

Cite this: *Chem. Sci.*, 2021, 12, 8096

All publication charges for this article have been paid for by the Royal Society of Chemistry

## Synthesis, structure, and reactivity of uranium(vi) nitrides†

Luciano Barluzzi,<sup>a</sup> Fang-Che Hsueh,<sup>a</sup> Rosario Scopelliti,<sup>b</sup> Benjamin E. Atkinson,<sup>b</sup> Nikolas Kaltsoyannis<sup>b</sup> and Marinella Mazzanti<sup>b</sup>\*<sup>a</sup>

Uranium nitride compounds are important molecular analogues of uranium nitride materials such as UN and UN<sub>2</sub> which are effective catalysts in the Haber–Bosch synthesis of ammonia, but the synthesis of molecular nitrides remains a challenge and studies of the reactivity and of the nature of the bonding are poorly developed. Here we report the synthesis of the first nitride bridged uranium complexes containing U(vi) and provide a unique comparison of reactivity and bonding in U(vi)/U(vi), U(vi)/U(v) and U(v)/U(v) systems. Oxidation of the U(v)/U(v) bis-nitride [K<sub>2</sub>{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>(μ-N))<sub>2</sub>], **1**, with mild oxidants yields the U(v)/U(vi) complexes [K{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>(μ-N))<sub>2</sub>], **2** and [K<sub>2</sub>{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>(μ-N)<sub>2</sub>(μ-l)}], **3** while oxidation with a stronger oxidant (“magic blue”) yields the U(vi)/U(vi) complex [{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>(μ-N)<sub>2</sub>(μ-thf)}], **4**. The three complexes show very different stability and reactivity, with N<sub>2</sub> release observed for complex **4**. Complex **2** undergoes hydrogenolysis to yield imido bridged [K<sub>2</sub>{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>(μ-NH))<sub>2</sub>], **6** and rare amido bridged U(vi)/U(vi) complexes [{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>(μ-NH)<sub>2</sub>(μ-thf)}], **7** while no hydrogenolysis could be observed for **4**. Both complexes **2** and **4** react with H<sup>+</sup> to yield quantitatively NH<sub>4</sub>Cl, but only complex **2** reacts with CO and H<sub>2</sub>. Differences in reactivity can be related to significant differences in the U–N bonding. Computational studies show a delocalised bond across the U–N–U for **1** and **2**, but an asymmetric bonding scheme is found for the U(vi)/U(vi) complex **4** which shows a U–N σ orbital well localised to U≡N and π orbitals which partially delocalise to form the U–N single bond with the other uranium.

Received 30th March 2021  
Accepted 30th April 2021

DOI: 10.1039/d1sc01796a

rsc.li/chemical-science

## Introduction

Metal nitride complexes continue to attract significant attention because of their key roles in the catalytic N<sub>2</sub> hydrogenation for ammonia production and in N-transfer processes.<sup>1</sup> Uranium nitride compounds provide molecular analogues of inorganic uranium nitride materials (UN, UN<sub>2</sub>, U<sub>2</sub>N<sub>3</sub>) which are effective catalysts in the Haber–Bosch synthesis of ammonia<sup>2</sup> and are considered as potential fuel for nuclear and space-power reactors.<sup>3</sup> Two examples of molecular uranium nitrides, both showing a diamond shaped arrangement of the two nitrides, were obtained from the cleavage of dinitrogen in ambient conditions.<sup>4</sup>

However, the development of rational synthetic routes to molecular uranium nitrides and the study of U–N bonding is still at an early stage.<sup>2b,5a–e</sup>

In recent years, a few mononuclear<sup>5e,6,7a,7b,5c,7c</sup> uranium terminal nitrides have been synthesised. A larger number of polynuclear uranium complexes containing bridging nitride has been reported. Most of the nitride bridged uranium complexes isolated so far contain uranium in the +IV oxidation state<sup>2b,4a,5b,8a–g</sup> with fewer examples containing U(III)<sup>9a,1c,9b</sup> or U(v).<sup>4a,8d,10</sup> Both terminal and bridging uranium nitrides have demonstrated high reactivity towards dinitrogen reduction, CO and CO<sub>2</sub> cleavage, and C–H activation.<sup>9b,11a–f</sup>

The reactivity of high valent uranium nitrides with H<sub>2</sub> is also of high current interest for modelling the activity of metal nitride catalysts in N<sub>2</sub> hydrogenation. The previous reports of hydrogenolysis by a terminal U(v) nitride,<sup>11e</sup> U(IV) nitride bridged complexes,<sup>9b,12</sup> and a U(v) bis-nitride<sup>10a</sup> are particularly remarkable considering the paucity of examples of direct hydrogenolysis by metal nitride complexes reported in the literature.<sup>1a,13a–f</sup>

After the first terminal U(vi) nitride was reported more than ten years ago,<sup>7b</sup> only two additional examples of U(vi) nitride complexes<sup>5e,14</sup> have been isolated very recently. Therefore, the knowledge of U(vi) nitrides lags far behind that of the oxide analogue uranyl(vi) (UO<sub>2</sub><sup>2+</sup>) which is the prevalent uranium form in nature. The scarce information available on U(vi) nitrides, mostly limited to gas phase and computational

<sup>a</sup>Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland. E-mail: marinella.mazzanti@epfl.ch

<sup>b</sup>Department of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, UK

† Electronic supplementary information (ESI) available: Synthetic methods, NMR spectra, computational details, crystallographic data. CCDC numbers: 2072156–2072160; 2080129. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1sc01796a



studies,<sup>15</sup> is due to the high chemical and photochemical reactivity of the U(vi) fragment.<sup>16,7b,11f</sup> In particular the diatomic rhombic (UN)<sub>2</sub> and (UN<sub>2</sub>)<sub>2</sub> fragments were so far only identified in matrix isolation experiments.<sup>13f</sup>

Oxidation of isolated U(v) nitrides, when available, allowed the synthesis of the analogous terminal<sup>7b</sup> or boron-capped U(vi) nitrides,<sup>17</sup> but demonstrated significant sensitivity to the reaction conditions<sup>7b</sup> and failed, so far, to produce U(vi)/U(vi) nitride bridged complexes.

Here we report the synthesis and characterization of the first example of a dinuclear U(vi) nitride which was obtained by oxidation of the previously reported U(v)/U(v) bis-nitride<sup>8f,10a</sup> [K<sub>2</sub>{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)}<sub>2</sub>(μ-N)<sub>2</sub>], **1**, with the strong oxidant tris(4-bromophenyl)ammoniumyl hexachloroantimonate (“magic blue”). The use of more common milder oxidants resulted in the isolation of the U(v)/U(vi) analogue.

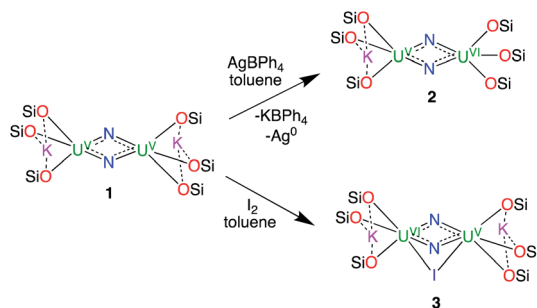
Studies of the molecular and electronic structure show very different bonding schemes for the two species that result in different reactivity.

## Results and discussion

### Synthesis of bis-nitride complexes

The synthesis of the targeted bis-nitride complexes of U(vi) was pursued by the oxidation of the previously reported complex **1** (ref. 8f) with different oxidizing agents (Scheme 1).

Reaction of **1** with 1 equiv. of AgBPh<sub>4</sub> in *d*<sub>8</sub>-toluene led to the full consumption of the starting material over the course of 5 days and the formation of a new species showing a broad resonance between 1.5 and −0.5 ppm. The reaction of complex **1** with 2 equiv. of AgBPh<sub>4</sub> resulted in the formation of the same species but with a faster consumption of the starting material (24 h). Cooling down the concentrated reaction mixture at −40 °C resulted in the formation of dark orange crystals of the mixed-valent complex [K{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)}<sub>2</sub>(μ-N)<sub>2</sub>], **2** in 65% yield. The reaction of complex **1** with 0.5 or 1 equiv. of I<sub>2</sub> in toluene led to the formation of the same U(v)/U(vi) complex as observed by <sup>1</sup>H NMR spectroscopy. Cooling down the reaction mixture at −30 °C afforded ochre yellow crystals of the complex [K<sub>2</sub>{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)}<sub>2</sub>(μ-N)<sub>2</sub>(μ-I)], **3**. The molecular structure of **3** indicates that the KI byproduct remains bound in the crystallised complex. The oxidation of **1** with larger excess of AgBPh<sub>4</sub> or I<sub>2</sub> failed to produce the desired U(vi)/U(vi) nitride and resulted



Scheme 1 Oxidation of complex **1** affording the complexes [K{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)}<sub>2</sub>(μ-N)<sub>2</sub>], **2** and [K<sub>2</sub>{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)}<sub>2</sub>(μ-N)<sub>2</sub>(μ-I)], **3**.

only in the formation of intractable mixtures of unidentified products.

Thus, in order to obtain a U(vi)/U(vi) bis-μ-nitride complex, we decided to use the stronger oxidant [N(C<sub>6</sub>H<sub>4</sub>Br)<sub>3</sub>][SbCl<sub>6</sub>], also known as “magic blue”.<sup>18</sup> Notably, we recently found that “magic blue” could be used to reach the high oxidation state +IV in lanthanide complexes supported by siloxide ligands.<sup>19</sup> Gratifyingly, the reaction of complex **1** with 2 equiv. of [N(C<sub>6</sub>H<sub>4</sub>Br)<sub>3</sub>][SbCl<sub>6</sub>] in thf resulted in the immediate formation of a single new species resonating at 1.44 ppm with a conversion of 94% measured by <sup>1</sup>H NMR spectroscopy. Cooling down the reaction mixture in toluene at −40 °C afforded orange crystals of the U(vi)/U(vi) complex [{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)}<sub>2</sub>(μ-N)<sub>2</sub>(μ-thf)], **4** in 35% yield. The low yield of the reaction, despite the almost quantitative conversion, reflects the high solubility of complex **4** in toluene and the separation steps necessary for the removal of the reaction byproducts. These results demonstrate that the use of a strong oxidizing agent such as an ammonium cation is necessary to oxidise the bis-nitride U(v)/U(v) to the U(vi)/U(vi) analogue. It should be noted that complex **4** undergoes decomposition if left in the reaction mixture for a long time before isolation, as indicated by <sup>1</sup>H NMR spectroscopy. The formation of new species is observed after 6 h with full consumption of complex **4** after 5 days. Cooling down the resulting decomposed reaction mixture in toluene at −40 °C overnight afforded light green crystals of the complex [U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)Cl(thf)<sub>2</sub>], **5**. The molecular structure of **5** and its description are reported in the ESI.† The presence of the chloride ligand suggests that the oxidised nitride reacts with the SbCl<sub>6</sub><sup>−</sup> anion. The non-innocence of the SbCl<sub>6</sub><sup>−</sup> anion in the oxidation of organometallic substrates was previously demonstrated.<sup>20</sup> Similar U(IV) halide species were also isolated upon reaction of the U(v) terminal nitride [U(Tren<sup>TIPS</sup>)N]<sup>7b</sup> with halide-containing oxidizing agents.<sup>7b</sup>

The molecular structure of complex **2** (Fig. 1) was determined by XRD studies and shows a dimeric U(v)/U(vi) complex bridged by two nitride ligands. Each U centre is pentacoordinated in a slightly distorted square pyramidal geometry and is

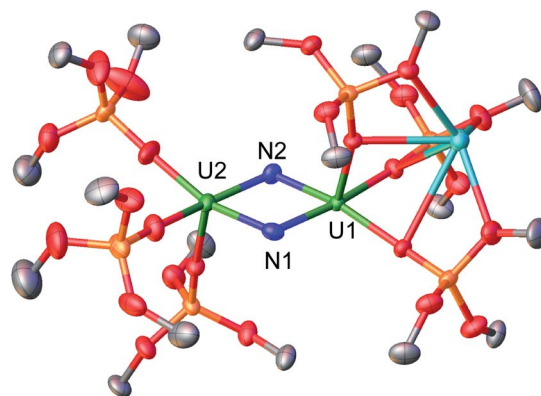


Fig. 1 Molecular structure of the complex [K{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)}<sub>2</sub>(μ-N)<sub>2</sub>], **2** with thermal ellipsoids drawn at the 50% probability level. The methyl groups of the *tert*-butyl moieties and the co-crystallized solvent molecules have been omitted for clarity.



bound to the two bridging nitrides and to three siloxide ligands. One set of siloxide ligands provides a O6 coordination pocket for the  $K^+$  counterion. The average U1–O<sub>sil</sub> distance of 2.17(1) Å is slightly longer than the average U2–O<sub>sil</sub> of 2.11(1) probably due to the presence of the  $K^+$  bound to the siloxide ligands. The U–N bond distances are all very similar (U1–N1 = 2.020(4) Å, U1–N2 = 2.067(4) Å, U2–N1 = 2.091(4) Å, and U2–N2 = 2.046(4) Å) and the average U–N bond distance of 2.06(3) Å is statistically equivalent to the one previously reported for complex **1** (2.06(6) Å).<sup>8f</sup> These values are consistent with the presence of U=N double bond character similar to that found in mono-nitride bridged uranium compounds (2.032(2)–2.080(4) Å).<sup>8d,8f,12b</sup> Overall, the metrical parameters indicate the presence of a charge delocalised species.

The molecular structure of **3** (Fig. S40†), as determined by XRD studies, shows the presence of a bis-nitride bridged dimeric U(v)/U(vi) complex which differs from **2** only by the presence of an additional bridging iodide ligand and an additional bound potassium cation. In **3**, two potassium cations are bound in each O6 coordination pocket formed by three siloxide ligands. The U–O<sub>sil</sub> distances (mean U–O = 2.190(5) Å) and the U–N bond distances (mean U–N = 2.13(5) Å) are nearly equivalent for the two U centres, suggesting no localization of the charge. The values of the U–N bond distances in **2** and **3** are only slightly longer than those found in **1** (2.022(5)–2.101(6) Å) and are comparable to the longer values reported for U<sup>VI</sup> = NR groups (2.034–2.068 Å).<sup>21</sup> In both complexes the two nitrides bind the uranium centres in a quite symmetric fashion with similar values of U–N distances.

The molecular structure of complex **4**, as determined by XRD studies (Fig. 2), shows a dimeric U(vi) complex bridged by two nitride and one thf ligand. The bridging mode adopted by the thf ligand is not common, but was previously reported in complexes of metal ions of the d, s and f block.<sup>22</sup> Each U atom is hexacoordinated in a distorted octahedral geometry bound by the three bridging ligands and three siloxide ligands. Asymmetric U–N bond distances are observed in complex **4**.

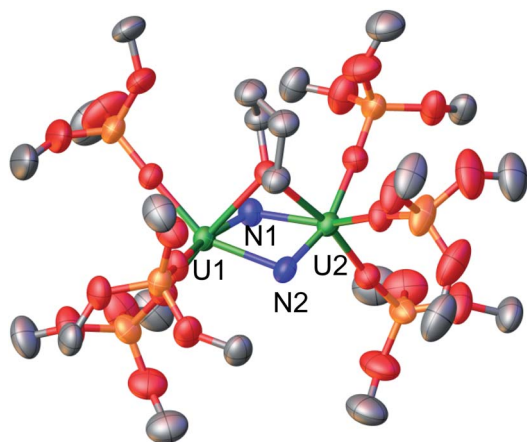


Fig. 2 Molecular structure of the complex  $\{[U(OSi(O^tBu)_3)_2(\mu-N)_2(\mu-thf)]\}_2$ , **4** with thermal ellipsoids drawn at the 50% probability level. The methyl groups of the *tert*-butyl moieties have been omitted for clarity.

In particular, short U–N distances (U1–N1 = 1.966(16) Å and U2–N2 = 1.850(12) Å) alternate with much longer distances (U1–N2 = 2.292(13) Å and U2–N1 = 2.252(16) Å). The longer distances are comparable to those found in uranium nitride clusters containing U–N single bonds (2.154(7)–to 2.399(5) Å).<sup>23,8b,4b</sup> The values of the shorter U–N distances in **4** are longer than those found in the only two previously reported terminal U(vi) nitrides (1.769(2) Å and 1.799(7) Å)<sup>7b,5e</sup> but similar to those found in borane capped U(vi) nitrides (1.880(4)–1.916(4) Å)<sup>17,6b</sup> and in tris- and tetrakis(imido) imido complexes (2.034–2.068 Å),<sup>21b</sup> consistent with the presence of U≡N multiple bond. The observed bonding scheme suggests that each nitride ligand binds one uranium cation with a triple bond and the other one with a single dative bond (Fig. 3). A similar alternate asymmetric bonding scheme was calculated for the matrix isolated U(vi) bis- $\mu$ -nitride  $[UN(\mu-N)]_2$  (U1–N1 = 1.859 Å, U1–N2 = 2.281 Å).<sup>15f</sup> An asymmetric binding mode is also found in the only two reported polynuclear U(vi) nitrides.<sup>14,8c</sup> In the trinuclear  $[(NH_3)_8U^{IV}(\mu-N)(NH_3)_5U^{VI}(\mu-N)U^{IV}(NH_3)_8]Br_8 \cdot 26NH_3$  a  $U^{VI}N_2$  fragment binds two  $[(NH_3)_8U^{IV}]^{4+}$  moieties through the bridging nitrides with  $U^{VI} \equiv N$  bond distances of 1.853(3) and 1.854(3) Å and  $U^{IV}$ –N distances of 2.304(3) and 2.300(3) Å.<sup>14</sup> In the dinuclear  $[Na(DME)_2][[(NR)_2(O)U(\mu-N)(CH_2SiMe_2NR)U(NR)_2]]_2$ , the  $NU^{VI}O$  fragment binds the  $[U^{IV}(CH_2SiMe_2NR)U(NR)_2]$  moiety through a bridging nitride with a  $U^{VI} \equiv N$  bond distance of 1.818(9) Å and a  $U^{IV}$ –N distance of 2.284(8) Å.<sup>8c</sup>

For U2 all the U–O<sub>sil</sub> bond distances are similar (2.09(1), 2.10(1) and 2.11(1) Å). In contrast, for U1 we observe a small shortening of the U–O<sub>sil</sub> bond *trans* to the nitride (2.068(9) Å; N–U–O = 161.8(6)°) compared the U–O<sub>sil</sub> bonds *cis* to the nitride (2.15(1) and 2.12(1) Å). Such shortening could be interpreted in terms of the inverse *trans* influence (ITI), a phenomenon previously observed for terminal U(vi) oxo and nitride complexes supported by strong  $\sigma$  and  $\pi$  donor ligands.<sup>24</sup>

Thus, the asymmetric binding mode found in **4** is very different from the more symmetric binding found both in the mixed valent U(vi)/U(v) bis nitride complexes **2** and **3** and in the previously reported U(v)/U(v) analogue **1**.

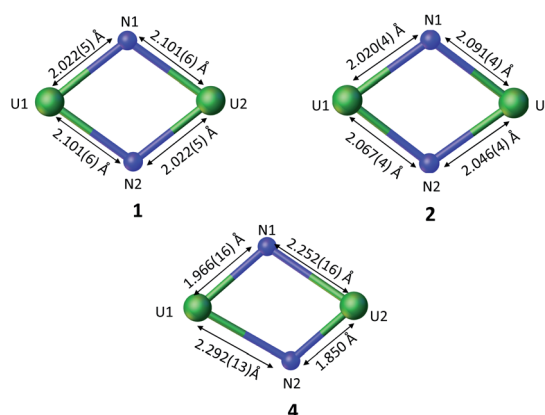


Fig. 3  $U_2N_2$  cores and structural parameters of the complexes **1**, **2**, and **4**.



### Stability and reactivity of the bis-nitride complexes

With these bis-nitride complexes in hand, their stability and reactivity were investigated and compared to that of recently isolated terminal U(v) and U(vi) nitrides.

The U(v)/U(v) bis-nitride **1** was reported to be stable both in solid state and in solution at room temperature for at least 5 days.

Similarly, once isolated the terminal U(vi) nitride [NBu<sub>4</sub>][U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>4</sub>(N)]<sup>5e</sup> was reported to be stable in solution for at least three weeks.<sup>5e</sup>

Complex **2** was also found to be stable in solid and in solution for at least 5 days.

Complexes **1**, **2**, and the terminal nitride [NBu<sub>4</sub>][U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>4</sub>(N)] showed no sign of decomposition when put under dynamic vacuum suggesting that nitride coupling and release of N<sub>2</sub> do not occur for these systems.

A significantly lower solution stability was found for complex **4** which slowly decomposes in a *d*<sub>8</sub>-thf solution under an N<sub>2</sub> or an Ar atmosphere to afford a complex mixture of products (Scheme 2).

The formation of new species was detected after 6 h and full decomposition was observed after 5 days giving rise to an intractable mixture of species. The decomposition of complex **4** was greatly affected by its exposure to dynamic vacuum. Full consumption of complex **4** was, indeed, observed after exposure to dynamic vacuum for 15 minutes. The reaction mixture obtained upon decomposition of complex **4** under Ar or under vacuum presents the same unidentified products as indicated by <sup>1</sup>H NMR spectroscopy. The observed low stability under dynamic vacuum of **4** is suggestive of dinitrogen release through nitride coupling. To test this possibility, the headspace of the reaction mixture after full decomposition of complex **4** under an Ar atmosphere was analyzed by GC-MS. The presence of N<sub>2</sub> was detected. Moreover, we found that addition of excess HCl to the reaction mixture obtained after exposure of **4** to vacuum showed only traces of NH<sub>4</sub>Cl, suggesting that the decomposition products do not contain nitride ligands (see below for observed production of NH<sub>4</sub>Cl from addition of acid to **4**). This suggests that the decomposition of complex **4** occurs *via* oxidative coupling of the nitride ligand.

Nitride coupling has not been reported in f-element chemistry, but slow N<sub>2</sub> release was previously observed for a tetrameric Fe bis-μ-nitride complex supported by a β-diketimate

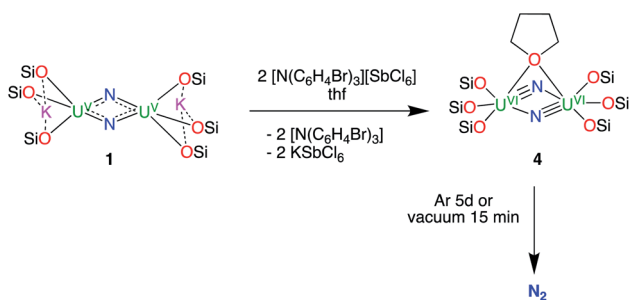
ligand in a benzene solution.<sup>25</sup> Electron rich transition metal terminal nitride species have also been reported to undergo spontaneous nitride coupling reactivity because of the presence of d electrons that populate the M–N π\* orbitals.<sup>1b,26</sup>

Density functional theory calculations (*vide infra*) identified two isomers of **4**, a U(v)/U(v) isomer bridged by N<sub>2</sub><sup>4–</sup> and a U(iv)/U(iv) N<sub>2</sub><sup>2–</sup> isomer, which are possible intermediates in a dinitrogen-evolution mechanism.

The reactivity of the U(v)/U(vi) and U(vi)/U(vi) bis-nitride towards CO, H<sub>2</sub>, and H<sup>+</sup> was investigated and compared with previous studies performed on the U(v)/U(v) bis-nitride<sup>10a</sup> and terminal U(vi) nitrides.<sup>11a,5e,11e</sup> The addition of 1 atm of CO to a degassed *d*<sub>8</sub>-toluene solution of complex [K{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>(μ-N)}<sub>2</sub>], **2** led to a colour change from brown-orange to light green over the course of 30 minutes and to the formation of an intractable mixture as observed by <sup>1</sup>H NMR spectroscopy. When the reaction was repeated with <sup>13</sup>CO, the <sup>13</sup>C NMR spectrum of the reaction mixture showed the presence of two paramagnetically shifted peaks at 215.71 and –162.60 ppm attributed to two U-bound <sup>13</sup>C-containing species. The observed resonances fall in the broad range of chemical shifts previously reported for U(iv) and U(m) bound isocyanate ligands (492.4 to –164 ppm).<sup>16,27</sup> When the reaction residue was hydrolysed with *p*D = 12 D<sub>2</sub>O, N<sup>13</sup>CO<sup>–</sup> was observed as the only <sup>13</sup>C-containing species by <sup>13</sup>C NMR spectroscopy. Quantitative <sup>13</sup>C NMR spectroscopy measured with respect to an added standard of CH<sub>3</sub><sup>13</sup>COONa revealed the formation of 2 equiv. of N<sup>13</sup>CO<sup>–</sup> per complex, thus proving that both nitride ligands are converted to isocyanate. The two-electron oxidation of two molecules of CO requires the two-electron reduction of both uranium centres in the U(v)/U(vi) complex **2**, involving the formation of U(m)–U(iv) species. Ligand redistribution is probably at the origin of the presence of multiple species. Similar reductive carbonylation reactivity was observed in U(v)<sup>11a</sup> and U(vi)<sup>11a,5e</sup> terminal nitride complexes. Such reactivity differs from that reported for the U(v)/U(v) complex **1**. Upon reaction with <sup>13</sup>CO, the two nitride ligands of complex **1** are instead converted to equimolar amounts of <sup>13</sup>CN<sup>–</sup> and N<sup>13</sup>CO<sup>–</sup> to yield the U(iv)–U(iv) complex [K<sub>2</sub>{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>(μ-O)(μ-CN)(μ-NCO)}].<sup>10a</sup> Therefore in complex **1** one nitride undergoes reductive carbonylation but the second nitride acts as a strong nucleophile and effects the cleavage of the CO molecule. The different reactivity observed for the mixed valent complex **2** can be assigned to its higher oxidation state that facilitates the reductive carbonylation process.

However, surprisingly exposure of *d*<sub>8</sub>-thf or *d*<sub>8</sub>-toluene solutions of the complex **4** to 1 atm of CO did not result in any reaction even after 6 days. Monitoring the evolution of the reactions by <sup>1</sup>H NMR spectroscopy revealed only the presence of decomposition products and no <sup>13</sup>C-containing species could be detected by <sup>13</sup>C NMR spectroscopy after hydrolysis of the reaction mixture with *p*D = 12 D<sub>2</sub>O.

The lack of reactivity of the U(vi)/U(vi) bis-nitride also contrasts with the high reactivity towards CO of the analogous terminal U(vi) nitride complex supported by four siloxide ligands [NBu<sub>4</sub>][U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>4</sub>(N)], bearing a U–N triple bond.<sup>5e</sup>



Scheme 2 Synthesis of complex [(U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>)<sub>2</sub>(μ-N)<sub>2</sub>(μ-thf)], **4** and its decomposition.



The only other reported terminal U(vi) nitride, the [U(vi)(Tren<sup>TIPS</sup>)N] complex,<sup>7b</sup> was found to react slowly with CO over the course of 16 h while the analogous [U(v)(Tren<sup>TIPS</sup>)N]<sup>-</sup> reacts immediately with the substrate. Such slower reaction observed for the U(vi) complex was interpreted in terms of sterical congestion at the U(vi) centre preventing binding of CO to the metal in the proposed reaction intermediate.<sup>11a</sup> A similar reasoning could be used to explain, at least in part, the lack of reactivity of the U(vi) bis-nitride complex **4** compared to the fast reaction of the U(v) analogue, complex **1**, with CO.

Complex **4** reacts rapidly with CO<sub>2</sub> in ambient conditions but the resulting products could not be identified.

Since we recently reported the rare ability of complex **1** to promote the oxidative cleavage of H<sub>2</sub> in ambient conditions, affording the reduced imido-bridged U(IV)/U(IV) complex [K<sub>2</sub>{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>(μ-NH)<sub>2</sub>}]<sub>2</sub>, **6**, we set out to investigate the reactivity of complexes **2** and **4** with H<sub>2</sub> (Scheme 3). Addition of 1 atm of H<sub>2</sub> to a *d*<sub>8</sub>-toluene solution of complex **2** led to its slow conversion over the course of 2 days to an equimolar mixture of two species resonating at 0.27 and -0.87 ppm. Monitoring the evolution of the reaction mixture *via* <sup>1</sup>H NMR spectroscopy did not reveal the presence of intermediate species. The resonance at -0.87 ppm was assigned to the previously reported complex [K<sub>2</sub>{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>(μ-NH)<sub>2</sub>}]<sub>2</sub>, **6**. The presence of **6** was also confirmed by single crystal X-ray diffractometry. Cooling down a concentrated toluene/thf reaction mixture at -40 °C led to the formation of light yellow crystals of complex **6** and light green crystals of the complex [{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>}]<sub>2</sub>(μ-NH<sub>2</sub>)<sub>2</sub>(μ-thf), **7**. The similar solubility of the complexes **6** and **7** prevented the isolation of analytically pure amounts of the latter from the reaction of complex **2** with H<sub>2</sub>.

Nevertheless, complex **7** could be independently synthesised upon protonation of complex [K<sub>2</sub>U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>(μ-NH)]<sub>2</sub>, **6** with 2 equiv. of the weak acid NEt<sub>3</sub>HBPh<sub>4</sub>, confirming the presence of amido bridging ligands in complex **7**.

The molecular structure of complex **7**, as determined by XRD studies (Fig. 4), shows a dimeric U(IV) complex bridged by two amido and one thf ligand. Each U centre is hexacoordinated in a distorted octahedral geometry. The bridging NH<sub>2</sub> linkage is unprecedented in uranium complexes. The U–N bond distances (U1–N1 = 2.441(7), U1–N2 = 2.443(7), U2–N1 = 2.436(10), U2–N2 = 2.455(8) Å) are elongated compared to the U–N<sub>imido</sub> distances in complex **6** (2.192(3)–2.273(3) Å) and are longer than

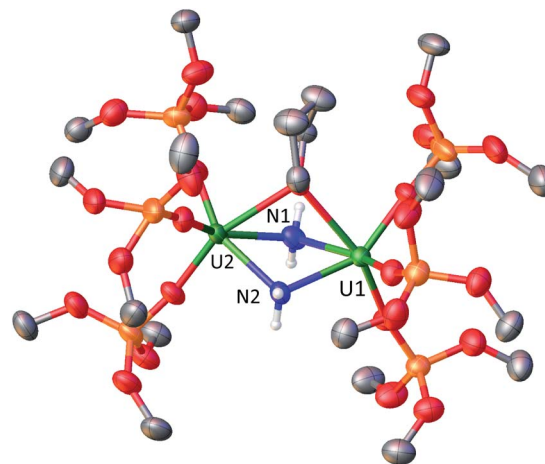


Fig. 4 Molecular structure of the complex [(U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>)<sub>2</sub>(μ-NH<sub>2</sub>)<sub>2</sub>(μ-thf)], **7** with thermal ellipsoids drawn at the 50% probability level. The methyl groups of the *tert*-butyl moieties have been omitted for clarity.

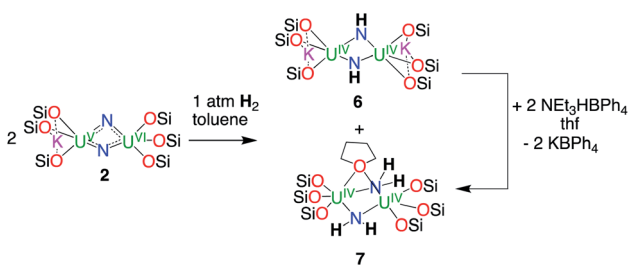
the distances found in the rare examples of terminal U–NH<sub>2</sub> complexes (2.183(6)–2.335(3) Å).<sup>7b,11e,28</sup> The reaction of complex **2** with H<sub>2</sub> is likely to involve first the oxidative cleavage of one molecule of H<sub>2</sub> to afford a transient U(IV)–U(V) bis-μ-NH followed by ligand scrambling affording complex **6** and a transient U(V)–U(V) bis-μ-NH complex. The latter immediately reacts with a second molecule of H<sub>2</sub> to afford complex **7** (Scheme S2†).

It should be noted that bis-imido U(IV)/U(IV) complex **6** does not react further with H<sub>2</sub> suggesting that a high oxidation state of the metal centre is required for an imido complex to effect oxidative cleavage of H<sub>2</sub>. Similar oxidative cleavage of H<sub>2</sub> was reported very recently for a terminal U(V)<sup>11e</sup> but terminal U(vi) nitrides did not react. The analogous nitride bridged complex U(vi)/U(vi) **4** also did not react with 1 atm of H<sub>2</sub>. Monitoring the evolution of the reaction of **4** with H<sub>2</sub> by <sup>1</sup>H NMR spectroscopy revealed only the presence of decomposition products.

These results seem to indicate that the presence of U(v) in the charge delocalised complex **2**, best described as a U 5.5+/U 5.5+ complex, results in a higher reactivity towards H<sub>2</sub> compared to the U(v)/U(v) and U(vi)/U(vi) analogues.

The computed mechanism of hydrogenolysis by the terminal U(v) complex [U<sup>V</sup>(Tren<sup>TIPS</sup>)(N)][K(B15C5)]<sub>2</sub> (Tren<sup>TIPS</sup> = N(CH<sub>2</sub>-CH<sub>2</sub>NSi<sup>+</sup>Pr<sub>3</sub>)<sub>3</sub><sup>3-</sup>; B15C5 = benzo-15-crown-5-ether) involves an heterolytic cleavage of H<sub>2</sub> and formation of a hydride imide U(v) intermediate followed by a 1,2 addition to yield the final U(III)–NH<sub>2</sub> complex. The observed reactivity of the terminal U(v) and lack of reactivity of the analogous U(vi) was explained in terms of a combination of the 5f-electron not being fully nonbonding, and the uranium(v)-nitride bond being highly polar.

A mechanism involving an heterolytic cleavage of H<sub>2</sub> to yield an imide hydride followed by hydride migration to the second nitride is likely to occur in both hydrogenation steps of the nitrides in complex **2**. A similar mechanism has also been computed for the hydrogenolysis effected by an iron bis-nitride complex very recently reported by Walter.<sup>13e</sup>



Scheme 3 Reactivity of complex **2** with H<sub>2</sub> yielding an equimolar mixture of the complexes [K<sub>2</sub>{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>(μ-NH)<sub>2</sub>}]<sub>2</sub>, **6** and [U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>(μ-NH<sub>2</sub>)<sub>2</sub>], **7**.



**Table 1** QTAIM and NBO charges,  $q(\text{U})$  and  $q(\text{N})$ , and U–N bond indices; the QTAIM delocalisation index  $\delta(\text{U}|\text{N})$  and the NBO Wiberg bond index  $\text{BO}_{\text{W}}(\text{U},\text{N})$

	QTAIM			NBO		
	$q(\text{U})$	$q(\text{N})$	$\delta(\text{U} \text{N})$	$q(\text{U})$	$q(\text{N})$	$\text{BO}_{\text{W}}(\text{U},\text{N})$
<b>1</b>	2.64, 2.64	−1.33, −1.33	1.45, 1.45, 1.20, 1.20	1.87, 1.87	−1.34, −1.34	1.47, 1.47, 1.19, 1.19
<b>2</b>	2.81, 2.66	−1.24, −1.21	1.14, 1.28, 1.39, 1.55,	1.88, 1.76	−0.91, −0.88	1.66, 1.48, 1.31, 1.16
<b>4</b>	2.85, 2.84	−1.11, −1.07	2.01, 1.95, 0.79, 0.73	1.88, 1.80	−0.72, −0.70	2.16, 2.10, 0.85, 0.78
<b>8</b>	2.78	−0.95	2.60	1.93	−0.69	2.76

Finally, despite being unreactive towards CO and H<sub>2</sub>, the nitride ligands in complex **4** react readily with H<sup>+</sup> to afford ammonia. A 100% conversion to NH<sub>4</sub>Cl (2 equiv. of NH<sub>4</sub>Cl per complex) was observed by <sup>1</sup>H NMR analysis of the products in *d*<sub>6</sub>-dmsO (dimethylsulfone was added as an internal standard for quantification) upon reaction of complex **4** with excess of a 2 M solution of HCl in diethylether.

Similarly, a 93% conversion to NH<sub>4</sub>Cl was observed upon reaction of **2** with a 2 M solution of HCl in diethylether. A lower yield to NH<sub>4</sub>Cl (78%) was observed<sup>10a</sup> upon the addition of HCl in the same conditions to complex **1**.

### Computational analysis

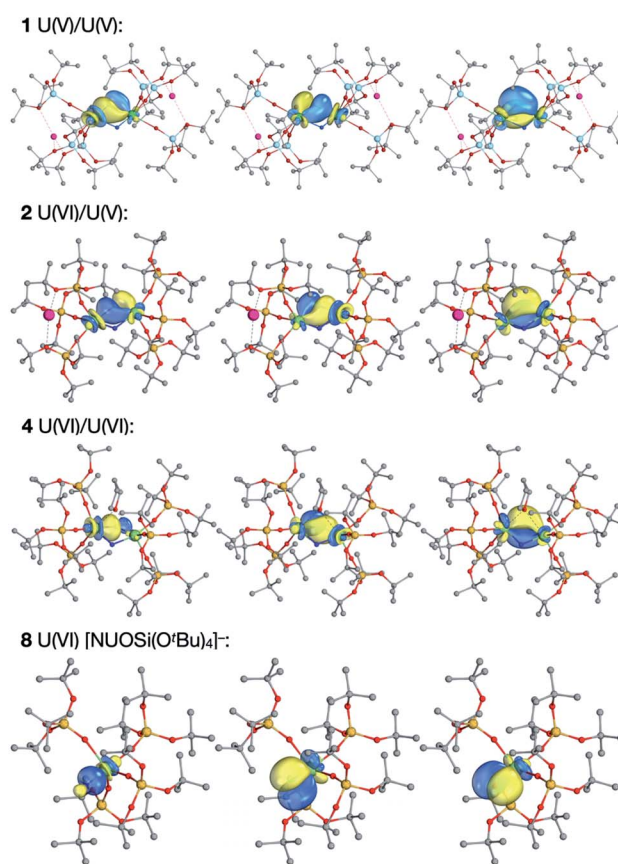
We performed DFT calculations on several of the diuranium species identified here to compare the uranium–nitrogen bonding across this set of similar complexes, *i.e.* the bis-nitrides **1**, **2** and **4**, and the terminal uranium nitride we recently reported, [NBu<sub>4</sub>][U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>4</sub>(N)]<sup>5c</sup> **8**. PBE0 calculations were performed at geometries in which the heavy atom positions were taken from experiment, with hydrogen positions optimised. Full computational methodology is given in the ESI.† For **1** (a U(v)/U(v) triplet) and **2** (a U(vi)/U(v) doublet, with the U(v) centre proximal to K<sup>+</sup>), singly occupied molecular orbitals are predominantly 5f<sub>U</sub> in character.

Natural Bond Orbital (NBO) and Quantum Theory of Atoms in Molecules (QTAIM) analyses were performed to obtain bond orders (the Wiberg bond index,  $\text{BO}_{\text{W}}(\text{U},\text{N})$ , in NBO and the QTAIM delocalisation index  $\delta(\text{U}|\text{N})$ ) and atomic charges, shown in Table 1. For **8**,  $\text{BO}_{\text{W}}(\text{U},\text{N}) = 2.76$  and  $\delta(\text{U}|\text{N}) = 2.60$ , indicating a strong triple bond. For **4**, the shorter pair of bonds have  $\text{BO}_{\text{W}}(\text{U},\text{N})$  of 2.16 and 2.10 for the 1.85 and 1.97 Å bonds respectively, and the longer pair of bonds have  $\text{BO}_{\text{W}}(\text{U},\text{N}) = 0.85$  and 0.78, *i.e.* the shorter pair of bonds have orders *c.* 2.6 times larger than the longer pair. A similar picture emerges from the QTAIM data, with  $\delta(\text{U}|\text{N})$  for the shorter pair of bonds *c.* 2.5 times greater than for the longer bonds, 2.01 and 1.95 *vs.* 0.79 and 0.73, respectively. By contrast, the U–N  $\text{BO}_{\text{W}}(\text{U},\text{N})$  in **1** vary from 1.17 to 1.47 and in **2** from 1.16 to 1.65, and the QTAIM varies from 1.20 to 1.45 in **1** and from 1.14 to 1.55 in **2**, *i.e.* the variation in bond orders in **1** and **2** is appreciably smaller than the substantial alternation observed in **4**.

The QTAIM charges for the U(v) centres in **1** and **2** are between 2.64–2.66, and the U(vi) centres in **2**, **4** and **8** between 2.78–2.85. Calculated charges are rarely as large as formal oxidation states, particularly for high oxidation state systems,

but the QTAIM charges for uranium atoms in the same formal oxidation state are in quite a small range, and distinguish U(v) from U(vi). By contrast, NBO charges are smaller than the analogous QTAIM values, and span a larger, overlapping range, with U(v) centres lying between 1.76 and 1.87, and U(vi) centres between 1.80 and 1.88.

We have also performed Intrinsic Bonding Orbital (IBO) analyses.<sup>29</sup> This technique localises orbitals *via* a projection onto a minimal quality basis set (Intrinsic Atomic Orbitals, IAOs), minimising the number of atoms the orbital is distributed over. Sets of the IBOs in the U<sub>2</sub>N<sub>2</sub> ring for the studied complexes are shown in Fig. 5. Orbitals are well localised onto one half of the U<sub>2</sub>N<sub>2</sub> ring (at least 99% in the IAO basis), with a similar set of orbitals being localised onto the opposite half



**Fig. 5**  $\alpha$  spin IBOs of the U<sub>2</sub>N<sub>2</sub> ring in **1**, **2** and **4**, and for the U≡N bond in **8**. The isosurfaces enclose 90% of the orbital.



(shown in Fig. S45 of the ESI†). The interpretation of the IBOs of **8** is unambiguous, with three bonding orbitals localised to  $\text{U}\equiv\text{N}$ , and a full  $\sigma^2\pi^4$  triple bond, consistent with the high values of  $\text{BO}_w(\text{U},\text{N})$  and  $\delta(\text{U}|\text{N})$ . The much smaller values of the bond order metrics for **1** and **2** are supported by the bonding IBOs, which are well delocalised across U–N–U. The significantly different bond orders for the shorter and longer bonds in **4** are also consistent with its IBOs, which show a U–N  $\sigma$  orbital well localised to  $\text{U}\equiv\text{N}$  but with  $\pi$  orbitals which partially delocalise to form the U–N single bond with the other uranium. The  $\sigma$  and two  $\pi$  orbitals have 3.8, 16.0 and 9.7% contribution respectively from the singly bound uranium (average 9.8%), and 39.2, 22.8 and 27.7% character from the triply bound uranium. By contrast, across the three bonding IBOs the delocalised **2** has an average character of 25.6% on one uranium (U–N = 2.02 Å) and 16.3% on the other (U–N = 2.09 Å). This change in bonding from **4** to **1** and **2** is similar to that calculated for the matrix isolated  $\text{U}(\text{vi})$  bis- $\mu$ -nitride  $[\text{UN}(\mu\text{-N})]_2$  described as a dimer of two  $\text{UN}_2$  units, while in the same study the  $\text{U}(\text{iii})$  species  $[\text{U}(\mu\text{-N})]_2$  was found to be highly delocalised.<sup>15f</sup>

Calculations using the PBE0 functional (full methodology is given in the ESI†) identified a  $\text{U}(\text{v})/\text{U}(\text{v})$  isomer bridged by  $\text{N}_2^{4-}$  with an energy of +0.5  $\text{kJ mol}^{-1}$ , and a  $\text{U}(\text{iv})/\text{U}(\text{iv})$   $\text{N}_2^{2-}$  isomer with an energy of –19.1  $\text{kJ mol}^{-1}$ , relative to the  $\text{U}(\text{vi})/\text{U}(\text{vi})$  bis-nitride isomer. The N–N bond lengths are 1.44 and 1.25 Å respectively, *i.e.* single and double bonds as expected for the  $\text{N}_2^{4-}$  and  $\text{N}_2^{2-}$  bridging ligands, and distinct from the observed N–N distance in **4**, 2.47(2) Å where the N–N bond is completely broken. Due to the challenges presented by the size of the molecule and multiple spin-crossovers we have not identified transition states linking these isomers, and our calculations were performed in the gas phase, but do suggest an energetically plausible route to oxidation of the nitrides, leading to  $\text{N}_2$  evolution.

## Conclusions

In conclusion we have been able to synthesise and characterise the first example of a molecular compound containing the cyclic  $\text{U}(\text{vi})\text{N}_2$  core previously only identified in gas phase experiments. We showed that the  $\text{U}(\text{vi})/\text{U}(\text{vi})$  bis-nitride (**4**) can be prepared from the oxidation of the  $\text{U}(\text{v})/\text{U}(\text{v})$  analogue (**1**) using a strong oxidizing agent, while weaker oxidizing agents only afford the  $\text{U}(\text{v})/\text{U}(\text{vi})$  analogues (**2** and **3**). The three compounds show different stability and reactivity. Notably, both **1** and **2** are stable in solution while **4** rapidly releases dinitrogen probably through  $\text{U}(\text{v})/\text{U}(\text{v})\text{N}_2^{4-}$  and  $\text{U}(\text{iv})/\text{U}(\text{iv})\text{N}_2^{2-}$  intermediates. The reactivity of **2** and **4** with CO,  $\text{H}_2$ , and  $\text{H}^+$  was explored and compared. Both complexes react with strong acids to yield  $\text{NH}_4^+$  quantitatively. Complex **4** does not react with CO or  $\text{H}_2$  while both nitrides in **2** undergo reductive carbonylation to yield  $2 \text{NCO}^-$ . The lack of reactivity of **4** with CO contrasts with the high reactivity with CO reported for the terminal  $\text{U}(\text{vi})$  nitride (**8**).<sup>5e</sup> Complex **2** also effects the cleavage of  $\text{H}_2$  to yield the bis-imido, **6** and bis-amido **7** providing a rare example of direct hydrogenolysis by a metal nitride. Computational studies show a very different bonding scheme for complexes **1** and **2** compared to

the  $\text{U}(\text{vi})$  bis-nitride **4**; the former shows a delocalised  $\pi$  bonding system while the latter has a U–N  $\sigma$  orbital well localised to  $\text{U}\equiv\text{N}$  but with  $\pi$  orbitals which partially delocalise to form the U–N single bond with the other uranium.

These results indicate that the delocalised  $\pi$  bonding system found in the complexes **1** and **2** stabilise the cyclic  $(\text{UN})_2$  structures defavouring  $\text{N}_2$  release compared to **4** and results in an higher nucleophilic reactivity of the nitrides towards CO and  $\text{H}_2$ .

## Authors contributions

L. B. carried out the synthetic experiments and analysed the experimental data; R. S. carried out the X-ray single crystal structure analyses; H.S. synthesised and characterised complexes **6** and **7**; B. E. A. and N. K. carried out and analysed the computational data. M. M. originated the central idea, coordinated the work, and analysed the experimental data. M. M., L. B., and B. E. A. wrote the manuscript with input from all co-authors.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

We acknowledge support from the Swiss National Science Foundation grant number 200021\_178793 and the Ecole Polytechnique Fédérale de Lausanne (EPFL). We thank R. Moinat and F. Sepulveda for carrying out the elemental and mass spectrometry analyses, F. Fadaei-Tirani for important contributions to the X-ray single crystal structure analyses. BEA and NK acknowledge the assistance given by Research IT, and the use of the Computational Shared Facility and the HPC Pool funded by the Research Lifecycle Programme at The University of Manchester.

## Notes and references

- (a) B. Askevold, J. T. Nieto, S. Tussupbayev, M. Diefenbach, E. Herdtweck, M. C. Holthausen and S. Schneider, *Nat. Chem.*, 2011, **3**, 532–537; (b) A. I. O. Suarez, V. Lyaskovskyy, J. N. H. Reek, J. I. van der Vlugt and B. de Bruin, *Angew. Chem., Int. Ed. Engl.*, 2013, **52**, 12510–12529; (c) M. Falcone, L. Chatelain, R. Scopelliti, I. Zivkovic and M. Mazzanti, *Nature*, 2017, **547**, 332–335; (d) N. B. Thompson, M. T. Green and J. C. Peters, *J. Am. Chem. Soc.*, 2017, **139**, 15312–15315; (e) L. R. Doyle, A. J. Wooles and S. T. Liddle, *Angew. Chem., Int. Ed. Engl.*, 2019, **58**, 6674–6677; (f) M. J. Chalkley, M. W. Drover and J. C. Peters, *Chem. Rev.*, 2020, **120**, 5582–5636; (g) S. Kim, F. Loose and P. J. Chirik, *Chem. Rev.*, 2020, **120**, 5637–5681; (h) J. Sun, J. Abbeneth, H. Verplancke, M. Diefenbach, B. de Bruin, D. Hunger, C. Wurtele, J. van Slageren, M. C. Holthausen and S. Schneider, *Nat. Chem.*, 2020, **12**, 1054–1059.



- 2 (a) F. Haber, *Angew. Chem.*, 1914, **27**, 473–477; (b) D. M. King and S. T. Liddle, *Coord. Chem. Rev.*, 2014, **266**, 2–15.
- 3 (a) R. B. Matthews, K. M. Chidester, C. W. Hoth, R. E. Mason and R. L. Petty, *J. Nucl. Mater.*, 1988, **151**, 334–344; (b) G. W. C. Silva, C. B. Yeamans, A. P. Sattelberger, T. Hartmann, G. S. Cereface and K. R. Czerwinski, *Inorg. Chem.*, 2009, **48**, 10635–10642.
- 4 (a) I. Korobkov, S. Gambarotta and G. P. A. Yap, *Angew. Chem., Int. Ed. Engl.*, 2002, **41**, 3433–3436; (b) X. Q. Xin, I. Douair, Y. Zhao, S. Wang, L. Maron and C. Q. Zhu, *J. Am. Chem. Soc.*, 2020, **142**, 15004–15011.
- 5 (a) L. Andrews, X. Wang, R. Lindh, B. O. Roos and C. J. Marsden, *Angew. Chem., Int. Ed. Engl.*, 2008, **47**, 5366–5370; (b) T. W. Hayton, *Chem. Commun.*, 2013, **49**, 2956–2973; (c) D. M. King, P. A. Cleaves, A. J. Wooles, B. M. Gardner, N. F. Chilton, F. Tuna, W. Lewis, E. J. L. McInnes and S. T. Liddle, *Nat. Commun.*, 2016, **7**; (d) B. E. Atkinson, H. S. Hu and N. Kaltsoyannis, *Chem. Commun.*, 2018, **54**, 11100–11103; (e) L. Barluzzi, R. Scopelliti and M. Mazzanti, *J. Am. Chem. Soc.*, 2020, **142**, 19047–19051.
- 6 (a) A. R. Fox and C. C. Cummins, *J. Am. Chem. Soc.*, 2009, **131**, 5716–5717; (b) M. A. Boreen, G. D. Rao, D. G. Villarreal, F. A. Watt, R. D. Britt, S. Hohloch and J. Arnold, *Chem. Commun.*, 2020, **56**, 4535–4538.
- 7 (a) 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; (b) D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Nat. Chem.*, 2013, **5**, 482–488; (c) N. Tsoureas, A. F. R. Kilpatrick, C. J. Inman and F. G. N. Cloke, *Chem. Sci.*, 2016, **7**, 4624–4632.
- 8 (a) W. J. Evans, S. A. Kozimor and J. W. Ziller, *Science*, 2005, **309**, 1835–1838; (b) G. Nocton, J. Pecaut and M. Mazzanti, *Angew. Chem., Int. Ed. Engl.*, 2008, **47**, 3040–3042; (c) S. Fortier, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2010, **132**, 6888–6889; (d) A. R. Fox, P. L. Arnold and C. C. Cummins, *J. Am. Chem. Soc.*, 2010, **132**, 3250–3251; (e) T. K. Todorova, L. Gagliardi, J. R. Walensky, K. A. Miller and W. J. Evans, *J. Am. Chem. Soc.*, 2010, **132**, 12397–12403; (f) C. Camp, J. Pecaut and M. Mazzanti, *J. Am. Chem. Soc.*, 2013, **135**, 12101–12111; (g) L. Maria, I. C. Santos, V. R. Sousa and J. Marcalo, *Inorg. Chem.*, 2015, **54**, 9115–9126.
- 9 (a) L. Chatelain, R. Scopelliti and M. Mazzanti, *J. Am. Chem. Soc.*, 2016, **138**, 1784–1787; (b) C. T. Palumbo, R. Scopelliti, I. Zivkovic and M. Mazzanti, *J. Am. Chem. Soc.*, 2020, **142**, 3149–3157.
- 10 (a) L. Barluzzi, L. Chatelain, F. Fadaei-Tirani, I. Zivkovic and M. Mazzanti, *Chem. Sci.*, 2019, **10**, 3543–3555; (b) J. Du, D. M. King, L. Chatelain, F. Tuna, E. J. L. McInnes, A. J. Wooles, L. Maron and S. T. Liddle, *Chem. Sci.*, 2019, **10**, 3738–3745.
- 11 (a) P. A. Cleaves, D. M. King, C. E. Kefalidis, L. Maron, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Angew. Chem., Int. Ed. Engl.*, 2014, **53**, 10412–10415; (b) M. Falcone, L. Chatelain and M. Mazzanti, *Angew. Chem., Int. Ed. Engl.*, 2016, **55**, 4074–4078; (c) M. Falcone, C. E. Kefalidis, R. Scopelliti, L. Maron and M. Mazzanti, *Angew. Chem., Int. Ed. Engl.*, 2016, **55**, 12290–12294; (d) K. C. Mullane, H. Ryu, T. Cheisson, L. N. Grant, J. Y. Park, B. C. Manor, P. J. Carroll, M. H. Baik, D. J. Mindiola and E. J. Schelter, *J. Am. Chem. Soc.*, 2018, **140**, 11335–11340; (e) L. Chatelain, E. Louyriac, I. Douair, E. Lu, F. Tuna, A. J. Wooles, B. M. Gardner, L. Maron and S. T. Liddle, *Nat. Commun.*, 2020, **11**; (f) M. Yadav, A. Metta-Magana and S. Fortier, *Chem. Sci.*, 2020, **11**, 2381–2387.
- 12 (a) M. Falcone, L. N. Poon, F. F. Tirani and M. Mazzanti, *Angew. Chem., Int. Ed. Engl.*, 2018, **57**, 3697–3700; (b) C. T. Palumbo, L. Barluzzi, R. Scopelliti, I. Zivkovic, A. Fabrizio, C. Corminboeuf and M. Mazzanti, *Chem. Sci.*, 2019, **10**, 8840–8849.
- 13 (a) S. D. Brown, M. P. Mehn and J. C. Peters, *J. Am. Chem. Soc.*, 2005, **127**, 13146–13147; (b) J. Schoffel, A. Y. Rogachev, S. D. George and P. Burger, *Angew. Chem., Int. Ed. Engl.*, 2009, **48**, 4734–4738; (c) F. S. Schendzielorz, M. Finger, C. Volkmann, C. Wurtele and S. Schneider, *Angew. Chem., Int. Ed. Engl.*, 2016, **55**, 11417–11420; (d) S. Kim, H. Y. Zhong, Y. Park, F. Loose and P. J. Chirik, *J. Am. Chem. Soc.*, 2020, **142**, 9518–9524; (e) M. Reiners, D. Baabe, K. Munster, M. K. 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) D. Sengupta, C. Sandoval-Pauker, E. Schueller, A. M. Encerrado-Manriquez, A. Metta-Magana, W. Y. Lee, R. Seshadri, B. Pinter and S. Fortier, *J. Am. Chem. Soc.*, 2020, **142**, 8233–8242.
- 14 S. S. Rudel, H. L. Deubner, M. Muller, A. J. Karttunen and F. Kraus, *Nat. Chem.*, 2020, **12**, 962–967.
- 15 (a) D. W. Green and G. T. Reedy, *J. Chem. Phys.*, 1976, **65**, 2921–2922; (b) R. D. Hunt, J. T. Yustein and L. Andrews, *J. Chem. Phys.*, 1993, **98**, 6070–6074; (c) P. Pykko, J. Li and N. Runeberg, *J. Phys. Chem.*, 1994, **98**, 4809–4813; (d) X. F. Wang, L. Andrews, B. Vlasisavljevich and L. Gagliardi, *Inorg. Chem.*, 2011, **50**, 3826–3831; (e) L. Andrews, X. F. Wang, Y. Gong and G. P. Kushto, *J. Phys. Chem. A*, 2014, **118**, 5289–5303; (f) B. Vlasisavljevich, L. Andrews, X. F. Wang, Y. Gong, G. P. Kushto and B. E. Bursten, *J. Am. Chem. Soc.*, 2016, **138**, 893–905.
- 16 R. K. Thomson, T. Cantat, B. L. Scott, D. E. Morris, E. R. Batista and J. L. Kiplinger, *Nat. Chem.*, 2010, **2**, 723–729.
- 17 A. R. Fox and C. C. Cummins, *J. Am. Chem. Soc.*, 2009, **131**, 5716–5717.
- 18 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877–910.
- 19 (a) C. T. Palumbo, I. Zivkovic, R. Scopelliti and M. Mazzanti, *J. Am. Chem. Soc.*, 2019, **141**, 9827–9831; (b) A. R. Willauer, C. T. Palumbo, F. Fadaei-Tirani, I. Zivkovic, I. Douair, L. Maron and M. Mazzanti, *J. Am. Chem. Soc.*, 2020, **142**, 5538–5542.
- 20 S. Fortier, J. R. Walensky, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2011, **133**, 11732–11743.





- 21 (a) N. H. Anderson, S. O. Odoh, Y. Y. Yao, U. J. Williams, B. A. Schaefer, J. J. Kiernicki, A. J. Lewis, M. D. Goshert, P. E. Fanwick, E. J. Schelter, J. R. Walensky, L. Gagliardi and S. C. Bart, *Nat. Chem.*, 2014, **6**, 919–926; (b) N. H. Anderson, J. Xie, D. Ray, M. Zeller, L. Gagliardi and S. C. Bart, *Nat. Chem.*, 2017, **9**, 850–855.
- 22 (a) T. Chlupaty, M. Bilek, J. Merna, J. Brus, Z. Ruzickova, T. Strassner and A. Ruzicka, *J. Chem. Soc., Dalton Trans.*, 2019, **48**, 5335–5342; (b) J. X. Liu, W. F. Chen, J. F. Li and C. M. Cui, *ACS Catal.*, 2018, **8**, 2230–2235; (c) S. Komorski, M. K. Leszczynski, I. Justyniak and J. Lewinski, *Inorg. Chem.*, 2016, **55**, 5104–5106.
- 23 W. J. Evans, K. A. Miller, J. W. Ziller and J. Greaves, *Inorg. Chem.*, 2007, **46**, 8008–8018.
- 24 H. S. La Pierre and K. Meyer, *Inorg. Chem.*, 2013, **52**, 529–539.
- 25 (a) K. C. MacLeod, D. J. Vinyard and P. L. Holland, *J. Am. Chem. Soc.*, 2014, **136**, 10226–10229; (b) E. O'Grady and N. Kaltsoyannis, *J. Chem. Soc., Dalton Trans.*, 2002, 1233–1239.
- 26 (a) M. G. Scheibel, B. Askevold, F. W. Heinemann, E. J. Reijerse, B. de Bruin and S. Schneider, *Nat. Chem.*, 2012, **4**, 552–558; (b) M. G. Scheibel, Y. I. Wu, A. C. Stueckl, L. Krause, E. Carl, D. Stalke, B. de Bruin and S. Schneider, *J. Am. Chem. Soc.*, 2013, **135**, 17719–17722; (c) J. Abbenseth, M. Finger, C. Wurtele, M. Kasanmascheff and S. Schneider, *Inorg. Chem. Front.*, 2016, **3**, 469–477.
- 27 C. Camp, L. Chatelain, C. E. Kefalidis, J. Pecaut, L. Maron and M. Mazzanti, *Chem. Commun.*, 2015, **51**, 15454–15457.
- 28 (a) G. F. Zi, L. Jia, E. L. Werkema, M. D. Walter, J. P. Gottfriedsen and R. A. Andersen, *Organometallics*, 2005, **24**, 4251–4264; (b) J. A. H. Frey, F. G. N. Cloke and S. M. Roe, *Organometallics*, 2015, **34**, 2102–2105.
- 29 G. Knizia, *J. Chem. Theory Comput.*, 2013, **9**, 4834–4843.

