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Small Molecule Activation by Multimetallic Uranium Complexes Supported by Siloxide Ligands

Luciano Barluzzi, [a] Marta Falcone, [a] and Marinella Mazzanti,*[a]

The synthesis and reactivity of uranium compounds supported by the tris- tertbutoxysiloxide ligand is surveyed. The multiple binding modes of the tert-butoxysiloxide ligand have proven very well suited to stabilize highly reactive homo- and heteropolymetallic complexes of uranium that have shown an unusual high reactivity towards small molecules such as CO_2, CS_2, chalcogens and azides. Moreover, these ligands have allowed the isolation of dinuclear nitride and oxide bridged complexes of uranium in various oxidation states. The ability of the tris- tertbutoxysiloxide ligands to trap alkali ions in these nitride or oxide complexes leads to unprecedented ligand based and metal based reduction and functionalization of N_2, CO, CO_2 and H_2

Introduction

In the current energetic context, the search for renewable alternatives to fossil fuels is attracting increasing attention towards the chemical low energy conversion of cheap and largely available C1 sources such as CO_2 and CO or N sources such as N_2 into higher value organic molecules.

CO_2 is a cheap, very largely available and renewable C1 source and as such, the possibility of using it in fine chemical synthesis, or converting it into liquid fuels is highly attractive.[1] CO is readily available as part of syngas (CO + H_2, usually obtained from coal or biomass) and is used as feedstock in the industrial Fischer–Tropsch process for production of alkanes, alkenes and alcohols. In this very energy demanding process, the reduction of CO by H_2 is catalyzed by heterogeneous cobalt or iron catalysts under high temperatures and pressures (200–350 °C, 20–44 bar).

Furthermore, in spite of the importance in agriculture of ammonia derived fertilizers, the only industrial process that uses dinitrogen as feedstock is the Haber-Bosch. This process is currently used for the production of large amounts of ammonia from dinitrogen and dihydrogen, but requires a metal catalyst, harsh conditions (about 450 °C and 300 bar) and consumes about 2% of the world's annual energy supply.

The sustainable transformation of small molecules such as CO_2 or N_2 remains a very challenging problem due to the low reactivity of such molecules. Metal complexes have been widely used to promote activation of small molecules in mild conditions. Uranium compounds offer an attractive alternative to metals of s, p and d block. Notably, the ability of 5f orbitals to participate in bonding, associated with the large size of the ion, its multiple oxidation states, and variable geometries and coordination numbers, confers unique properties and reactivity to uranium compounds rendering them a competitive perspective in catalytic applications.[2] Uranium compounds have demonstrated unique reactivity in the activation of inert bonds such as C-H [3] and of small molecules such as CO_2, CO, H_2, H_2O, N_2.[4] It has also been demonstrated that uranium compounds can be implemented in synthetic cycles on the cusp of catalysis, including the remarkable transformation of CO and H_2 into methanol in ambient conditions.[4b, 5] Moreover, molecular uranium compounds have been recently used to develop efficient electrocatalysts[6], while uranium(III) nitride materials were reported since 1910 to act as effective catalysts for the Haber process.[7] Efforts in this area have been summarized in several recent reviews.[2b, 4c, 8] Here we just recall some examples that are most relevant for the work presented in this feature.

A few rare examples of mononuclear complexes of uranium binding CO, [9] N_2[10] or CO_2[4a] in a terminal fashion were reported (Figure 1). In the carbonyl and dinitrogen U(III) complexes, the CO and N_2 bonds are unchanged with respect to the free molecule, suggesting a very low degree of activation. The ability of U(III) complexes to bind CO contrasts with the lack of reported carbonyl complexes of Ln(III) and is interpreted in terms of a more covalent U-C interaction. In contrast, an important degree of activation is reported for the bound CO_2 in the $[U\{(^{Ad}ArO)_3tacn\}(\eta^1\text{-}OCO)]$ complex, which exhibits an

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

unprecedented end-on bound CO_2 unit. The structural and spectroscopic data suggested the presence of a U(IV) complex of the charge-separated $CO_2^{-\cdot}$ radical anion (U(IV)–(OCO$^{-\cdot}$).[4a] The unusual reactivity of [U{(AdArO)3tacn}] was explained in terms of the sterical protected environment provided by the bulky (AdArO)3tacn system that stabilises an end-on bound $CO_2^{-\cdot}$ radical anion. This was confirmed by the reactivity of the U(III) complex of the less bulky ligand system (tBuArO)3tacn, leading to CO_2 cleavage and resulting in the formation of a very stable bridging oxo species and CO.[11] Beside this very unique example,
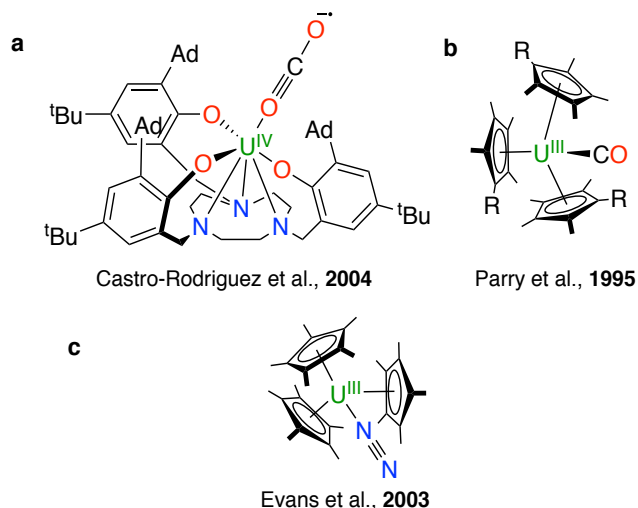
Figure 1 Coordinated carbon dioxide to uranium in a radical form (a), carbonyl complex of a U(III) complex (b), monometallic U(III) complex of N_2

reduction of CO, CO_2 or N_2 at U(III) centres involves, in the vast majority of reported studies, mono-electron transfer by mononuclear complexes of uranium (III). In most cases two mononuclear complexes bind the substrate and effect reduction to afford a dinuclear complex where two uranium(IV) centres are bridged by the reduced substrate. In these systems, each uranium ion is involved in one-electron transfer process. Computational studies have shown that both uranium cooperatively participate in the activation of the substrate.

In Scheme 1 and 2 some key examples of this type of reactivity with CO_2,[12] CS_2,[13] CO[14] and N_2[15,10] are summarized.

Reduction of CO_2 resulted in the cleavage of one CO bond, reductive disproportionation and reductive dimerization depending on the electronic and steric properties of the supporting ligands.[4c, 12]

CO reduction by U(III) mixed sandwich or amide complexes afforded a range of linear and cyclic homologation products $(C_nO_n)^{2-}$, the ethynediolate[5b, 14, 16] (n = 2), deltate (n = 3) [14], and squarate (n=4)[17] dianions.

The reaction of two U(III) complexes supported by various ligands leads to side-on bridged dinitrogen complexes where the extent of dinitrogen reduction varies from 0[15] to -2[18](Scheme 2). In most of these complexes N_2 binding is reversible and any attempt to cleave or further functionalize the uranium bound dinitrogen resulted in N_2 displacement.[15, 18]

These results anticipated that cooperative binding of substrates by homo- and hetero-multimetallic U(III) complexes would be
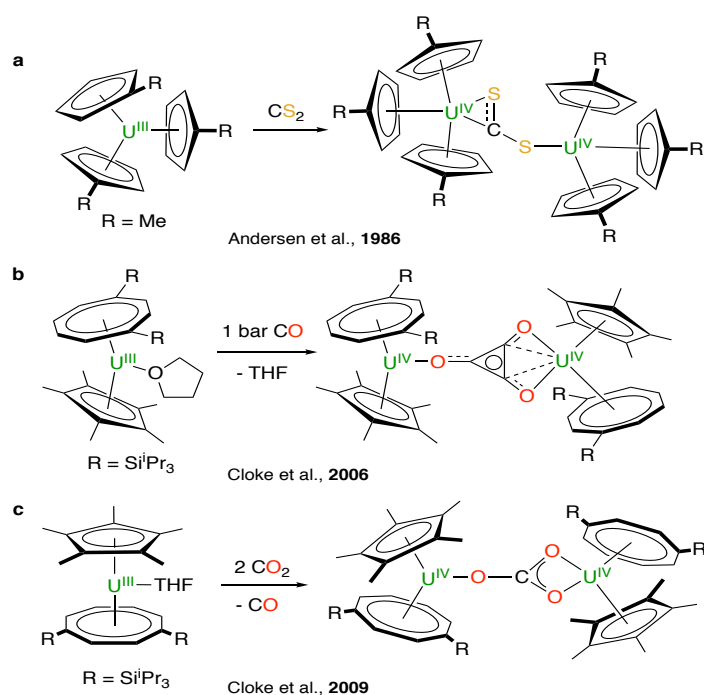

Scheme 1: Carbon disulfide reduction (a), carbon monoxide reductive cyclotrimerization (b) and reductive disproportionation of carbon dioxide (c) by trivalent uranium metallocenes

more effective in the reduction of small molecules but examples of such systems remain extremely rare for uranium.[4d, 19,19d] Particularly relevant is the fact that the first example of two-electron reduction of N_2 at a uranium centre was reported for a heterodimetallic U/Mo system (Scheme 3).[19b]

The only example of dinitrogen cleavage reported for a uranium complex was isolated from the reduction of the U(III) complex [(Et8-calix[4]tetrapyrrole)U-(dme)][K(dme)] under nitrogen and is likely to involve a highly reactive U(II) intermediate.[20] So far,
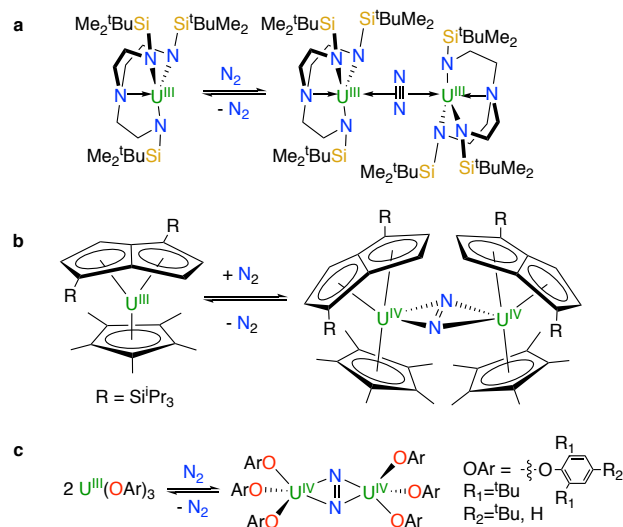
Scheme 2 Reversible coordination/reduction of dinitrogen by U(III) complexes side-on coordination (a), two electron reduction to afford the side-on N_2^{2-} bridged diuranium(IV) complexes with Cp ligands (b) and aryloxide ligands (c)

complete cleavage of the strong CO and N_2 triple bond by a
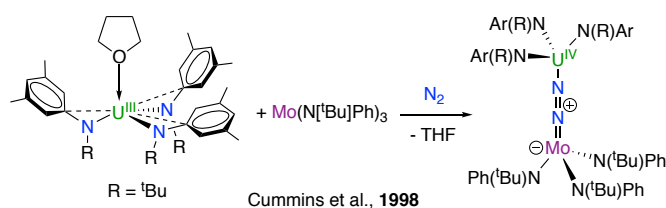
Scheme 3: Non-reversible two-electron reduction of dinitrogen by an heterometallic U/Mo system.

uranium(III) system has not been reported , but carefully tailored multimetallic complexes should be able to effect such transformations and some progresses in this direction are presented in this article.

Siloxides as supporting ligands in uranium chemistry

A broad range of siloxide ligands have been used in d-block chemistry[21] and, to some extent, in lanthanide chemistry.[22] However, beside the recent work from our group featured in this article, only one additional example of the use of siloxides in uranium chemistry has been reported.[23] Arnold and coworkers reported the reaction of the bulky trimesitylsilanol $HOSi(Mes)_3$ (Mes = mesityl, $2,4,6\text{-}Me_3C_6H_2$) with ULN_3 (N = $N(SiMe_3)_2$).[23] The protonolysis reaction did not allow the isolation of a siloxide supported U(III) complex, but, when performed under dinitrogen atmosphere, leads to the isolation of the dinitrogen complex $\{[U\{OSi(Mes)_3\}_3]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)\}$ alongside with other byproducts. The complex was shown to be very stable and to contain a reduced N_2^{2-} moiety, but no reactivity of the bound N_2 was reported.

The tris- tertbutoxysiloxide ligand

Tert-butoxysiloxide ligands have multiple binding modes (Figure
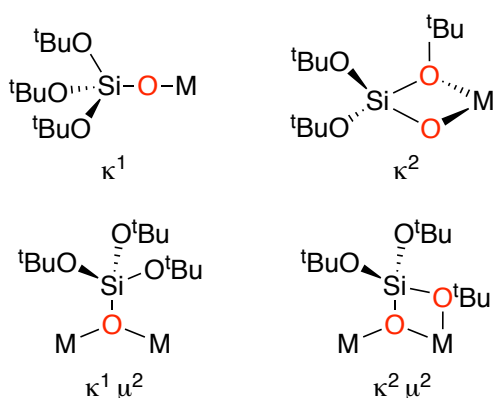
Figure 2: Binding modes of the tris-tertbutoxysiloxide ligand.

2) and have been used extensively as supporting ligands in d-block chemistry[21c, 24] and more sparsely in lanthanide chemistry[22a, 22d, 22e, 22h, 25] , but never, prior to the work of our group, in uranium chemistry. We found that tert-butoxysiloxide ligands can be used to build homopolymetallic or
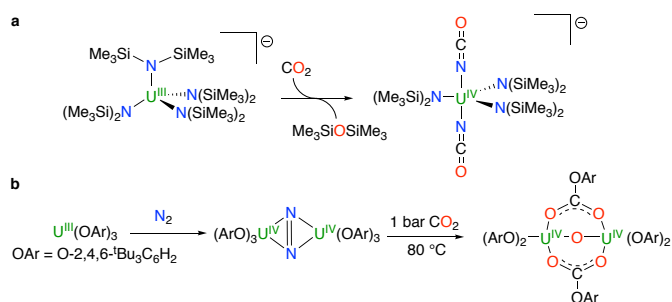

Scheme 4: CO_2 insertion reactions into the M–L bond.

heteropolymetallic complexes of uranium in low oxidation state. Moreover, due to their lower basicity, they are less prone to insertion of small molecules in the M-L bond as found for monodentate phenoxides[18a] or amides[26] (Scheme 4). Such properties make them attractive supporting ligands for the design of metal complexes capable of promoting small molecule activation.[4d, 22e]
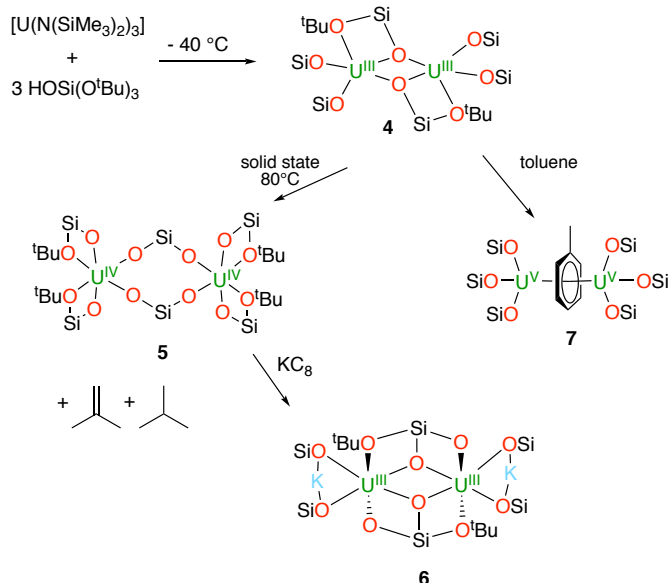
Synthesis of uranium siloxide complexes

The homoleptic U(IV) complex $[U(OSi(OtBu)_3)_4]$, **1** is easily obtained from the reaction of $[UI_4(OEt_2)_2]$ with the potassium salt of the tris-tertbutoxysiloxide ligand (Scheme 5).[27] The solid-state structure of crystals of **1**, isolated from hexane[4d], clearly shows the ability of the siloxide to act as a polydentate supporting ligand in the absence of coordinating solvents or other substrates. The structure of **1** isolated from THF or pyridine shows that the butoxy oxygen atom can be easily displaced by coordinating substrates such as THF or pyridine.[27] The reaction of **1** with 1 equiv of KC_8 at room temperature leads to the formation of the neutral heterodimetallic U(III) "ate" complex $[KU(OSi(O^tBu)_3)_4]$, **2**. This complex is stable in solid state and in solution up to 100 °C. ^1H NMR studies showed that the potassium cation remains bound in toluene solution in the pocket formed by the oxygen atoms of the siloxide ligands confirming the heterodimetallic nature of the "ate" complex **2**. Addition of crown ether to **2** affords the ion-pair analogue $[K(18c6)][U(OSi(O^tBu)_3)_4]$, **3**.[19a] The homoleptic dinuclear complex of U(III) $[U(OSi(O^tBu)_3)_3]_2$, **4**, can be synthesised in high yield from the metathesis reaction of
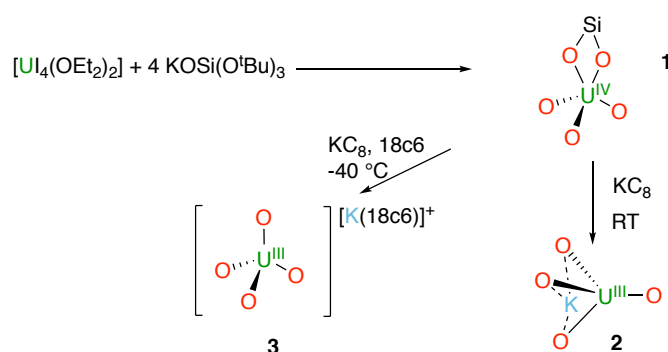
Scheme 5: Synthesis of the homoleptic complex $[U(OSi(O^tBu)_3)_4]$, **1** and its reduction reactions performed in presence or absence of crown ether to afford the heterodimetallic complex **2** or the ion-pair analogue, **3**, respectively.

the tris amide complex [U(N(SiMe₃)₂)₃] with the silanol ligand (Scheme 6).[4d] This dinuclear complex is stable in the solid state and in hexane at -40°C, but decomposes slowly at room temperature.

Decomposition is fast when the solid is heated at 80°C affording

Scheme 6: Synthesis of the homoleptic dinuclear complex of U(III), [U(OSi(OtBu)₃)₃]₂, 4. The decomposition of 4 in solid state leads to the siloxide/silandiolate diuranium(IV) complex, 5, which is further reduced to the diuranium(III) analogue, 6. Complex 4 reduces toluene to yield the diuranium(V) inverse sandwich complex 7 (Tertbutyl groups of unbound tertbutoxide groups are omitted).

the dinuclear U(IV) complex [U(OSi(OtBu)₃)₂(μ-O₂Si(OtBu)₂)]₂, 5. The formation of 5 from 4 involves the oxidative cleavage of two tertbutyl groups from the siloxide ligand affording a new dianionic silandiolate ligand.[28] The heteroleptic complex 5 can be reduced with potassium to afford the new U(III)-U(III) complex [K(THF)U(OSi(OtBu)₃)₂(μ-O₂Si(OtBu)₂)]₂ 6 in high yield. Complex 6 is the first example of a U(III) complex containing both siloxide and silandiolate ligands, and provides a potential precursor for reactivity studies.

The diuranium(III) siloxide complex 4 is also unstable in toluene, where clean reduction of toluene occurs to afford the inverted arene sandwich [{U(OSi(OtBu)₃)₃}₂(μ-η⁶:η⁶-C₇H₈)], 7 which was identified as the product of four-electron reduction of toluene (U(V)-(arene)⁴⁻-U(V)). Complex 4 dissociates in coordinating solvents (THF) to afford the mononuclear solvate analogue.

The complexes 2, 3 and 4 provide a versatile platform to investigate cooperative effects in small molecule activation by U(III) complexes.

Reactivity of siloxides-supported uranium complexes

Reaction with heteroallenes (CO₂ and CS₂)

In scheme 7 are summarized the reactions of the complexes 2, 3 and 4 with CS₂. The dinuclear complex [U(OSi(OtBu)₃)₃]₂, 4, effects the two-electron reaction of CS₂ in ambient conditions to afford [{U(OSi(OtBu)₃)₃}₂{ μ-CS₂}], 8[4d] where the CS₂²⁻ ligand

bridges two U(IV) centres in a rare[29] μ-η²(C,S1):η²(S1,S2)
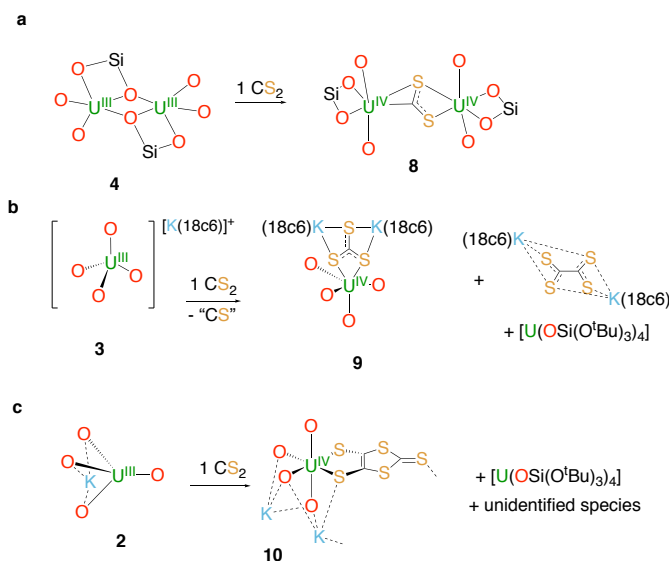
Scheme 7: Reduction of CS₂ (a) by 4 to give the bridging CS₂²⁻ diuranium(IV) complex 8, (b) by 3 and (c) by 2 (Only the the bound oxygen atoms of the siloxides are shown here and in the following schemes).

fashion. This is only the second example of a diuranium(IV) complex bridged by a CS₂²⁻ ligand. The [(RC₅H₄)₃U]₂[μ-η¹:η²-CS₂] complex was obtained from the reduction of CS₂ by the U(III) complex [(RC₅H₄)₃U]. [13]

In contrast, Meyer et al. reported the formation of a mixture of trithiocarbonate and a tetrathiooxalate complexes from reduction of CS₂ by the trivalent uranium complex of a multidentate phenolate [(AdArO)₃N)U(DME)].[30] DFT studies on these phenolate systems identified a CS₂²⁻ bridged U(IV)/U(IV) dimer as the most reasonable intermediate in the formation of trithiocarbonate and tetrathiooxalate, [31] but this intermediate was not experimentally observed. In contrast, DFT studies indicated that complex 8 is the most stable product of the reaction of 4 with 1equiv of CS₂ and that any further reaction from the bimetallic complex 8 to yield sulfide, thiocarbonate or tetrathiooxalate complexes are either thermodynamically or kinetically unfavourable, in agreement with the experimental observation of the complex 8 as the only product.[4d]

However, when the number of siloxide ligands bound to the uranium(III) centres is increased from 3 to 4, the reaction with CS₂ proceeds differently, leading to the formation of the reductive coupling and disproportionation products that are rapidly released from the coordination sphere of the metal centre due to the steric bulkiness of the "ate" complexes.[32] The "ate" complex 3, and the heterodimetallic 2 both effect the parallel reductive dimerization and reductive disproportionation of CS₂. However, ¹³C NMR studies show that the presence of the bound Lewis acidic potassium cation in 2 leads preferentially to the reductive dimerization of CS₂, while the reductive disproportionation pathway is favoured by the "ate" complex 3. The unstable intermediates [U(OSi(OtBu)₃)₄(μ₃-CS₃)K₂(18c6)₂], 9 and [U(OSi(OtBu)₃)₄K₂(C₃S₅)]ₙ 10 containing bound trithiocarbonate, and bound dmit dianion (dmit²⁻ = C₃S₅²⁻ = 1,3-dithiole-2-thione-4,5-dithiolate, formed from the reaction

of $C_2S_4^{2-}$ with CS) were isolated and crystallographically characterized.[32]

The terminal trithiocarbonate **9** was found to rapidly release the K_2CS_3 substrate, rendering the system attractive for the development of catalytic cycles.[32] The differences in reactivity between complexes **3** and **2** were interpreted in terms of different multimetallic U-K cooperativity. In contrast, the lower stability of the putative CS_2^{2-} intermediates is probably the result of combined electronic and steric factors introduced by the additional electron-rich, bulky siloxide present in **3** and **2** compared to **4**.

CO_2 also reacts in ambient conditions with complexes **2**, **3** and **4**. The reactions are summarized in Scheme 8.

The dinuclear tris-siloxide complex **4** effects the reductive disproportionation of CO_2 to afford the carbonate-bridged diuranium(IV) complex [{U(OSi(O^tBu)_3)_3}_2{μ-η^1:η^2-CO_3}], **11**, and
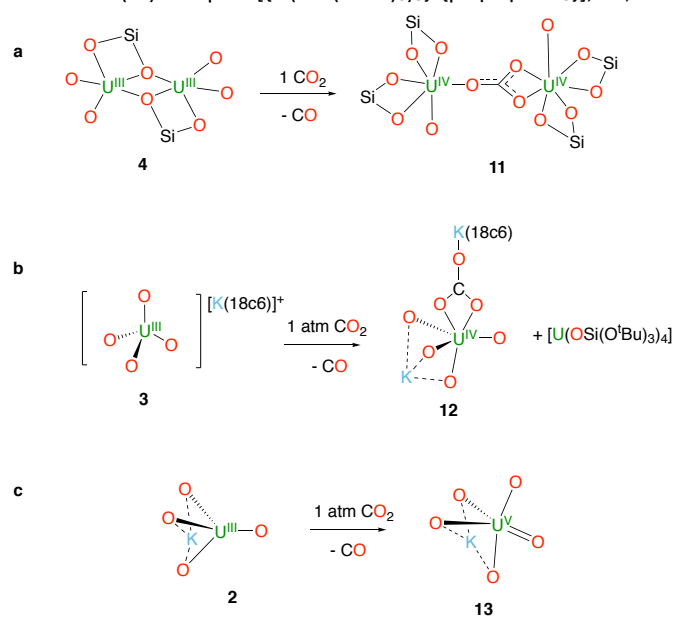
Scheme 8: Carbon dioxide reduction reactions by the dinuclear U(III) complex **4** to give the bridging carbonate dinuclear U(IV) complex **11** (a); carbon dioxide reduction by the *ate* and the heterobimetallic complexes **3** and **2**, to give the U(IV) carbonate complex **12** (b) and the U(V) terminal oxo complex **13** (c).

CO.[4d] The reductive disproportionation of CO_2 to CO and uranium carbonate derivatives had been previously reported for mixed sandwich U(III),[12] and tris(aryloxide) systems.[5a, 33] However, the reaction mechanism proposed for the reaction of **4** with CO_2, on the base of DFT computational studies, differs significantly from the previously reported systems. In the case of mononuclear U(III) complexes of polydentate tris(aryloxide) and mixed sandwich ligands, a diuranium(IV) oxo bridged intermediate was postulated to form upon extrusion of CO from a bimetallic intermediate species [U(IV)]–(CO_2^{2-})–[U(IV)]. The oxo dimer further inserts a second CO_2 molecule to afford the final carbonate.[34] In contrast, in the case of **4** the carbonate complex formation occurs through an alternative mechanism where the attack of CO_2 and release of CO are concerted.[4d]

This concerted mechanism of CO_2 reduction is probably favoured by the dinuclear nature of complex **4**, which is, so far, the only dinuclear complex of uranium reported to activate CO_2. The reactivity of **4** with carbon dioxide contrasts with that

reported for mononuclear uranium(III) complexes supported by monodentate aryloxide or amide ligands for which no carbonate adducts were isolated and multiple reduction and insertion products were identified.[18a, 26] This could be ascribed to the different electronic and steric properties of the siloxide supporting ligand confirming their interest as alternative ancillary ligand in U(III) chemistry. However, the role of the dimetallic nature of complex **4** should not be underestimated.
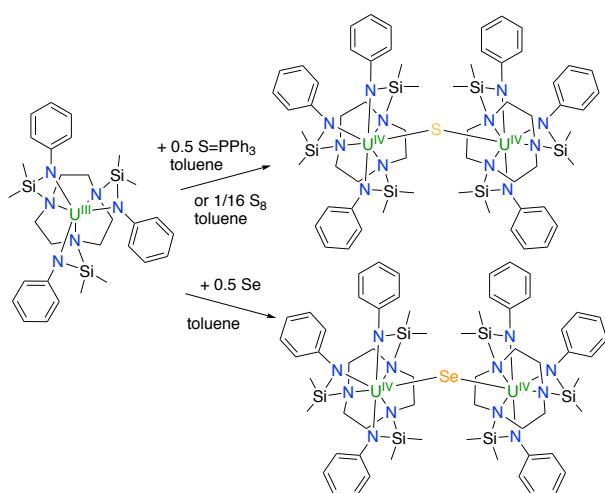
The ion pair complex **3** readily reacts in ambient condition with CO_2 to afford CO, the terminal U(IV) carbonate complex [(18c6)K(μ-η^1:η^2CO_3)U(OSi(O^tBu)_3)_3K], **12**, and the U(IV) complex **1**. Complex **12** shows higher stability compared to **11** with respect to ligand scrambling over time in toluene solution. The presence of the coordinating [K(18c6)]^+ cation binding the carbonate group may play a role in the stabilization of the mononuclear product.[19a]

Thus, both the dinuclear tris-siloxide complex **4** and the mononuclear tetrasiloxide complex **3** promote selectively the reductive disproportionation of CO_2. This reactivity is remarkably different from the reactivity with CS_2. Notably, the tris-siloxide **4** leads to a stable [{U(OSi(OtBu)_3)_3}_2{μ-CS_2^{2-}}] intermediate, while both reductive disproportionation and reductive dimerization of CS_2 were observed with the bulky tetrasiloxide complex **3.** The pathway leading to reductive dimerization of CO_2 to oxalate was not observed for **3**. Oxalate formation from CO_2 is rare and only three examples have been reported for uranium(III) that were obtained as the kinetic products of the reaction controlled by steric effects.[35] In contrast, the heterodimetallic complex **2** shows a dramatically different and unprecedented (in uranium chemistry) reactivity with CO_2. Complex **2** effects the two-electron reduction of CO_2 in ambient conditions leading to the terminal U(V) oxo complex [UO(OSi(O^tBu)_3)_3_4K], **13** and CO.[19a] This reaction is the first example of the two-electron reductive cleavage of CO_2 mediated by a single U(III) complex. One example of two-electron reductive cleavage of CO_2 had been previously reported but involved the concerted oxidation of two U(III) complexes.[11] Notably, addition of carbon dioxide to the U(III) complex [((^{tBu}ArO)_3tacn)U] resulted in the formation of an oxo-bridged diuranium(IV) species with extrusion of carbon monoxide. In general, all previously reported examples of CO_2 reduction by U(III) complexes involved two metal complexes transferring one electron each.[4c, 35-36] The reactivity of the heterodimetallic complex **2** is remarkable both because two-electron redox transfer is generally rare in uranium chemistry[27, 37] and terminal U(V) oxo complexes are not common. Notably, the formation of terminal uranium(V) oxo complexes from the reaction of U(III) with oxo-transfer reagents requires the use of bulky ligands preventing the formation of more stable dinuclear oxo-bridged U(IV) complexes and a careful choice of the oxo-transfer agents.[38] U(V) mono-oxo complexes have also been obtained by the reductive cleavage of nitrite by a U(IV) complex,[39] and from the metathesis of a U(V)–imido complex with CO_2.[40] The dramatic difference in the reactivity of complexes **2** and **3** with carbon dioxide was explained in terms of the presence of a coordinated potassium cation in proximity to the uranium centre in complex **2**. The association of a highly

reducing U(III) ion and an electropositive potassium cation is likely to result in the cooperative binding and activation of carbon dioxide. A similar coordination mode has been characterized at a Co^{I}-M (M= Li, Na) site.[41] DFT studies support the significant influence of the potassium atom as well as the cooperative effect between the metal centres in CO$_2$ transformation.[19a]
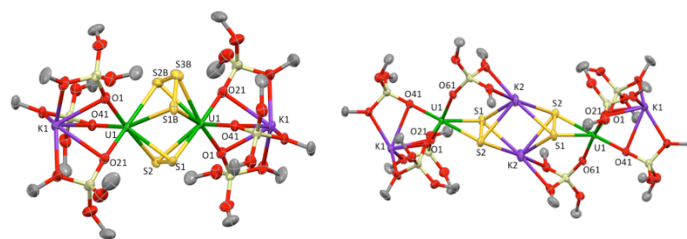
Reaction with chalcogen transfer reagents; synthesis of chalcogenide complexes

Activation of chalcogens and functionalization of chalcogenides is attracting increasing interest in uranium chemistry[42] due to its relevance in catalysis and in spent nuclear fuel processing. However, examples of activation of elemental chalcogens by uranium compounds remain relatively scarce and have mostly
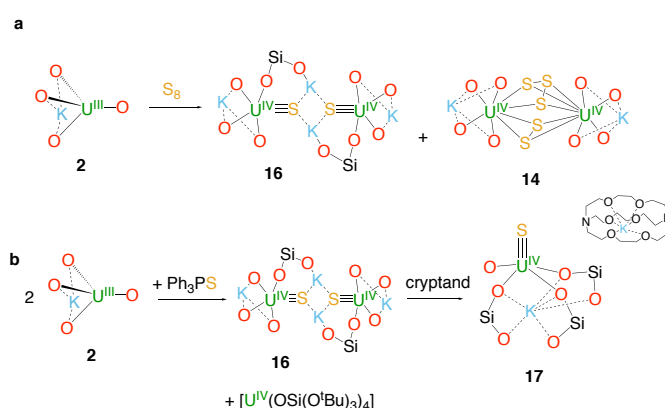
Figure 3: Molecular structure of the trisulfide complex **14** (left) and the disulfide complex **15** (right).

The use of bulky ligands has often been employed to favour the formation of terminal sulfide complexes. However, the reaction of [KU(OSi(O^{t}Bu)$_3$)$_4$], **2** with 0.125 equiv S$_8$ leads to a complex mixture of compounds from which the disulfide

Scheme 10: Reactions of the heterodimetallic complex **2** with S$_8$ (a) and Ph$_3$PS (b) yielding the U(IV) potassium-capped sulfide, **16** complex and the U(IV) non-capped sulfide complex, **17**

[K$_2$U(S$_2$)(OSi(O^{t}Bu)$_3$)$_4$]$_2$, **14** and the trisulfide [K(μ-S$_2$)(μ-S$_3$){U(OSi(O^{t}Bu)$_3$)$_3$}$_2$]$_2$, **15** diuranium(IV) dimer were isolated[46] (Figure 3).

In contrast, a rare potassium capped ([SU(OSi(O^{t}Bu)$_3$)$_4$K$_2$]$_2$), **16** or non-capped ([SU(OSi(O^{t}Bu)$_3$)$_4$K][Kcryptand]), **17** U(IV) terminal sulfide, (Scheme 10) could be selectively formed by reacting **2** with Ph$_3$PS with or without the presence of cryptand.[46]

Interestingly, if **2** is pre-treated with cryptand, no reaction is observed whit Ph$_3$PS, which unambiguously demonstrated that the presence of a bound potassium cation is crucial in the S-transfer reaction between [U(OSi(O^{t}Bu)$_3$)$_4$K] and Ph$_3$PS. This dramatic difference in reactivity was explained in terms of steric differences leading to a reduced access of the S$_8$ substrate to the metal centre. However, cooperative binding of uranium and

Scheme 9: Synthesis of sulfide-bridged and selenide-bridged complexes of U(IV) with the tacn-based ligand system.

resulted in the single electron oxidation of the uranium centre even in the presence of an excess of chalcogen, which is formally a two-electron oxidizing agent. Notably, U(III) mononuclear complexes are known to promote the reduction of elemental sulfur providing a pathway to sulfide bridged diuranium(IV) complexes (Scheme 9 shows a representative example from ref[37a]). [37a, 43] In contrast, the reaction of a dinuclear U(III) complex with excess sulfur was reported to lead to a persulfide bridged diuranium(IV) complex.[19c] The formation of the persulfide versus sulfide species could be explained by a cooperative binding of sulfur by the two metal centres associated to simultaneous one electron transfer, while the reaction of mononuclear U(III) complexes is likely to proceed via the formation of a terminal U(V) sulfide that further reacts with another U(III) complex. The first terminal U(IV) sulfide was reported by Hayton and coworkers by using a ylide protecting group that disfavours the formation of bridging sulfide complexes during sulfur transfer from S$_8$ to U(III) amido complex.[44] Single electron chalcogen reduction was also reported for dimeric bis(imido) U(V) complexes leading to the formation of E^{2-} or [E$_4$]$^{2-}$ (E = S, Se) bridged diuranium(VI) complexes.[45]

potassium centre to the sulfur are likely to play an important role in reactivity.

A few studies of the reactivity of bridging and terminal chalcogenides have been reported with different ancillary
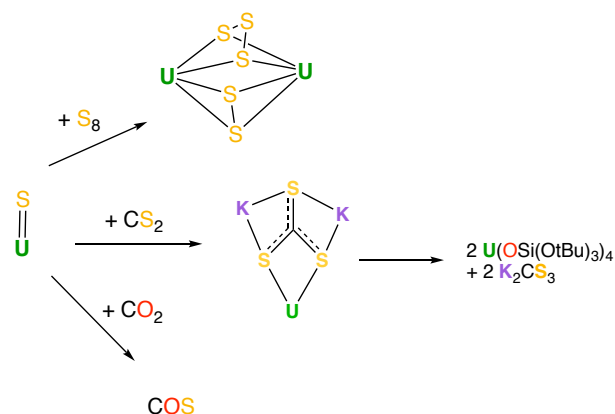
Scheme 11: Reactivity of the capped and terminal sulfides with S_8, CS_2 and

ligands. Terminal[47] and bridging[48] chalcogenides were reported to further activate elemental chalcogens to afford terminal and bridging polychalcogenido uranium complexes respectively. The activation of CS_2, CO_2, and COS by chalcogenide-bridged complexes has also been reported for the [{((^{Ad}ArO)$_3$N)U}$_2$(μ-E)] (E =S, Se) and leads to trithiocarbonate bridged [{((^{Ad}ArO)$_3$N)U}$_2$(μ-κ_2:κ_2-CS$_3$)][31] and mixed-chalcogeno carbonate bridged complexes of the types U−CO$_2$E−U (E = S, Se), U−CS$_2$E−U (E = O, Se), and U−COSSe−U.[49]

In our group, we investigated the reactivity of the capped and terminal sulfides with S_8, CS_2 and CO_2 (Scheme 11). Excess sulfur leads to polychalcogenide-bridged complexes as a result of loss of one siloxide ligand, but the reaction with CS_2 leads to the formation of terminal trithiocarbonate complexes that release the bound K_2CS_3 over time. The trithiocarbonate intermediate complex [U(OSi(O^{t}Bu)$_3$)$_4$(μ_3-κ_2:κ_2: κ_2-CS$_3$)K$_2$(18c6)$_2$],**9**, was isolated and crystallographically characterized from the direct reaction of the ion-pair complex [K(18c6)][U(OSi(O^{t}Bu)$_3$)$_4$], **3**, with CS_2. [32] The reaction of the terminal sulfide **17** with CO_2 leads to free COS probably from the decomposition of a U(IV)-CO_2S intermediate.[46]

Surprisingly, U(V) terminal sulfides could not previously be obtained from the activation of S_8 by U(III) complexes, probably due to the high nucleophilic nature of such compounds that results in fast reaction with unreacted U(III). We succeeded in preparing the first example of a terminal U(V) terminal sulfide via metathesis of the U(V) imido [K(2.2.2-cryptand)][U(NAd){OSi(O^{t}Bu)$_3$}$_4$], **18**[27] (see the following chapter for the synthesis of imido complexes) with H_2S to give [K(2.2.2-cryptand)][US{OSi(O^{t}Bu)$_3$}$_4$], **19** (Scheme 12).[50] Based on DFT calculations, triple-bond character with a strong covalent interaction is suggested for the U^V=S bond. The terminal U(V) sulfide rapidly reacts with CS_2 to afford a terminal U(V) trithiocarbonate [K(2.2.2-cryptand)][U(CS$_3$){OSi(OtBu)$_3$}$_4$], **20** that was also obtained from the metathesis of **18** with CS_2 probably via the highly reactive terminal U(V) sulfide intermediate. [50]

In contrast to the difficulty encountered in obtaining terminal sulfide complexes, the formation of a terminal U(V) monoxo
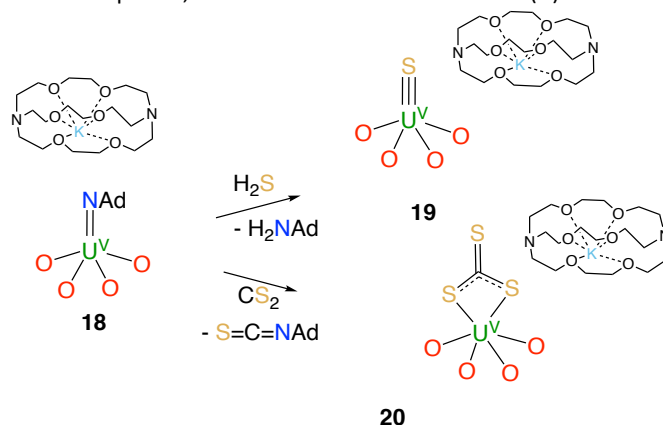
Scheme 12: Syntheses of the terminal U(V) sulfide complex, **19** and of the U(V) trithiocarbonate complex, **20**.

complex is quite straightforward and can be achieved by reacting the bulky tetrasiloxide complex **2** with pyridine N-oxide or even with CO_2.

Several diuranium(IV) oxo-bridged have been reported, [5a, 33, 38, 51] but, surprisingly, the controlled synthesis of a diuranium(IV) bridging oxide revealed to be significantly more difficult than expected with tris-tertbutoxysiloxide as supporting ligand. Notably, the reaction of **4** with classical oxygen transfer agents such as PyNO, Me$_3$NO or N_2O only led to complicated mixtures of products including uranyl(VI) species. Only the use of the N_2O adduct of the N-heterocyclic carbene 1,3-dimesitylimidazol-2-ylidene (IMes) IMesN$_2$O[52] in THF at −80°C (Scheme 13) allowed the synthesis of the oxo-bridged diuranium(IV) complex [{U(OSi(O^{t}Bu)$_3$)$_3$}$_2$(μ-O)], **21**, in 79% yield.[53] The ability of the IMesN$_2$O to selectively produce the oxodiuranium(IV) complex could be due to the higher reaction rates of this reagent[54] compared to the other used oxygen transfer agents.
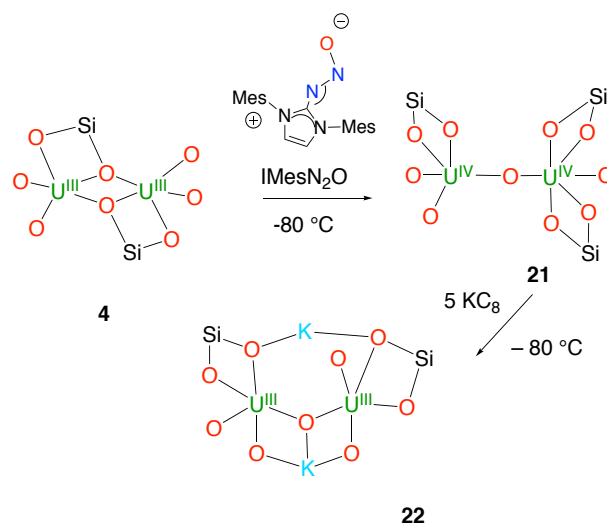
Scheme 13: Reaction of **4** with IMesN$_2$O to afford the diuranium(IV) oxo-bridged complex **21** and its reduction with excess KC$_8$ to afford the diuranium(III) oxo-bridged complex **22**.

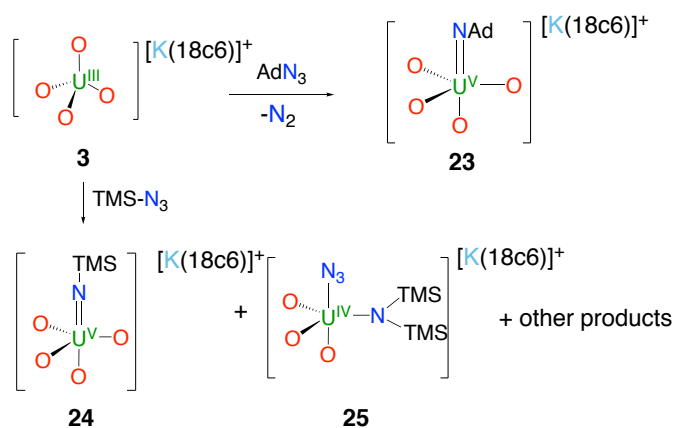Oxo-bridged molecular complexes are attractive models for metal oxide catalysts but usually contain metal centres in high oxidation state. The unique example of a crystallographically characterized U(III)-O-U(III) complex[55] was obtained from adventitious oxygen source during the reduction of a U(III) complex. The reduction of the oxo-bridged diuranium(IV) complex, **21**, leads to the multimetallic U(III) complex [K$_2$\{[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-O)\}], K$_2$U-O-U, **22.** This result confirms the ability of the tertbutoxysiloxide ligand to stabilize multimetallic complexes of uranium in low oxidation states and provides a new precursor for studying the reactivity of dinuclear complexes of U(III) with small molecules.

Reaction with organic azides

The diuranium(III) complex **4** and the ion pair complex **3** show a different reactivity with organic azides (Scheme 14 and Scheme 15). Complex **4** reacts with adamantyl azide affording the U(IV) complex [U(OSi(O^{t}Bu)$_3$)$_4$], **1**, and a dinuclear bis-imido complex of uranium(VI) [U$_2$(NAd)$_4$(OSi(O^{t}Bu)$_3$)$_4$], **26**. The bis-imido complex presents a cation-cation interaction[56] (CCI) between two [U(NAd)$_2$]$^{2+}$ units with a U-N-U angle of 108.4(5)° and a non-planar arrangement of the two imido groups. Both [U(NAd)$_2$]$^{2+}$ motifs are nearly linear and can be seen as nitrogen analogues
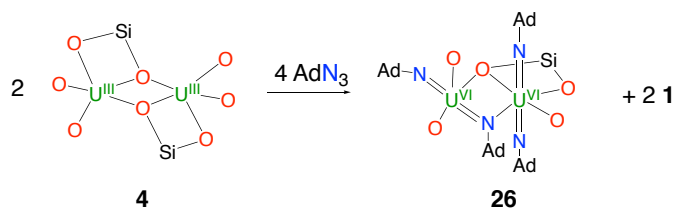
Scheme 14: Reaction of the uranium(III) complex, **3** with organic azides.

Scheme 15: Reaction of the neutral uranium(III) complex, **4** with adamantyl azide.

literature.[37g] However, such complexes may provide desirable precursors for reactivity studies or synthesis of otherwise non accessible compounds such as the terminal U(V) sulfide **19**.

Reaction with metal azides: synthesis of uranium nitrides

In view of the high reactivity of the U(III) siloxide complexes with heteroallenes, we became interested in investigating their reactivity with the isoelectronic azide (N$_3^-$) as a possible route to uranium nitride complexes. Metal azides are, indeed, known as versatile precursors for the obtention of nitride complexes. Uranium nitrides are of great fundamental interest for investigating multiple M-Ligand bonding[37b, 59] and nitride transfer reactivity. The synthesis and study of molecular nitride complexes is also attractive because of the importance of UN materials as potential alternative nuclear fuel.[59b, 60] Moreover, we were particularly interested by the high activity of UN materials reported by Haber in the catalytic conversion of N$_2$ and H$_2$ to NH$_3$.[7] The first examples of uranium nitrides were

of the UO$_2^{2+}$ moiety. The dinuclear complex **26** provided the first example of a uranium(VI) trans-bisimido complex showing a cation-cation interaction between the two imido groups.

Examples of dinuclear bis-imido complexes are rare in uranium chemistry[57] and they all present a diamond-shaped geometry. The reaction is likely to proceed with the formation of a U(V) azide that then disproportionates to U(VI) and U(IV) accompanied by ligand scrambling.
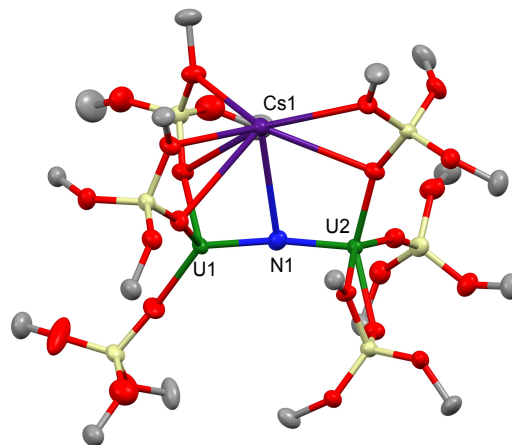
The bulky environment provided by the four siloxides in complex **3** prevents disproportionation during the reaction with the bulky adamantyl azide affording a stable U(V) terminal imido complex. Less bulky amides such as TMS-azide failed to stabilize the U(V) complex. Probably the bulky environment provided by the siloxide ligands and the adamantyl substituents are key in preventing U(V) disproportionation. The tendency of U(V) imido complexes to undergo disproportionation, even if to a less extent that uranyl(V) compounds,[58] is probably the reason of the limited number of isolated compounds reported in the

Figure 4: Molecular structure of **29**, probability at 50%, hydrogen atoms and methyl groups are omitted for clarity

obtained by Evans and then by our group from the reaction of U(III) complexes with metal azides, but led to multimetallic (3-8 uranium atoms) clusters containing both bridging nitrides and bridging azide ligands.[61] A series of stable nitride bridged diuranium,(U(IV)/U(IV); U(V)/U(IV); U(V)/U(V)) complexes containing a linear U=N=U motif were subsequently reported by Cummins and coworkers. The parent diuranium(IV) complex was prepared from the reaction of a U(III) tris-amide species with unprotected azide and then stepwise oxidized.[62] Only a

handful of additional examples of dinuclear and terminal nitrides have been reported to this date from the reaction of U(III) with azides, suggesting that the choice of reaction conditions and supporting ligands is critical in the isolation of stable uranium nitrides. [27, 37b, 59b, 63]

We found that only the dinuclear complex **4** would react in a controlled manner with metal azides to afford a nitride compound in high yield. In contrast, the reaction of the bulky tetra-siloxide complex **3** with cesium azide led to the formation
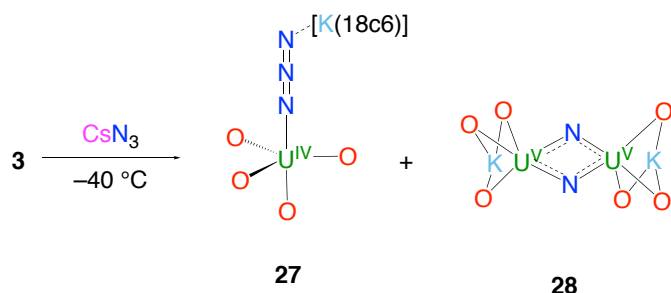
Scheme 16: Reaction of the ion-paired uranium(III) complex, **3** with cesium azide.

of multiple products from which we could isolate only a few crystals of the U(IV) azido complex [K(18c6)U(N$_3$)(OSi(O^{t}Bu)$_3$)$_4$], **27** and of the di μ-nitride diuranium(V) complex [KU(μ-N)(OSi(O^{t}Bu)$_3$)]$_2$ **28**.[27] (Scheme 16).

If a synthetic route to the terminal azide complex could be identified it could provide access to a terminal nitride complex. The most interesting features in the structure of **28** is the presence of two nitride atoms bridging two U(V) centres in a diamond-shaped geometry. Complex **28** is the first example of a U$_2$N$_2$ core isolated from the reaction of U(III) with azides. The formation of this unprecedented U(V)/U(V) complex may involve a highly reactive U(V) terminal nitride intermediate that affords the bis(nitride) complex trough the loss of one siloxide ligand. The crowded environment and the high complex charge
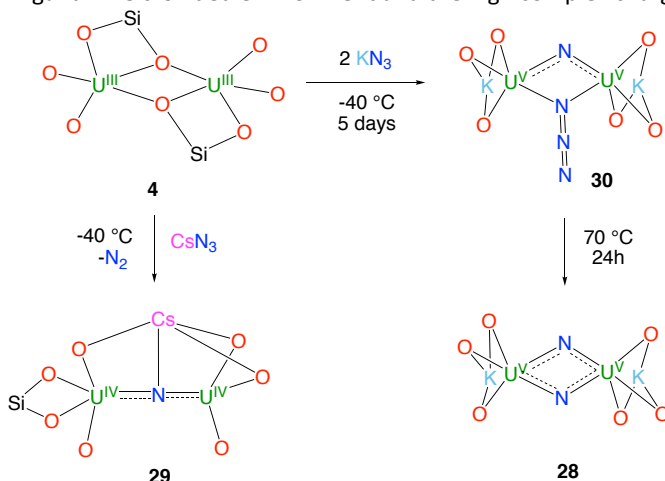
Scheme 17: Reaction of **4** with alkali azides to afford the nitride-bridged complex **29** and the diuranium(V) nitride-azide-bridged complex **30**. Thermolysis of **30** to afford the diuranium(V) bis(nitride)-bridged complex **28**.

result in a low stability of the putative terminal nitride intermediate and in the impossibility to trap it. This is in line

with the high reactivity demonstrated by the elusive uranium nitride intermediate [UN{N(SiMe$_3$)$_2$}(C5Me$_5$)$_2$] which engages in intramolecular C-H bond activation[64] and by the isolated terminal U(V) nitride. [37b]

The reaction of the dinuclear tris-siloxide complex **4** with CsN$_3$ (Scheme 17) affords the nitride bridged diuranium(IV) complex [Cs(μ-N){U(OSi(O^{t}Bu)$_3$)$_3$}$_2$], **29** in 47% yield.[27] The reaction is likely to proceed via the formation of an azide-bridged complex that eliminate dinitrogen to afford the final nitride. The solid-state structure of **29** (Figure 4) consists of a heterotrinuclear (U,U,Cs) complex where two U(IV) cations are held together by a bridging nitride N^{3-} ligand in a nearly linear fashion (U-N-U angle : 170.2(3)°) 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.
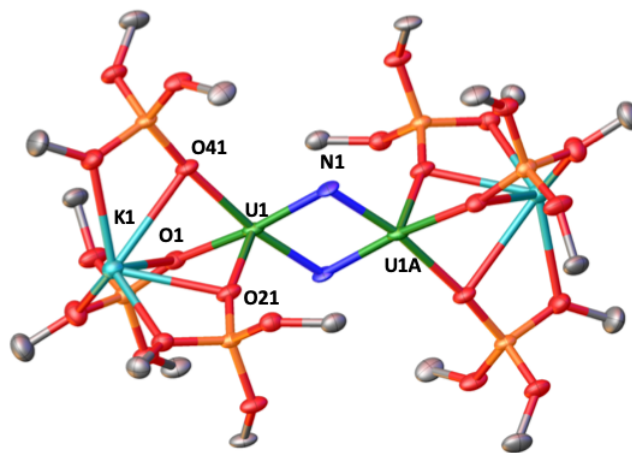
These values are similar to those found in other nitride-bridged

Figure 5: Molecular structure of **28**; probability at 50%; hydrogen atoms and methyl groups are omitted for clarity. Selected bond distances [Å] U1–N1, 2.022(5); U1–O$^-_{avg}$, 2.23(3)

diuranium(IV) complexes presenting a linear U=N=U fragment (U=N distance ranging from 2.05 to 2.09 Å and U-N-U angle ranging from 159 to 175 °).[61b, 62, 63b, 63h, 65] An important structural feature of the complex **29** compared to the other linear nitride-bridged U(IV)/U(IV) complexes is its heteropolymetallic neutral nature. Notably, in **29** the six siloxides act as multidentate bridging ligands binding the Cs$^+$ cation through 6 tert-butoxy oxygen atoms. The Cs$^+$ cation lies at the apical position of the nitride ligand and remains bound in a solution of toluene or THF as indicated by the fact that a different species is obtained upon addition of cryptand to a solution of **29**.

The bis-nitride bridged diuranium(V) complex can be prepared in 53% yield from the reaction of **4** with 2 equivs of potassium azide followed by heating at 70°C. These diuranium complexes provide a good substrate for comparative studies of the reactivity of bridging nitrides for different oxidation states of uranium. The X Ray crystals structure of complex **28** is presented in Figure 5.

Surprisingly all nitride complexes reported up to 2016 contained uranium in high oxidation state (U(IV), U(V), U(VI), in spite of the
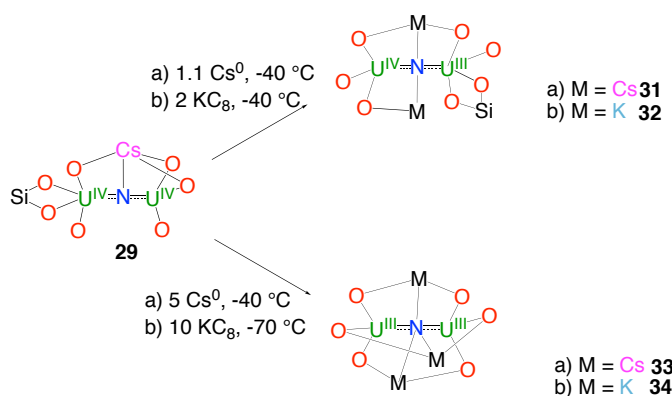
Scheme 18: Syntheses of the U(III)/U(IV) bridging nitride, and of the U(III)/U(III) bridging nitride with cesium and potassium cations

fact that one of the global objectives behind the synthesis of these species was to model the properties of U(III)N material.

In our group, we investigated the reduction of diuranium(IV) complex **29** with different reducing agents. Stepwise reduction of **29** with 1 equiv or a large excess of Cs^0 in THF at -40°C and under argon afforded the U(III)/U(IV) complex $Cs_2\{(\mu-N)[U(OSi(O^tBu)_3)_3]_2\}$, **31** and the U(III)/U(III) complex $Cs_3\{(\mu-N)[U(OSi(O^tBu)_3)_3]_2\}$, **33,** respectively (Scheme 18).[63f]

When the diuranium(IV) nitride complex **29** is reacted with excess KC_8 (10 equivs) in THF at −70 °C, the potassium analogue $[K_3\{[U(OSi(O^tBu)_3)_3]_2(\mu-N)\}]$, **34**, was isolated in 70% yield.[19d]

The nature of the cation bound to the U(III) complexes has a strong impact on their solution and solid-state stability. The cesium analogue is stable only few hours even at low temperature rendering more difficult the study of its reactivity. The solid-state structure of the U(III)/U(IV) and U(III)/U(III) nitrides presents respectively two and three cations bound in the pockets formed by the siloxide ligands (the X-Ray crystal structure of complex **34** is presented in Figure 6). The cations also bind the nitride group in a linear (**31**) or triangular fashion (**33**, **34**). In the U(III)/U(III) complexes the strong binding of the cation (K^+ or Cs^+) creates a flexible metallo-ligand framework that holds together the two uranium centres in close proximity. The cations could not be removed by addition of cryptand, showing that they are tightly bound. In all these U(III) containing complexes, the values of the U-N distances in the $Cs_2U^{III}NU^{IV}$, $Cs_3U^{III}NU^{III}$, and $K_3U^{III}NU^{III}$ complexes (Table 1) and the linear arrangement of the UNU core suggest the presence of U^{III}-N multiple bonding. The variation in the U=N bond lengths with variation of the oxidation state in the Cs_xUNU cores is larger than what observed in linear $U^{IV}NU^{IV}$ and U^VNU^V cores supported by bulky amides. This larger difference is most likely due to the presence of a different number of bound cations in the siloxide complexes leading to a reduced electron density in the UNU core.

More recently, computational studies showed a marked covalent character of the $K_3U^{III}NU^{III}$ with a U-N bond order of 1.4.[66] Moreover, magnetic data measured for $K_3U^{III}NU^{III}$ at variable temperature show a maximum at 23 K in the χ versus T plot showing that the two uranium centres are antiferromagnetically coupled at low temperature. These results indicate that nitride ligands can promote magnetic communication between U(III) centres.

	CsUNU, **29**	Cs₂UNU, **31**	Cs₃UNU, **33**	K₃UNU, **34**
U1-N	2.058(5) Å	2.099(12) Å	2.1495(12) Å	2.129(14) Å
U2-N	2.079(5) Å	2.243(25) Å	2.1495(12) Å	2.111(14)Å
U-O$_{avg}$	2.19(3) Å	2.243(25) Å	2.282(24) Å	2.303(7) Å
M1-N	3.393(4) Å	3.276(12) Å	3.348(8) Å	3.115(7) Å
M2-N	-	3.635(12) Å	3.348(8) Å	3.017(16) Å
M3-N	-	-	3.22(2)	3.243 (15)Å
U-N-U	170.2(3)°	169.1(7)°	174.2(11)°	173.7(7)°

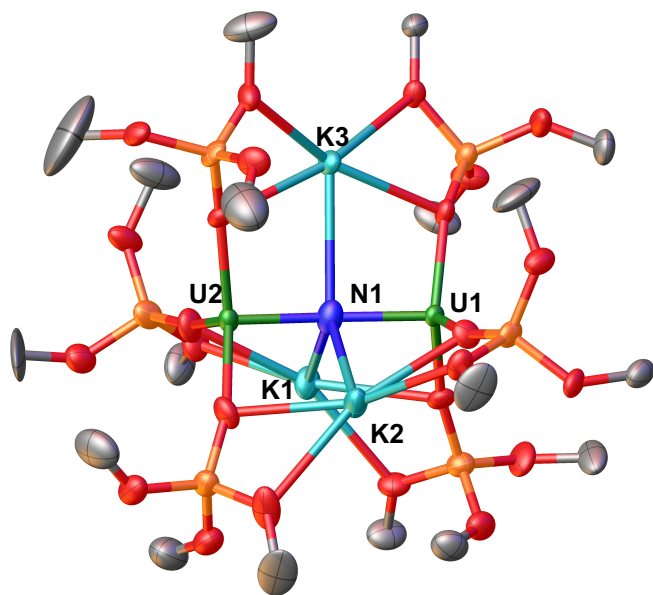**Table 1**: Comparative structural parameters of complexes **29**, **31**, **33**, and **34**

Figure 6: Molecular structure of **34**, probability at 50%, hydrogen atoms and methyl groups are omitted for clarity

Reactivity of siloxide-supported nitride bridged complexes
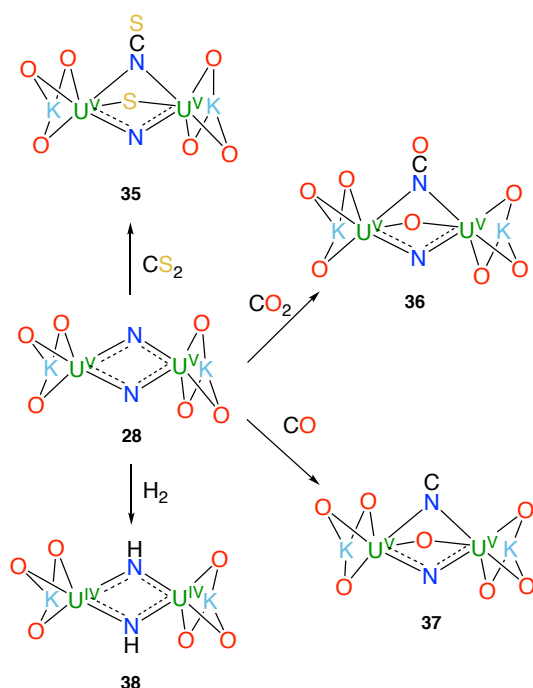
Scheme 19: Reactivity of the diuranium(V) bis-nitride complex **28** with CS_2, CO_2, CO and H_2.

The study of the reactivity of metal nitrides is of high relevance for the future development of catalytic processes directed to build organic molecules with added value such as amino acids, pharmaceuticals or agrochemicals [67] from cheap raw material such as N_2, CO_2, CO. N-C bond formation reactions are particularly important in this context. [68] Metal nitrides are important intermediates in the biological and industrial conversion of N_2 to ammonia and N-H formation is a crucial step in both processes. In this context, a wide range of studies has been directed to the development of metal complexes able to effect dinitrogen transformation in mild conditions.[69] Particularly desirable would be the use of cheap and/or largely available molecules such as H_2, CO or CO_2 in combination with dinitrogen for the synthesis of ammines and new organic products. However, examples of direct dinitrogen cleavage by H_2, CO or CO_2 are extremely rare[70].

Examples of N-C bond formation from the reaction of carbon dioxide[71a, 71b { Brask, 2002 #22948, 71c, 71d] or carbon monoxide [63e, 72] with activated nitride complexes of transition metals or hydrogenolysis by d-block metal nitride are also extremely rare.[69a, 72a, 73]

These reactions may involve electron transfer from the metal to the substrate or just the functionalization of the highly nucleophilic nitride group.

Very little is known of the reactivity of uranium nitrides in spite of their relevance in nuclear industry[60] and their activity as catalysts[2a, 7] in the Haber process. Prior to studies from our group of the reactivity of uranium nitrides, a seminal study from the Cummins group of the reactivity of the $U^V N U^V$ core supported by bulky amides fragment with NaCN showed that

the cyanide acts as a two-electron reducing agent while inserting into the nitride to yield a $U^{IV}N=C=NU^{IV}$ species.[62] The same complex was reported not to react with carbon monoxide. In contrast, the terminal uranium(V) nitride $[U(TrenTIPS)(N)][Na(12C4)_2]$ (TrenTIPS= $N(CH_2CH_2NSi^iPr_3)_3$) effects the two electron oxidation of CO to afford cyanate via attack of the nucleophilic nitride to the antibonding orbitals of CO.[63e] These contrasting results seemed to point to a reduced reactivity of uranium bound bridging nitrides and incited us to explore the reactivity of siloxide supported nitride bridged complexes.

Reactivity of uranium(V) nitride bridged complexes

The diuranium(V) bis(nitride) **28** demonstrated high nucleophilic reactivity towards diverse small molecules which is summarized in Scheme 19.[53] The reactivity of a toluene solution of **28** with one equiv of CS_2 led to CS_2 cleavage affording the sulfide-thiocyanate complex $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu-N)(\mu-S)(\mu-NCS)\}]$, **35**. Cleavage of CS_2 and concomitant formation of NCS^- was also observed for the U(IV) bridging nitride **29** (see next section) and for U(V) and U(VI) terminal nitrides.[74] In none of these cases, though, a uranium sulfide could be isolated. For complex **29** and the U(V) terminal nitride $[NU(Tren^{TIPS})][K(B15C5)_2]$ a putative uranium sulfide further reacts with CS_2 to give a trithiocarbonate ligand.[74] The different reactivity of **28** could be explained in terms of higher steric

hindrance around the sulfide. In contrast, the U(VI) terminal nitride $[NU(Tren^{TIPS})]$ cleaves CS_2 affording a U(IV) terminal thiocyanate and elemental sulfur.[74] The reaction of a toluene solution of complex **28** with 1 equiv of CO_2 led to C-O cleavage resulting in the isolation of the oxo-cyanate-complex $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu-N)(\mu-O)(\mu-NCO)\}]$, **36**. A similar reactivity leading to oxo and cyanate ligands is also observed for the U(V) and the U(VI) terminal nitrides $[NU(Tren^{TIPS})][K(B15C5)_2]$ and $[NU(Tren^{TIPS})]$.[74]

The reaction of **28** with 2 equivs of CO at room temperature affords the complex [K$_2${[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-NC)(μ-O)(μ-NCO)}], **37**. Two equivs of CO react with the two bridging nitride ligands with different outcomes. In fact, one nitride cleaves the CO triple bond affording a cyanido and an oxo complex, while the second nitride undergoes reductive carbonylation to form a cyanate ligand with the concomitant reduction of the two U centres from U(V) to U(IV). Thus, both ligand-based and metal-based reactivity are observed. The formation of thiocyanate, cyanate, and cyanide was confirmed by structural studies and ^{13}C NMR analysis of the products after reaction with ^{13}CS$_2$, ^{13}CO$_2$ and ^{13}CO.[53]

The complete cleavage of the CO triple bond (one of the strongest bonds in nature) in ambient conditions is particularly remarkable and is probably the result of the cooperative binding of CO by the two metal centres. Notably, CO cleavage is not observed in the reaction of terminal nitrides with CO which leads to reductive carbonylation.[74] Complete CO cleavage is a key step in the Fischer-Tropsch hydrocarbon production from CO and H$_2$ but examples of complete cleavage of CO by molecular complexes remain rare.[75]

The reactivity of complex **28** with 1 atm of H$_2$ in ambient conditions is remarkable in that the bis-nitride effects the oxidative cleavage of H$_2$ in mild conditions to yield the bis-imido complex [KU(μ-NH)(OSi(O^{t}Bu)$_3$)]$_2$, **38**.[53] Notably, cleavage of H$_2$ by metal-nitride is a rarely observed event.

The reaction pathway probably does not involve H$_2$ coordination to the metal centre but direct attack of H$_2$ to the two nucleophilic nitrides as previously reported for a terminal iridium complex.[76] The reactivity of complex **28** with H$_2$ is a likely model of the intermediates formed during the conversion of N$_2$ and H$_2$ into ammonia promoted by uranium nitrides in the Haber-Bosch process.

Reactivity of uranium(IV) nitride bridged complexes

The overnight thermolysis of **29** at 80°C in toluene solution resulted in the complete transformation of **29** to afford the new imido bridged siloxide/silandiolate diuranium(IV) complex Cs{(μ-N^{t}Bu)(μ-O$_2$Si(O^{t}Bu)$_2$)U$_2$(OSi(O^{t}Bu)$_3$)$_5$}, **39**. The thermolysis reaction leads to cleavage of a C-O bond of one siloxide ligand and to tert-butyl group transfer to the bridging nitride resulting in the formation of a new N-C bond. This reactivity demonstrated the strong nucleophilic character of the bridging nitride in **29** and incited to explore the reactivity with small molecules summarized in Scheme 20.

We found that the bridging nitride in the U(IV)/U(IV) complex **29** acts as a strong nucleophile towards CS$_2$, CO$_2$[77] and CO[77] leading to C-S or C-O cleavage and N-C bond formation yielding respectively the thiocyanate/trithiocarbonate complex Cs{(μ-NCS)(μ-CS$_3$)[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$}, **(43)**, the oxo/cyanate complex Cs{(μ-NCO)(μ-O)[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$}, **(44)**, and the oxo/cyanide complex Cs[{U(OSi(OtBu)$_3$)$_3$}$_2$(μ-CN)(μ-O)], **(41)** respectively. The high nucleophilic character of the U(IV)/U(IV) nitride leads to complete cleavage of the CO triple bond as observed for the
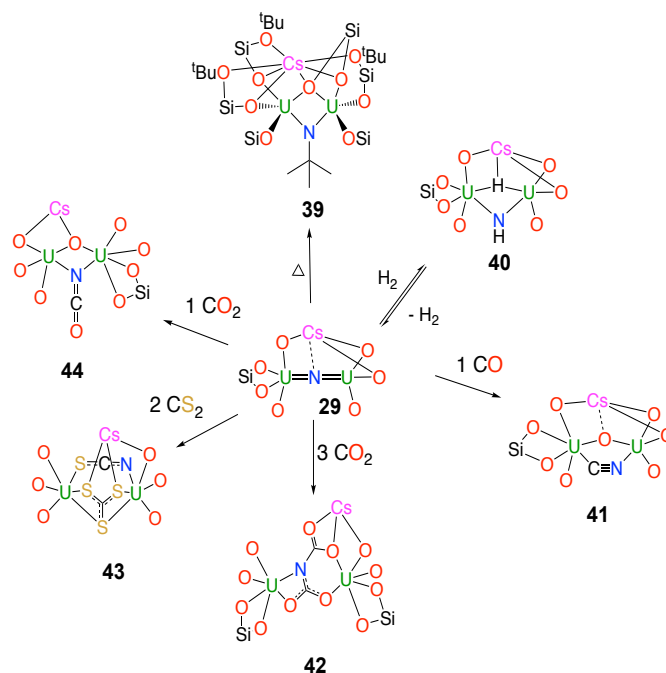
Scheme 20: Thermolysis and reactivity with CS$_2$, CO$_2$, CO and H$_2$ of the diuranium(IV) bridging nitride, complex **29**.

bis-nitride **28**. The cyanide in **41** is easily alkylated by MeOTf to afford MeCN.

Addition of excess (more than 3 equivs) CO$_2$ to **29** led to the unprecedented electrophilic addition of 2 CO$_2$ molecules to the bridging nitride affording the bis-carbamate complex Cs{(μ-NC$_2$O$_4$)[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$},**(42)**. The CsUNU core behaves as a Frustrated Lewis Pair and such reactivity encouraged to explore its ability to cleave H$_2$. In spite of their relevance in biological and industrial dinitrogen reduction the formation of imido-hydrido species from H$_2$ addition to metal-nitrides or metal-dinitrogen complexes remains extremely rare.[78] The bifunctional Lewis acid-Lewis base character of complex **29**, led to the reversible heterolytic cleavage of dihydrogen under ambient conditions to afford the reversible formation of the parent imide-hydride complex [Cs{U(OSi(O^{t}Bu)$_3$)$_3$}$_2$(μ-H)(μ-NH)], **40**.[79] This complex can transfer the hydride to acetonitrile and CO$_2$ to afford azavinylidene and formate insertion products respectively.

Reactivity of nitride bridged diuranium(III) complexes

The reaction between Cs$_3${(μ-N)[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$}, **33** and 1 equiv of ^{13}CS$_2$ led to the formation of the complex [(Cs(THF))$_2${[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-S)$_2$}], **45**[63f] and of N^{13}CS$^-$ suggesting that the transfer of the nitride ligand and the concomitant cleavage of a C=S double bond occurred. The oxidation of the U ions from U(III) to U(IV) indicates that metal-based reactivity has also occurred and that other unidentified species must be formed.

More remarkable is the ability of complex Cs$_3${(μ-N)[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$}, **33** to react with dinitrogen in ambient conditions. The concomitant formation of decomposition products, though, prevented the successful isolation of the
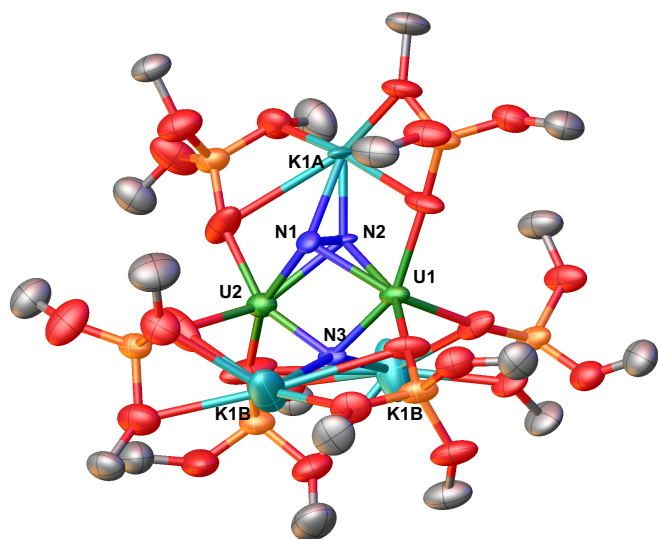
Figure 7: Molecular structure of **46**, probability at 50%, hydrogen atoms and methyl groups are omitted for clarity. Selected bond distances [Å] U_{avg}–N3, 2.069(3); N1–N2, 1.521(18

newly formed species. The increased stability of [K$_3$\{[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-N)\}], **34** in solid state and in solution makes it, in fact, a better candidate to investigate the reactivity towards dinitrogen. When complex **34** is exposed to an atmosphere of N$_2$ in solid state or in a toluene solution, the complex [K$_3$\{[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-N)(μ-η^2:η^2-N$_2$)\}], **46** is formed. Dinitrogen undergoes a four-electron reduction to N$_2^{4-}$ concomitantly with the oxidation of each U ion from U(III) to U(V).[19d] Theoretical investigation suggests that the removal of a Cs$^+$ in **33** is more favourable than the analogue process with K$^+$ in **34**.[80] Thus, upon the rearrangement of the siloxide framework required to bind N$_2$, decomposition processes are more favoured in **33** than **34**. The N$_2$ binding and functionalization reactivity is summarized in Scheme 22.
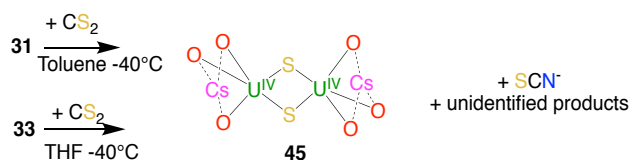
Scheme 21: Reactivity with CS$_2$ of the diuranium(IV/III) and the diuranium (III) bridging nitride, complexes **31** and **33**.

The oxidation state of the U ions and the extent of dinitrogen reduction in **46** was confirmed by SQUID magnetometry, EPR, and Raman spectroscopy. The X-ray crystal structure of **46** (Figure 7) shows that the UNU angle changes from 173.7(8)° in complex **33** to 106.0(5)° in complex **46**. Such a striking difference in the UNU angle upon binding and reduction of N$_2$ confirms the ability of the siloxide ligands to create a flexible ligand framework which holds together the two uranium centres during the reaction with dinitrogen. Four-electron reduction of dinitrogen is known for group 4 d-metals.[81] but is unprecedented in f element chemistry.[8d] Moreover, until very recently, N$_2$ functionalization had never been reported for
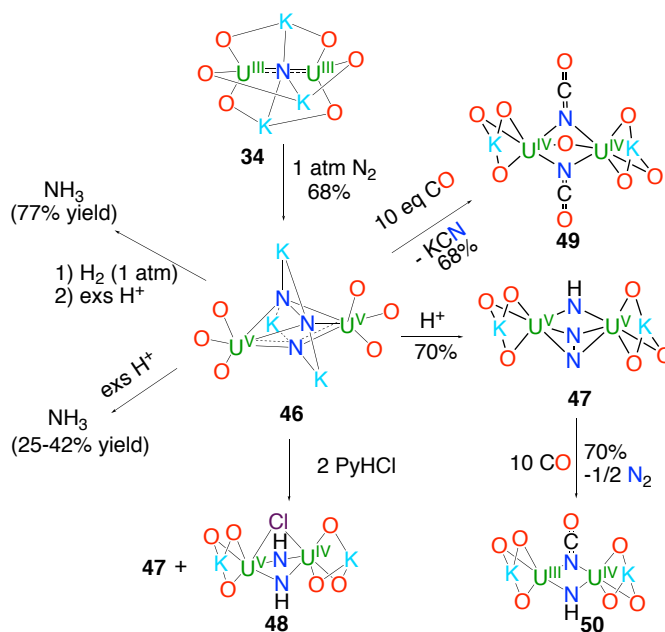
Scheme 22: Reactivity with N$_2$ of the diuranium (III) bridging nitride **34**., affording the nitride hydrazido bridged diuranium (V) complex **46** and its subsequent reactivity with H$^+$, CO, and H$_2$.

dinitrogen complexes of f-elements which usually undergo N$_2$ displacement upon addition of H$_2$ or CO.

The protonation reaction of the complex **46** with 1 equiv of 2,4,6-tri-tertbutylphenol led only to nitride protonation and to the formation of the mono protonated complex [K$_2$\{[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-NH)(μ-η^2:η^2-N$_2$)\}], **47**.

In contrast, when complex **46** is reacted with stronger acids such as PyHCl, HCl or HBAr^F, the protonation of the hydrazido ligand also occurs and crystals of the complex [K$_2$\{[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-NH)$_2$(μ-Cl)\}], **48** have been obtained. Moreover, when 20 equivs of PyHCl are added to complex **46** and d$_6$-dmso is added to the solid crude reaction mixture, ^{14}NH$_4$Cl can be identified in the reaction mixture by ^{1}H NMR spectroscopy. A mixture of ^{14}NH$_4$Cl and ^{15}NH$_4$Cl, distinguishable in the ^{1}H NMR spectrum by their different multiplicity, is observed when the reaction is repeated with [K$_3$\{[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-N)(μ-η^2:η^2-^{15}N$_2$)\}], ^{15}N-**46**, suggesting that the nitride and hydrazide groups can exchange. The yield in NH$_4^+$, detected by quantitative ^{1}H NMR spectroscopy, ranges from 25% to 42% depending on the acid used, but can be increased by performing a preliminary reduction of **46** with H$_2$. Hydrogenation of N$_2$ with H$_2$ is a highly desirable feature, even though it has been accomplished only for a few complexes. Complex **46** is completely consumed when exposed to 1 atm of H$_2$ at RT for 2-3 weeks. The ^{1}H NMR spectrum of the final reaction mixture is uninformative, and no NH$_3$ could be detected in the headspace of the reaction mixture. Nevertheless, when an excess of HCl in ethereal solution is added to the crude reaction mixture, quantitative ^{1}H NMR spectroscopy in d$_6$-dmso reveals the formation of NH$_4$Cl in 77% yield, suggesting that reactivity with H$_2$ actually affords the cleavage of the N-N single bond of the hydrazido ligand. [19d]

Reactivity of **46** and **47** with CO also provides the first examples of N functionalization of bound dinitrogen in f element complexes. The reaction of complex **46** (K$_2$UN(N$_2$)U) with an excess of CO affords the complex [K$_2${[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-O)(μ-NCO)$_2$}], **49** and the concomitant formation of KCN. Thus, both reductive carbonylation and cleavage of the CO triple bond are achieved by, respectively, the hydrazido and the nitride ligands. The reduced reactivity of the imido ligand in complex **47** compared to the nitride ligand in complex **46** leads to a different reactivity towards CO. In fact, the reaction of complex **47** with excess CO affords the mixed valent U(III)/U(IV) complex [K$_2${[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-NH)(μ-NCO)}], **50** and free N$_2$.[79] Thus, in this case, the addition of CO leads to disproportionation of the hydrazido ligand. Attempts to reduce **50** to regenerate the diuranium(III) complex **34** have not been successful so far. If such reduction could be easily performed, the catalytic generation of cyanate from CO and N$_2$ may become accessible.

Reactivity of Siloxide-Supported Uranium(III) Oxide Complexes

N$_2$ activation and functionalization by oxide bridged diuranium(III) complexes

The highly reducing nature of the [K$_2${[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-O)}], K$_2$U-O-U, **22** was evidenced by its reactivity with the inert N$_2$ molecule that affords the dinitrogen complex [K$_2${[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-O)(μ-η^2:η^2-N$_2$)}], **51**.[66] The N$_2$ binding and functionalization reactivity of **22** is summarized in Scheme 23.

The crystallographically determined N-N bond distance together with SQUID magnetometry measurements confirmed the nature of the U centres in **51** to be U(V), in agreement with the presence of a bound N$_2^{4-}$ ligand. These data suggest a similar degree of activation of the bound N$_2$ in **51** as that found in the nitride N$_2$ complex **46**. However, important differences were found in the reactivity of the bound dinitrogen. The reaction of **51** with 3 equivs of CO affords the formation of the complex [K$_2${[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-O)$_2$(μ-NCN)}], **52**.[66] Such a reactivity is different from the one observed for the complexes [K$_3${[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-N)(μ-η^2:η^2-N$_2$)}], **46**, and
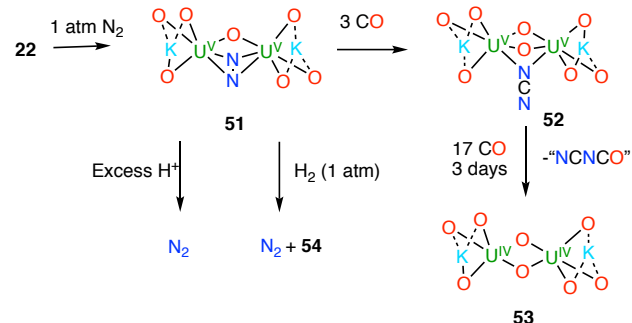
Scheme 23. Reactivity with N$_2$ of the diuranium (III) bridging oxo **22**, affording the oxo hydrazido bridged diuranium (V) complex **51** and its subsequent reactivity with CO, H$_2$, and H$^+$

[K$_2${[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-NH)(μ-η^2:η^2-N$_2$)}], **47**, in which the formation of cyanate ligands with concomitant reduction of the

U centres was observed. This novel reactivity suggests that the reduction of the U cations in complex **51** is less accessible, but, when an excess of CO (10-100 equivs) is added, the slow transformation into a new species is observed. In particular the bis U(IV) complex [K$_2${[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-O)}], **53** is formed. More surprising is the difference in reactivity compared to complex **46** observed for reactions with H$_2$ and H$^+$. In both cases, N$_2$ is released from the complex **51** and no NH$_3$ or NH$_4^+$ could be detected. In contrast when complex **46** is reacted with H$^+$, NH$_4^+$ is formed with a yield of 25-42% which is increased to 80% if **46** is pre-treated with H$_2$. Moreover, when complex **51** is reacted with 1 atm of H$_2$, release of N$_2$ and concomitant formation of the complex [K$_2${[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-O)(μ-H)$_2$}], **54** is observed (see following paragraph for the synthesis and characterization). Such a different reactivity is originated from important differences in the nature of bonding and in the electronic structure of the oxide and nitride complexes. Notably, the measurements of magnetic susceptibility in function of temperature show the presence of antiferromagnetic coupling between the two uranium ions of the nitride bridged complexes **34** and **46**, but show that the oxide bridged counterparts **22** and **51** behave as independent paramagnets. Moreover, computational studies show a different binding scheme for the two complexes, with a degree of covalency in the U-N$_{nitride}$ bonding but not in the U-O$_{oxo}$ one. Furthermore, while in complex **46** the nitride ligand does participate in the bonding and in the subsequent activation of N$_2$, the oxo ligand in complex **51** acts as a spectator ligand.

These results show that linkers used to build polymetallic uranium systems can have dramatic electronic effects in dinitrogen activation and functionalization. Cations may also play a role in tuning such differences in reactivity and should be further explored.

H$_2$ Cleavage by oxide bridged diuranium(III) complexes
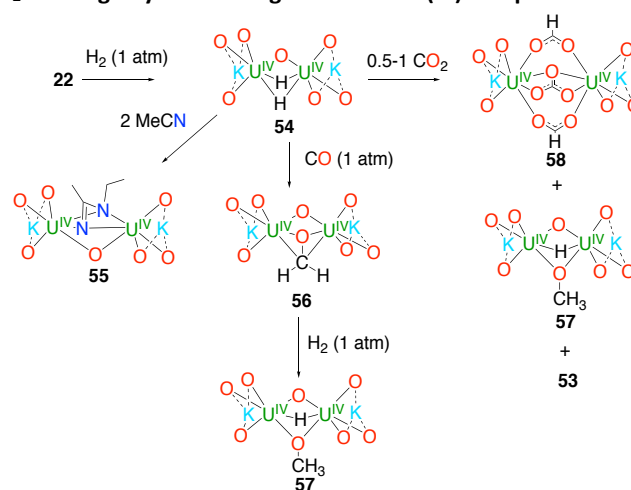
Scheme 24: H$_2$ cleavage by **22**, affording the oxo bis-hydride bridged diuranium (V) complex, **54** and its subsequent reactivity with CO, MeCN, and

Complex **54** is a rare example of a stable uranium(IV) bis-hydride that can be prepared from the reaction of **22** with 1 atm of H$_2$.[82] The bis hydride complex **54** shows a remarkable stability

towards H_2 release, making it an attractive candidate for being used in hydride transfer reactivity. Notably, the reaction of **54** with 2 equivs of MeCN afforded the complex $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}O)(\mu\text{-}\kappa^2\text{-}NC(CH_3)NCH_2CH_3)\}]$, **55** (Scheme 24) where the reductive coupling of two acetonitrile molecules has occurred following hydride transfer from the uranium to the nitrile. The reaction between complex **54** and 1 equiv of CO affords the oxomethylene complex $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}O)(\mu\text{-}CH_2O)\}]$, **56** trough the four-electron reduction of CO and the concomitant oxidation of the two hydride bridging ligands. Complex **56** was found to irreversibly cleave H_2 in ambient conditions to afford the methoxide complex $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}O)(\mu\text{-}H)(\mu\text{-}CH_3O)\}]$, **57** in 75% yield.[82]

Complex **54** also effect the direct reduction of CO_2 to methoxide which the first example of such reactivity in f-element chemistry.

These results show that polynuclear oxide-supported hydrides are excellent candidates for the conversion of CO and CO_2 to methoxide. These systems also provide competent models of the surface mediated hydride transfer to CO or CO_2 at metal oxide surfaces in the heterogeneously catalysed Fischer-Tropsch process. The transformation of H_2 an CO into methanol could be driven catalytically if conditions for the addition of H_2 to complex **57** could be identified.

Conclusions

The tris- tertbutoxysiloxide ligand has proven to be particularly well suited to support the formation of stable homo and heteropolymetallic complexes of uranium that have shown high ligand and metal-based reactivity towards small molecule fixation and functionalization. These simple ligands allow, by binding several metals, to build flexible frameworks for the multimetallic cooperative binding and activation of small molecules. The role of the ligand electronics and of nature of the counterion in reactivity remains ambiguous and comparative studies using other simple ligands and diverse counterions will be required to further understand it.

The presented results show that the reactivity of the uranium(III) complexes supported by siloxide ligands can be tuned simply by changing the number of ligands. We have shown that, in mononuclear complexes, the increase in number of ligands allows to increase the steric hindrance which does not result in reduced reactivity but facilitates the removal of the CO_2 or CS_2 reduction products from the uranium coordination sphere. These experiments suggest that catalytic cycles should be easily implemented without strong coordination of reduction products such as carbonate or thiocarbonate being a limitation. Analogous synthetic cycles were implemented for the reduction of CO_2 to carbonate and CO by uranium(III) complexes supported by bulky polydentate amine-phenolate ligands,[5a] but in the non-optimized conditions carbonate binding by uranium leads to insoluble products and to the termination of the cycle. Ideally, one should be able to drive such reactions electrochemically. The first example of the use uranium(III) compounds in electrocatalysis was recently reported for the H_2 production from H_2O[6] and it can be anticipated that use of uranium(III) compounds as electrocatalysts can be extended to CO_2 and N_2 reduction.

The use of simple nitride and oxide linkers for assembling compounds containing more than one uranium(III) centre allowed to demonstrate that an unique reactivity results from the cooperative binding of dinitrogen or hydrides by two uranium cations. Notably, the four electrons reduction of dinitrogen is promoted by both the oxo- and nitride bridged diuranium(III) complexes affording diuranium(V) complexes of N_2^{4-}. Moreover, it is remarkable that the uranium-bound dinitrogen can be functionalized by CO, CO_2 and even H_2 and in some cases results in the reduction of the uranium centers. In these stoichiometric processes, new molecules, such as cyanate and cyanamide, are built from readily available substrates (CO and N_2). Despite the fact that N_2 functionalization was also reported for group 4 metals,[81] the increased redox flexibility of uranium renders its compounds well suited for developing catalytic cycles (chemical and electrochemical). The nitride linker is involved in the reactivity of the dinuclear dinitrogen complexes but the more robust oxide linker may be implemented in catalytic cycles for the transformation of small molecules if the system electronics can be properly tuned.

Very recently, we have shown that replacement of siloxides with amide ligands leads to very different reactivity of the uranium bound nitride.[83] We foresee that a careful combined tuning of the electronics of the linkers and ancillary ligand should lead to systems where reducing reactants such as hydrogen or CO may be used to restore the uranium(III) precursor alone or in combination with reducing agents. Such studies should open the way to the development of uranium-based catalysts for dinitrogen functionalization and provide a better understanding of dinitrogen reduction by polymetallic compounds.

Conflicts of interest

"There are no conflicts to declare".

Acknowledgements

Notes and references

1.   (a)M. Aresta, *Carbon Dioxide as a Chemical Feedstock*, Wiley VCH, 2010; (b)E. E. Benson, C. P. Kubiak, A. J. Sathrum and J. M. Smieja, *Chem. Soc. Rev.*, 2009, **38**, 89-99.

2.   (a)H. Liu, T. Ghatak and M. S. Eisen, *Chem. Commun.*, 2017, **53**, 11278-11297; (b)A. R. Fox, S. C. Bart, K. Meyer and C. C. Cummins, *Nature*, 2008, **455**, 341-349.

3.   P. L. Arnold, S. M. Mansell, L. Maron and D. McKay, *Nat. Chem.*, 2012, **4**, 668-674.

4.   (a)I. Castro-Rodriguez, H. Nakai, L. N. Zakharov, A. L. Rheingold and K. Meyer, *Science*, 2004, **305**, 1757-1759; (b)A. S. P. Frey, F. G. N. Cloke, M. P. Coles, L. Maron and T. Davin, *Angew. Chem. Int. Ed. Engl.*, 2011, **50**, 6881-6883; (c)H. S. La Pierre and K. Meyer, in *Prog. Inorg. Chem.*, ed. K. D. Karlin, JOHN WILEY & SONS INC, HOBOKEN, 2014, vol. 58, pp. 303-415; (d)V. Mougel, C. Camp, J. Pecaut, C. Coperet, L. Maron, C. E. Kefalidis and M. Mazzanti, *Angew. Chem. Int. Ed. Engl.*, 2012, **51**, 12280-12284.

5.   (a)A. C. Schmidt, A. V. Nizovtsev, A. Scheurer, F. W. Heinemann and K. Meyer, *Chem. Commun.*, 2012, **48**, 8634-8636; (b)B. M. Gardner, J. C. Stewart, A. L. Davis, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Proc Natl Acad Sci USA*, 2012, **109**, 9265-9270.

6.   D. P. Halter, F. W. Heinemann, J. Bachmann and K. Meyer, *Nature*, 2016, **530**, 317-321.

7.   *Haber, F Ammonia German patent DE 229126 Pat.*, 1909.

8.   (a)P. L. Arnold and Z. R. Turner, *Nat. Rev. Chem.*, 2017, **1**; (b)P. L. Arnold, *Chem. Commun.*, 2011, **47**, 9005-9010; (c)B. M. Gardner and S. T. Liddle, *Eur. J. Inorg. Chem.*, 2013, **2013**, 3753-3770; (d)M. D. Walter, in *Advances in Organometallic Chemistry, Vol 65*, ed. P. J. Perez, 2016, vol. 65, pp. 261-377; (e)O. T. Summerscales and F. G. N. Cloke, in *Organometallic and Coordination Chemistry of the Actinides*, ed. T. E. AlbrechtSchmitt, 2008, vol. 127, pp. 87-117; (f)S. C. Bart and K. Meyer, in *Struct. Bond.*, 2008, vol. 127, pp. 119-176; (g)T. Andrea and M. S. Eisen, *Chem. Soc. Rev.*, 2008, **37**, 550-567; (h)S. T. Liddle, *Angew. Chem. Int. Ed. Engl.*, 2015, **54**, 8604-8641.

9.   (a)J. G. Brennan, R. A. Andersen and J. L. Robbins, *J. Am. Chem. Soc.*, 1986, **108**, 335-336; (b)J. Parry, E. Carmona, C. Simon and M. Hursthouse, *J. Am. Chem. Soc.*, 1995, **117**, 2649-2650; (c)W. J. Evans, S. A. Kozimor, G. W. Nyce and J. W. Ziller, *J. Am. Chem. Soc.*, 2003, **125**, 13831-13835.

10.   W. J. Evans, S. A. Kozimor and J. W. Ziller, *J. Am. Chem. Soc.*, 2003, **125**, 14264-14265.

11.   I. Castro-Rodriguez and K. Meyer, *J. Am. Chem. Soc.*, 2005, **127**, 11242-11243.

12.   O. T. Summerscales, A. S. P. Frey, F. Geoffrey, N. Cloke and P. B. Hitchcock, *Chem. Commun.*, 2009, 198-200.

13.   J. G. Brennan, R. A. Andersen and A. Zalkin, *Inorg. Chem.*, 1986, **25**, 1756-1760.

14.   O. T. Summerscales, F. G. N. Cloke, P. B. Hitchcock, J. C. Green and N. Hazari, *Science*, 2006, **311**, 829-831.

15.   P. Roussel and P. Scott, *J. Am. Chem. Soc.*, 1998, **120**, 1070-1071.

16.   P. L. Arnold, Z. R. Turner, R. M. Bellabarba and R. P. Tooze, *Chem. Sci.*, 2011, **2**, 77-79.

17.   O. T. Summerscales, F. G. N. Cloke, P. B. Hitchcock, J. C. Green and N. Hazari, *J. Am. Chem. Soc.*, 2006, **128**, 9602-9603.

18.   (a)S. M. Mansell, N. Kaltsoyannis and P. L. Arnold, *J. Am. Chem. Soc.*, 2011, **133**, 9036-9051; (b)G. Cloke, F. N. and P. B. Hitchcock, *J. Am. Chem. Soc.*, 2002, **124**, 9352-9353.

19.   (a)O. Cooper, C. Camp, J. Pécaut, C. E. Kefalidis, L. Maron, S. Gambarelli and M. Mazzanti, *J. Am. Chem. Soc.*, 2014, **136**, 6716-6723; (b)A. L. Odom, P. L. Arnold and C. C. Cummins, *J. Am. Chem. Soc.*, 1998, **120**, 5836-5837; (c)P. L. Arnold, C. J. Stevens, N. L. Bell, R. M. Lord, J. M. Goldberg, G. S. Nichol and J. B. Love, *Chem. Sci.*, 2017, **8**, 3609-3617; (d)M. Falcone, L. Chatelain, R. Scopelliti, I. Zivkovic and M. Mazzanti, *Nature*, 2017, **547**, 332-335.

20.   I. Korobkov, S. Gambarotta and G. P. A. Yap, *Angew. Chem. Int. Ed. Engl.*, 2002, **41**, 3433-3436.

21.   (a)P. T. Wolczanski, *Polyhedron*, 1995, **14**, 3335-3362; (b)D. R. Neithamer, R. E. Lapointe, R. A. Wheeler, D. S. Richeson, G. D. Vanduyne and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1989, **111**, 9056-9072; (c)C. Krempner, *Eur. J. Inorg. Chem.*, 2011, 1689-1698.

22.   (a)T. J. Boyle and L. A. M. Ottley, *Chem. Rev.*, 2008, **108**, 1896-1917; (b)A. Willauer, D. Toniolo, F. Fadaei-Tirani, Y. Yang, S. Laurent and M. Mazzanti, *J. Chem. Soc.-Dalton Trans.*, 2019, DOI: 10.1039/c1039dt00554d; (c)R. P. Kelly, D. Toniolo, F. F. Tirani, L. Maron and M. Mazzanti, *Chem. Commun.*, 2018, **54**, 10268-10271; (d)R. P. Kelly, L. Maron, R. Scopelliti and M. Mazzanti, *Angew. Chem. Int. Ed. Engl.*, 2017, **56**, 15663-15666; (e)J. Andrez, J. Pecaut, P.-A. Bayle and M. Mazzanti, *Angew. Chem. Int. Ed. Engl.*, 2014, **53**, 10448-10452; (f)D. Toniolo, A. Willauer, R. Scopelliti, J. Andrez, Y. Yang and L. Maron, *Chem. Eur. J.*, 2019; (g)V. Lorenz, A. Fischer, S. Giessmann, J. W. Gilje, Y. Gun'ko, K. Jacob and F. T. Edelmann, *Coord. Chem. Rev.*, 2000, **206**, 321-368; (h)G. Lapadula, M. P. Conley, C. Coperet and R. A. Andersen, *Organometallics*, 2015, **34**, 2271-2277.

23.   S. M. Mansell, J. H. Farnaby, A. I. Germeroth and P. L. Arnold, *Organometallics*, 2013, **32**, 4214-4222.

24.   (a)S. Lysenko, B. Haberlag, C. G. Daniliuc, P. G. Jones and M. Tamm, *Chemcatchem*, 2011, **3**, 115-118; (b)J. Jarupatrakorn and T. D. Tilley, *J. Chem. Soc.-Dalton Trans.*, 2004, 2808-2813; (c)K. L. Fujdala and T. D. Tilley, *Chem. Mater.*, 2001, **13**, 1817-1827; (d)F. Blanc, C. Coperet, J. Thivolle-Cazat, J. M. Basset, A. Lesage, L. Emsley, A. Sinha and R. R. Schrock, *Angew. Chem. Int. Ed. Engl.*, 2006, **45**, 1216-1220; (e)D. Werner and R. Anwander, *J. Am. Chem. Soc.*, 2018, **140**, 14334-14341; (f)K. L. Fujdala and T. D. Tilley, *Chem. Mater.*, 2004, **16**, 1035-1047; (g)M. P. Coles, C. G. Lugmair, K. W. Terry and T. D. Tilley, *Chem. Mater.*, 2000, **12**, 122-131.

25.   (a)J. Friedrich, Y. S. Qiao, C. Maichle-Mossmer, E. J. Schelter and R. Anwander, *J. Chem. Soc.-Dalton Trans.*, 2018, **47**, 10113-10123; (b)J. Friedrich, C. Maichle-Mossmer and R. Anwander, *Chem. Commun.*, 2017, **53**, 12044-12047; (c)M. Nishiura, Z. M. Hou and Y. Wakatsuki, *Organometallics*, 2004, **23**, 1359-1368; (d)Z. M. Hou and Y. Wakatsuki, *J. Organomet. Chem.*, 2002, **647**, 61-70; (e)A. Fischbach, M. G. Klimpel, M. Widenmeyer, E. Herdtweck, W. Scherer and R. Anwander, *Angew. Chem. Int. Ed. Engl.*, 2004, **43**, 2234-2239.

26.   C. Camp, L. Chatelain, C. E. Kefalidis, J. Pecaut, L. Maron and M. Mazzanti, *Chem. Commun.*, 2015, **51**, 15454-15457.

27. C. Camp, J. Pecaut and M. Mazzanti, *J. Am. Chem. Soc.*, 2013, **135**, 12101-12111.

28. C. Camp, C. E. Kefalidis, J. Pecaut, L. Maron and M. Mazzanti, *Angew. Chem. Int. Ed. Engl.*, 2013, **52**, 12646-12650.

29. C. Bianchini, C. Mealli, A. Meli, A. Orlandini and L. Sacconi, *Angewandte Chemie-International Edition in English*, 1979, **18**, 673-674.

30. (a)O. P. Lam and K. Meyer, *Polyhedron*, 2012, **32**, 1-9; (b)O. P. Lam, F. W. Heinemann and K. Meyer, *Angew. Chem. Int. Ed. Engl.*, 2011, **50**, 5965-5968.

31. O. P. Lam, L. Castro, B. Kosog, F. W. Heinemann, L. Maron and K. Meyer, *Inorg. Chem.*, 2012, **51**, 781-783.

32. C. Camp, O. Cooper, J. Andrez, J. Pecaut and M. Mazzanti, *J. Chem. Soc.-Dalton Trans.*, 2015, **44**, 2650-2656.

33. O. P. Lam, S. C. Bart, H. Kameo, F. W. Heinemann and K. Meyer, *Chem. Commun.*, 2010, **46**, 3137-3139.

34. (a)L. Castro, O. P. Lam, S. C. Bart, K. Meyer and L. Maron, *Organometallics*, 2010, **29**, 5504-5510; (b)L. Castro, C. E. Kefalidis, D. McKay, S. Essafi, L. Perrin and L. Maron, *J. Chem. Soc.-Dalton Trans.*, 2014, **43**, 12124-12134.

35. (a)N. Tsoureas, L. Castro, A. F. R. Kilpatrick, F. G. N. Cloke and L. Maron, *Chem. Sci.*, 2014, **5**, 3777-3788; (b)C. J. Inman, A. S. P. Frey, A. F. R. Kilpatrick, F. G. N. Cloke and S. M. Roe, *Organometallics*, 2017, **36**, 4539-4545; (c)A.-C. Schmidt, F. W. Heinemann, C. E. Kefalidis, L. Maron, P. W. Roesky and K. Meyer, *Chem. Eur. J.*, 2014, **20**, 13501-13506.

36. R. J. Kahan, J. H. Farnaby, N. Tsoureas, F. G. N. Cloke, P. B. Hitchcock, M. P. Coles, S. M. Roe and C. Wilson, *J. Organomet. Chem.*, 2018, **857**, 110-122.

37. (a)C. Camp, M. A. Antunes, G. Garcia, I. Ciofini, I. C. Santos, J. Pecaut, M. Almeida, J. Marcalo and M. Mazzanti, *Chem. Sci.*, 2014, **5**, 841-846; (b)D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Science*, 2012, **337**, 717-720; (c)J. G. Brennan and R. A. Andersen, *J. Am. Chem. Soc.*, 1985, **107**, 514-516; (d)D. S. J. Arney and C. J. Burns, *J. Am. Chem. Soc.*, 1993, **115**, 9840-9841; (e)I. Castro-Rodriguez and K. Meyer, *Chem. Commun.*, 2006, 1353-1368; (f)W. J. Evans and S. A. Kozimor, *Coord. Chem. Rev.*, 2006, **250**, 911-935; (g)C. R. Graves and J. L. Kiplinger, *Chem. Commun.*, 2009, 3831-3853.

38. S. Fortier, J. L. Brown, N. Kaltsoyannis, G. Wu and T. W. Hayton, *Inorg. Chem.*, 2012, **51**, 1625-1633.

39. A. J. Lewis, P. J. Carroll and E. J. Schelter, *J. Am. Chem. Soc.*, 2013, **135**, 511-518.

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

41. S. Gambarotta, F. Arena, C. Floriani and P. F. Zanazzi, *J. Am. Chem. Soc.*, 1982, **104**, 5082-5092.

42. M. Ephritikhine, *Coord. Chem. Rev.*, 2016, **319**, 35-62.

43. (a)O. P. Lam, F. W. Heinemann and K. Meyer, *Chem. Sci.*, 2011, **2**, 1538-1547; (b)J. L. Brown, G. Wu and T. W. Hayton, *Organometallics*, 2013, **32**, 1193-1198; (c)D. E. Smiles, G. Wu and T. W. Hayton, *New J. Chem.*, 2015, **39**, 7563-7566; (d)J. G. Brennan, R. A. Andersen and A. Zalkin, *Inorg. Chem.*, 1986, **25**, 1761-1765.

44. J. L. Brown, S. Fortier, R. A. Lewis, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2012, **134**, 15468-15475.

45. L. P. Spencer, P. Yang, B. L. Scott, E. R. Batista and J. M. Boncella, *Inorg. Chem.*, 2009, **48**, 11615-11623.

46. J. Andrez, J. Pecaut, R. Scopelliti, C. E. Kefalidis, L. Maron, M. W. Rosenzweig, K. Meyere and M. Mazzanti, *Chem. Sci.*, 2016, **7**, 5846-5856.

47. D. E. Smiles, G. Wu and T. W. Hayton, *Inorg. Chem.*, 2014, **53**, 12683-12685.

48. S. M. Franke, F. W. Heinemann and K. Meyer, *Chem. Sci.*, 2014, **5**, 942-950.

49. O. P. Lam, S. M. Franke, F. W. Heinemann and K. Meyer, *J. Am. Chem. Soc.*, 2012, **134**, 16877-16881.

50. R. P. Kelly, M. Falcone, C. A. Lamsfus, R. Scopelliti, L. Maron, K. Meyer and M. Mazzanti, *Chem. Sci.*, 2017, **8**, 5319-5328.

51. (a)L. Castro, O. P. Lam, S. C. Bart, K. Meyer and L. Maron, *Organometallics*, 2010, **29**, 5504-5510; (b)J. C. Berthet, M. Lance, M. Nierlich, J. Vigner and M. Ephritikhine, *J. Organomet. Chem.*, 1991, **420**, C9-C11; (c)A. S. P. Frey, F. G. N. Cloke, M. P. Coles and P. B. Hitchcock, *Chem. Eur. J.*, 2010, **16**, 9446-9448.

52. (a)A. G. Tskhovrebov, B. Vuichoud, E. Solari, R. Scopelliti and K. Severin, *J. Am. Chem. Soc.*, 2013, **135**, 9486-9492; (b)A. G. Tskhovrebov, E. Solari, M. D. Wodrich, R. Scopelliti and K. Severin, *Angew. Chem. Int. Ed. Engl.*, 2012, **51**, 232-234.

53. L. Barluzzi, L. Chatelain, F. Fadaei-Tirani, I. Zivkovic and M. Mazzanti, *Chem. Sci.*, 2019, **10**, 3543 - 3555.

54. T. D. Palluccio, E. V. Rybak-Akimova, S. Majumdar, X. C. Cai, M. G. Chui, M. Temprado, J. S. Silvia, A. F. Cozzolino, D. Tofan, A. Velian, C. C. Cummins, B. Captain and C. D. Hoff, *J. Am. Chem. Soc.*, 2013, **135**, 11357-11372.

55. W. J. Evans, S. A. Kozimor and J. W. Ziller, *Polyhedron*, 2004, **23**, 2689-2694.

56. N. N. Krot and M. S. Grigoriev, *Russ. Chem. Rev.*, 2004, **73**, 89-100.

57. (a)J. G. Brennan, R. A. Andersen and A. Zalkin, *J. Am. Chem. Soc.*, 1988, **110**, 4554-4558; (b)L. P. Spencer, E. J. Schelter, P. Yang, R. L. Gdula, B. L. Scott, J. D. Thompson, J. L. Kiplinger, E. R. Batista and J. M. Boncella, *Angew. Chem. Int. Ed. Engl.*, 2009, **48**, 3795-3798.

58. (a)V. Mougel, J. Pecaut and M. Mazzanti, *Chem. Commun.*, 2012, **48**, 868-870; (b)V. Mougel, P. Horeglad, G. Nocton, J. Pécaut and M. Mazzanti, *Chem. Eur. J.*, 2010, **16**, 14365-14377; (c)P. L. Arnold, J. B. Love and D. Patel, *Coord. Chem. Rev.*, 2009, **253**, 1973-1978.

59. (a)T. W. Hayton, *Chem. Commun.*, 2013, **49**, 2956-2973; (b)D. M. King and S. T. Liddle, *Coord. Chem. Rev.*, 2014, **266**, 2-15.

60. G. W. C. Silva, C. B. Yeamans, A. P. Sattelberger, T. Hartmann, G. S. Cerefice and K. R. Czerwinski, *Inorg. Chem.*, 2009, **48**, 10635-10642.

61. (a)G. Nocton, J. Pecaut and M. Mazzanti, *Angew. Chem. Int. Ed. Engl.*, 2008, **47**, 3040-3042; (b)W. J. Evans, S. A. Kozimor and J. W. Ziller, *Science*, 2005, **309**, 1835-1838.

62. A. R. Fox, P. L. Arnold and C. C. Cummins, *J. Am. Chem. Soc.*, 2010, **132**, 3250-3251.

63.   (a)S. Fortier, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2010, **132**, 6888-6889; (b)L. Maria, I. C. Santos, V. R. Sousa and J. Marcalo, *Inorg. Chem.*, 2015, **54**, 9115-9126; (c)D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Nat. Chem.*, 2013, **15**, 482-488; (d)D. M. King, J. McMaster, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake and S. T. Liddle, *J. Am. Chem. Soc.*, 2014, **136**, 5619-5622; (e)P. A. Cleaves, D. M. King, C. E. Kefalidis, L. Maron, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Angew. Chem. Int. Ed. Engl.*, 2014, **53**, 10412-10415; (f)L. Chatelain, R. Scopelliti and M. Mazzanti, *J. Am. Chem. Soc.*, 2016, **138**, 1784-1787; (g)D. M. King, P. A. Cleaves, A. J. Wooles, B. M. Gardner, N. F. Chilton, F. Tuna, W. Lewis, E. J. L. McInnes and S. T. Liddle, *Nat. Commun.*, 2016, **7**; (h)N. Tsoureas, A. F. R. Kilpatrick, C. J. Inman and F. G. N. Cloke, *Chem. Sci.*, 2016, **7**, 4624-4632.

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

65.   J. Du, D. M. King, L. Chatelain, F. Tuna, E. J. L. McInnes, A. J. Wooles, L. Maron and S. T. Liddle, *Chem. Sci.*, 2019, **10**, 3738-3745.

66.   M. Falcone, L. Barluzzi, J. Andrez, F. F. Tirani, I. Zivkovic, A. Fabrizio, C. Corminboeuf, K. Severin and M. Mazzanti, *Nat. Chem.*, 2019, **11**, 154–160.

67.   S. D. Roughley and A. M. Jordan, *J. Med. Chem.*, 2011, **54**, 3451-3479.

68.   M. Aresta and A. Dibenedetto, *J. Chem. Soc.-Dalton Trans.*, 2007, 2975-2992.

69.   (a)R. J. Burford and M. D. Fryzuk, *Nature Reviews Chemistry*, 2017, **1**, Article Number: UNSP 0026; (b)M. P. Shaver and M. D. Fryzuk, *Adv. Synth. Catal.*, 2003, **345**, 1061-1076.

70.   (a)D. J. Knobloch, E. Lobkovsky and P. J. Chirik, *Nat. Chem.*, 2010, **2**, 30-35; (b)M. D. Fryzuk, J. B. Love, S. J. Rettig and V. G. Young, *Science*, 1997, **275**, 1445-1447.

71.   (a)S. P. Semproni and P. J. Chirik, *J. Am. Chem. Soc.*, 2013, **135**, 11373-11383; (b)S. P. Semproni and P. J. Chirik, *Angew. Chem. Int. Ed. Engl.*, 2013, **52**, 12965-12969; (c)J. S. Silvia and C. C. Cummins, *J. Am. Chem. Soc.*, 2010, **132**, 2169-2170; (d)J. M. Smith, *Prog. Inorg. Chem.*, 2014, **58**, 417-470.

72.   (a)B. Askevold, J. T. Nieto, S. Tussupbayev, M. Diefenbach, E. Herdtweck, M. C. Holthausen and S. Schneider, *Nat. Chem.*, 2011, **3**, 532-537; (b)J. J. Scepaniak, R. P. Bontchev, D. L. Johnson and J. M. Smith, *Angew. Chem. Int. Ed. Engl.*, 2011, **50**, 6630-6633; (c)B. L. Tran, M. Singhal, H. Park, O. P. Lam, M. Pink, J. Krzystek, A. Ozarowski, J. Telser, K. Meyer and D. J. Mindiola, *Angew. Chem. Int. Ed. Engl.*, 2010, **49**, 9871-9875; (d)J. S. Silvia and C. C. Cummins, *J. Am. Chem. Soc.*, 2009, **131**, 446-447; (e)S. P. Semproni, C. Milsmann and P. J. Chirik, *Angew. Chem. Int. Ed. Engl.*, 2012, **51**, 5213-5216.

73.   I. Klopsch, M. Kinauer, M. Finger, C. Wurtele and S. Schneider, *Angew. Chem. Int. Ed. Engl.*, 2016, **55**, 4786-4789.

74.   P. A. Cleaves, C. E. Kefalidis, B. M. Gardner, F. Tuna, E. J. L. McInnes, W. Lewis, L. Maron and S. T. Liddle, *Chem. Eur. J.*, 2017, **23**, 2950-2959.

75.   J. A. Buss and T. Agapie, *Nature*, 2016, **529**, 72-75.

76.   J. Schoffel, A. Y. Rogachev, S. D. George and P. Burger, *Angew. Chem. Int. Ed. Engl.*, 2009, **48**, 4734-4738.

77.   M. Falcone, L. Chatelain and M. Mazzanti, *Angew. Chem. Int. Ed. Engl.*, 2016, **55**, 4074-4078.

78.   (a)M. P. Shaver and M. D. Fryzuk, *J. Am. Chem. Soc.*, 2005, **127**, 500-501; (b)S. D. Brown, M. P. Mehn and J. C. Peters, *J. Am. Chem. Soc.*, 2005, **127**, 13146-13147.

79.   M. Falcone, L. N. Poon, F. F. Tirani and M. Mazzanti, *Angew. Chem. Int. Ed. Engl.*, 2018, **57**, 3697-3700.

80.   D. Panthi, O. Adeyiga, N. K. Dandu and S. O. Odoh, *Inorg. Chem.*, 2019, **58**, 6731-6741.

81.   Y. Ohki and M. D. Fryzuk, *Angew. Chem. Int. Ed. Engl.*, 2007, **46**, 3180-3183.

82.   M. Falcone, R. Scopelliti and M. Mazzanti, *J. Am. Chem. Soc.*, 2019, **141**, 9570-9577.

83.   C. T. Palumbo, L. Barluzzi, R. Scopelliti, I. Zivkovic, A. Fabrizio, C. Corminboeuf and M. Mazzanti, *Chem. Sci.*, 2019, https://doi.org/10.1039/C1039SC02149C.

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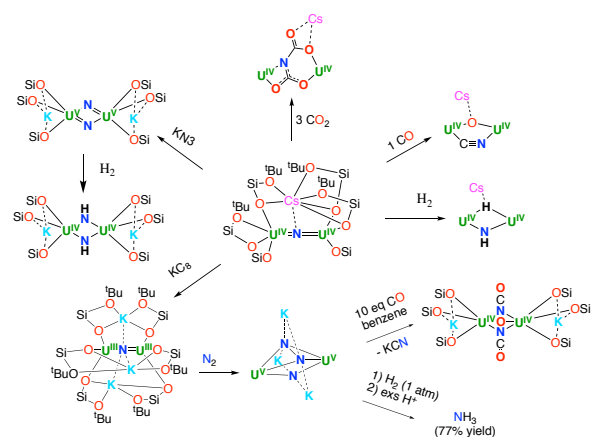
An overview of the small molecule activation chemistry of polynuclear complexes of uranium supported by the tert-butoxysiloxide ligand.