Subscriber access provided by University of South Dakota

Article

Tuning Uranium-Nitrogen Multiple Bond Formation with Ancillary Siloxide Ligands.

Clement Camp, Jacques Pecaut, and Marinella Mazzanti

J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/ja405815b • Publication Date (Web): 19 Jul 2013

Downloaded from http://pubs.acs.org on July 20, 2013

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

ACS Publications
High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Tuning Uranium-Nitrogen Multiple Bond Formation with Ancillary Siloxide Ligands.

Clément Camp[a], Jacques Pécaut[a] and Marinella Mazzanti*[a]

[a]Laboratoire de Reconnaissance Ionique et Chimie de Coordination, SCIB, UMR-E3 CEA-UJF, INAC, CEA-Grenoble, 17 rue des Martyrs, F-38054 Grenoble Cedex 09

Supporting Information Placeholder

ABSTRACT: The new homoleptic "ate" U(III) siloxide $[K(18c6)][U(OSi(O^tBu)_3)_4]$, **2** has been prepared in 69% yield by reduction of $[U(OSi(O^tBu)_3)_4]$, **3** with KC_8. The reaction of the neutral U(III) siloxide complex $[U(OSi(O^tBu)_3)_2(\mu\text{-}OSi(O^tBu)_3)]_2$, **1** with adamantyl azide leads to the isolation of the dinuclear U(VI) imido complex $[U_2(NAd)_4(OSi(O^tBu)_3)_4]$, **4**. The X-ray crystal structure shows the presence of a "cation-cation interaction" between the two $[U(NAd)_2]^{2+}$ groups. In contrast the reactions of **2** with the trimethylsilyl and adamantyl azides afford the U(V) imido complexes $[K(18c6)][U(NSiMe_3)(OSi(O^tBu)_3)_4]$ **5-TMS** and $[K(18c6)][U(NAd)(OSi(O^tBu)_3)_4]$ **5-Ad** pure in 48 % and 66 % yield respectively. The reaction of **2** with CsN_3 in THF at -40°C yields a mixture of products from which the azido U(IV) complex $[K(18c6)][U(N_3)(OSi(O^tBu)_3)_4]$, **7** and the the μ-nitrido di-uranium(V) complex $[KU(\mu\text{-}N)(OSi(O^tBu)_3)]_2$, **8** were isolated. The crystal structure of **8** shows the presence of a rare U_2N_2 core with two nitrido atoms bridging two uranium centers in a diamond-shaped geometry. In contrast, the reaction of **1** with CsN_3 affords the diuranium(IV) complex $Cs\{(\mu\text{-}N)[U(OSi(O^tBu)_3)_3]_2\}$, **9** presenting a nitrido ligand bridging two uranium and one cesium cations. These results show the importance of the coordination environment in the outcome of the reaction of U(III) with azides.

Introduction :

Nitrido and imido complexes have been the focus of numerous studies in transition metal chemistry due to their important implication in nitrogen fixation, atom and group transfer reactions, and catalysis.[1,2] Since the first reports in the 80's of uranium-imido complexes[3,4] there has been also an increased interest for actinide compounds containing metal-nitrogen multiple bonding.[5-9] The focus of actinide scientists on such compounds has been driven by the possibility of promoting novel reactivity and catalytic transformations as a result of the larger size of actinides and of the involvement of f orbitals in bonding.[10-12] Moreover actinide imido and nitrido complexes are particularly attractive species for gaining a better understanding of the nature of bonding in molecular actinide species[13-18] which is relevant to the problem of spent nuclear fuel reprocessing.[19-23] Interest in uranium nitrides is also arising from the possibility of using uranium nitride as an alternative nuclear fuel in generation-IV power reactors because of its higher melting point and enhanced thermal conductivity compared to the currently used uranium oxides.[24,25] A classic route to metal-imides and metal-nitrides involves the reaction of organic and inorganic azides with reducing metal complexes.[2,26] In uranium chemistry several U(VI) cis-bis(imido) and terminal U(V) mono(imido) complexes[4-6,12,18,26-35] have been obtained from U(IV) and U(III) precursors respectively in a two-electron transfer with organic azides. In contrast U(VI) and U(V) bis(imido) complexes presenting the imido groups in a *trans* configurations have proven elusive using the azide route, but few examples of these compounds have been recently reported using alternative synthetic procedures.[16,36-39]

Fewer uranium nitrides have been reported compared to imido complexes.[34,41-47] Besides two examples of uranium nitrides isolated from the dinitrogen reduction by a U(III) complex,[40,41] they have been obtained from the reaction of low valent uranium with inorganic azides.

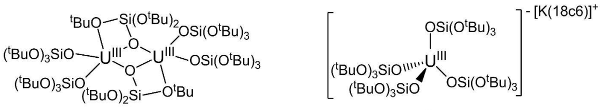
Depending on the ligand environment this reaction has led to the synthesis of terminal borane-capped nitrides,[42] dinuclear bridging nitrides,[43,44] large azido/nitrido clusters,[45-47] transient mononuclear nitride promoting intramolecular C-H activation,[48] or stable terminal nitrides.[33,49]

Differing steric and electronic environments at the uranium center have a critical impact on the formation of nitrido and imido complexes, on their geometry, stability and reactivity. For example the optimal tuning of the steric and electronic environment has been the key to the recent isolation of the first uranium complexes containing a terminal nitride.[33,49]

However, only a very limited number of studies have explored the effect of different steric environments in similar ligand systems.[12,18,50]

We have recently shown that bulky siloxide ligands, due to their $\sigma+\pi$ donating ability and their multiple binding modes,[51,52] provide an attractive alternative coordination environment for the stabilization of highly reactive trivalent uranium complexes.

Chart 1. U(III) siloxide complexes $[U(OSi(O^tBu)_3)_3]_2$, **1** and $[K(18c6)][U(OSi(O^tBu)_3)_4]$ **2**.



1 **2**

Here we investigate the reactivity with organic and inorganic azides of two U(III) systems presenting a different number of alkoxy(siloxide) ligands, the neutral tris-siloxide dimer $[U(OSi(O^tBu)_3)_3]_2$,**1**[53] and the new monomeric "ate" complex $[K(18c6)][U(OSi(O^tBu)_3)_4]$ **2** (Chart 1). It should be noted that studies on uranium "ate"-salts are rare[28,34,40,54-58] mostly due to the general belief that such compounds will result in a saturated coordination sphere and limited reactivity. Here we show that both the neutral and the "ate" complexes **1** and **2** react with organic and inorganic azides. The difference in steric demand and charge results in a very different outcome of the reactivity for the two U(III) siloxide species providing new insight into the formation of U=N multiple bonding and affording new imido and nitride complexes of uranium.

Results and discussion:

Mononuclear U(IV) and U(III) tetra-siloxide complexes.

The reaction of $[UI_4(OEt_2)_2]$ with 4 equiv of the potassium salt of tris-tertiobutoxysilanol $KOSi(OtBu)_3$ in THF affords, after recrystallization from hexane and drying in vacuum, the uranium(IV) homoleptic complex $[U(OSi(O^tBu)_3)_4]$ **3**, in 88% yield (Scheme 1). This complex was first isolated in our group from the ligand redistribution of a silanol carbonate U(IV) complex.[53] This compound is fully soluble in polar solvents (THF, pyridine) and in hydrocarbon solvents (hexane, toluene). In the solid state structure of **3** one siloxide ligand adopts a bidentate coordination mode, while the three other siloxide ligands are coordinated in a terminal monodentate fashion (see supporting information). A single proton resonance is observed in the ^1H NMR spectrum of **3** in deuterated *n*-hexane or toluene solutions suggesting that the coordination of the O^tBu group is labile in solution or involved in fast exchange.

Single crystals obtained from saturated pyridine solutions of $[U(OSi(O^tBu)_3)_4]$ were analyzed by X-ray diffraction and revealed that this homoleptic structure is not retained in coordinating solvent. The crystal structure of the green pyridine adduct $[U(OSi(O^tBu)_3)_4(py)_2]$ **3-py**, set out in Figure 1, shows that the uranium center is hexacoordinated with a distorted octahedral geometry by four terminal monodentate silanol ligands and two pyridine molecules bound in a *cis* fashion. The $U-O^-$ bond distances ($U-O_{avg}$ 2.177(12) Å) are slightly longer than what is found in **3**, and lie in the usual range of what is observed in other U(IV) alkoxide and siloxide compounds.[53,59-62] The structures of complexes **3** and **3-py** highlight the ability of the $OSi(O^tBu)_3$ ligand to adapt its coordination mode to its environment, allowing the stabilization of the low-coordinate uranium in both coordinating and non coordinating solvents.

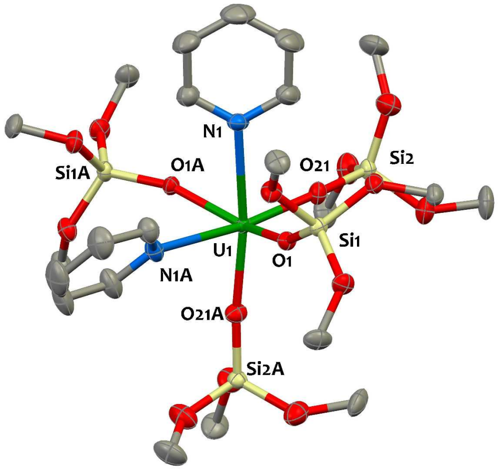
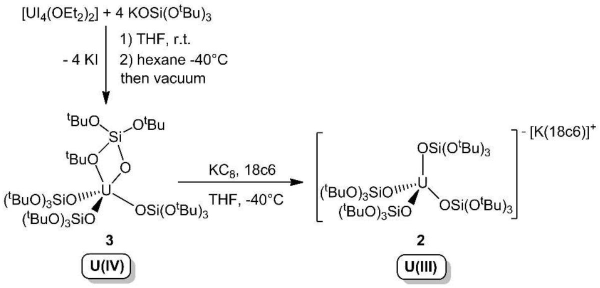


Figure 1. Ellipsoid plot for $[U(OSi(O^tBu)_3)_4(py)_2]$ **3-py** crystallized from pyridine; probability 50%. Disorder, hydrogen atoms and methyl groups are omitted for clarity. Bond distances (Å): $U1-O_{avg}$ 2.177(12), U1-N1 2.630(3). (O1A = O1 -x+1,y,-z+3/2)

Scheme 1. Synthesis of $[K(18c6)][U(OSi(O^tBu)_3)_4]$, **2**.



The reduction of complex **3** with potassium graphite in THF performed in the presence of 18c6 crown ether affords the uranium(III) "ate" complex $[K(18c6)][U(OSi(O^tBu)_3)_4]$ **2,** which was isolated pure in 69% yield (Scheme 1). The X-ray diffraction analysis shows the presence of an ion-pair structure composed of a K(18c6) cation and of a $[U(OSi(O^tBu)_3)_4]$ anion (Figure 2). The uranium ion is coordinated by four terminal siloxide groups with a tetrahedral geometry. The measured U-O bond lengths of the terminal siloxide (mean $U-O_{siloxide}$ = 2.228(17) Å) are longer than in complex **3** (mean $U-O_{siloxide}$ = 2.13(4) Å) and are in the range of typical U-O distances in uranium(III) siloxide and alkoxide complexes.[53,59,61] The difference in the coordination mode adopted by one of the siloxide ligand in the U(III) complex **2**, with respect to the homoleptic U(IV) complex **3** (monodentate versus bidentate) is probably the result of the difference in electron density. The U(III) cation is larger in size than the U(IV) and thus it should favour higher coordination numbers but the higher electron-rich character of trivalent uranium might disfavour the coordination of the butoxide group.

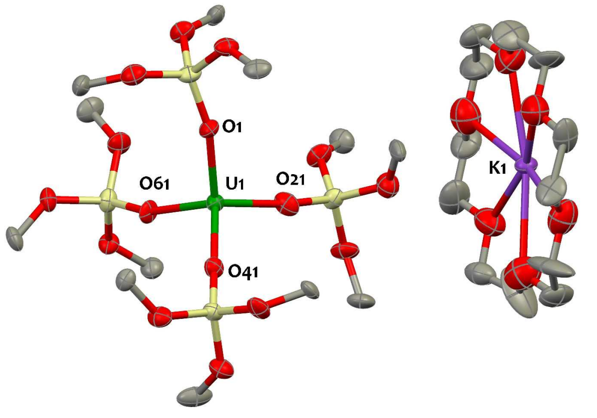


Figure 2. Ellipsoid plot for $[K(18c6)][U(OSi(O^tBu)_3)_4]$ **2** crystallized from toluene; probability 50%. Hydrogen atoms, methyl groups and solvent molecules are omitted for clarity. Bond distance (Å): $U1\text{-}O_{avg}$ 2.228(17).

The room temperature magnetic moment (2.63 μ_B) measured using the Evans method[63] for a THF solution of **2** falls in the range of the values reported for other U(III) coordination compounds.[31,64-66] This value is lower than the theoretical value (3.62 μ_B) calculated for a $5f^3$ ion with a full spin-orbit coupling as often observed in trivalent uranium complexes.[67]

The proton NMR of **2** in THF and toluene solution shows the presence of one signal for the siloxide protons and one signal for the 18c6 protons in agreement with the presence of S_4 symmetric solution species. The UV-visible absorption spectrum of **2** recorded from THF solution (see supporting information) displays a large band centered at $\lambda = 366$ nm ($\varepsilon = 3420$ $L.cm^{-1}.mol^{-1}$). This absorption, which is responsible of the orange color of the complex, is attributed to a $5f^3 \rightarrow 5f^2 6d^1$ transition, a classical feature of U(III) complexes.[68-70] A series of less intense ($\varepsilon < 150$ $L.cm^{-1}.mol^{-1}$) sharp resonances that we assign to $5f \rightarrow 5f$ transitions are spread over the entire recorded range above 500 nm. In comparison, the spectrum recorded for the complex **3-THF** (see supporting information) exhibits much weaker ($\varepsilon < 50$ $L.cm^{-1}.mol^{-1}$) $5f \rightarrow 5f$ transitions, with a maximum centered at $\lambda = 608$ nm as usually observed for U(IV) complexes.[31]

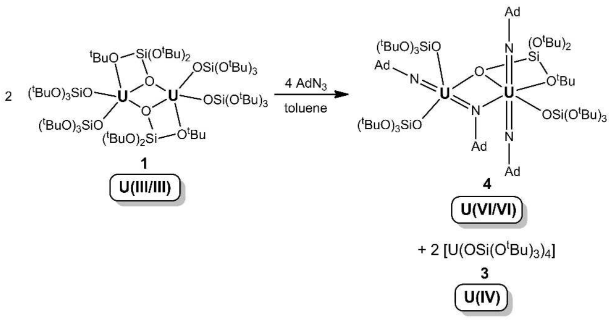
Anionic U(III) complexes are less common than their neutral analogues and mostly limited to cyclopentadienyl and cyclooctatetraenyl derivatives.[34] Other examples of "ate"-salt complexes of U(III) have been reported with calix[4]tetrapyrrole and bulky silylamido ligands.[34,40,71] Moreover, the reactivity of "ate" complexes of U(III) supported by electron donor ligands has been little explored compared to their neutral counterparts.

The "ate"-salt complex **2** and the previously reported neutral analogue complex $[U(OSi(O^tBu)_3)_2(\mu\text{-}OSi(O^tBu)_3)]_2$, **1**, provide interesting systems for investigating the effect of charge and steric bulk in the reactivity of U(III) complexes. The current interest in nitrido and imido complexes of high-valent uranium prompted us to investigate the reactivity of these siloxide complexes with organic and inorganic azides.

Reactivity with organic azides.

The reaction of the previously reported neutral U(III) siloxide complex $[U(OSi(O^tBu)_3)_2(\mu\text{-}OSi(O^tBu)_3)]_2$, **1**[53] with adamantyl azide (one equivalent per uranium) (Scheme 2) leads to the immediate formation of the U(IV) complex $[U(OSi(O^tBu)_3)_4]$, **3**, and of the dinuclear bis-imido complex of uranium(VI) $[U_2(NAd)_4(OSi(O^tBu)_3)_4]$, **4**, in ratio 2:1 (See ^1H NMR in supporting information).

Scheme 2. Reaction of $[U(OSi(O^tBu)_3)_2(\mu\text{-}OSi(O^tBu)_3)]_2$, **1** with adamantyl azide.



Complex **4** crystallizes from hexane solution in the monoclinic space group $P2_1/n$, and its solid-state molecular structure is represented in Figure 3. The dinuclear complex contains a cation-cation interaction[72] between two $[U(NAd)_2]^{2+}$ units (U1-N3-U2 angle = 108.4(5)°). The two $[U(OSi(O^tBu)_3)_2(NAd)_2]$ moieties are also held together by a bridging siloxide with a U···U distance of 3.7687(7) Å. Both $[U(NAd)_2]^{2+}$ motifs are nearly linear (N1-U1-N2 angle = 173.6(5)° ; N3-U2-N4 angle = 169.2(5)°) and can be seen as nitrogen analogues of the UO_2^{2+} moiety. The U=N imido bond distances for the terminal imido groups are short ($U{=}N_{avg}$ = 1.89(5) Å), in agreement with a multiple uranium-nitrogen bonding, and fall in the range of those reported for U(VI) imido complexes.[16,27,28,35-37,39,73-76] The U=N bond distance of the imido group (U2-N3 = 1.957(10) Å) involved in the cation-cation interaction is, as expected, longer than those of the terminal imido groups but significantly shorter than the U1-N3 bond length (2.661(12) Å), in agreement with the formulation proposed. The arrangement of the two imido groups is not planar (See figure 3b) (with N4U2N3U1 and N1U1N2N2 planes almost perpendicular at 85.23 °). This differs from the previously reported cation-cation complexes of pentavalent uranyl which all show a T-shaped or diamond shaped coplanar arrangement.[38,77-79] [80,81] The coordination geometry of U2 is best described as a distorted trigonal bipyramid with three $OSi(O^tBu)_3$ ligands occupying the equatorial plane. U1 is hexacoordinated in a highly distorted octahedral geometry by two adamantyl imidos in trans position, one terminal monodentate siloxy ligand, one bridging bidentate siloxy ligand and one bridging imido ligand.

While cis-bis(imido) complexes of U(VI) have been known since 1992,[27,28,35,73],[82] only in 2005 the first example of stable U(VI) trans-bis(imido) complexes, $[U(NR)_2I_2(THF)_2]$, were prepared from the reaction of uranium metal or U(III) with iodine and alkyl- or arylamines.[37,74] A few other examples of U(VI) trans-bis(imido) complexes in different ligand environments have been prepared in the last few years[16,36,39,75,76] which have shown interesting reactivity.[74,83,84] Compound **4** provides a new example of uranium(VI) trans-bis(imido) complex and the first one showing a cation-cation interaction between the two imido groups. Examples of dinuclear bis-imido complexes are rare in uranium chemistry[38,85] and they all present a diamond-shaped geometry. Cation-cation interaction between uranyl groups is found in several recently reported uranyl(V) complexes,[77,78,86] but only rarely observed in uranyl(VI) complexes.[86-88]

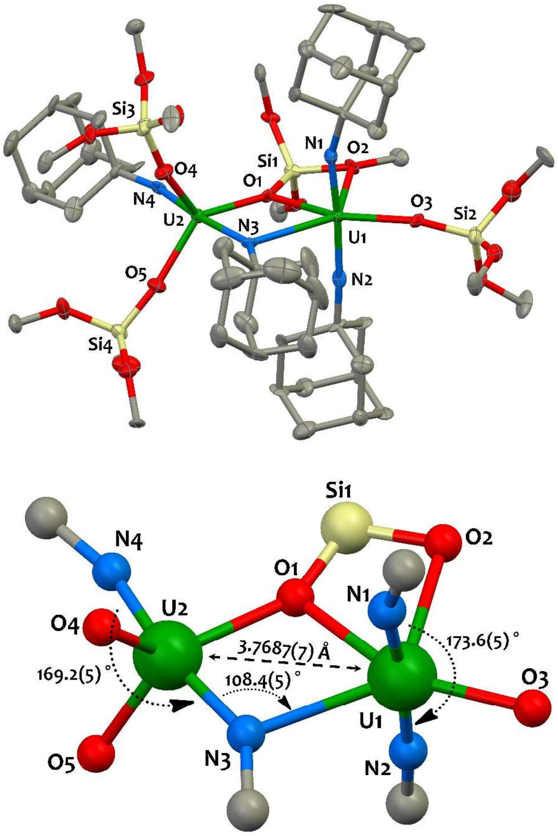


Figure 3. (top) Ellipsoid plot for $[U_2(NAd)_4(OSi(O^tBu)_3)_4]$ **4** crystallized from hexane; probability 50%. Hydrogen atoms and methyl groups are omitted for clarity. Bond distances (Å) and angles (°): U-O$_{avg}$ 2.20(2), U=N$_{avg}$ 1.937(7), U2-N3 ;= 1.957(10), U1-N3 = 2.661(12), U1-N3-U2 =108.4(5), N1-U1-N2 = 173.6(5), N3-U2-N4 =169.2(5); (bottom) detail of the bis-imido cation-cation core in **4**.

The formation of the complexes **3** and **4** from the reaction of **1** with adamantly azide could be the result of the disproportionation of an unstable U(V) bis(imido) intermediate. While the disproportionation reaction of uranyl(V) to yield uranyl(VI) and U(IV) species in aqueous or organic media[86,89-93] has been the subject of high interest in past and more recent years, to the best of our knowledge there are no previous reports of the disproportionation of uranyl(V) imido complexes.

However, one example of the formation of a U(VI) imido complex and of a U(IV) complex from the reaction of U(III) with organic azides has been reported.[35] The mechanism proposed by the authors is based on previously reported reactivity of U(V) imides with U(III)[94] and involves the comproportionation of the U(V) intermediate $[(C_5Me_5)_2UCl(N{=}R)]$ with the U(III) starting complex $\{Na[(C_5Me_5)_2UCl_2]\}$ to afford the imido $[(C_5Me_5)_2U(N{=}R)]$ and the bis-chloride $[(C_5Me_5)_2UCl_2]$ U(IV) complexes. Further reaction of the U(IV) imido with azide yields the U(VI) cis-bis(imido) product. A similar mechanism could also be invoked for the formation of **3** and **4** from **1** as alternative to the disproportionation route. (see supporting for the scheme of the two possible mechanisms). Further work will be directed to further investigate this reactivity.

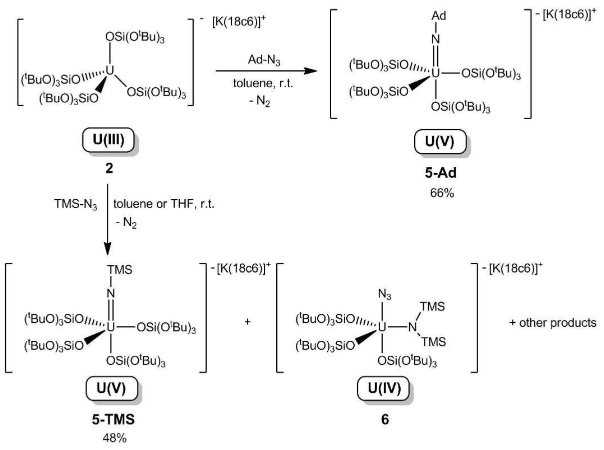
We have also studied the reaction of the “ate” salt complex **2** with organic azides in order to investigate how the increased steric bulk and the difference in charge and redox potential influence the outcome of the reaction with respect to complex **1.**

The reaction of complex **2** with trimethylsilyl and adamantyl azides in toluene proceeds quickly at room temperature with a colour change from orange to dark brown to afford the uranium(V) imido complexes, respectively $[K(18c6)][U(NSiMe_3)(OSi(O^tBu)_3)_4]$ **5-TMS** and $[K(18c6)][U(NAd)(OSi(O^tBu)_3)_4]$ **5-Ad** which were isolated pure in 48 % and 66 % yield respectively (Scheme 3). **5-TMS** and **5-Ad** provide new examples of stable U(V) mono(imido) complexes.

Complex **2** activates organic azides but the resulting U(V) imido complexes do not undergo disproportionation as observed in the case of complex **1** (Scheme 2).

The increased steric bulk and the anionic charge of the **5-TMS** and **5-Ad** complexes compared to a neutral tris-siloxide imido complex probably disfavour a bimolecular mechanism, and thereby prevent the disproportionation.

Scheme 3. Reaction of $[K(18c6)][U(OSi(O^tBu)_3)_4]$ **2** with organic azides.



These anionic heteroleptic complexes are highly soluble in toluene and are stable in solution for several days. The ^{1}H NMR spectra of both compounds are in agreement with a C_3-symmetry for the complexes in solution with respectively one and four proton resonances for the $SiMe_3$ and the adamantyl groups. The UV-visible spectra of both complexes (see supporting information) display a broad unresolved band in the UV-visible region attributed to charge transfer transitions. In addition, a weaker Laporte-forbidden f→f transition is observed around 910 nm. The value of the magnetic moment per uranium, measured at 298 K using the Evans method,[63] for a toluene solution of **5-TMS** (2.12 μ_B) and **5-Ad** (2.34 μ_B) is close to the calculated effective magnetic moment at room temperature for a U(V) 5f^1 complex (2.54 μ_B) and is similar to the value found in other U(V) imido complexes.[26,31]

Structural data for both compounds were obtained by X-ray diffraction analysis. In both complexes, the uranium cation is pentacoordinated in a distorted trigonal bipyramid geometry by three monodentate siloxyde ligands in the equatorial plane and one monodentate siloxyde ligand and a trimethylsilyimido or an adamantylimido ligand, in **5-TMS** and **5-Ad** respectively, in axial position. The short U-N bond distances, respectively of 1.889(11) Å for **5-TMS** and 1.937(7) Å for **5-Ad,** lie in the lower side of the range of U=N distances (1.89 to 2.12 Å) in previously reported U(V) imido complexes.[4,7,17,18,26,29,31,36,38] The U-N-R (R = $SiMe_3$, Ad) angles (163.4(5)° and 172.3(5)°) are close to linearity. The short U=N bond distance and the linear U-N-R angle are structural features characteristic of a strong pi interaction between the two donating lone pairs of the nitrogen atom and the f-orbitals of the uranium cation and are indicative of the multiple bonding between the imido moiety and the uranium centre.[5,6]

The U-O bond distances in **5-TMS** ($U\text{-}O_{avg}$ = 2.16(2) Å) and **5-Ad** ($U\text{-}O_{avg}$ = 2.20(2) Å) are in the same range than the ones in **2** ($U\text{-}O_{avg}$ = 2.228(17) Å). In both complexes, the U-O bond distances for the siloxide group opposite to the amido group (2.130(7) Å for **5-TMS** and 2.180(6) Å for **5-Ad**) are slightly shorter than the U-O distances observed for the three siloxide ligands in the equatorial plane (average $U\text{-}O_{eq}$ bond distance 2.173(9) Å for **5-TMS** and 2.21(2) Å for **5-Ad**). This is expected as the axial position is less sterically constrained than the equatorial ones, allowing a closer approach of the sterically hindered tris(tert-butoxy)siloxide axial ligand. Additionally this could be further amplified by an inverse trans influence interaction which typically occurs in high-valent U(V) and U(VI) systems bearing multiply bonded imido and oxo ligands.[18,95,96]

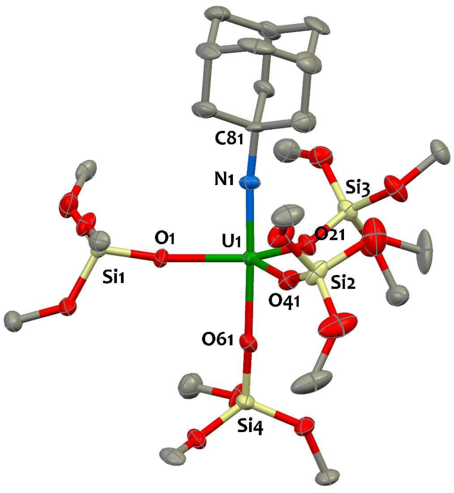


Figure 4. Ellipsoid plot for of the anion in $[K(18c6)][U(NAd)(OSi(O^tBu)_3)_4]$ **5-Ad** crystallized from hexane; probability 50%. [K(18c6)] counter cation, hydrogen atoms, methyl groups and solvent molecules are omitted for clarity. Bond distances (Å): $U1\text{-}O_{avg}$ 2.20(2), U1-N1 1.937(7).

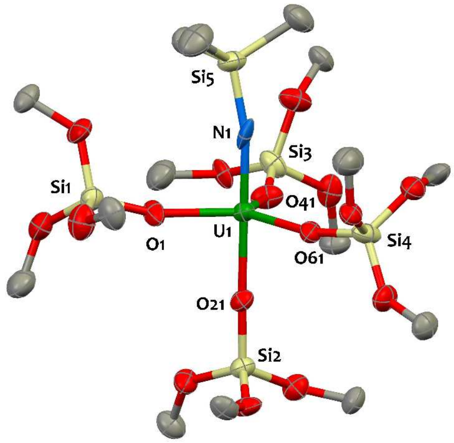


Figure 5. Ellipsoid plot for of the anion in $[K(18c6)][U(NSiMe_3)(OSi(O^tBu)_3)_4]$ **5-TMS** crystallized from toluene; probability 50%. [K(18c6)] counter cation, hydrogen atoms, disordered atoms, methyl groups and solvent molecules are omitted for clarity. Bond distances (Å): $U1\text{-}O_{avg}$ 2.16(2), U1-N1 1.889(11).

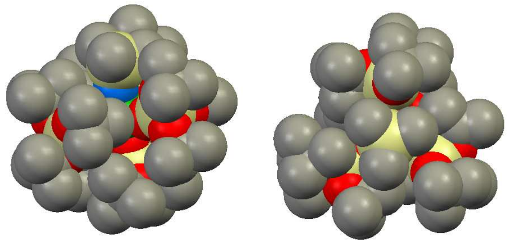


Figure 6. Space-filling representations of the anion in [K(18c6)][U(NSiMe$_3$)(OSi(O^{t}Bu)$_3$)$_4$] **5-TMS** crystallized from toluene. [K(18c6)] counter cation, hydrogen atoms and solvent molecules are omitted for clarity.

A probable reason for the limited number of isolated U(V) imido compounds[7] is that, depending on the supporting ligands and on the azide substituent, the reaction of U(III) complexes with organic azides can follow alternative pathways leading to multiple products.[12,18,26,31,32]

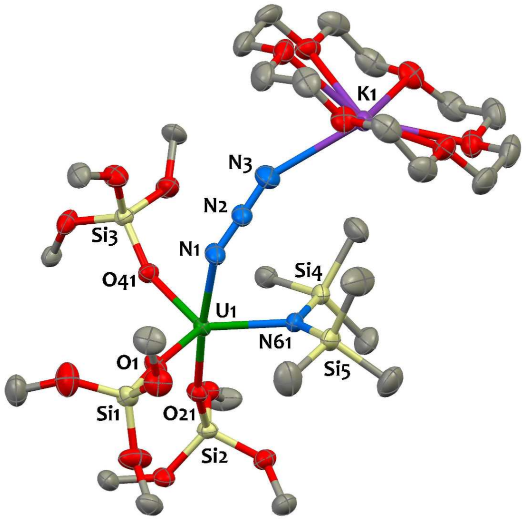


Figure 7. Ellipsoid plot for of the anion in [U(N$_3$-[K(18c6)U(N$_3$)(N(SiMe$_3$)$_2$(OSi(O^{t}Bu)$_3$)$_3$], **6** crystallized from toluene; probability 50%. Hydrogen atoms, methyl groups from OSiO^{t}Bu ligands and solvent molecules are omitted for clarity. Bond distances (Å): U1-O$_{avg}$ 2.146(8), U1-N61 2.330(4), U1-N1 2.409(4), N1-N2 1.184(5), N2-N3 1.157(6).

Notably, the imido complex **5-TMS** is isolated in low yield (48%) and the ^{1}H NMR spectrum of the reaction mixture of **2** with trimethylsilyl azide shows the presence of several by-products. After separation of pure **5-TMS** from the reaction mixture, few crystals of the azido-amido complex [K(18c6)U(N$_3$)(N(SiMe$_3$)$_2$(OSi(O^{t}Bu)$_3$)$_3$] **6** were obtained from the concentrated mother liquor. The solid-state structure (Figure 7) shows that the uranium cation in **6** is pentacoordinated in a distorted trigonal bipyramid fashion by one azido ligand in apical position, three monodentate siloxy ligands and one silylamido ligand in the equatorial plane. The silylamido ligand and the azido ligand are found in a cis-arrangement (N61-U1-N1 angle: 80.93(13)°).

The isolation of an U(IV) azido-amido complex from the reaction of U(III) with an organic azide is unprecedented and is probably the result of the high reactivity of the nucleophilic imido complex **5-TMS** with TMS-N$_3$ which should lead to new interesting imido-group transfer chemistry.[97]

The different reactivity observed with TMS-N$_3$ compared to that with Ad-N$_3$ and leading to the formation of **6** could arise from the higher stability of the silicon based trimethylsily radical compared to the carbon based adamantyl radical in a possible radical transfer pathway.[12]

The redox properties of **5-TMS** and **5-Ad** in THF solution were investigated by electrochemistry. The cyclovoltammetric curves recorded for the U(V) imidos in THF solution (see supporting information) show that it is possible to oxidize them to U(VI) imidos. The U(VI)/U(V) process is reversible, and occurs at $E_{1/2}$ = -0.7 V and -1.0 V vs the Fc$^+$/Fc couple respectively for **5-TMS** and **5-Ad**. The +0.3 V shift in potential indicates that the N-Ad ligand favours the +VI oxidation state due to the higher electron-donor character of the adamantyl group. An irreversible reduction process is observed at E_{pc} = -2.9 V and -3.2 V vs the Fc$^+$/Fc couple respectively for **5-TMS** and **5-Ad**, and is attributed to the reduction to U(IV). The separation between uranium oxidation and reduction processes in both systems is similar (ΔE = 2.2 V).

To our knowledge, electrochemical studies of U(V) imidos is limited to the complexes of the general formula [U(Cp)$_2$(NAr)(X)] (Ar = 2,4,6-^{t}Bu$_3$-C$_6$H$_2$, 2,6-^{i}Pr$_2$-C$_6$H$_3$; X = F, Cl, Br, I) reported by Kiplinger et al.[17] These species exhibit much higher potential (range : 0.11 V to -0.19 V) for the U(VI)/U(V) couple. The lower value for the oxidation of the U(V) imido observed with the siloxide ligands vs the Cp and halide ones is in agreement with the stronger electron-donating character of the siloxide ligands and with the anionic character of the complexes **5-TMS** and **5-Ad**. The observed U(VI)/U(V) redox potential compares well with those reported for homoleptic U(V) ate complexes bearing highly electron-rich ligands [UL$_6$]$^-$ (L = O^{t}Bu, CH$_2$SiMe$_3$, NC$_5$H$_{10}$, N=C^{t}BuPh)[54-56,75,98] ranging from -1.12 V, to -1.52 V vs the Fc$^+$/Fc couple.

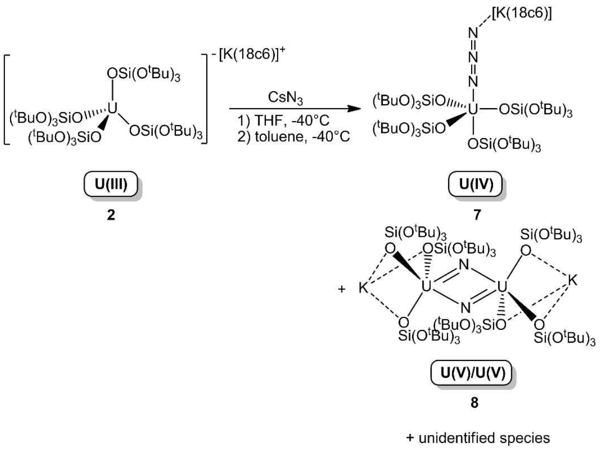
These preliminary studies suggest that these monomeric anionic U(V) imido compounds provide convenient attractive precursors for exploring the chemistry of high valent uranium.

The observed high reactivity of the “ate” complex **2** with organic azides prompted us to investigate the possibility of obtaining nitrido complexes in this novel ligand environment from the reaction of **2** with inorganic azides.

Nitride formation from the reaction of U(III) siloxides with CsN$_3$.

The reaction of [K(18c6)][U(OSi(O^{t}Bu)$_3$)$_4$] **2** with cesium azide in THF at -40°C proceeded in 24 hours to afford a complex mixture of compounds. From this mixture two types of crystals, pale blue/green and brown diamond-shaped plates, formed at -40°C. X-ray diffraction studies show the presence of the U(IV) azido complex $[K(18c6)U(N_3)(OSi(O^tBu)_3)_4]$, **7** (see supporting information) and of the di μ-nitrido diuranium(V) complex $[KU(\mu\text{-}N)_2(OSi(O^tBu)_3)]_2$ **8**.

Scheme 4. Reaction of $[K(18c6)][U(OSi(O^tBu)_3)_4]$ **2** with cesium azide.



The structure of **8** is shown in Figure 8. The molecule has a crystallographically imposed symmetry center in between the two uranium cations. The most interesting feature in the structure of **8** is the presence of two nitrido atoms bridging two uranium centers in a diamond-shaped geometry. Only one example of diamond-shaped U_2N_2 nitride has been previously reported for a diuranium mixed valent complex U(V)/U(IV) isolated from dinitrogen reduction.[40] However, complex **8** is the first example of a U_2N_2 core obtained from the reaction of U(III) with azides.

The overall neutral charge of the complex is consistent with a formal +V oxidation state for each uranium cation, coordinated to six monoanionic siloxide ligands and two trianionic nitrido ligands in a distorted square pyramid geometry. Bond valence sum calculations are in agreement with a U(V) oxidation state (see supporting). The U_2N_2 core in **8** is planar, with a N1···N1A separation of 2.479(8) Å ruling out the presence of a chemical bond between the two nitrogen atoms. The U···U separation is 3.2960(6) Å. The short U-N bond distances (2.101(6) and 2.023(5) Å) indicate a multiple bond character and are similar to the values of U-N bond distances found in other nitride bridged uranium compounds.[40,46] All the metrical parameters including the U-N-U angles (106.1(2)° in **8** in the U_2N_2 core are similar to those found in the U_2N_2 core of the U(IV)/U(V) complex supported by a calix[4]tetrapyrrole ligand[40] although a shorter U···U distance is found in **8** (3.2960(6) Å in **8** and 3.355(6) Å in $[\{K(dme)(calix[4]tetrapyrrole)U\}_2(\mu\text{-}NK)_2]$-$[K(dme)_4]$[40]) as expected given the higher oxidation state of the uraniums in **8**. A similar U_2N_2 diamond-shaped core is also found in three reported example of dinitrogen (μ-η^2:η^2-N_2) bridged diuranium complexes[60,99,100] but with metrical parameters compatible with the presence of a bridging diazenido ligand.

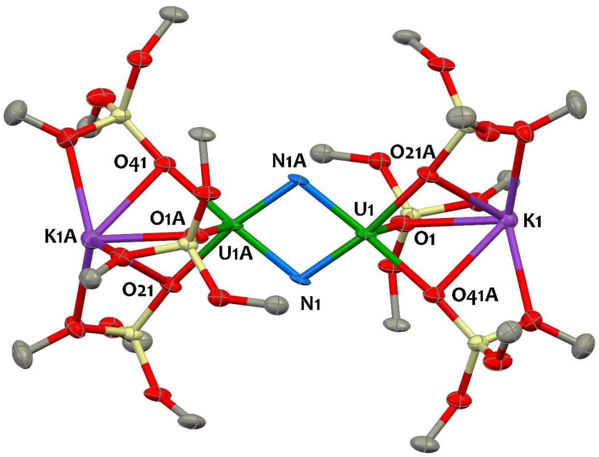


Figure 8. Ellipsoid plot for $[KU(\mu\text{-}N)(OSi(O^tBu)_3)_3]_2$ **8** crystallized from toluene; probability 50%. Hydrogen atoms, methyl groups and solvent molecules are omitted for clarity. Bond distances (Å) and angles (deg): $U1\text{-}O_{avg}$ 2.23(3), U1-N1 2.022(5), U1-N1A 2.101(6), U1-U1A 3.2960(6), N1-N1A 2.479(8), U1-N1-U1A 106.1(2).

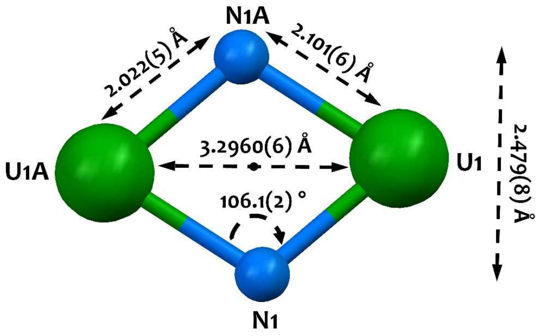
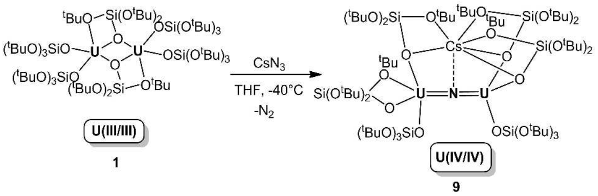


Figure 9. $U_2(\mu\text{-}N)_2$ core view and metric parameters from the crystal structure of **8**.

The formation of this unprecedented U(V)/U(V) complex is likely to occur trough a highly reactive U(V) terminal nitrido intermediate supported by the crowded environment provided by the four siloxides by elimination of N_2 from a U(III) azido intermediate. The highly charged tetrasiloxide terminal nitride will then afford the dinitrido complex trough the loss of one siloxide ligand. An alternative intermediate involving a diuranium complex with a bridging azide ligand is less probable. Attempts to prepare complex **8** pure in significant amounts failed, preventing further characterization of this complex. Attempts to trap a transient terminal nitride were also unsuccessful. This is in line with the high reactivity demonstrated by the elusive uranium nitride intermediate $[UN\{N(SiMe_3)_2\}(C_5Me_5)_2]$ which engages in intramolecular C-H bond activation yielding the U(IV) amido complex $(C_5Me_5)(C_5Me_4CH_2NH)U[N(SiMe_3)_2]$.[48] A recently isolated terminal U(V) nitride also shows an extreme reactivity and its isolation and solution stability are very dependent on the experimental conditions.[49] The high reactivity of the complex **2** with TMSCl, pyridine or $[B(C_6F_6)]_3$ prevents their use for trapping a possible terminal nitrido intermediate.[2,42,49]

Since in the final complex **8** only three coordinated siloxide ligands are bound to the uranium center, we have also investigated the reactivity of the tris-siloxide U(III) complex previously reported.

Scheme 5. Synthesis of the dinuclear uranium(IV)/uranium(IV) nitride Cs{(μ-N)[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$} **9**.



The reaction of [U(OSi(O^{t}Bu)$_3$)$_2$(μ-OSi(O^{t}Bu)$_3$)]$_2$, **1**, with cesium azide was performed in THF at -40°C. The reaction proceeds in 24 hours to afford the complex Cs{(μ-N)[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$} **9** in 47 % yield (Scheme 5). This compound is soluble in THF, toluene and hexane, and is crystallized upon cooling a saturated toluene solution to -40°C. The crystal structure determined by X-ray studies is presented in Figure 10. It consists of a heterotrinuclear (U,U,Cs) complex. Two uranium(IV) cations are held together by a bridging nitrido N^{3-} ligand in a nearly linear fashion (U-N-U angle : 170.2(3)°) and with short U-N nitride bond distances (U1-N1 2.058(5) Å, U2-N1 2.079(5) Å) in agreement with the presence of a multiple U=N bond. These values are close to those found for the two other reported uranium nitrides containing the linear U=N=U fragment (U=N distance ranging from 2.05 to 2.09 Å and U-N-U angle ranging from 160 to 175 °).[43,46]

Uranium nitride complexes remain rare and complex **9** is only the second example of a dinuclear uranium nitride complex featuring a linear U(IV)-N-U(IV) motif. The closely related dinuclear anionic U(IV)-N-U(IV) complex [(μ-N)(U(N[*t*-Bu]Ar)$_3$)$_2$]Na has been previously obtained from the reaction of the tris-amido complex {(THF)U(N[*t*-Bu]Ar)$_3$} (Ar = 3,5-$Me_2C_6H_3$) with sodium azide.[43] The main difference between the structure of the later anionic nitride complex and that of complex **9** is the neutral character of complex **9** and its heterometallic structure. Notably, a cesium cation is held in the structure through the coordination of three siloxy ligands which act as bridging bidentate μ-η^2 ligands. This cesium cation lies at the exact apical position of the nitride ligand (U1-N1-Cs1 angle: 86.6(1)°), pointing at the 2p$_z$ filled orbital of the N^{3-} ligand, with a Cs-N distance of 3.393(4) Å. The coordination of the alkaline cation by the siloxide ligands results in a disymmetric structure. While U1 is coordinated by one terminal siloxide and two siloxides bridging the U and Cs centers, U2 is coordinated by a terminal siloxide ligand, a siloxide ligand bridging the U and Cs centers and a third one acting as a bidentate O$^-$/O^{t}Bu ligand. Thus U1 is tetracoordinated in a pseudo-tetrahedral geometry while U2 is pentacoordinated in a distorted square pyramidal environment. The mean value for the U-O$^-$ bond distances (U-O$^-_{avg}$ = 2.19(3) Å) are in the range of those found in other U(IV)-siloxide complexes. This, together with bond valence sum calculations and variable-temperature magnetic moment measurements (see supporting information) confirm the U(IV)-N^{3-}-U(IV) formulation for the complex. This compound slowly decomposes in THF solution at r.t. over 1 week.

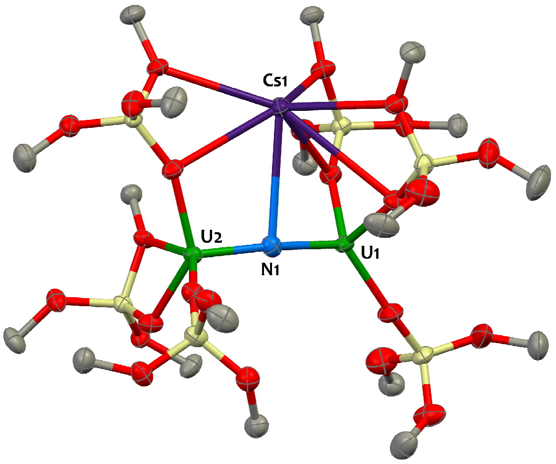


Figure 10. Ellipsoid plot for Cs{(μ-N)[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$} **9**, crystallized from a saturated hexane solution ; probability 50%, Hydrogen atoms and methyl groups are omitted for clarity. Bond distances (Å) and angles (deg): U1-N1 2.058(5), U2-N1 2.079(5), U1-O$^-_{avg}$ 2.183(14), U2-OtBu 2.713(4), U2-O$^-_{avg}$ 2.19(3).

The formation of this linear nitride could involve a mononuclear nitride or an azido bridged dinuclear complex as intermediates. The later intermediate is supported by the outcome of the reaction of the U(III) complex **1** with the isoelectronic CS_2 molecule which affords the dinuclear complex U(IV)-$(CS_2)^{2-}$-U(IV) complex.[53] The different outcome of the reaction with CsN_3 for the complexes **1** and **2** clearly underlines the importance of the coordination environment for the control of the reactivity and for determining the structure of the final product.

The isolation of the bis-nitride U(V) dimer suggests that it might be possible to find conditions leading to mononuclear nitrides using siloxides as supporting ligands. Moreover the synthesis of the heterotrimetallic complex **9** provides a nice precursor for heteropolymetallic nitrido systems. Future studies will be directed to investigate the reaction mechanism and the bonding of these systems and to identify the conditions for the isolation of mononuclear and polynuclear nitride species.

Concluding Remarks.

A new stable homoleptic “ate” U(III) tetra-siloxide complex has been prepared by reduction of its U(IV) analogue. The reaction of this complex and of the neutral U(III) tris-siloxide analogue $[U(OSi(O^tBu)_3)_2(\mu\text{-}OSi(O^tBu)_3)]_2$ with organic and inorganic azides leads to the formation of different products. Notably, while the reaction of the U(III) tetrakis-siloxide with organic azides affords new examples of stable U(V) imido complexes, the same reaction with the tris-siloxide U(III) complex leads to the formation of a dimeric bis(imido) complex of U(VI) via a highly reactive U(V) intermediate. This complex presents an unprecedented cation-cation interaction of the two *trans*-imido groups. The different outcome of the reaction of the U(III) tris- and tetrakis- siloxide complexes with organic azides shows the important role of the steric environment in stabilizing U(V) imido species. A very different outcome is also observed in the reaction of the U(III) tris and tetrakis- siloxide complexes with CsN_3. A clean reaction occurs with the U(III) tris-siloxide complex leading to a rare heterometallic nitrido bridged diuranium(IV) complex. In contrast the reaction of the U(III) tetra-siloxide leads to a complex mixture of products from which we isolated a dinitrido bridged di-uranium(V) complex which is likely to form trough a terminal nitride intermediate.

These results show that the siloxide ligands provide a versatile tool to modulate the steric and electronic environment of low-valent uranium and to prepare new mononuclear and polynuclear species containing U=N multiple bonds. Future studies will be directed to investigated the nature of bonding and the reactivity of these systems.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise noted, all manipulations were carried out at ambient temperature under an inert argon atmosphere using Schlenk techniques and an MBraun glovebox equipped with a purifier unit. The water and oxygen levels were always kept at less than 1 ppm. Glassware was dried overnight at 130°C before use.

^{1}H and ^{13}C NMR spectroscopy experiments were carried out using NMR tubes adapted with J. Young valves. ^{1}H NMR spectra were recorded on Bruker 200 MHz and Varian Mercury 400 MHz spectrometers. ^{13}C NMR spectra were recorded on Bruker 50 MHz spectrometer. NMR chemical shifts are reported in ppm with solvent as internal reference.

Elemental analyses were performed under argon by Analytische Laboratorien GMBH at Lindlar, Germany.

UV-visible spectroscopy measurements were carried out with a Varian Cary 50 Probe spectrophotometer in quartz cells (optical path lengths: 1 mm) adapted with Young valves.

Mass spectra were acquired on a LXQ-linear ion trap (Thermo Scientific, San Jose, CA, USA), equipped with an electrospray source in a THF solution which was prepared and filtered on microporous filters in the glove-box and maintained under argon until injection in the spectrometer. Electrospray full scan spectra, in the range of m/z 50 – 3000 amu, were obtained by infusion through fused silica tubing at 2 – 10 μL min^{-1}. The LXQ calibration (m/z 50-2000) was achieved according to the standard calibration procedure from the manufacturer (mixture of caffeine/MRFA and Ultramark 1621). The LXQ calibration (m/z 2000-4000) was performed with ES tuning mix (Agilent). The temperature of the heated capillary of the LXQ was set to the range of 180 – 220 °C, the ion spray voltage was in the range of 1 – 3 kV with an injection time of 5 - 100 ms. The experimental isotopic profile was compared in each case to the theoretical one.

Starting materials. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. The solvents were purchased from Aldrich or Eurisotop (deuterated solvents) in their anhydrous form, conditioned under argon and vacuum distilled from K/benzophenone (toluene, hexane, pyridine and THF). All reagents were dried under high-vacuum for 7 days prior to use. Syntheses were performed using glass-covered stirring bars. Depleted uranium turnings were purchased from the "Société Industrielle du Combustible Nucléaire" of Annecy (France). $(^tBuO)_3SiOH$ was purchased from ABCR chemicals and sublimed prior to use. $[UI_4(OEt_2)_2]$,[101] $[U(OSi(O^tBu)_3)_2(\mu\text{-}OSi(O^tBu)_3)]_2$,[53] were prepared according to the published procedures. $(^tBuO)_3SiOK$ was prepared upon reaction of $(^tBuO)_3SiOH$ with one equivalent of KH in THF.

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.

Caution: Because of their potentially explosive character, all reactions involving azido compounds should be carried out with care, in small quantities and using appropriate protection.

Synthesis of $[U(OSi(O^tBu)_3)_4]$ 3.

A solution of $[UI_4(OEt_2)_2]$ (227.5 mg, 0.25 mmol, 1 equiv.) in THF (2 mL) was added to a solution of $KOSi(O^tBu)_3$ (308.0 mg, 1.02 mmol, 4 equiv.) in THF (2 mL). The reaction mixture was stirred at room temperature for 4 hours. The resulting light blue suspension was filtered to remove KI and the green filtrate was evaporated to dryness to give a microcrystalline pale green solid. This solid was dissolved twice in 3 mL of hexane, triturated, and evaporated to dryness. The resulting solid was dissolved in 1 mL hexane and cooled to -40°C. After 12 hours, blue crystals were recovered and dried *in vacuo* for 4 hours giving $[U(OSi(O^tBu)_3)_4]$, **3** as a light lilac powder (289.0 mg, 0.22 mmol, 88 % yield). Single crystals suitable for X-ray diffraction analysis were obtained upon cooling a concentrated toluene solution of $[U(OSi(O^tBu)_3)_4]$ to -40°C. Recrystallization of this complex in pyridine afforded green single crystals of $[U(OSi(O^tBu)_3)_4(py)_2]$, **3-Py**.

^1H NMR (200 MHz, hexane-d_{14}, 298 K): δ = 0.98 (s, 108H, CH_3).

^1H NMR (200 MHz, toluene-d_8, 298 K): δ = 1.06 (s, 108H, CH_3).

^1H NMR (200 MHz, THF-d_8, 298 K): δ = 1.9 (br s, 108H, CH_3).

^1H NMR (200 MHz, py-d_5, 298 K): δ = 1.90 (s, 54H, CH_3) ; 1.90 (s, 54H, CH_3).

^1H NMR (200 MHz, py-d_5, 263 K): δ = 9.7 (br s, 54H, CH_3) ; -2.7 (br s, 54H, CH_3).

^1H NMR (200 MHz, py-d_5, 353 K): δ = 3.1 (br s, 108H, CH_3).

^{13}C NMR (50 MHz, hexane-d_{14}, 298 K): δ = 28.99 (s, CH_3), 68.33 (s, $OC(CH_3)_3$).

^{13}C NMR (50 MHz, toluene-d_8, 298 K): δ = 31.29 (s, CH_3), 67.74 (s, $OC(CH_3)_3$).

Anal. Calcd for $[U(OSi(O^tBu)_3)_4]$: $C_{48}H_{108}O_{16}Si_4U$: C 44.6; H 8.4; N 0.0; Found: C 44.3; H 8.3; N <0.2.

ES-MS: m/z= 1313.5 $[M+Na]^+$; 1329.5 $[M+K]^+$.

Synthesis of $[K(18c6)][U(OSi(O^tBu)_3)_4]$ 2.

KC_8 (25.3 mg; 0.187 mmol, 1.5 eq) was added to a cold (- 40°C) solution of $[U(OSi(O^tBu)_3)_4]$ (161.0 mg, 0.125 mmol, 1 equiv.) and 18-crown-6 (32.9 mg, 0.125 mmol, 1 equiv.) in THF (2 mL). The resulting dark orange suspension was stirred for 1 hour at -40° C. The suspension was centrifuged, the supernatant was collected and the solvent was removed *in vacuo*. The resulting solid was washed with 1 mL hexane and 6 x 1 mL toluene and dried *in vacuo* to give $[K(18c6)][U(OSi(O^tBu)_3)_4]$, **2** as an orange solid in 69% yield (138 mg, 0.087 mmol). Recrystallisation of this orange solid in toluene produced X-ray quality crystals of **2**.

^1H NMR (400 MHz, toluene-d_8, 298 K): δ 3.40 (s, 24H, 18c6), -0.15 (brs, 108H, $OC(CH_3)_3$).

^1H NMR (400 MHz, THF-d_8, 298 K): δ 3.64 (s, 24H, 18c6), 1.18 (brs, 108H, $OC(CH_3)_3$).

Anal. Calcd for $[K(18c6)][U(OSi(O^tBu)_3)_4]$: $C_{60}H_{132}O_{22}Si_4KU$: C 45.2; H 8.3; N 0.00; Found: C 45.0; H 8.3; N <0.1.

ES-MS: m/z= 1290.4 $[U(OSi(O^tBu)_3)_4]^-$.

Reaction of 1 with AdN_3, isolation of 4.

A vial was charged with $[U(OSi(O^tBu)_3)_2(\mu\text{-}OSi(O^tBu)_3)]_2$ (123.5 mg, 0.060 mmol, 1 equiv.) and the compound was dissolved in 5 mL toluene. To this brown solution was added a 5 mL toluene solution of AdN_3 (21.3 mg, 0.120 mmol, 2 equiv.) and the reaction mixture was vigorously stirred for 4 hours at room temperature. A strong N_2 bubbling was observed. The resulting dark brown solution was taken to dryness and the residue was extracted with 0.5 mL hexane, filtered and the filtrate was cooled to -40°C. Crystals were grown from this solution in 2 days. The crystals were collected and dried *in vacuo* to give **4** as a brown crystalline solid (22.2 mg, 0.010 mmol, yield of 35 % calculated taking account of the reaction stoechiometry). The presence of small amounts (~ 6%) of the second reaction product (**3**) in this solid prevented the obtention of a satisfactory elemental analysis. Brown crystals of **4** suitable for XRD were grown similarly.

^1H NMR (200 MHz, toluene-d_8, 298 K): δ 2.29 (brs, 3H, $H_{adamantyl}$), 1.91 (brs, 9H, $H_{adamantyl}$), 1.83 (brs, 108H, $OC(CH_3)_3$), 1.54 (brs, 3H, $H_{adamantyl}$), 1.23 (brs, 6H, $H_{adamantyl}$), 1.12 (brs, 18H, $H_{adamantyl}$), 0.67 (brs, 18H, $H_{adamantyl}$).

ES-MS: m/z= 2141.7 $[M+OH]^-$.

Synthesis of $[K(18c6)][U(NSiMe_3)(OSi(O^tBu)_3)_4]$ 5-TMS.

100 μL of a 0.94 M THF solution of trimethylsilyl azide (0.094 mmol, 1 equiv.) were added to a cold (-40°C) 2 mL THF solution of $[K(18c6)][U(OSi(O^tBu)_3)_4]$ (150.0 mg; 0.094mmol, 1 equiv.). An immediate color change from dark orange to brown was observed together with N_2 evolution. The resulting solution was stirred for 30 minutes before the solvent was removed *in vacuo*. The resulting brown oil was extracted with 2 mL toluene, filtered and the filtrate was stored 48 hours at -40° C to afford $[K(18c6)][U(NSiMe_3)(OSi(O^tBu)_3)_4]$, **5-TMS** as a brown crystalline solid in 48% yield (75.5 mg, 0.045 mmol). Similar procedure was followed to produce brown triangular shaped single crystals suitable for X-ray diffraction.

^1H NMR (400 MHz, toluene-d_8, 298 K): δ 10.98 (s, 9H, $SiMe_3$), 3.51 (s, 24H, 18c6), -0.25 (brs, 108H, $OC(CH_3)_3$).

Anal. Calcd for $[K(18c6)][U(NSiMe_3)(OSi(O^tBu)_3)_4]$: $C_{63}H_{141}O_{22}Si_4NKU$: C 45.0; H 8.5; N 0.8; Found: 44.5; H 8.2; N 0.9.

ES-MS: Due to the extreme reactivity of this compound towards dioxygen, it was not possible to acquire a mass spectrum for this compound. Indeed, even when taking all the usual precautions, the only compound observed in the spectra was the uranyl(VI) tris-siloxy $[UO_2(OSi(O^tBu)_3)_3]^-$ complex (m/z= 1059.5).

The remaining pale brown filtrate was cooled down to -40°C. This afforded pale blue single crystals of $[K(18c6)][U(N_3)(N(SiMe_3)_2(OSi(O^tBu)_3)_3]$, **6** suitable for X-ray diffraction.

The reaction of **2** with TMS-N_3 was also performed in toluene but the outcome of the reaction was similar to the one observed in THF.

Synthesis of [K(18c6)][U(NAd)(OSi(O^tBu)$_3$)$_4$] 5-Ad.

A toluene solution (2 mL) of adamantylazide (11.1 mg, 0.063 mmol, 1 equiv.) was added to a 4 mL toluene suspension of [K(18c6)][U(OSi(O^tBu)$_3$)$_4$] (100.0 mg; 0.063 mmol, 1 equiv.). Immediately, the orange suspension turned dark brown, all the solid solubilized and a strong N_2 bubbling was observed. The resulting solution was stirred for 2 hours before filtration. The filtrate was taken to dryness and extracted with 2 mL hexane. The brown suspension was filtered and the brown filtrate was cooled to -40°C for 24 hours to afford [K(18c6)][U(NAd)(OSi(O^tBu)$_3$)$_4$], **5-Ad** as a brown crystalline solid (72.1 mg, 0.041 mmol, 66 %). Single crystals suitable for X-ray diffraction were grown by slow evaporation of a hexane solution of the complex. This complex is highly soluble in toluene.

^{1}H NMR (400 MHz, toluene-d_8, 298 K): δ 21.83 (brs, 6H, $H_{adamantyl}$), 14.93 (s, 3H, $H_{adamantyl}$), 10.61 (d, 3H, $H_{adamantyl}$), 8.45 (d, 3H, $H_{adamantyl}$), 3.48 (s, 24H, 18c6), -0.73 (brs, 108H, OC(CH_3)$_3$).

Anal. Calcd for [K(18c6)][U(NAd)(OSi(O^tBu)$_3$)$_4$]: $C_{70}H_{147}O_{22}N_1Si_4K_1U_1$: C 48.2; H 8.5; N 0.8; Found C 48.0; H 8.3; N 0.9.

ES-MS: Due to the extreme reactivity of this compound towards dioxygen, it was not possible to acquire a mass spectrum for this compound. Indeed, even when taking all the usual precautions, the only compound observed in the spectra was the uranyl(VI) tris-siloxy [UO_2(OSi(O^tBu)$_3$)$_3$]$^-$ complex (m/z= 1059.5).

Reaction of [K(18-c-6)][U(OSi(O^tBu)$_3$)$_4$] with CsN_3.

A vial was charged with [K(18c6)][U(OSi(O^tBu)$_3$)$_4$] (50.0 mg, 0.031 mmol, 1 equiv.) and the compound was dissolved in 2 mL THF at -40°C. This solution was added onto CsN_3 (5.5 mg, 0.031 mmol, 1 equiv.) and the reaction mixture was vigorously stirred with a glass-coated stir bar for 24 hours at -40°C. The resulting brownish red solution was taken to dryness and the residue was extracted with 2 mL toluene, filtered and the filtrate was cooled at -40°C. Two types of crystals suitable for XRD were grown from this solution : pale blue rectangular parallelepipeds of [K(18c6)][U(N_3)(OSi(O^tBu)$_3$)$_4$] **7** and brown rhombus-faced parallelepipeds of [KU(μ-N)$_2$(OSi(O^tBu)$_3$)$_3$]$_2$, **8**.

^{1}H NMR (400 MHz, toluene-d_8, 298 K) of crystals of **8** shows only one peak at -1.76 ppm.

Synthesis of Cs{(μ-N)[U(OSi(O^tBu)$_3$)$_3$]$_2$} 9.

A vial was charged with [U(OSi(O^tBu)$_3$)$_2$(μ-OSi(O^tBu)$_3$)]$_2$ (124.9 mg, 0.061 mmol, 1 equiv.) and the compound was dissolved in 2 mL THF and cooled to -40°C. This cold solution was added onto cold CsN_3 (10.7 mg, 0.061 mmol, 1 equiv.) and the reaction mixture was vigorously stirred with a glass-coated stir bar for 24 hours at -40°C. The resulting brownish red solution was taken to dryness and the residue was extracted with 2 mL hexane, filtered and the filtrate was cooled to -40°C. Crystals were grown from this solution in 10 days. The crystals were collected and dried *in vacuo* to give **9** as a pure crystalline solid (63.6 mg, 0.029 mmol, 47 %). Brown-red crystals of **9** suitable for XRD were grown by slow evaporation of a hexane solution of **9**.

ES-MS: m/z= 1957.8 ([9 - Si(O^tBu)$_3$ + 2H]$^+$), 1027.6 ([U(OSi(O^tBu)$_3$)$_3$]$^+$).

^{1}H NMR (200 MHz, toluene-d_8, 298 K): δ = -1.16 (s, 108H, CH_3), -2.49 (s, 54H, CH_3).

Anal. Calcd for 2: $C_{72}H_{162}CsNO_{24}Si_6U_2$: C 39.2; H 7.4; N 0.6; Found C 38.9; H 7.5; N, 0.8.

Electrochemical Methods. Cyclic voltammetry data were carried out at room temperature in an argon-filled glovebox described above. Data were collected using a Biologic SP-300 potentiostat connected to a personal computer. All samples were 2 mM in complex with 0.1 M [Bu_4N][PF_6] supporting electrolyte in THF solution. The experiments were carried out with a vitrous carbon working electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode. Potential calibration was performed at the end of each data collection cycle using the ferrocene/ferrocenium [(C_5H_5)$_2$Fe]$^{+/0}$ couple as an internal standard.

X-ray Crystallography. Diffraction data were taken using an Oxford-Diffraction XCallibur S kappa geometry diffractometer (Mo-Kα radiation, graphite monochromator, λ = 0.71073 Å). To prevent evaporation of co-crystallised solvent molecules the crystals were coated with light hydrocarbon oil and the data were collected at 150 K. The cell parameters were obtained with intensities detected on three batches of 5 frames. The crystal-detector distance was 4.5 cm. The number of settings and frames has been established taking in consideration the Laue symmetry of the cell by CrysAlisPro Oxford-diffraction software.[102] 289 for **3**, 662 for **3-py**, 141 for **2**, 252 for **4**, 384 for **5-Ad**, 221 for **5-TMS**, 509 for **6**, 492 for **7**, 444 for **8** and 1019 for **9** narrow data were collected for 1° increments in ω with a 2 s exposure time for **3**, 20 s for **3-py**, 300 s for **2**, 150 s for **4**, 98 s for **5-Ad**, 90 s for **5-TMS**, 15 s for **6**, 4 s for **7**, 110 s for **8** and 10 s for **9**. Unique intensities detected on all frames using the Oxford-diffraction Red program were used to refine the values of the cell parameters. The substantial redundancy in data allows empirical absorption corrections to be applied using multiple measurements of equivalent reflections with the ABSPACK Oxford-diffraction program.[102] Space groups were determined from systematic absences, and they were confirmed by the successful solution of the structure. The structures were solved by direct methods using the SHELXTL 6.14 package.[103] All non-hydrogen atoms were found by difference Fourier syntheses and refined on F^2. Hydrogen atoms were fixed in ideal position except for **3-py** where hydrogen atoms from the pyridine and the Si1 silanol moieties were found by Fourier synthesis and refined. Full crystallographic details are given in Tables 1 and 2.

ASSOCIATED CONTENT

Supporting Information. ^{1}H NMR, ESI/MS and UV-vis spectra, magnetic and electrochemistry data, crystallographic and structural details, X-ray crystallographic data and files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

* marinella.mazzanti@cea.fr

Author Contributions

All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

We thank Colette Lebrun for her help with mass spectroscopy characterizations. We acknowledge support from the Commissariat à l'Energie Atomique, Direction de l'Energie Nucléaire, RBPCH program and from the "Agence Nationale de la Recherche", (ANR-10-BLAN-0729).

REFERENCES

(1) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988.

(2) Eikey, R. A.; Abu-Omar, M. M. *Coord. Chem. Rev.* **2003**, *243*, 83-124.

(3) Cramer, R. E.; Panchanatheswaran, K.; Gilje, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 1853-1854.

(4) Brennan, J. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 514-516.

(5) Hayton, T. W. *Dalton Trans* **2010**, *39*, 1145-1158.

(6) Hayton, T. W. *Chem. Commun.* **2013**, *49*, 2956-2973.

(7) Graves, C. R.; Kiplinger, J. L. *Chem. Commun.* **2009**, 3831-3853.

(8) Andrea, T.; Eisen, M. S. *Chem. Soc. Rev.* **2008**, *37*, 550-567.

(9) Ren, W. S.; Zi, G. F.; Walter, M. D. *Organometallics* **2012**, *31*, 672-679.

(10) Fox, A. R.; Bart, S. C.; Meyer, K.; Cummins, C. C. *Nature* **2008**, *455*, 341-349.

(11) Diaconescu, P. L. *Nat. Chem.* **2010**, *2*, 705-706.

(12) Castro-Rodriguez, I.; Meyer, K. *Chem. Commun.* **2006**, 1353-1368.

(13) Belkhiri, L.; Lissillour, R.; Boucekkine, A. *Theochem-J. Mol. Struct.* **2005**, *757*, 155-164.

(14) Neidig, M. L.; Clark, D. L.; Martin, R. L. *Coord. Chem. Rev.* **2013**, *257*, 394-406.

(15) Spencer, L. P.; Yang, P.; Minasian, S. G.; Jilek, R. E.; Batista, E. R.; Boland, K. S.; Boncella, J. M.; Conradson, S. D.; Clark, D. L.; Hayton, T. W.; Kozimor, S. A.; Martin, R. L.; MacInnes, M. M.; Olson, A. C.; Scott, B. L.; Shuh, D. K.; Wilkerson, M. P. *J. Am. Chem. Soc.* **2013**, *135*, 2279-2290.

(16) Spencer, L. P.; Yang, P.; Scott, B. L.; Batista, E. R.; Boncella, J. M. *Inorg. Chem.* **2009**, *48*, 2693-2700.

(17) Graves, C. R.; Yang, P.; Kozimor, S. A.; Vaughn, A. E.; Clark, D. L.; Conradson, S. D.; Schelter, E. J.; Scott, B. L.; Thompson, J. D.; Hay, P. J.; Morris, D. E.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 5272-5285.

(18) Lam, O. P.; Franke, S. M.; Nakai, H.; Heinemann, F. W.; Hieringer, W.; Meyer, K. *Inorg. Chem.* **2012**, *51*, 6190-6199.

(19) Wietzke, R.; Mazzanti, M.; Latour, J.-M.; Pecaut, J.; Cordier, P.-Y.; Madic, C. *Inorg. Chem.* **1998**, *37*, 6690-6697.

(20) Mazzanti, M.; Wietzke, R.; Pécaut, J.; Latour, J.-M.; Maldivi, P.; Remy, M. *Inorg. Chem.* **2002**, *41*, 2389-2399.

(21) Denecke, M. A.; Panak, P. J.; Burdet, F.; Weigl, M.; Geist, A.; Klenze, R.; Mazzanti, M.; Gompper, K. *C. R. Chim.* **2007**, *10*, 872-882.

(22) Hudson, M. J.; Harwood, L. M.; Laventine, D. M.; Lewis, F. W. *Inorg. Chem.* **2013**, *52*, 3414-3428.

(23) Panak, P. J.; Geist, A. *Chem. Rev.* **2013**, *113*, 1199-1236.

(24) Streit, M.; Ingold, F. *J. Eur. Ceram. Soc.* **2005**, *25*, 2687-2692.

(25) Silva, G. W. C.; Yeamans, C. B.; Ma, L. Z.; Cerefice, G. S.; Czerwinski, K. R.; Sattelberger, A. P. *Chem. Mat.* **2008**, *20*, 3076-3084.

(26) Bart, S. C.; Anthon, C.; Heinemann, F. W.; Bill, E.; Edelstein, N. M.; Meyer, K. *J. Am. Chem. Soc.* **2008**, *130*, 12536-12546.

(27) Arney, D. S. J.; Burns, C. J.; Smith, D. C. *J. Am. Chem. Soc.* **1992**, *114*, 10068-10069.

(28) Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 9448-9460.

(29) Zalkin, A.; Brennan, J. G.; Andersen, R. A. *Acta Crystallogr. Sect. C-Cryst. Struct. Commun.* **1988**, *44*, 1553-1554.

(30) Roussel, P.; Boaretto, R.; Kingsley, A. J.; Alcock, N. W.; Scott, P. *J. Chem. Soc.-Dalton Trans.* **2002**, 1423-1428.

(31) Castro-Rodriguez, I.; Olsen, K.; Gantzel, P.; Meyer, K. *J. Am. Chem. Soc.* **2003**, *125*, 4565-4571.

(32) Lam, O. P.; Heinemann, F. W.; Meyer, K. *C. R. Chim.* **2010**, *13*, 803-811.

(33) King, D. M.; Tuna, F.; McInnes, E. J. L.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Nat. Chem.* **2013**, *15*, 482-488.

(34) Evans, W. J.; Kozimor, S. A. *Coord. Chem. Rev.* **2006**, *250*, 911-935.

(35) Warner, B. P.; Scott, B. L.; Burns, C. J. *Angew. Chem. Int. Ed.* **1998**, *37*, 959-960.

(36) Jilek, R. E.; Spencer, L. P.; Lewis, R. A.; Scott, B. L.; Hayton, T. W.; Boncella, J. M. *J. Am. Chem. Soc.* **2012**, *134*, 9876-9878.

(37) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Palmer, P. D.; Batista, E. R.; Hay, P. J. *Science* **2005**, *310*, 1941-1943.

(38) Spencer, L. P.; Schelter, E. J.; Yang, P.; Gdula, R. L.; Scott, B. L.; Thompson, J. D.;

Kiplinger, J. L.; Batista, E. R.; Boncella, J. M. *Angew. Chem. Int. Ed.* **2009**, *48*, 3795-3798.

(39) Spencer, L. P.; Yang, P.; Scott, B. L.; Batista, E. R.; Boncella, J. M. *Inorg. Chem.* **2009**, *48*, 11615-11623.

(40) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 3433-3436.

(41) Todorova, T. K.; Gagliardi, L.; Walensky, J. R.; Miller, K. A.; Evans, W. J. *J. Am. Chem. Soc.* **2010**, *132*, 12397-12403.

(42) Fox, A. R.; Cummins, C. C. *J. Am. Chem. Soc.* **2009**, *131*, 5716-5717.

(43) Fox, A. R.; Arnold, P. L.; Cummins, C. C. *J. Am. Chem. Soc.* **2010**, *132*, 3250-3251.

(44) Fortier, S.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2010**, *132*, 6888-6889.

(45) Nocton, G.; Pecaut, J.; Mazzanti, M. *Angew. Chem. Int. Ed.* **2008**, *47*, 3040-3042.

(46) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *Science* **2005**, *309*, 1835-1838.

(47) Evans, W. J.; Miller, K. A.; Ziller, J. W.; Greaves, J. *Inorg. Chem.* **2007**, *46*, 8008-8018.

(48) Thomson, R. K.; Cantat, T.; Scott, B. L.; Morris, D. E.; Batista, E. R.; Kiplinger, J. L. *Nat. Chem.* **2010**, *2*, 723-729.

(49) King, D. M.; Tuna, F.; McInnes, E. J. L.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Science* **2012**, *337*, 717-720.

(50) Spencer, L. P.; Gdula, R. L.; Hayton, T. W.; Scott, B. L.; Boncella, J. M. *Chem. Commun.* **2008**, 4986-4988.

(51) Wolczanski, P. T. *Polyhedron* **1995**, *14*, 3335-3362.

(52) Marciniec, B.; Maciejewski, H. *Coord. Chem. Rev.* **2001**, *223*, 301-335.

(53) Mougel, V.; Camp, C.; Pecaut, J.; Coperet, C.; Maron, L.; Kefalidis, C. E.; Mazzanti, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 12280-12284.

(54) Fortier, S.; Wu, G.; Hayton, T. W. *Inorg. Chem.* **2008**, *47*, 4752-4761.

(55) Seaman, L. A.; Wu, G.; Edelstein, N.; Lukens, W. W.; Magnani, N.; Hayton, T. W. *J. Am. Chem. Soc.* **2012**, *134*, 4931-4940.

(56) Fortier, S.; Walensky, J. R.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2011**, *133*, 11732-11743.

(57) Jantunen, K. C.; Haftbaradaran, F.; Katz, M. J.; Batchelor, R. J.; Schatte, G.; Leznoff, D. B. *Dalton Trans.* **2005**, 3083-3091.

(58) Lewis, A. J.; Williams, U. J.; Carroll, P. J.; Schelter, E. J. *Inorg. Chem.* **2013**, *52*, 7326-7328.

(59) Vandersluys, W. G.; Sattelberger, A. P. *Chem. Rev.* **1990**, *90*, 1027-1040.

(60) Mansell, S. M.; Kaltsoyannis, N.; Arnold, P. L. *J. Am. Chem. Soc.* **2011**, *133*, 9036-9051.

(61) Clark, D. L.; Sattelberger, A. P.; Vandersluys, W. G.; Watkin, J. G. *J. Alloy. Compd.* **1992**, *180*, 303-315.

(62) Mora, E.; Maria, L.; Biswas, B.; Camp, C.; Santos, I.; Pécaut, J.; Cruz, A.; Carretas, J. M.; Marçalo, J.; Mazzanti, M. *Organometallics* **2013**, *32*, 1409–1422.

(63) Evans, D. F. *J. Am. Chem. Soc.* **1959**, 2003-2005.

(64) Rinehart, J. D.; Harris, T. D.; Kozimor, S. A.; Bartlett, B. M.; Long, J. R. *Inorg. Chem.* **2009**, *48*, 3382-3395.

(65) Moro, F.; Mills, D. P.; Liddle, S. T.; Slangeren, J. *Angew. Chem. Int. Ed. Engl.* **2013**, *52*, 1-5.

(66) Antunes, M. A.; Pereira, L. C. J.; Santos, I. C.; Mazzanti, M.; Marcalo, J.; Almeida, M. *Inorg. Chem.* **2011**, *50*, 9915-9917.

(67) Morss, L. R.; Edelstein, N. M.; Fuger, J. *The Chemistry of the Actinide and Transactinide Elements*; Springer: Dordrecht, 2006.

(68) Drozdzynski, J. *Coord. Chem. Rev.* **2005**, *249*, 2351-2373.

(69) Lam, O. P.; Feng, P. L.; Heinemann, F. W.; O'Connor, J. M.; Meyer, K. *J. Am. Chem. Soc.* **2008**, *130*, 2806-2816.

(70) Bart, S. C.; Heinemann, F. W.; Anthon, C.; Hauser, C.; Meyer, K. *Inorg. Chem.* **2009**, *48*, 9419-9426.

(71) Evans, W. J.; Lee, D. S.; Rego, D. B.; Perotti, J. M.; Kozimor, S. A.; Moore, E. K.; Ziller, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 14574-14582.

(72) Krot, N. N.; Grigoriev, M. S. *Russ. Chem. Rev.* **2004**, *73*, 89-100.

(73) Evans, W. J.; Traina, C. A.; Ziller, J. W. *J. Am. Chem. Soc.* **2009**, *131*, 17473-17481.

(74) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Batista, E. R.; Hay, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 10549-10559.

(75) Seaman, L. A.; Fortier, S.; Wu, G. A.; Hayton, T. W. *Inorg. Chem.* **2011**, *50*, 636-646.

(76) Swartz, D. L.; Spencer, L. P.; Scott, B. L.; Odom, A. L.; Boncella, J. M. *Dalton Trans.* **2010**, *39*, 6841-6846.

(77) Nocton, G.; Horeglad, P.; Pecaut, J.; Mazzanti, M. *J. Am. Chem. Soc.* **2008**, *130*, 16633-16645.

(78) Mougel, V.; Horeglad, P.; Nocton, G.; Pecaut, J.; Mazzanti, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 8477-8480.

(79) Arnold, P. L.; Hollis, E.; White, F. J.; Magnani, N.; Caciuffo, R.; Love, J. B. *Angew. Chem. Int. Ed.* **2011**, *50*, 887-890.

(80) Chatelain, L.; Mougel, V.; Pecaut, J.; Mazzanti, M. *Chem. Sci.* **2012**, *3*, 1075-1079.

(81) Mougel, V.; Chatelain, L.; Pecaut, J.; Caciuffo, R.; Colineau, E.; Griveau, J. C.; Mazzanti, M. *Nat. Chem.* **2012**, *4*, 1011-1017.

(82) Brown, D. R.; Denning, R. G. *Inorg. Chem.* **1996**, *35*, 6158-6163.

(83) Spencer, L. P.; Yang, P.; Scott, B. L.; Batista, E. R.; Boncella, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 2930-2931.

(84) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Batista, E. R. *J. Am. Chem. Soc.* **2006**, *128*, 12622-12623.

(85) Brennan, J. G.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1988**, *110*, 4554-4558.

(86) Mougel, V.; Horeglad, P.; Nocton, G.; Pecaut, J.; Mazzanti, M. *Chem. Eur. J.* **2010**, *16*, 14365-14377.

(87) Sullens, T. A.; Jensen, R. A.; Shvareva, T. Y.; Albrecht-Schmitt, T. E. *J. Am. Chem. Soc.* **2004**, *126*, 2676-2677.

(88) Alekseev, E. V.; Krivovichev, S. V.; Depmeier, W.; Siidra, O. I.; Knorr, K.; Suleimanov, E. V.; Chuprunov, E. V. *Angew. Chem. Int. Ed.* **2006**, *45*, 7233-7235.

(89) Ekstrom, A. *Inorg. Chem.* **1974**, *13*, 2237-2241.

(90) Newton, T. W.; Baker, F. B. *Inorg. Chem.* **1965**, *4*, 1166-1170.

(91) Arnold, P. L.; Love, J. B.; Patel, D. *Coord. Chem. Rev.* **2009**, *253*, 1973-1978.

(92) Steele, H.; Taylor, R. J. *Inorg. Chem.* **2007**, *46*, 6311-6318.

(93) Nocton, G.; Horeglad, P.; Pécaut, J.; Mazzanti, M. *J. Am. Chem. Soc.* **2008**, *130*, 16633–16645.

(94) Brennan, J. G.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1988**, *110*, 4554-4558.

(95) La Pierre, H. S.; Meyer, K. *Inorg. Chem.* **2013**, *52*, 529-539.

(96) Kovacs, A.; Konings, R. J. M. *ChemPhysChem* **2006**, *7*, 455-462.

(97) Castro-Rodriguez, I.; Nakai, H.; Meyer, K. *Angew. Chem. Int. Ed.* **2006**, *45*, 2389-2392.

(98) Meyer, K.; Mindiola, D. J.; Baker, T. A.; Davis, W. M.; Cummins, C. C. *Angew. Chem. Int. Ed.* **2000**, *39*, 3063-3066.

(99) Roussel, P.; Scott, P. *J. Am. Chem. Soc.* **1998**, *120*, 1070-1071.

(100) Cloke, G., F. N.; Hitchcock, P. B. *J. Am. Chem. Soc.* **2002**, *124*, 9352-9353.

(101) Carmichael, C. D.; Jones, N. A.; Arnold, P. L. *Inorg. Chem.* **2008**, *47*, 8577-8579.

(102) CrysAlisPro CCD; CrysAlisPro RED ; ABSPACK; CrysAlis PRO. Agilent Technologies: Yarnton, England., Agilent (2010).

(103) Sheldrick, G. M.; 6.14 ed.; Inc, B. A., Ed. Madison,Wisconsin, USA, 1997.

Table of Contents (TOC):