

# CO Cleavage and CO<sub>2</sub> Functionalization under Mild Conditions by a Multimetallic CsU<sub>2</sub> Nitride Complex

Marta Falcone<sup>§</sup>, Lucile Chatelain, Rosario Scopelliti, and Marinella Mazzanti\*

<sup>§</sup>SCS-DSM Award for best poster presentation in Inorganic & Coordination Chemistry

**Abstract:** Novel efficient chemical processes involving cheap and widely accessible carbon dioxide or carbon monoxide under mild conditions for the production of valuable chemical products are highly desirable in the current energetic context. Uranium nitride materials act as high activity catalysts in the Haber-Bosch process but the reactivity of molecular nitride compounds remains unexplored. Here we review recent results obtained in our group showing that a multimetallic nitride complex [Cs{[U(OSi(O<sup>t</sup>Bu)<sub>3</sub>]<sub>2</sub>(μ-N)}] (**1**) with a CsU<sup>IV</sup>-N-U<sup>IV</sup> core, is able to promote N–C bond formation due to its strong nucleophile behaviour. In particular, complex **1**, in the presence of excess CO<sub>2</sub> leads to a remarkable dicarbamate product. The multimetallic CsU<sup>IV</sup>-N-U<sup>IV</sup> nitride also readily cleaves the C=O bond under mild conditions.

**Keywords:** CO<sub>2</sub> activation · CO cleavage · N–C bond formation · Nitrides · Uranium



*Marta Falcone* was born in Domo-dossola (Italy). She did first 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 de Lausanne (EPFL). She is currently carrying out her research in the group of the Prof. Marinella Mazzanti. Her current research is centered on the development of highly reactive complexes of elements for the transformation of cheap and widely available molecules such as CO<sub>2</sub>, N<sub>2</sub> and CO into value-added organic compounds.

## 1. Introduction

Uranium nitrides are interesting candidates for application in the development of more efficient nuclear fuels,<sup>[1]</sup> in catalytic N-transfer reactions and small molecule transformation.<sup>[2]</sup> The reactivity of uranium nitrides remains practically unexplored but the recent characterization of stable mononuclear and dinuclear nitride complexes of uranium in oxidation states ranging from +3 to +5<sup>[3]</sup> renders accessible the study of the reactivity of these species. Reactions that lead to N–C bond formation are of great interest, as they are involved in the synthesis of value-added chemicals such as amino acids or pharmaceutical.<sup>[4]</sup> It is desirable to design synthetic methods involving the use of cheap and available C<sub>1</sub> feedstock such as carbon dioxide.<sup>[5]</sup> A handful of examples of transition metals complexes able to form N–C bonds from carbon dioxide and activated dinitrogen or nitride complexes<sup>[6,7]</sup> have been reported but before our reports reviewed here,<sup>[8,9]</sup> elements molecular nitrides had not been shown to react with CO<sub>2</sub>. Another readily available C<sub>1</sub> feedstock used in industry for the production of a wide variety of chemicals such as methanol, acetic acid, phosgene and hydrocarbons<sup>[10]</sup> is carbon monoxide. The cleavage of the carbon oxygen bond, one of the strongest bonds in chemistry (dissociation energy at 298 K = 1076 kJ mol<sup>-1</sup>) is achieved in the Fischer-Tropsch process, used for hydrocarbon production from CO and H<sub>2</sub>. This process requires the use of heterogeneous

transition-metal catalysts at elevated temperatures.<sup>[11]</sup> It is an important current challenge to explore new, mild conditions for the CO cleavage reaction, in the search of new routes for the production of functionalized organic molecules. The direct addition of CO to a metal-nitride is rare and it is observed only for highly nucleophilic nitride complexes,<sup>[3n,12]</sup> usually leading to the release of the resulting cyanate ligand.<sup>[3n,12d]</sup> Only a few examples of CO cleavage by metal complexes have been reported so far that led to the formation of metal-carbide complexes and oxo clusters.<sup>[13]</sup> The binding<sup>[14]</sup> and the reduction<sup>[15]</sup> of CO by uranium(III) complexes has been demonstrated. Deltate,<sup>[16]</sup> squarate<sup>[16b,17]</sup> or ethyenediolate dianions<sup>[18]</sup> have been identified as products in the reaction of uranium(III) compounds with CO. Here, we review the previously reported<sup>[8,9]</sup> ability of the nitride-bridged diuranium(IV) complex, [Cs{[U(OSi(O<sup>t</sup>Bu)<sub>3</sub>]<sub>2</sub>(μ-N)}] (**1**),<sup>[19]</sup> to promote N–C bond formation in the reaction with small molecules. The nitride group, bridging two uranium(IV) centers, is highly nucleophilic, and its ability to lead to N–C bond formation allowed us to characterize several new compounds. In particular, in the reactions with CS<sub>2</sub>, CO<sub>2</sub><sup>[8]</sup> and CO,<sup>[9]</sup> a cyanate/thiocyanate complex, a dicarbamate complex and a cyanide/oxo complex were formed, respectively. The unusually high nucleophilic character of the nitride leads to complete cleavage of the CO triple bond. We also demonstrated<sup>[9]</sup> that the direct methylation of the nitride complex **1** leads to Lewis-acid-

\*Correspondence: Prof. Dr. M. Mazzanti  
Institut des Sciences et Ingénierie Chimiques  
Ecole Polytechnique Fédérale de Lausanne (EPFL)  
CH-1015 Lausanne  
E-mail: marinella.mazzanti@epfl.ch

assisted disproportionation of the uranium atom, a completely new reactivity in nitride chemistry.

## 2. Reaction with CO<sub>2</sub> and CS<sub>2</sub>: N–C Bond Formation

We recently showed<sup>[8]</sup> that complex [Cs{[U(OSi(O<sup>t</sup>Bu)<sub>3</sub>]<sub>2</sub>(μ-N)}] (**1**), can be stored at –40 °C, in solution but decomposes at higher temperatures (Scheme 1a). In particular, complex **1** undergoes thermolysis at 80 °C in toluene to afford the new imido-bridged siloxide/silandiolate diuranium(IV) complex, [Cs{U<sub>2</sub>(OSi(O<sup>t</sup>Bu)<sub>3</sub>)(μ-N<sup>t</sup>Bu)(μ-O<sub>2</sub>Si(O<sup>t</sup>Bu)<sub>2</sub>)}] (**2**), in 65% yield. Single crystals suitable for X-ray diffraction were obtained, and the resulting structure of **2** (Fig. 1) clearly showed that a new *tert*-butylimido bridging group is formed as a consequence of the nucleophilic attack of the nitride on a *tert*-butyl group of the ligand. Similar reactivity, with elimination of isobutene, has been reported for the diuranium(III) complex [U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>2</sub>(μ-OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>2</sub>].<sup>[20]</sup> The two U–N<sub>imido</sub> bond lengths found for the *tert*-butylimido bridge are 2.300(3) and 2.398(3) Å, slightly longer than those of dinuclear U(IV) imido complexes (2.156(8)–2.378(3) Å).<sup>[21]</sup>

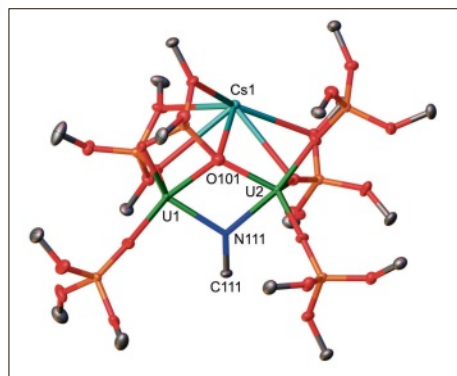
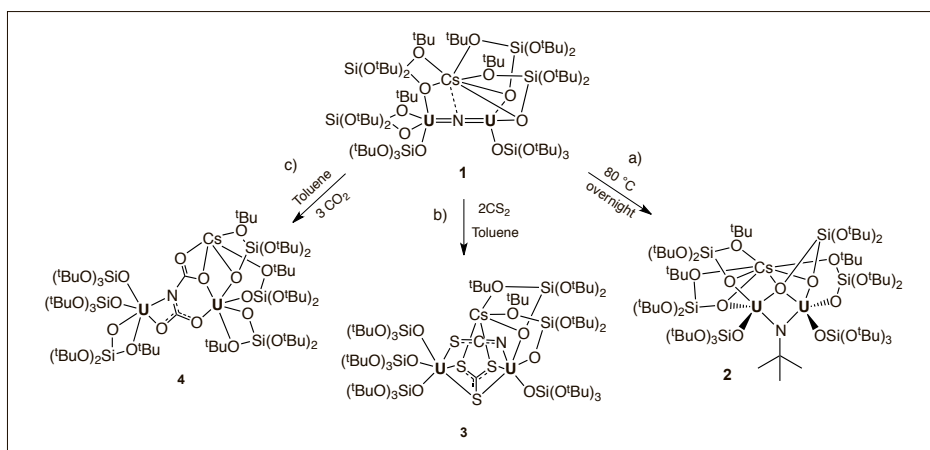


Fig. 1. Thermal ellipsoid drawing of complex **2**; probability 50%. Only one carbon atom of the <sup>t</sup>Bu groups is shown for clarity. ©Wiley-VCH Verlag GmbH & Co. KGaA. Figure adapted from ref. [8] with permission.

The high nucleophilicity of the bridging nitride inspired us to investigate the reactivity of this complex towards CS<sub>2</sub> and CO<sub>2</sub>. We have shown<sup>[8]</sup> that the reaction of **1** with two equiv. CS<sub>2</sub> (Scheme 1b) results in the prompt formation of complex [Cs{[U(OSi(O<sup>t</sup>Bu)<sub>3</sub>]<sub>2</sub>(μ-NCS)(μ-CS<sub>3</sub>)}] (**3**) (58% yield). The crystal structure of **3** (Fig. 2) shows the presence of a bridging thiocyanate and a bridging trithiocarbonate ligand, binding the two uranium atoms and the cesium cation in a μ<sub>3</sub>-κ<sup>2</sup>:κ<sup>2</sup>:κ<sup>2</sup> fashion. In the CS<sub>3</sub><sup>2-</sup> unit the charge is clearly delocalised, as indicated by the C–S bond lengths (1.740(12), 1.682(9), 1.712(10)



Scheme 1. Reactivity of complex **1**: <sup>t</sup>Bu transfer from the ligand to the nitrogen atom to form complex **2** (a); reaction with 2CS<sub>2</sub> to form complex **3** (b); reaction with CO<sub>2</sub> to form complex **4** (c). The products were stored at –40 °C.

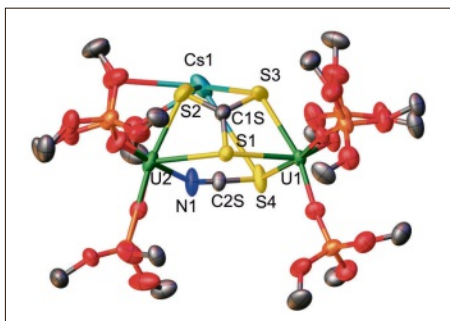


Fig. 2. Thermal ellipsoid drawing of complex **3**; probability 50%. Only one carbon atom of the <sup>t</sup>Bu groups is shown for clarity. ©Wiley-VCH Verlag GmbH & Co. KGaA. Figure adapted from ref. [8] with permission.

Å). While two other examples of uranium trithiocarbonate complexes were previously reported,<sup>[22]</sup> S-bound thiocyanate ligands could not be found in the Cambridge Structural Database.

The presence of the bridging NCS<sup>-</sup> and CS<sub>3</sub><sup>2-</sup> ligands was confirmed by <sup>13</sup>C NMR in toluene-d<sub>8</sub> (resonances at 124.0 ppm and 195.8 ppm). The presence of the thiocyanate ligand was also confirmed by IR, which shows two ν(<sup>13</sup>CN) stretches at 2006 and 2085 cm<sup>-1</sup>.<sup>[23]</sup>

We have also reported<sup>[8]</sup> that when only 1 equiv. CS<sub>2</sub> is added to **1**, the <sup>13</sup>C NMR spectrum in DMSO-d<sub>6</sub> shows the presence of free NCS<sup>-</sup>. This indicates that the formation of complex **3** probably results from the reaction of a sulphide/thiocyanate-bridged intermediate, [Cs{[(μ-NCS)(μ-S)[U(OSi(O<sup>t</sup>Bu)<sub>3</sub>]<sub>2</sub>]}]’, with a second equiv. of CS<sub>2</sub>. Previous examples of nucleophilic addition of CS<sub>2</sub> were shown for a sulphide-bridged diuranium(IV) complex<sup>[22a]</sup> and for a V(v) terminal nitride.<sup>[7b]</sup>

We recently reported<sup>[8]</sup> that addition of CO<sub>2</sub> to complex **1** results in a different reactivity. Complex [Cs{[U(OSi(O<sup>t</sup>Bu)<sub>3</sub>]<sub>2</sub>(μ-NC<sub>2</sub>O<sub>4</sub>)}] (**4**) was formed after addition at low temperature (–70 °C) of 3 equiv. CO<sub>2</sub>

to **1** (Scheme 1c). The crystal structure of **4** (Fig. 3) shows a dicarbamate ligand, bridging the two uranium atoms forming two fused rings that share one of the new N–C bonds. One carbamate oxygen is slightly out of the plane of the dicarbamate ligand and is bound to the cesium cation. In the fragment O122–C121–O121 the negative charge is delocalised (O121–C121 and C121–O122 bond lengths of 1.292(5) and 1.282(4) Å) while the double bond character of the C122–O124 bond (1.229(6) Å) with respect to C122–O123 (1.317(4) Å) suggests charge localisation.

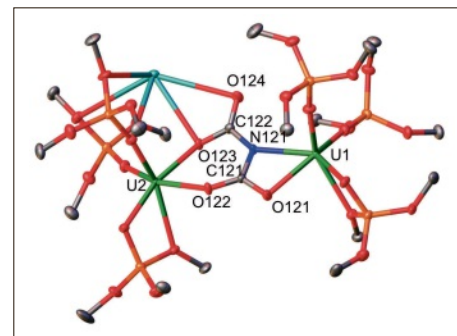


Fig. 3. Thermal ellipsoid drawing of complex **4**; probability 50%. Only one carbon atom of the <sup>t</sup>Bu groups is shown for clarity. ©Wiley-VCH Verlag GmbH & Co. KGaA. Figure adapted from ref. [8] with permission.

Thus our recent report<sup>[8]</sup> described the unprecedented insertion of CO<sub>2</sub> into a metal nitride, yielding a dicarbamate ligand. Indeed, complexes with the N(CO<sub>2</sub>)<sub>2</sub><sup>3-</sup> ligand have never been reported, as the synthesis of the protonated species is not trivial.<sup>[24]</sup> The insertion reactions of CO<sub>2</sub> into U<sup>III</sup>–N<sub>amide</sub> or U<sup>IV</sup>–N<sub>amide</sub> bonds resulting in the formation of U(III) or U(IV) O-bound carbamate complexes<sup>[25]</sup> or U(IV) isocyanate complexes<sup>[26]</sup> had been reported previously by other groups. However, complex **4** provided the first example of CO<sub>2</sub> insertion into a U–N<sub>nitride</sub> bond.

### 3. Reaction with Carbon Monoxide: C–O Bond Cleavage and N–C Bond Formation.

We recently showed<sup>[9]</sup> that the addition of stoichiometric amounts of CO or <sup>13</sup>CO to complex [Cs{[U(OSi(O<sup>t</sup>Bu)<sub>3</sub>]<sub>3</sub>]<sub>2</sub>(μ-N)}] (**1**) in toluene at room temperature (Scheme 2a) results in an immediate reaction. The <sup>1</sup>H NMR spectrum shows the appearance of a single new signal at –1.34 ppm. Blue crystals of the complex [Cs{[U(OSi(O<sup>t</sup>Bu)<sub>3</sub>]<sub>3</sub>]<sub>2</sub>(μ-CN)(μ-O)}] (**5**) were isolated in 60% yield at –40 °C (Fig. 4). The solid-state structure of **5** shows the presence of a diuranium(IV) complex where two uranium atoms are bridged by one oxo ligand and one cyanide ligand. This indicates that the bridging nitride of **1** promotes the ready cleavage of carbon monoxide. The resulting cyanide ligand adopts a bridging mode with U–C (2.609(7) Å) and U–N (2.576(6) Å) bond distances comparable to those reported for cyanide bridged diuranium(IV) complexes (2.549(8)–2.583(2) Å).<sup>[27]</sup>

The reductive carbonylation reactions of U(V) and U(VI) mononuclear nitrides were reported to afford U<sup>III</sup>-OCN and U<sup>IV</sup>-OCN complexes respectively.<sup>[3n]</sup> The reactivity of complex **1** is remarkably different and shows the importance of the multi-metallic cooperativity of the two uranium centres and of the Cs<sup>+</sup> cation to afford complete scission of CO. The importance of such cooperative effect was also evidenced by DFT studies.<sup>[9]</sup>

In order to confirm the presence of a cyanide ligand in complex **5** and to investigate the possibility of transferring the cyanide ligand to organic substrates, complex **5** was reacted with Me<sub>3</sub>SiI and with MeOTf (Scheme 2). The <sup>13</sup>C NMR spectrum after addition of Me<sub>3</sub>SiI to complex **5** showed the appearance of a signal at 126.3 ppm, assigned to the cyanide group of the Me<sub>3</sub>Si<sup>13</sup>CN.<sup>[12e]</sup> The formation of CH<sub>3</sub><sup>13</sup>CN, after addition of MeOTf to complex **5**, was also confirmed by <sup>13</sup>C NMR, which shows a signal at 113 ppm.

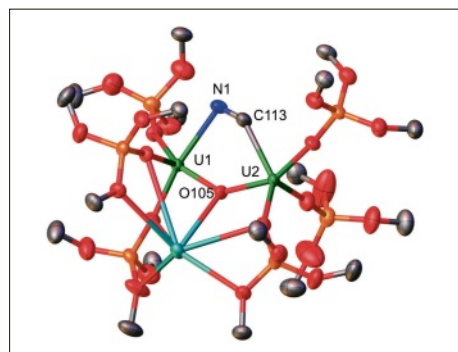
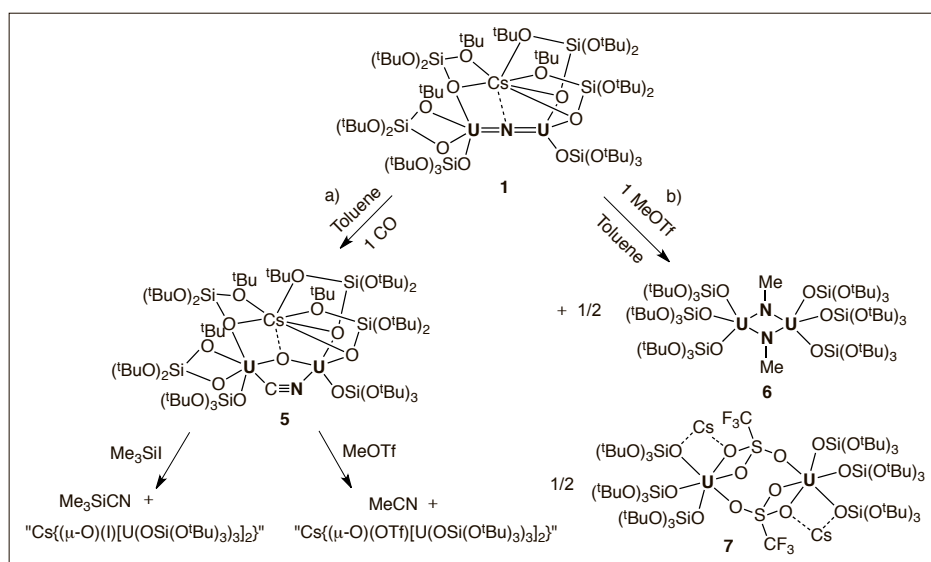


Fig. 4. Molecular structure of complex **5**. Thermal ellipsoids depicted at 50% probability. Only one carbon atom of the <sup>t</sup>Bu groups is shown for clarity. Figure adapted from ref. [9].



Scheme 2. Reactivity of complex **1**: CO cleavage reaction under ambient conditions to afford complex **5** (a) and subsequent addition of the electrophiles MeOTf and Me<sub>3</sub>SiI to afford MeCN and Me<sub>3</sub>SiCN; methylation reaction with MeOTf to form complexes **6** and **7** (b).

We also showed<sup>[9]</sup> that the reaction of **1** with one equivalent of MeOTf at room temperature results in a slow reaction affording a mixture of complexes [U<sup>V</sup>(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(μ-NMe)<sub>2</sub> (**6**) and Cs<sub>2</sub>[{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(μ-OTf)<sub>2</sub>·2(C<sub>7</sub>H<sub>8</sub>) (**7**) (Scheme 2b). The solution was kept at –40 °C and light blue crystals of the bis(imido) complex **6** were recovered after 24 h. Attempts to isolate the two products in a pure form from this reaction were not successful. However, the reaction of complex **1** with 2 equiv. MeOTf resulted in the isolation of complex **7** in 60% yield.

The crystal structure of **6** (Fig. 5a) shows two independent diuranium(V) complexes (only one is shown in Fig. 5a) where two uranium atoms are bridged by two methylimido ligands. The solid-state structure of **7** (Fig. 5b) shows a diuranium(III) complex where two uranium atoms are bridged by two triflate anions, each one binding the two uranium centres and a cesium cation.

Thus, the alkylation of **1** promotes the valence disproportionation of U(IV) into U(V) and U(III). This exceptional reactivity is remarkable since U(III) and U(V) complexes are usually more prone to disproportionation,<sup>[28]</sup> while U(IV) complexes are generally much more stable.

### 4. Conclusion

In conclusion our recent work<sup>[8,9]</sup> demonstrated that nitride functionalization with heteroallenes is readily effected by uranium. The work opens up new selective pathways for the synthesis of new organic molecules from cheap CO<sub>2</sub> feedstock and metal nitrides. Moreover, the high nucleophilic reactivity of the nitride ligand in the

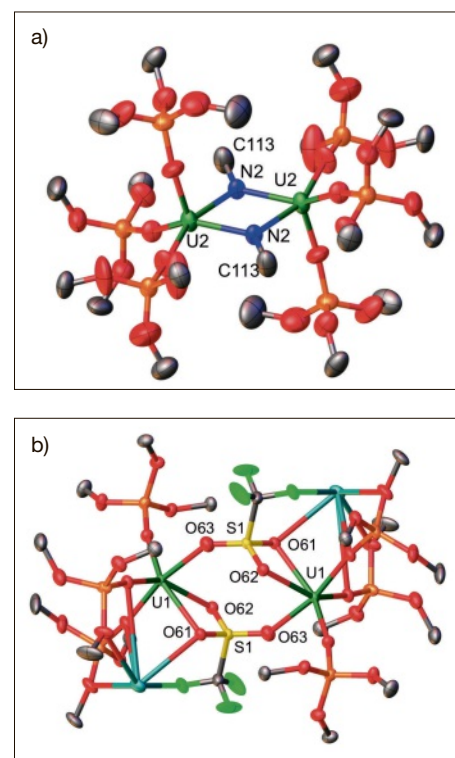


Fig. 5. Thermal ellipsoid drawing of complex **6** (only one complex is displayed) (a) and for Cs<sub>2</sub>[{U(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(μ-OTf)<sub>2</sub>·2(C<sub>7</sub>H<sub>8</sub>) **7** (b); probability 50%. Only one carbon atom of the <sup>t</sup>Bu groups is shown for clarity. Figure adapted from ref [9].

heterodimetallic CsU=N=U nitride led to the first example of complete cleavage of CO by a nitride complex under ambient conditions. The CO cleavage affords a new complex containing two U(IV) cations bridged by an oxo and a cyanide group. This complex can transfer the cyanide group to electrophiles leading to N–C bond



formation and release of organic molecules such as CH<sub>3</sub>CN or CH<sub>3</sub>SiCN.

The potential of these multimetallic uranium nitrides is highlighted by the fact that bridging nitrides of transition metals are often inert. The work demonstrated the possibility of implementing the selective synthesis of organic molecules from abundant and cheap CO and CO<sub>2</sub> feedstocks using metal nitrides. Such novel reactivity of uranium nitrides will certainly promote the development of new methods that involve both stoichiometric and catalytic N–C bond formation.

### Acknowledgements

We acknowledge support from the Swiss National Science Foundation and from the Ecole Polytechnique Fédérale de Lausanne (EPFL).

Received: February 10, 2017

- [1] a) A. R. Fox, S. C. Bart, K. Meyer, C. C. Cummins, *Nature* **2008**, *455*, 341; b) M. J. Monreal, P. L. Diaconescu, *Nat. Chem.* **2010**, *2*, 423; c) G. W. C. Silva, C. B. Yeaman, A. P. Sattelberger, T. Hartmann, G. S. Cerefece, K. R. Czerwinski, *Inorg. Chem.* **2009**, *48*, 10635.
- [2] a) F. Haber, Vol. DE 229126, Haber, F. Ammonia German patent DE 229126, **1909**; b) A. R. Fox, S. C. Bart, K. Meyer, C. C. Cummins, *Nature* **2008**, *455*, 341; c) M. S. Eisen, *Top. Organomet. Chem.* **2010**, *31*, 157.
- [3] a) D. M. King, S. T. Liddle, *Coord. Chem. Rev.* **2014**, *266*, 2; b) T. W. Hayton, *Chem. Commun.* **2013**, *49*, 2956; c) W. J. Evans, S. A. Kozimor, J. W. Ziller, *Science* **2005**, *309*, 1835; d) I. Korobkov, S. Gambarotta, G. P. A. Yap, *Angew. Chem. Int. Ed.* **2002**, *41*, 3433; e) T. K. Todorova, L. Gagliardi, J. R. Walensky, K. A. Miller, W. J. Evans, *J. Am. Chem. Soc.* **2010**, *132*, 12397; f) G. Nocton, J. Pecaut, M. Mazzanti, *Angew. Chem. Int. Ed.* **2008**, *47*, 3040; g) S. Fortier, G. Wu, T. W. Hayton, *J. Am. Chem. Soc.* **2010**, *132*, 6888; h) A. R. Fox, P. L. Arnold, C. C. Cummins, *J. Am. Chem. Soc.* **2010**, *132*, 3250; i) C. Camp, J. Pecaut, M. Mazzanti, *J. Am. Chem. Soc.* **2013**, *135*, 12101; j) L. Maria, I. C. Santos, V. R. Sousa, J. Marcalo, *Inorg. Chem.* **2015**, *54*, 9115; k) R. K. Thomson, T. Cantat, B. L. Scott, D. E. Morris, E. R. Batista, J. L. Kiplinger, *Nat. Chem.* **2010**, *2*, 723; l) D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Nat. Chem.* **2013**, *15*, 482; m) D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Science* **2012**, *337*, 717; n) 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; o) L. Chatelain, R. Scopelliti, M. Mazzanti, *J. Am. Chem. Soc.* **2016**, *138*, 1784; p) N. Tsoureas, A. F. R. Kilpatrick, C. J. Inman, F. G. N. Cloke, *Chem. Sci.* **2016**, *7*, 4624.
- [4] S. D. Roughley, A. M. Jordan, *J. Med. Chem.* **2011**, *54*, 3451.
- [5] M. Aresta, A. Dibenedetto, *J. Chem. Soc.-Dalton Trans.* **2007**, 2975.
- [6] a) W. H. Bernskoetter, E. Lobkovsky, P. J. Chirik, *Angew. Chem. Int. Ed.* **2007**, *46*, 2858; b) D. J. Knobloch, H. E. Toomey, P. J. Chirik, *J. Am. Chem. Soc.* **2008**, *130*, 4248.
- [7] a) J. M. Smith, *Prog. Inorg. Chem.* **2014**, *58*, 417; b) J. K. Brask, V. Dura-Vila, P. L. Diaconescu, C. C. Cummins, *Chem. Commun.* **2002**, 902; c) J. S. Silvia, C. C. Cummins, *J. Am. Chem. Soc.* **2010**, *132*, 2169.
- [8] M. Falcone, L. Chatelain, M. Mazzanti, *Angew. Chem. Int. Ed.* **2016**, *55*, 4074.
- [9] M. Falcone, C. E. Kefalidis, R. Scopelliti, L. Maron, M. Mazzanti, *Angew. Chem. Int. Ed.* **2016**, *55*, 12290 [10] G. W. Parshall, S. D. Ittel, 'Homogeneous Catalysis. The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes', 2nd ed., Wiley Interscience, **1992**.
- [11] H. Schulz, *Appl. Catal. A* **1999**, *186*, 3.
- [12] a) B. Askevold, J. T. Nieto, S. Tussupbayev, M. Diefenbach, E. Herdtweck, M. C. Holthausen, S. Schneider, *Nat. Chem.* **2011**, *3*, 532; b) J. J. Scepaniak, R. P. Bontchev, D. L. Johnson, J. M. Smith, *Angew. Chem. Int. Ed.* **2011**, *50*, 6630; c) B. L. Tran, M. Singhal, H. Park, O. P. Lam, M. Pink, J. Krzystek, A. Ozarowski, J. Telsler, K. Meyer, D. J. Mindiola, *Angew. Chem. Int. Ed.* **2010**, *49*, 9871; d) J. S. Silvia, C. C. Cummins, *J. Am. Chem. Soc.* **2009**, *131*, 446; e) S. P. Semproni, C. Milsman, P. J. Chirik, *Angew. Chem. Int. Ed.* **2012**, *51*, 5213.
- [13] a) F. Calderazzo, U. Englert, A. Guarini, F. Marchetti, G. Pampaloni, A. Segre, *Angew. Chem. Int. Ed.* **1994**, *33*, 1188; b) N. M. West, A. J. M. Miller, J. A. Labinger, J. E. Bercaw, *Coord. Chem. Rev.* **2011**, *255*, 881; c) D. R. Neithamer, R. E. Lapointe, R. A. Wheeler, D. S. Richeson, G. D. Vanduyne, P. T. Wolczanski, *J. Am. Chem. Soc.* **1989**, *111*, 9056; d) R. L. Miller, P. T. Wolczanski, A. L. Rheingold, *J. Am. Chem. Soc.* **1993**, *115*, 10422; e) T. Shima, Z. Hou, *J. Am. Chem. Soc.* **2006**, *128*, 8124; f) J. Ballmann, F. Pick, L. Castro, M. D. Fryzuk, L. Maron, *Organometallics* **2012**, *31*, 8516; g) A. S. Batsanov, J. A. Cabeza, M. G. Crestani, M. R. Fructos, P. Garcia-Alvarez, M. Gille, Z. Lin, T. B. Marder, *Angew. Chem. Int. Ed.* **2016**, *55*, 4707; h) P. A. Belmonte, F. G. N. Cloke, R. R. Schrock, *J. Am. Chem. Soc.* **1983**, *105*, 2643; i) J. A. Buss, T. Agapie, *Nature* **2016**, *529*, 72; j) D. J. Knobloch, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2010**, *132*, 10553; k) T. Matsuo, H. Kawaguchi, *J. Am. Chem. Soc.* **2005**, *127*, 17198; l) H. Braunschweig, M. A. Celik, R. D. Dewhurst, S. Kachel, B. Wennemann, *Angew. Chem. Int. Ed.* **2016**, *55*, 5076.
- [14] a) J. G. Brennan, R. A. Andersen, J. L. Robbins, *J. Am. Chem. Soc.* **1986**, *108*, 335; b) J. Parry, E. Carmona, S. Coles, M. Hursthouse, *J. Am. Chem. Soc.* **1995**, *117*, 2649; c) W. J. Evans, S. A. Kozimor, G. W. Nyce, J. W. Ziller, *J. Am. Chem. Soc.* **2003**, *125*, 13831.
- [15] I. Castro-Rodriguez, K. Meyer, *J. Am. Chem. Soc.* **2005**, *127*, 11242.
- [16] a) O. T. Summerscales, F. G. N. Cloke, P. B. Hitchcock, J. C. Green, N. Hazari, *Science* **2006**, *311*, 829; b) A. S. Frey, F. G. N. Cloke, P. B. Hitchcock, I. J. Day, J. C. Green, G. Aitken, *J. Am. Chem. Soc.* **2008**, *130*, 13816.
- [17] O. T. Summerscales, F. G. N. Cloke, P. B. Hitchcock, J. C. Green, N. Hazari, *J. Am. Chem. Soc.* **2006**, *128*, 9602.
- [18] a) P. L. Arnold, Z. R. Turner, R. M. Bellabarba, R. P. Tooze, *Chem. Sci.* **2011**, *2*, 77; b) S. M. Mansell, N. Kaltsoyannis, P. L. Arnold, *J. Am. Chem. Soc.* **2011**, *133*, 9036; c) B. M. Gardner, J. C. Stewart, A. L. Davis, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 9265.
- [19] C. Camp, J. Pecaut, M. Mazzanti, *J. Am. Chem. Soc.* **2013**, *135*, 12101.
- [20] C. Camp, C. E. Kefalidis, J. Pecaut, L. Maron, M. Mazzanti, *Angew. Chem. Int. Ed.* **2013**, *52*, 12646.
- [21] a) J. G. Brennan, R. A. Andersen, A. Zalkin, *J. Am. Chem. Soc.* **1988**, *110*, 4554; b) J. L. Stewart, R. A. Andersen, *New J. Chem.* **1995**, *19*, 587; c) R. C. Schnabel, B. L. Scott, W. H. Smith, C. J. Burns, *J. Organomet. Chem.* **1999**, *591*, 14.
- [22] a) O. P. Lam, L. Castro, B. Kosog, F. W. Heinemann, L. Maron, K. Meyer, *Inorg. Chem.* **2012**, *51*, 781; b) C. Camp, O. Cooper, J. Andrez, J. Pecaut, M. Mazzanti, *J. Chem. Soc.-Dalton Trans.* **2015**, *44*, 2650.
- [23] M. A. S. Goher, *Coll. Czech. Chem. Commun.* **1977**, *42*, 1478.
- [24] R. B. MacMullin, *US. Pat.* **43178**, **1935**.
- [25] P. J. Fagan, J. M. Manriquez, S. H. Vollmer, C. S. Day, V. W. Day, T. J. Marks, *J. Am. Chem. Soc.* **1981**, *103*, 2206.
- [26] C. Camp, L. Chatelain, C. E. Kefalidis, J. Pecaut, L. Maron, M. Mazzanti, *Chem. Commun.* **2015**, *51*, 15454.
- [27] a) J.-C. Berthet, P. Thuery, M. Ephritikhine, *J. Chem. Soc.-Dalton Trans.* **2015**, *44*, 7727; b) A. Herve, Y. Bouzidi, J.-C. Berthet, L. Belkhir, P. Thuery, A. Boucekkine, M. Ephritikhine, *Inorg. Chem.* **2014**, *53*, 6995.
- [28] 'The Chemistry of the Actinide and Transactinide Elements', Eds. L. R. Morss, N. Edelstein, J. Fuger, J. J. Katz, 3rd ed., Springer, Dordrecht, **2006**.