecaut and M. Mazzanti, J. Am. Chem. Soc., 2013, 135, 12101–12111; (d) T. W. Hayton, J. Am. Chem. Soc., 2013, 135, 2956–2973; (e) C. Camp, M. A. Antunes, G. Garcia, I. Ciofini, I. C. Santos, J. Pecaut, M. Almeida, J. Marcelo and M. Mazzanti, Chem. Sci., 2014, 5, 841–846; (f) O. Cooper, C. Camp, J. Pécaut, C. E. Kefalidis, L. Maron, S. Gambarelli and M. Mazzanti, J. Am. Chem. Soc., 2014, 136, 6716–6723; (g) D. P. Halter, F. W. Heinemann, J. Bachmann and K. Meyer, Nature, 2016, 530, 317–321; (h) N. Tsoureas, A. F. R. Kilpatrick, C. J. Inman and F. G. N. Cloke, Chem. Sci., 2016, 7, 4624–4632; (i) B. M. Gardner, C. E. Kefalidis, E. Lu, D. Patel, E. J. L. McInnes, F. Tuna, A. J. Woolles, L. Maron and S. T. Liddle, Nat. Commun., 2017, 8, 1898; (j) N. S. Settineri, A. A. Shiua and J. Arnold, Chem. Commun., 2018, 54, 10913–10916.

5 (a) D. S. J. Arney and C. J. Burns, J. Am. Chem. Soc., 1995, 117, 9448–9460; (b) J. L. Kiplinger, D. E. Morris, B. L. Scott and C. J. Burns, Chem. Commun., 2002, 30–31; (c) J. L. Brown, S. Fortier, G. Wu, N. Kaltsoyannis and T. W. Hayton, J. Am. Chem. Soc., 2013, 135, 5352–5355; (d) A. J. Lewis, P. J. Carroll and E. J. Schelter, J. Am. Chem. Soc., 2013, 135, 13185–13192; (e) E. L. Lu, O. J. Cooper, J. McMaster, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake and S. T. Liddle, Angew. Chem., Int. Ed. Engl., 2014, 53, 6696–6700; (f) N. T. Rice, K. McCabe, J. Bacs, L. Maron and H. S. La Pierre, J. Am. Chem. Soc., 2020, 142, 7368–7373; (g) R. J. Ward, P. Rungthanaphatsophon, I. del Rosal, S. P. Kelley, L. Maron and J. R. Walensky, Chem. Sci., 2020, 11, 5830–5835.

6 (a) J. M. Manriquez, P. J. Fagan, T. J. Marks, S. H. Vollmer, C. S. Day and V. W. Day, J. Am. Chem. Soc., 1979, 101, 5075–5078; (b) P. J. Fagan, J. M. Manriquez, T. J. Marks, C. S. Day, S. H. Vollmer and V. W. Day, Organometallics, 1982, 1, 170–180; (c) P. L. Diaconescu, P. L. Arnold, T. A. Baker, D. J. Mindiola and C. C. Cummins, J. Am. Chem. Soc., 2000, 122, 6108–6109; (d) W. J. Evans, S. A. Kozimor and J. W. Ziller, Chem. Commun., 2005, 4681–4683; (e) G. F. Zi, L. Jia, E. L. Werkema, M. D. Walter, J. P. Gottfriedsen and R. A. Andersen, Organometallics, 2005, 24, 4251–4264; (f) W. J. Evans, K. A. Miller,
