Four-electron Reduction and Functionalization of N_2 by a Uranium(III) Bridging Nitride

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Abstract: N_2 is a cheap and widely available but very unreactive molecule. Notably, the only industrial process for the conversion of dinitrogen is the Haber-Bosch process to form ammonia, but under very harsh conditions (high temperature and pressure). Here, we review our recent research leading to the reduction of dinitrogen by four electrons, under ambient conditions by a uranium(III) bridging nitride, K_3U-N-U, where two uranium(III) cations are linked by a nitride group and a flexible metal–ligand scaffold. We also show that the bound dinitrogen can be further functionalized under mild conditions: the addition of acid, hydrogen and protons or carbon monoxide to the uranium hydrazido complex yields to the cleavage of the N-N single bond and to the formation of new N–H and N–C bonds.

Keywords: Dinitrogen · Nitrides · Uranium(III)

Marta Falcone was born in Domo-dossola (Italy). She first did a Bachelor in Chemistry at the University of Parma and then a Master in Organic Chemistry at the University of Pisa. In March 2015 she joined the PhD program at the Ecole Polytechnique Fédérale of Lausanne (EPFL). She is currently carrying out her research in the group of coordination chemistry of Prof. Marinella Mazzanti. Her current research is centred on the development of highly reactive complexes of f elements for the transformation of cheap and widely available molecules such as CO_2, N_2 and CO into value-added organic compounds.

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1. Introduction

The functionalization of dinitrogen under mild conditions is an attractive route for the use of this resource in the production of ammonia or other value-added nitrogen-containing compounds. Molecular complexes capable of binding and even reducing dinitrogen have been identified but examples of further transformation of bound dinitrogen leading to N–H or N–C bond formation remain rare.[1] Before iron-based catalysts were used in the Haber-Bosch process, uranium and uranium nitride were claimed to be the most effective catalysts for the production of ammonia from dinitrogen.[2] However, only a few examples of uranium(III) complexes that bind dinitrogen are known today.[3]

Multimetallic assemblies are thought to be involved in the stoichiometric and catalytic reduction of N_2 by compounds of d-block[1a,c–e,4] or f-block elements[4e,5] and the cooperative binding of dinitrogen by transition metals and alkali metal ions is crucial in dinitrogen activation,[1d,5b,6] but the polymetallic assemblies involved in dinitrogen activation are not well defined in most cases. Indeed, in most examples of dinitrogen cleavage, the active polymetallic species are generated *in situ* during the reduction of mononuclear precursors with strong reducing agents such as alkali metals under a nitrogen atmosphere.[1d,4b,c,5b,c] Here, we review recent results[7] obtained in our group showing a new approach that involves the use of a flexible multimetallic nitride-bridged K_3U-N-U core supported by a potassium-siloxide framework to bind N_2 at the two uranium centres and to effect its four-electron reduction. The multimetallic K_3U-N-U core in complex $[K_3\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}N)\}]$ (**1**) is able to bind dinitrogen and to effect its four-electron reduction under mild conditions to afford a N_2^{4-} moiety that is easily functionalized by hydrogen and/or protons or CO, leading to complete N–N cleavage, and N–H and N–C bond formation.

While current industrial processes and biological nitrogen fixation involve iron-based multi-metallic sites, the high activity reported for uranium nitrides in the Haber-Bosch process and the results reviewed[7] here indicate that molecular uranium compounds can demonstrate high reactivity in dinitrogen reduction and functionalization. This could for example eventually lead to the use of the large amounts of weakly radioactive uranium produced as waste in nuclear power production as valuable catalysts.[8,9]

2. N2 Binding and Protonation

The low valent uranium complex $[K_3\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}N)\}]$ (**1**) is easily obtained by reduction of the diuranium(IV) nitride-bridged complex, $[Cs\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}N)\}]$,[10] in THF at –70 °C (Scheme 1).

Complex **1** showed more stability both in solid state and in solution with respect to the Cs complex $[Cs_3\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}N)\}]$,[11] allowing for more controlled reactivity. The difference in stability probably originates from the higher Lewis

acidity of the potassium cation compared to the Cs cation that reduces the electron density at the K_3U-N-U core stabilized by the strong coordination of the K cations by the supporting siloxide ligands.

The molecular structure of **1** (Fig. 1a) presents a heterometallic K_3U-N-U core where two uranium(III) cations are linked by a nitride group. Three K^+ cations also bind the nitride group in a triangle perpendicular to the linear $U^{III}\!\cdots\!N\!\cdots\!U^{III}$ fragment, with a geometry comparable to the caesium complex, $[Cs_3\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}N)\}]$, Cs_3U-N-U. The U–U distance in **1** (4.234(2) Å) is only slightly shorter than that found in the Cs analogue (4.293(1) Å) but the K^+ cations are significantly closer to the nitride than the Cs^+ atoms in the Cs_3U-N-U core.

The reaction of **1** with one atmosphere of N_2 at room temperature affords the diuranium(V) complex, $[K_3\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}N)(\mu\text{-}\eta^2\text{-}N_2)\}]$ (**2**) (Scheme 2a).

In complex **1**, the two highly reducing uranium ions are maintained in close proximity by the nitride group and the flexible potassium-siloxide framework, affording an ideal geometry for N_2 binding and reduction. Indeed, when the multimetallic complex **1** in solid state or in solution, is exposed to N_2 (0.5–1 atm) (Scheme 2a) at room temperature, we observe an immediate change in colour from deep purple to brown. Brown crystals of $[K_3\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}N)(\mu\text{-}\eta^2\text{-}N_2)\}]$ (**2**) were isolated in 68% yield from a toluene solution that was stored at –40 °C.

The flexible framework created by the siloxide ligands that bind the two uranium atoms and potassium cations, plays an important role as it allows the U-N-U core to bend upon N_2 binding. Moreover, the choice of the cation is crucial, as the same complex with caesium leads to complicated reaction mixtures.

The N_2 activation is not reversible, as the proton NMR shows the presence of the same species after dynamic vacuum is applied to the solid or after cycles of freeze-pump-thaw degassing are performed on a toluene or THF solution of **2**. Only one example of non-reversible N_2 binding by an uranium compound has been reported previously in the homobimetallic complex, $[U(OC_6H_2\text{-}Bu^t_3\text{-}2,4,6)_3]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$,[3c] where the N_2 ligand is reduced to N_2^{2-} with concomitant oxidation of the uranium to U^{IV}. Stable N_2 binding and reduction to N_2^{2-} is also observed in a heterobimetallic (U/Mo) complex.[3b] The structure of **2** (Fig. 2b) shows the two uranium(V) centres (U–U distance of 3.305(1) Å), bridged by one nitride group and a side-on-bound hydrazido group (N_2^{4-}). The U–N3 distance (2.069(2) Å) is in the range of reported U–N distances for nitride-bridged uranium compounds and is indicative of U–N
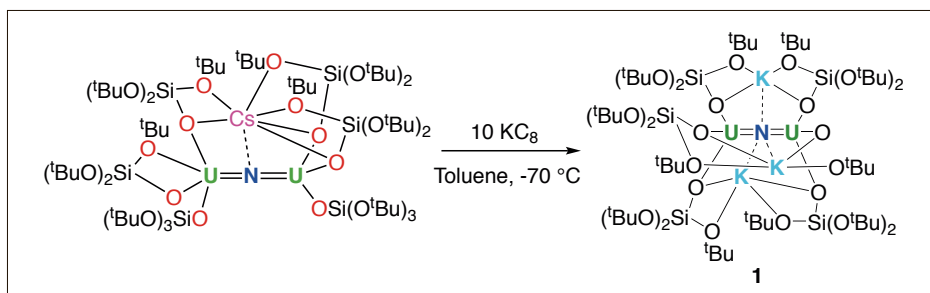
Scheme 1. Reduction of $[K_3\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}N)\}]$ with excess KC_8 to give complex **1**. Caution: depleted uranium (primary isotope ^{238}U) is a weak α-emitter (4.197 MeV) with a half-life of 4.47×10^9 years. Manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere glovebox in a radiation laboratory equipped with α- and β-counting equipment.
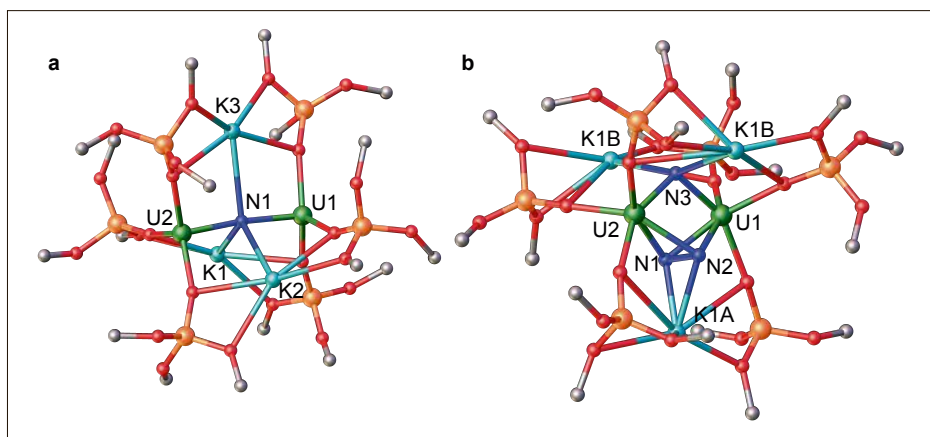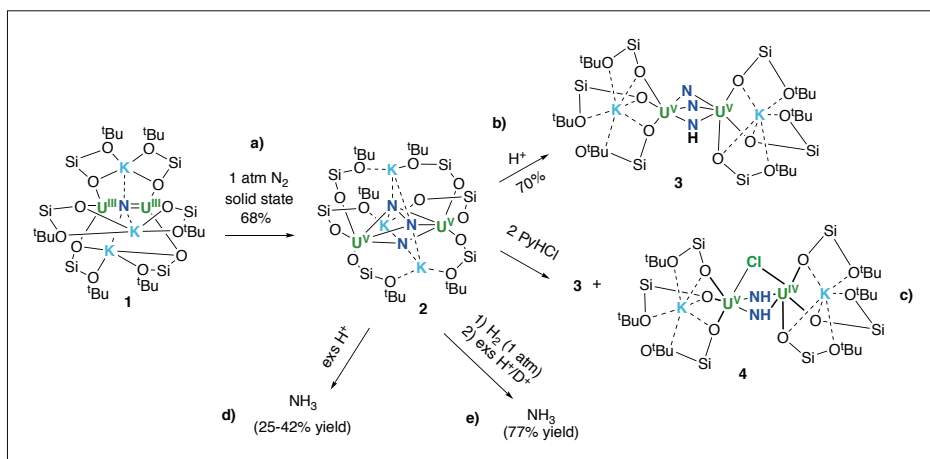

Fig. 1. Molecular structures of $[K_3\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}N)\}]$ (**1**) (a), and $[K_3\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}N)(\mu\text{-}\eta^2\text{-}N_2)\}]$ (**2**) (b). Thermal ellipsoids depicted at 50% probability. Hydrogen atoms and methyl groups are not shown. Only one position for the N atoms is shown for **2** (nitrogen atoms in the core are disordered over three positions with 0.33 occupancy each). Picture reproduced from *Nature* **2017**, *547*, 332–335.[7]

Scheme 2. N_2 reduction and functionalization reactions effected by complex $[K_3\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}N)\}]$ (**1**); a) N_2 reduction to afford the hydrazido complex, $[K_3\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}N)(\mu\text{-}\eta^2\text{-}N_2)\}]$ (**2**); b) and c) reactions with acids of the nitride and hydrazide in complex **2**, to give complexes $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}NH)(\mu\text{-}\eta^2\text{-}N_2)\}]$ (**3**) and $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}NH)_2(\mu\text{-}Cl)\}]$ (**4**), respectively; d) reaction of **2** with acids leads to ammonia; e) hydrogen addition to complex **2**, followed by acid addition, to give ammonia.

multiple bonding.[10–12] The $U_2(\mu\text{-}\eta^2\text{-}N_2)$ fragment shows U–N bond distances going from 2.311(13) Å to 2.163 (13) Å, in agreement with U–N single bonds.[13] The N–N bond length (mean N–N value of 1.521(18) Å) in complex **2** is in the range of values (1.377–1.548 Å) reported for hydrazido complexes of group 4 metals and

samarium resulting from dinitrogen reduction effected by non-isolated low-valent species[1c,4b,c] and comparable to the bond length in hydrazine, H_2NNH_2 (1.47 Å).

The uranium cations were confirmed to be in +V oxidation state, by EPR and variable-temperature magnetic data. These results showed the first example of four-elec-

tron reduction of dinitrogen by a uranium complex. Moreover, for the previously reported uranium complexes capable of activating dinitrogen, no reactivity of the N_2-bound fragment was performed. We reported that **2** can be easily functionalized with hydrogen and/or protons.

Complex $[K_3\{[U(OSi(O^tBu)_3)_3]_2(\mu-N)(\mu-\eta^2-N_2)\}]$ (**2**) was reacted with one equivalent of 2,4,6-tri-*tert*-butylphenol (Scheme 2b) to give the mono-protonated compound, $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu-NH)(\mu-\eta^2-N_2)\}]$ (**3**) in 70% yield. The crystal structure of complex **3** (Fig. 2a) shows two $[K\{U(OSi(O^tBu)_3)_3\}]$ fragments bridged by a NH^{2-} ligand and the N_2^{4-} ligand. The U–N1 and U–N2 distances in the U–N_2^{4-} fragment are essentially unchanged compared to those in complex **2**. Instead, the mean value of the U–N3 distances (2.11(5) Å) is coherent with a U^V imido-bridged species[13] and it is longer than the U-N$_{nitride}$ distance found in complex **2** (2.069(2) Å). This indicates that the protonation occurs selectively at the nitride nitrogen. When stronger acids such as PyHCl, HCl or $HBAr^F$ are used, protonation of the hydrazido ligand is also observed (Scheme 2c). The addition of PyHCl to complex **2** results in the formation of several protonation products, even after the addition of only one equivalent of acid. After the addition of two equivalents of PyHCl to complex **2**, a few crystals of a di-protonated species were isolated. The parameters found in the X-ray structure are in agreement with the assignment of a di-uranium(IV/V) bis(imido)-bridged complex, $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu-NH)_2(\mu-Cl)\}]$ (**4**) (Fig. 2b). The reduction of one of the uranium(V) cations to U^{IV} and the loss of one nitrogen atom can be interpreted in terms of the oxidative elimination of dinitrogen as a result of the disproportionation of the bound hydrazido ligand.

When an excess of PyHCl (20 equiv.) is added to **2**, ammonium chloride was detected in the proton NMR spectrum in dmso-d_6. The same experiment was carried out with the ^{15}N-labelled compound $[K_3\{[U(OSi(O^tBu)_3)_3]_2(\mu-N)(\mu-\eta^2-^{15}N_2)\}]$, which was prepared from the reaction of **1** with $^{15}N_2$. The resulting ^1H NMR spectrum shows two sets of peaks for $^{15}NH_4Cl$ (doublet) and $^{14}NH_4Cl$ (triplet) with a ratio 1:0.85. This experiment demonstrates that by protonating complex **2**, dinitrogen can be completely cleaved. Yields in ammonia of 25, 35 and 42% (Scheme 2d) were observed when an excess of $HBAr^F$ PyHCl or HCl was added to complex **2**.

The direct hydrogenation of dinitrogen with hydrogen in mild conditions is a desirable target that so far has only been observed for very few dinitrogen complexes.[4b,c,14] Since uranium nitrides are efficient catalysts in the Haber pro-
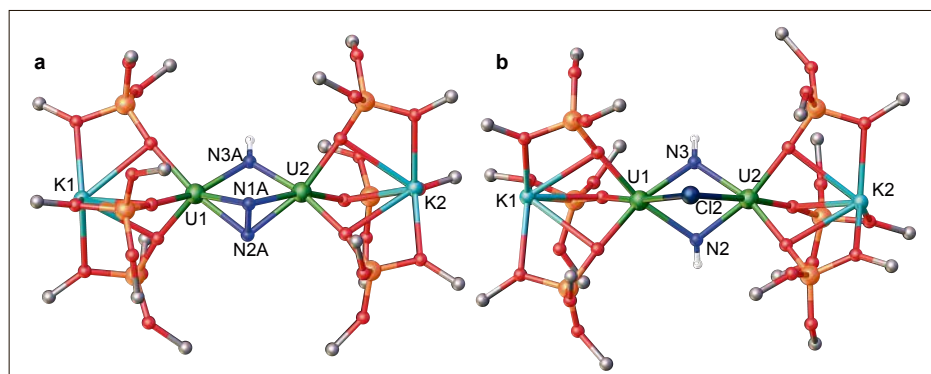

Fig. 2. Molecular structure of $[K_2[U(OSi(O^tBu)_3)_3]_2(\mu-NH)(\mu-\eta^2-N_2)\}]$ (**3**) (a), and complex $[K_2[U(OSi(O^tBu)_3)_3]_2(\mu-NH)_2(\mu-Cl)\}]$ (**4**) (b). Thermal ellipsoids depicted at 50% probability. Hydrogen atoms and methyl groups are not shown. The disorder for complex **3** and **4** of the N atoms (and Cl for **4**) over two positions is omitted. Picture reproduced from *Nature* **2017**, *547*, 332–335.[7]

cess we also investigated the possibility of functionalizing the bound N_2 in **2** with hydrogen. Letting complex **2** stand under one atm of H_2 at room temperature results in the slow consumption of the complex **2** over two to three weeks. The final proton NMR shows only one peak, corresponding to free ligand. No formation of ammonia is observed in the headspace, but the addition of $HCl(Et_2O)$ to the residue leads to formation of ammonia in 77% yield. The high yield of ammonia formed from the hydrogenation/protonation reaction suggests that the reaction of the bound hydrazido moiety with H_2 does not proceed with N_2 elimination. The nitride complex **1** is the first reported example of a molecular uranium complex capable of promoting the transformation of dinitrogen into ammonia.

## 3. Functionalization of Bound N_2 with CO

In order to confirm the high degree of reduction of the bound dinitrogen in complex **2**, and to further explore the possibility of ligand-promoted reduction and cleavage of the bound dinitrogen we have reacted complex **2** with CO. Notably, Chirik and co-workers have previously demonstrated that in group 4 complexes (where the met-

al cannot supply the six electrons required for complete N_2 cleavage) the N_2^{4-} moiety can be reduced by addition of CO and completely cleaved, resulting in N–C and C–C bond formation.[1a]

Complex **2** reacted with excess CO (10 to 20 equiv.) in toluene or benzene to afford complex $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu-O)(\mu-NCO)_2\}]$ (**5**) with the uranium atoms in the +IV oxidation state, bridged by an oxo and two cyanate ligands (Scheme 3a). The ^{13}C NMR spectrum in D_2O shows the presence of the peaks at 163.9 and 130 ppm assigned to CN^- and NCO^- respectively.

The solid-state structure of complex **5** determined by X ray crystallography is shown in Fig. 3a and it shows the presence of two $[K\{U(OSi(O^tBu)_3)_3\}]$ groups bridged by an oxo group (O^{2-}) and two cyanate (OCN^-), with angle values of 108.7(3)° for U1-O-U2 and 88.0(3)° and 89.0(3)° for the two $UN_{cyanate}U$.

The nitride is responsible for the nucleophilic addition of CO, resulting in the complete cleavage of CO with formation of an oxo ligand and extrusion of the cyanide as KCN. We recently described[15] a nitride-bridged diuranium(IV) complex, $[Cs\{[U(OSi(O^tBu)_3)_3]_2(\mu-N)\}]$, capable of cleaving the CO triple bond under mild conditions. Uranium(V) and uranium(VI) terminal nitrides were shown to be able to
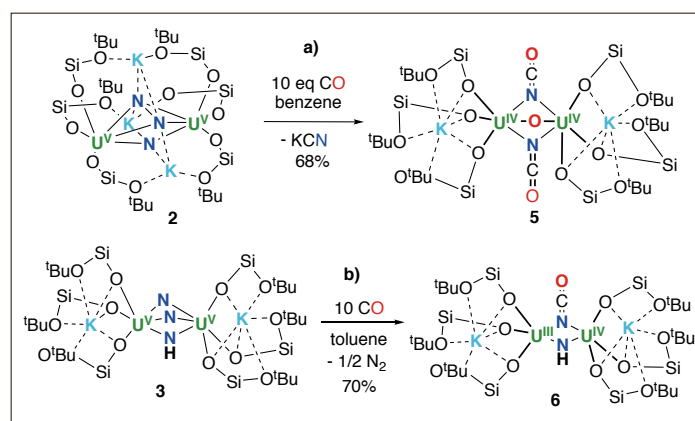
Scheme 3. a) Reactions of $[K_3\{[U(OSi(O^tBu)_3)_3]_2(\mu-N)(\mu-\eta^2-N_2)\}]$ (**2**) with an excess of CO to afford $[K_2\{[U(OSi(OtBu)_3)_3]_2(\mu-O)(\mu-NCO)_2\}]$ (**5**); b) reaction of **3** with an excess of CO to afford complex $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu-NH)(\mu-NCO)\}]$ (**6**).
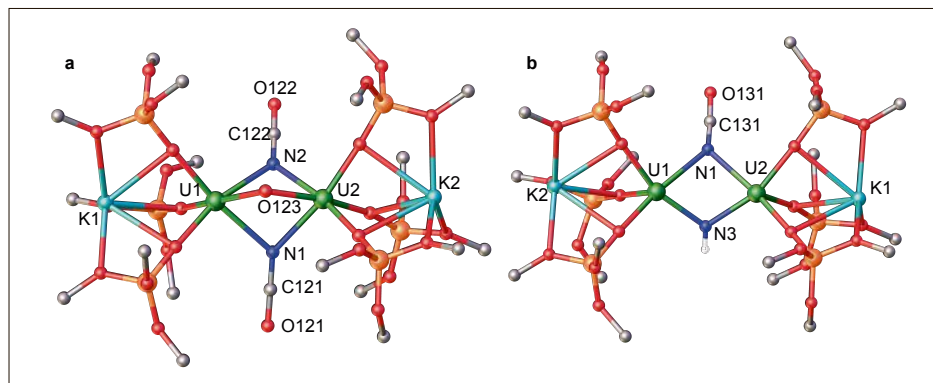
Fig. 3. Molecular structures of [K$_2${[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-O)(μ-NCO)$_2$}] (**5**) (a), and [K$_2${[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-NH)(μ-NCO)}] (**6**) (b). Thermal ellipsoids depicted at 50% probability. Hydrogen atoms and methyl groups are not shown. The disorder of the NCO ligand in **6** over two positions is omitted. Picture reproduced from *Nature* **2017**, *547*, 332–335.[7]

undergo reductive carbonilation to afford cyanate,[16] but reductive carbonylation of dinitrogen metal complexes is unprecedented. These results showed that the highly activated dinitrogen in complex **2** can be completely cleaved and functionalized under ambient conditions by CO. This reactivity differs from that reported by Chirik for ligand-induced cleavage of dinitrogen in U^{IV} and Hf^{IV} metallocene complexes. Notably, the formation of N–C and C–C bonds, affording the [N$_2$C$_2$O$_2$]$^{4-}$ (oxamidide) fragment does not involve redox events on the metal centre.[1a,17]

The protonated nitride group in complex [K$_2${[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-NH)(μ-η^2-N$_2$)}] (**3**) led to reduced reactivity with CO (Scheme 3b).

^{13}C NMR spectroscopy in D$_2$O shows a signal at 130.0 ppm assigned to cyanate. Brown crystals of complex [K$_2${[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-NH)(μ-NCO)}] (**6**) were isolated in 70% yield from the toluene reaction mixture after 24 hours at room temperature.

The solid-state structure of **6** (Fig. 3b) shows the presence of one imido (NH^{2-}) and one cyanate (NCO$^-$) ligand bridging the two uranium atoms in +III and +IV oxidation state, in a diamond shaped geometry. The U–NH distance (mean value of 2.18(3) Å) is in agreement with uranium in the +III oxidation state and is longer than that of complex **3** (2.10(5) Å). Examples of U^{III}/U^{IV} imido-bridged compounds have not been reported, but the U–NH distance falls in the range of imido-bridged U^{IV} complexes.[18]

In complex **6**, the two uranium centres have undergone an overall three-electron reduction while one of the hydrazido nitrogens has undergone a formal one-electron reduction to afford NCO$^-$, with concomitant two-electron oxidation of the carbonyl carbon atom. The stoichiometry of the reductive carbonylation of the hydrazido complex **3** requires the concomitant elimination of dinitrogen that was confirmed by gas-chromatography of the headspace. The formation of **6** is the first example of CO-induced disproportionation of a N$_2^{4-}$ moiety.

4. Conclusions

In summary, in our recent work[7] we have shown a novel approach that enabled the characterization of a multimetallic molecular species that is able to bind and effect the four-electron reduction of N$_2$. The flexible metal–ligand framework provides an optimal arrangement for the cooperative binding and activation of dinitrogen. It should be possible to extend this approach to other metals, provided that their low-valent nitride complexes can be stabilized.

The potassium-siloxide framework is certainly crucial in the assembly of a flexible but stable U-N-U core that can bend upon N$_2$ binding. The addition of hydrogen and/or protons to the resulting dinitrogen complex affords stoichiometric amounts of ammonia, thus providing the first molecular model for the species involved in the uranium catalysed Haber-Bosch process. The activated dinitrogen can also be cleaved and functionalized by CO, providing a route for building organonitrogen compounds from cheap resources. These results represent an important advance in the development of new molecular systems for the catalytic transformation of N$_2$.

[1] a) D. J. Knobloch, E. Lobkovsky, P. J. Chirik, *Nat. Chem.* **2010**, *2*, 30; b) L. P. Spencer, B. A. MacKay, B. O. Patrick, M. D. Fryzuk, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 17094; c) Y. Ohki, M. D. Fryzuk, *Angew. Chem. Int. Ed.* **2007**, *46*, 3180; d) M. M. Rodriguez, E. Bill, W. W. Brennessel, P. L. Holland, *Science* **2011**, *334*, 780; e) K. C. MacLeod, P. L. Holland, *Nat. Chem.* **2013**, *5*, 559.
[2] F. Haber, Vol. DE 229126, Haber, F Ammonia German patent DE 229126, **1909**.
[3] a) F. G. N. Cloke, P. B. Hitchcock, *J. Am. Chem. Soc.* **2002**, *124*, 9352; b) A. L. Odom, P. L. Arnold, C. C. Cummins, *J. Am. Chem. Soc.* **1998**, *120*, 5836; c) S. M. Mansell, N. Kaltsoyannis, P. L. Arnold, *J. Am. Chem. Soc.* **2011**, *133*, 9036; d) W. J. Evans, S. A. Kozimor, J. W. Ziller, *J. Am. Chem. Soc.* **2003**, *125*, 14264; e) P. Roussel, P. Scott, *J. Am. Chem. Soc.* **1998**, *120*, 1070.
[4] a) C. E. Laplaza, C. C. Cummins, *Science* **1995**, *268*, 861; b) J. A. Pool, E. Lobkovsky, P. J. Chirik, *Nature* **2004**, *427*, 527; c) M. D. Fryzuk, J. B. Love, S. J. Rettig, V. G. Young, *Science* **1997**, *275*, 1445; d) B. A. MacKay, M. D. Fryzuk, *Chem. Rev.* **2004**, *104*, 385; e) M. D. Walter, *Adv. Organomet. Chem.* **2016**, *65*, 261; f) K. Arashiba, Y. Miyake, Y. Nishibayashi, *Nat. Chem.* **2011**, *3*, 120.
[5] a) W. J. Evans, M. Fang, G. Zucchi, F. Furche, J. W. Ziller, R. M. Hoekstra, J. I. Zink, *J. Am. Chem. Soc.* **2009**, *131*, 11195; b) S. Gambarotta, J. Scott, *Angew. Chem. Int. Ed.* **2004**, *43*, 5298; c) W. J. Evans, D. S. Lee, D. B. Rego, J. M. Perotti, S. A. Kozimor, E. K. Moore, J. W. Ziller, *J. Am. Chem. Soc.* **2004**, *126*, 14574.
[6] a) T. Shima, S. W. Hu, G. Luo, X. H. Kang, Y. Luo, Z. M. Hou, *Science* **2013**, *340*, 1549; b) Y. Lee, F. T. Sloane, G. Blondin, K. A. Abboud, R. Garcia-Serres, L. J. Murray, *Angew. Chem. Int. Ed.* **2015**, *54*, 1499; c) S. F. McWilliams, P. L. Holland, *Acc. Chem. Res.* **2015**, *48*, 2059.
[7] M. Falcone, L. Chatelain, R. Scopelliti, I. Zivkovic, M. Mazzanti, *Nature* **2017**, *547*, 332.
[8] A. R. Fox, S. C. Bart, K. Meyer, C. C. Cummins, *Nature* **2008**, *455*, 341.
[9] D. P. Halter, F. W. Heinemann, J. Bachmann, K. Meyer, *Nature* **2016**, *530*, 317.
[10] C. Camp, J. Pecaut, M. Mazzanti, *J. Am. Chem. Soc.* **2013**, *135*, 12101.
[11] L. Chatelain, R. Scopelliti, M. Mazzanti, *J. Am. Chem. Soc.* **2016**, *138*, 1784.
[12] a) I. Korobkov, S. Gambarotta, G. P. A. Yap, *Angew. Chem. Int. Ed.* **2002**, *41*, 3433; b) A. R. Fox, P. L. Arnold, C. C. Cummins, *J. Am. Chem. Soc.* **2010**, *132*, 3250.
[13] L. P. Spencer, E. J. Schelter, P. Yang, R. L. Gdula, B. L. Scott, J. D. Thompson, J. L. Kiplinger, E. R. Batista, J. M. Boncella, *Angew. Chem. Int. Ed.* **2009**, *48*, 3795.
[14] B. Askevold, J. T. Nieto, S. Tussupbayev, M. Diefenbach, E. Herdtweck, M. C. Holthausen, S. Schneider, *Nat. Chem.* **2011**, *3*, 532.
[15] M. Falcone, C. E. Kefalidis, R. Scopelliti, L. Maron, M. Mazzanti, *Angew. Chem. Int. Ed.* **2016**, *55*, 12290.
[16] P. A. Cleaves, D. M. King, C. E. Kefalidis, L. Maron, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem. Int. Ed.* **2014**, *53*, 10412.
[17] D. J. Knobloch, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2010**, *132*, 10553.
[18] a) J. G. Brennan, R. A. Andersen, A. Zalkin, *J. Am. Chem. Soc.* **1988**, *110*, 4554; b) D. M. King, J. McMaster, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake, S. T. Liddle, *J. Am. Chem. Soc.* **2014**, *136*, 5619.