



Cite this: *Chem. Commun.*, 2015, 51, 15454

Received 10th August 2015,  
Accepted 27th August 2015

DOI: 10.1039/c5cc06707c

www.rsc.org/chemcomm

## CO<sub>2</sub> conversion to isocyanate via multiple N–Si bond cleavage at a bulky uranium(III) complex†

Clément Camp,<sup>ab</sup> Lucile Chatelain,<sup>abc</sup> Christos E. Kefalidis,<sup>d</sup> Jacques Pécaut,<sup>ab</sup> Laurent Maron<sup>\*cd</sup> and Marinella Mazzanti<sup>\*c</sup>

**The reaction of the sterically saturated uranium(III) tetrasilylamido complex [K(18c6)][U(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>4</sub>] with CO<sub>2</sub> leads to CO<sub>2</sub> insertion into the U–N bond affording the stable U(IV) isocyanate complex [K(18c6)][U(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub>(NCO)<sub>2</sub>]<sub>n</sub> that was crystallographically characterized. DFT studies indicate that the reaction involves the [2+2] cycloaddition of a double bond of O=C=O to the U–N(SiMe<sub>3</sub>)<sub>2</sub> bond and proceeds to the final product through multiple silyl migration steps.**

The reactivity of uranium(III) with small molecules such as CO<sub>2</sub>, CO or N<sub>2</sub> has been attracting increasing interest in recent years due to the ability of uranium to promote unusual transformations.<sup>1,2</sup> Bulky amides have been successfully used in uranium chemistry, as innocent ancillary ligands, as alternatives to the ubiquitous cyclopentadienyl systems.<sup>3</sup> In particular the simple neutral [U(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub>]<sup>14</sup> complex has provided a versatile precursor and has demonstrated interesting reactivity<sup>5</sup> including arene reduction and functionalization,<sup>6</sup> CO activation,<sup>7</sup> and nitride formation.<sup>8</sup> In contrast, the ability of the U–N bonds to undergo insertion reactions has been much less explored compared to U–C σ-bonds.<sup>1c</sup> Only a few examples of insertion of CO<sub>2</sub> into U(III)–NR<sub>2</sub> and U(IV)–NR<sub>2</sub> bonds leading to the formation of U(III)<sup>9</sup> and U(IV) carbamates<sup>10</sup> have been reported. Examples of the insertion of CO<sub>2</sub> into metal–silylamide bonds have been reported<sup>11</sup> for main group, d-block and f-block metals<sup>12</sup> but are much rarer than the insertion of CO<sub>2</sub> into N-alkylamide bonds. In particular, [U<sup>III</sup>(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub>] was reported to react with CO<sub>2</sub> to give O=C=NSiMe<sub>3</sub> and a second product identified as the tetravalent uranium silanolate [U(OSiMe<sub>3</sub>)<sub>4</sub>].<sup>12a</sup>

Herein we show that the reaction of CO<sub>2</sub> with the sterically saturated uranium(III) tetrasilylamido complex [K(18c6)][U(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>4</sub>], **1**, leads to CO<sub>2</sub> insertion into the U–N bond and to the formation of the stable U(IV) isocyanate complex [K(18c6)][U(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub>(NCO)<sub>2</sub>]<sub>n</sub> **2**. DFT studies were used in combination with reactivity studies to investigate the mechanism leading to the formation of complex **2**. Complex **2** provides a rare example of cyanate formation at a uranium center. To date there have been only three examples of uranium-mediated OCN<sup>−</sup> formation and they involve the reaction of CO with a nitride,<sup>13</sup> imido<sup>14</sup> or nitrosyl complex.<sup>15</sup>

Complex **1** was prepared from [U(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>4</sub>]<sup>16</sup> according to the previously reported procedure.<sup>17</sup> The reaction of **1** with 2.5 equivalents of carbon dioxide proceeded slowly (completed after 48 hours) at room temperature affording after workup and recrystallization the U(IV) bis-cyanate complex [K(18c6)][U(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub>(NCO)<sub>2</sub>]<sub>n</sub>, **2** as a pale pink microcrystalline solid in 48% yield (Scheme 1). The stoichiometry of this reaction requires the presence of additional uranium compounds and reduced by-products (U(III) has been oxidized to U(IV)) that have not been isolated. THF solutions of **2** are stable for at least 48h at room temperature. The <sup>1</sup>H NMR spectrum for **2** recorded from deuterated THF at room temperature displays a broad resonance at −10.9 ppm corresponding to the three equivalent {N(SiMe<sub>3</sub>)<sub>2</sub>} moieties together with a resonance at 4.7 ppm for the potassium crown ether counter cation.

The X-ray crystal structure of **2** shows the presence of a 1D coordination polymer (Fig. 1). The uranium environment is trigonal bipyramidal with three silylamido ligands at equatorial

<sup>a</sup> Univ. Grenoble Alpes, INAC-SCIB, F-38000 Grenoble, France

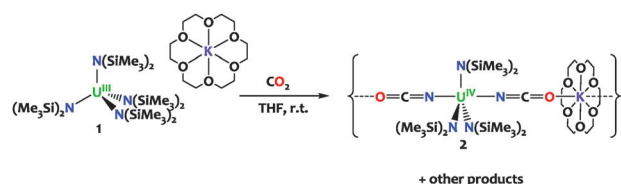
<sup>b</sup> CEA, INAC-SCIB, Reconnaissance Ionique et Chimie de Coordination, 17 Rue des Martyrs, F-38000 Grenoble, France

<sup>c</sup> Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.

E-mail: marinella.mazzanti@epfl.ch

<sup>d</sup> LPCNO, CNRS & INSA, UPS, Université de Toulouse, 135 Avenue de Rangueil, F-31077 Toulouse, France

† Electronic supplementary information (ESI) available: Synthetic details, full crystallographic data, <sup>1</sup>H and <sup>13</sup>C NMR spectra, ESI/MS spectra and computational data are included. CCDC 1417064. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc06707c



Scheme 1



positions and two NCO<sup>-</sup> anions at apical positions. A K(18c6) cation bridges two NCO ligands from two distinct uranium complexes. The U1–N<sub>amido</sub> bond distances fall in the range of what was observed in the U(IV) silylamido species. Notably the structure of **2** is closely related to the isoelectronic azide species [Na(THF)<sub>4</sub>][U{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>3</sub>(N<sub>3</sub>)<sub>2</sub>] reported by Hayton and coworkers<sup>5e</sup> featuring similar geometry and uranium-ligand bond distances. The three atoms X=C=X' units are disordered across the mirror plane of the *P21/m* space group and refine equally well when N or O or a mixture of both are used at the X and X' positions. Thus, the X-ray data do not allow us to discriminate between a cyanate (coordination through O) and an isocyanate (coordination through N) ligand. Similar disorder issues were observed in the [Me<sub>2</sub>Al(μ-OsSiMe<sub>3</sub>)<sub>2</sub>Mg(THF)<sub>2</sub>(μ-OCN)]<sub>3</sub> complex<sup>11c</sup> and in the dimeric U(IV) complex [U(η-C<sub>8</sub>H<sub>6</sub>{Si<sup>i</sup>Pr<sub>3</sub>-1,4<sub>2</sub>})(η-Cp\*)(NCO)]<sub>2</sub>.<sup>15</sup> However, in most previously reported U(IV) complexes the NCO ligand is N-bound<sup>18</sup> and DFT calculations are in agreement with an N-bound coordination (see below and ref. 13). Therefore the structure was refined with N-bound OCN ligands (Fig. 1). The two U–N<sub>NCO</sub> bond distances at 2.337(3) and 2.338(4) Å are in the range of those found in the few uranium isocyanate complexes reported (2.338(3),<sup>13</sup> 2.389(6)<sup>18b</sup> and 2.336(5) Å<sup>19</sup>).

The absorption band at 2201 cm<sup>-1</sup> in the IR spectrum of **2** was assigned to the asymmetric stretching mode ν<sub>NCO</sub>. This value is similar to those found in the few terminal<sup>18</sup> or bridging<sup>15</sup> U(IV) and U(III)<sup>13</sup> isocyanate complexes reported (2199–2122 cm<sup>-1</sup>).

All the spectroscopic and analytical data (see ESI†) support the assignment of the three atoms in **2** as NCO ligands. Notably the quaternary carbon (after reaction with <sup>13</sup>CO<sub>2</sub>) resonance at δ = 492.4 ppm in the <sup>13</sup>C NMR spectrum, the microanalytical data, and the parent ion in the mass spectrum for the anion [U(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub>(NCO)<sub>2</sub>]<sup>-</sup> (*m/z* = 802.4) are in agreement with the assigned formula.

<sup>1</sup>H and <sup>13</sup>C NMR studies of the reaction of **1** with <sup>13</sup>CO<sub>2</sub> were performed. After addition of 1 equivalent of <sup>13</sup>CO<sub>2</sub> the reaction leads to the slow disappearance of the <sup>1</sup>H signals assigned to complex **1** with completion after 48 hours. The <sup>13</sup>C NMR spectrum of the final reaction mixture shows the presence of a signal at 307 ppm that

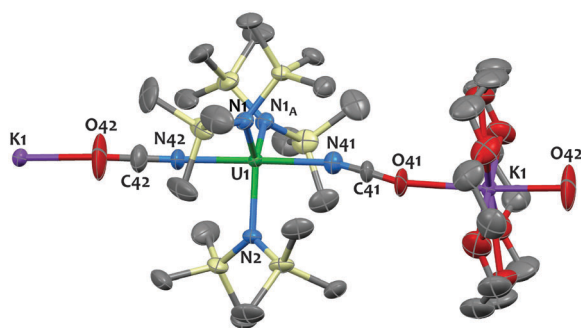


Fig. 1 Solid-state molecular structure of [K(18c6)][U(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub>(NCO)<sub>2</sub>]<sub>n</sub> **2** crystallized from THF/hexane. Hydrogen atoms and disorder are omitted for clarity. Uranium (green), potassium (purple), silicon (yellow), nitrogen (blue), oxygen (red) and carbon (grey) atoms are represented with 30% probability ellipsoids. Selected bond distances [Å] and angles [deg]: U1–N1 2.2679(2), U1–N2 2.2696(2), U1–O/N42 = 2.3358(1), U1–O/N41 = 2.3370(1), X42–C42–X'42 = 171.6(1), X41–C41–X'41 = 175.5(1).

could be assigned to the quaternary carbon of a carbamate or an isocyanate intermediate. No evident color change was observed during the reaction. Additional <sup>13</sup>C NMR signals are also observed in the 5.6–1.8 ppm region. Further addition of 1 equivalent of <sup>13</sup>CO<sub>2</sub> leads to a slow color change of the reaction mixture from dark purple to light pink. <sup>13</sup>C NMR monitoring of the reaction showed a slow evolution with time with the disappearance of the <sup>13</sup>C NMR signal at 307 ppm and the appearance of the <sup>13</sup>C NMR signal at 492.4 ppm assigned to the isocyanate complex **2**. All the <sup>13</sup>C NMR resonances in the 5.6–1.8 ppm region remained present in the final <sup>13</sup>C NMR spectrum but with increased intensity. In particular, two signals at 0.07 ppm in the <sup>1</sup>H NMR spectrum and at 1.84 ppm in the <sup>13</sup>C NMR spectrum were assigned to the hexamethyldisiloxane (SiMe<sub>3</sub>)<sub>2</sub>O by-product. Signals for SiMe<sub>3</sub>NCO were not observed. The <sup>1</sup>H NMR spectrum of the final reaction mixture showed the resonances assigned to complex **2** and additional broad shifted resonances assigned to unidentified U(IV) products. Mass spectrometry studies showed the presence of [U<sub>2</sub>(OSiMe<sub>3</sub>)<sub>9</sub>]<sup>-</sup> and [U<sub>2</sub>(NCO)(OSiMe<sub>3</sub>)<sub>8</sub>]<sup>-</sup> species (see ESI†).

In order to shed light on the mechanistic aspects of this peculiar reactivity outcome, DFT investigations using the B3PW91 functional were performed. The system of choice is the full anionic system [U(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>4</sub>]<sup>-</sup>, where the counter-cation is not taken into account.<sup>13</sup> The anionic [U(IV)–CO<sub>2</sub>]<sup>-</sup> intermediate **Int1** is formed from the electronic reduction of CO<sub>2</sub> that occurs at the coordination to the initial U(III) complex (so-called coordination-induced reduction).<sup>20</sup> The first step of the mechanism involves the [2+2] cyclo-addition of a double bond from the O=C=O<sup>•</sup> radical anion to the U–N(SiMe<sub>3</sub>)<sub>2</sub> bond, as it is shown in Fig. 2. The activation barrier for this process is found to be relatively small (14.8 kcal mol<sup>-1</sup>). In particular, in the transition state the amide group that is involved in the insertion step is considerably far from the uranium center, at a non-bonding distance (*d*<sub>U–N</sub> = 3.63 Å). The nature of this late-transition state is most probably due to the directionality of the occupied molecular orbital of the nitrogen with respect to the electrophilic carbon of the carbon dioxide molecule. Moreover, the steric hindrance of the ligand environment may also play an important role in the non-bonding situation between the nitrogen and the uranium, providing a logical explanation for the outcome of this step. In particular, the IRC calculation did not converge into

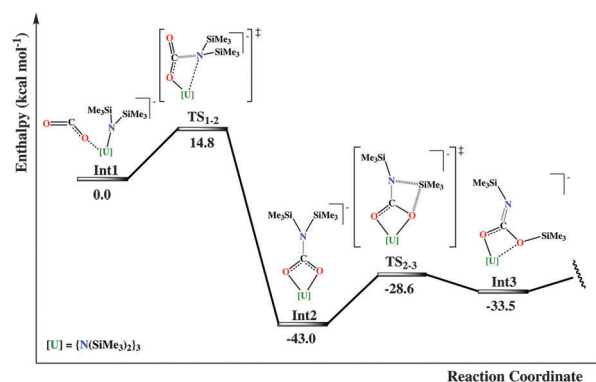


Fig. 2 Part of the energy profile that leads to the formation of the isocyanate complex **2**.



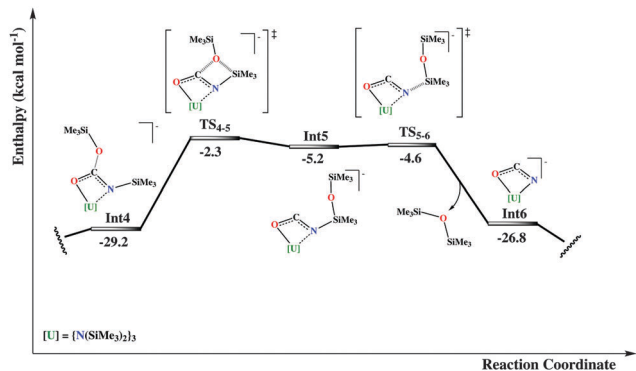


Fig. 3 Part of the energy profile that leads to the formation of the isocyanate complex **2**.

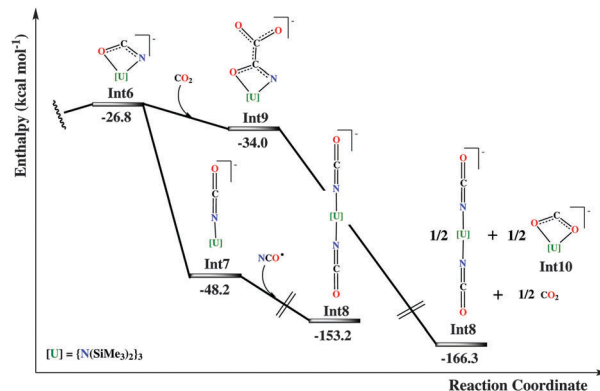


Fig. 4 Part of the energy profile that leads to the formation of the isocyanate complex **2**.

an O,N-bound carbamate intermediate, but instead into an O,O-bound one (**Int2**), with a subsequent significant drop in enthalpy energy ( $43.0 \text{ kcal mol}^{-1}$  with respect to the  $\text{CO}_2$  reduced adduct).

From the ligated dianionic O,O-bound carbamate the reaction can proceed through a sequence of two successive silyl migration steps (Fig. 2 and 3).

More specifically, the first step refers to the migration of the trimethylsilyl group from the nitrogen atom to one oxygen of the carbamate group, surmounting a moderate activation energy barrier of  $14.4 \text{ kcal mol}^{-1}$ . From the ensuing intermediate, **Int3**, rotation around the  $\text{O}_{\text{siloxyde}}-\text{C}$  bond of the silyl group is required for the Si atom to approach the coordinated oxygen atom, for the second migration to occur. This isomerization is an almost thermo-neutral process, with enthalpy energy difference of only  $4.3 \text{ kcal mol}^{-1}$  in favor of **Int3**. The following migration of the silyl group is more energy demanding than the previous one, with an accessible activation energy barrier of  $26.9 \text{ kcal mol}^{-1}$  in terms of  $\Delta H^\ddagger$ .

In the following intermediate, **Int5**, a kind of cyanate fragment has been formed, now developing an  $\eta^2\text{-N,O}$ -type coordination with the uranium atom. This fragment can easily expel a siloxane molecule, which is observed experimentally, through an almost barrierless energy micro-step, *via* **TS<sub>5-6</sub>**. The resulting intermediate, **Int6**, is formally described as an  $\text{OCN}^{2-}$  complex of U(IV). At this point, one can envision two different potential paths, the first corresponding to the isomerization of the cyanate group to give a terminal bonded isocyanate complex or to the nucleophilic attack by a second  $\text{CO}_2$  molecule on the carbon atom of the  $\text{OCN}^{2-}$  moiety (Fig. 4). The first possibility results in an important stabilization energy of  $21.4 \text{ kcal mol}^{-1}$  with respect to the  $\eta^2$ -bound one. Then a putative free NCO radical (originating from a second uranium complex) can coordinate the vacant coordination site of **Int7**, on the axial position, *trans* to the other isocyanate, of the trigonal bipyramid. This can be done through two different coordination modes since  $\text{OCN}^-$  is an ambident ligand. Even though both correspond to highly exothermic processes (more than  $100 \text{ kcal mol}^{-1}$  stabilization energy), the N-bound intermediate, **Int8**, is more stable than the O-bound one, (see **Int8'** in the ESI<sup>†</sup>), by almost  $10 \text{ kcal mol}^{-1}$ . This observation suggests that most probably the two OCN groups in the X-ray structure of complex **2** are bound to the uranium through

their nitrogen atoms while the oxygen atoms bind the potassium atoms of the  $\text{K}(\text{18c6})$  cation.

Besides, since the experimental reactivity is found to be influenced by the number of  $\text{CO}_2$  equivalents reacted with U(III), a second  $\text{CO}_2$  molecule can undergo a nucleophilic attack at the carbon of the  $\eta^2$ -cyanate group in intermediate **Int6** (Fig. 4). This will result in the formation of an oxalate-like complex, **Int9**. Such reactivity is reminiscent of the oxalate formation in U(III) chemistry.<sup>21</sup> Two molecules of **Int9** can then disproportionate in order to give the bis-cyanate product **Int8** and a  $\text{CO}_2^{2-}$  complex (**Int10**). Also in this route, an important stabilization energy is found (almost  $130 \text{ kcal mol}^{-1}$ ). Attempts to compute a reaction pathway involving the insertion of  $\text{CO}_2$  into a U(III) species were not successful but showed that such a pathway is higher in energy.

In conclusion the bulky uranium(III) tetrasilylamido complex  $[\text{K}(\text{18c6})][\text{U}(\text{N}(\text{SiMe}_3)_2)_4]$  reacts with  $\text{CO}_2$  to afford a rare example of a U(IV) isocyanate complex. DFT computational studies suggest that the reaction proceeds through carbon dioxide reduction followed by the [2+2] cyclo-addition of the carbonyl double bond of the reduced carbon dioxide to the  $\text{U}-\text{N}(\text{SiMe}_3)_2$  bond and multiple silyl migration. The reactivity of this bulky "ate" complex differs from that reported for the neutral analogue  $[\text{U}(\text{N}(\text{SiMe}_3)_2)_3]$ <sup>12a</sup> highlighting the importance of the coordination environment for controlling the  $\text{CO}_2$  conversion at the uranium center.

This work was supported by the CEA, the Swiss National Science Foundation, and by the EPFL. We thank O. Cooper for recording some analytical data. LM is member of the Institut Universitaire de France. Humboldt Foundation and Calmip are also acknowledged.

## Notes and references

- (a) P. L. Arnold, *Chem. Commun.*, 2011, 47, 9005–9010; (b) O. P. Lam and K. Meyer, *Polyhedron*, 2012, 32, 1–9; (c) H. S. La Pierre and K. Meyer, *Prog. Inorg. Chem.*, ed. K. D. Karlin, 2014, vol. 58, pp. 303–415; (d) S. T. Liddle, *Angew. Chem., Int. Ed.*, 2015, 54, 8604–8641.
- (a) A. R. Fox, S. C. Bart, K. Meyer and C. C. Cummins, *Nature*, 2008, 455, 341–349; (b) M. S. Eisen, *C–X Bond Formation*, ed. A. Vigalok, 2010, vol. 31, pp. 157–184; (c) M. B. Jones and A. J. Gaunt, *Chem. Rev.*, 2013, 113, 1137–1198.
- (a) D. M. King and S. T. Liddle, *Coord. Chem. Rev.*, 2014, 266, 2–15; (b) A. R. Fox, P. L. Arnold and C. C. Cummins, *J. Am. Chem. Soc.*, 2010, 132, 3250–3251; (c) P. L. Diaconescu and C. C. Cummins,



- J. Am. Chem. Soc.*, 2002, **124**, 7660–7661; (d) P. L. Diaconescu, *Acc. Chem. Res.*, 2010, **43**, 1352–1363; (e) B. M. Gardner and S. T. Liddle, *Chem. Commun.*, 2015, **51**, 10589–10607.
- 4 (a) R. A. Andersen, *Inorg. Chem.*, 1979, **18**, 1507–1509; (b) L. R. Avens, S. G. Bott, D. L. Clark, A. P. Sattelberger, J. G. Watkin and B. D. Zwick, *Inorg. Chem.*, 1994, **33**, 2248–2256.
- 5 (a) D. L. Clark, M. M. Miller and J. G. Watkin, *Inorg. Chem.*, 1993, **32**, 772–774; (b) C. J. Burns, D. L. Clark, R. J. Donohoe, P. B. Duval, B. L. Scott and C. D. Tait, *Inorg. Chem.*, 2000, **39**, 5464–5468; (c) H. Nakai, X. L. Hu, L. N. Zakharov, A. L. Rheingold and K. Meyer, *Inorg. Chem.*, 2004, **43**, 855–857; (d) S. Fortier, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2010, **132**, 6888–6889; (e) S. Fortier, G. Wu and T. W. Hayton, *J. Chem. Soc., Dalton Trans.*, 2010, **39**, 352–354; (f) S. Fortier, N. Kaltsoyannis, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2011, **133**, 14224–14227; (g) S. Fortier, J. R. Walensky, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2011, **133**, 6894–6897; (h) S. Fortier, J. L. Brown, N. Kaltsoyannis, G. Wu and T. W. Hayton, *Inorg. Chem.*, 2012, **51**, 1625–1633; (i) A. J. Lewis, E. Nakamaru-Ogiso, J. M. Kikkawa, P. J. Carroll and E. J. Schelter, *Chem. Commun.*, 2012, **48**, 4977–4979; (j) A. J. Lewis, U. J. Williams, P. J. Carroll and E. J. Schelter, *Inorg. Chem.*, 2013, **52**, 7326–7328; (k) W. J. Evans, D. S. Lee, D. B. Rego, J. M. Perotti, S. A. Kozimor, E. K. Moore and J. W. Ziller, *J. Am. Chem. Soc.*, 2004, **126**, 14574–14582; (l) K. C. Mullane, A. J. Lewis, H. Yin, P. J. Carroll and E. J. Schelter, *Inorg. Chem.*, 2014, **53**, 9129–9139.
- 6 P. L. Arnold, S. M. Mansell, L. Maron and D. McKay, *Nat. Chem.*, 2012, **4**, 668–674.
- 7 P. L. Arnold, Z. R. Turner, R. M. Bellabarba and R. P. Tooze, *Chem. Sci.*, 2011, **2**, 77–79.
- 8 S. Fortier, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2010, **132**, 6888–6889.
- 9 E. M. Matson, P. E. Fanwick and S. C. Bart, *Organometallics*, 2011, **30**, 5753–5762.
- 10 (a) K. W. Bagnall and E. Yanir, *J. Inorg. Nucl. Chem.*, 1974, **36**, 777–779; (b) P. J. Fagan, J. M. Manriquez, S. H. Vollmer, C. S. Day, V. W. Day and T. J. Marks, *J. Am. Chem. Soc.*, 1981, **103**, 2206–2220; (c) S. C. Bart, C. Anthon, F. W. Heinemann, E. Bill, N. M. Edelstein and K. Meyer, *J. Am. Chem. Soc.*, 2008, **130**, 12536–12546; (d) J. A. H. Frey, G. N. Cloke and S. M. Roe, *Organometallics*, 2015, **34**, 2102–2105.
- 11 (a) W. Sattler and G. Parkin, *J. Am. Chem. Soc.*, 2011, **133**, 9708–9711; (b) M. T. Whited, A. J. Kosanovich and D. E. Janzen, *Organometallics*, 2014, **33**, 1416–1422; (c) H. Phull, D. Alberti, I. Korobkov, S. Gambarotta and P. H. M. Budzelaar, *Angew. Chem., Int. Ed.*, 2006, **45**, 5331–5334; (d) L. R. Sita, J. R. Babcock and R. Xi, *J. Am. Chem. Soc.*, 1996, **118**, 10912–10913; (e) C. A. Stewart, D. A. Dickie, M. V. Parkes, J. A. Saria and R. A. Kemp, *Inorg. Chem.*, 2010, **49**, 11133–11141.
- 12 (a) S. M. Mansell, N. Kaltsoyannis and P. L. Arnold, *J. Am. Chem. Soc.*, 2011, **133**, 9036–9051; (b) P. L. Arnold, Z. R. Turner, A. I. Germeroth, I. J. Casely, G. S. Nichol, R. Bellabarba and R. P. Tooze, *J. Chem. Soc., Dalton Trans.*, 2013, **42**, 1333–1337.
- 13 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.*, 2014, **53**, 10412–10415.
- 14 I. Castro-Rodriguez and K. Meyer, *Chem. Commun.*, 2006, 1353–1368.
- 15 A. S. P. Frey, F. G. N. Cloke, M. P. Coles and P. B. Hitchcock, *Chem. – Eur. J.*, 2010, **16**, 9446–9448.
- 16 A. J. Lewis, U. J. Williams, P. J. Carroll and E. J. Schelter, *Inorg. Chem.*, 2013, **52**, 7326–7328.
- 17 L. C. J. Pereira, C. Camp, J. T. Coutinho, L. Chatelain, P. Maldivi, M. Almeida and M. Mazzanti, *Inorg. Chem.*, 2014, **53**, 11809–11811.
- 18 (a) M. J. Crawford, P. Mayer, H. Noth and M. Suter, *Inorg. Chem.*, 2004, **43**, 6860–6862; (b) I. Castro-Rodriguez, H. Nakai and K. Meyer, *Angew. Chem., Int. Ed.*, 2006, **45**, 2389–2392; (c) R. K. Thomson, B. L. Scott, D. E. Morris and J. L. Kiplinger, *C. R. Chim.*, 2010, **13**, 790–802; (d) C. Camp, N. Settineri, J. Lefevre, A. R. Jupp, J. M. Goicoechea, L. Maron and J. Arnold, *Chem. Sci.*, 2015, DOI: 10.1039/C5SC02150B.
- 19 I. Castro-Rodriguez, H. Nakai, L. N. Zakharov, A. L. Rheingold and K. Meyer, *Science*, 2004, **305**, 1757–1759.
- 20 (a) L. Castro, C. E. Kefalidis, D. McKay, S. Essafi, L. Perrin and L. Maron, *J. Chem. Soc., Dalton Trans.*, 2014, **43**, 12124–12134; (b) C. E. Kefalidis, L. Castro, A. Yahia, L. Perrin and L. Maron, *Computational Methods in Lanthanide and Actinide Chemistry*, John Wiley & Sons Ltd, Chichester, UK, 2015.
- 21 (a) A.-C. Schmidt, F. W. Heinemann, C. E. Kefalidis, L. Maron, P. W. Roesky and K. Meyer, *Chem. – Eur. J.*, 2014, **20**, 13501–13506; (b) N. Tsoureas, L. Castro, A. F. R. Kilpatrick, F. G. N. Cloke and L. Maron, *Chem. Sci.*, 2014, **5**, 3777–3788; (c) L. Castro, O. P. Lam, S. C. Bart, K. Meyer and L. Maron, *Organometallics*, 2010, **29**, 5504–5510.

