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Uranium triamidoamine chemistry

Benedict M. Gardner and Stephen T. Liddle*

Triamidoamine (Tren) complexes of the p- and d-block elements have been well-studied, and they display a diverse array of chemistry of academic, industrial and biological significance. Such in-depth investigations are not as widespread for Tren complexes of uranium, despite the general drive to better understand the chemical behaviour of uranium by virtue of its fundamental position within the nuclear sector. However, the chemistry of Tren–uranium complexes is characterised by the ability to stabilise otherwise reactive, multiply bonded main group donor atom ligands, construct uranium–metal bonds, promote small molecule activation, and support single molecule magnetism, all of which exploit the steric, electronic, thermodynamic and kinetic features of the Tren ligand system. This *Feature Article* presents a current account of the chemistry of Tren–uranium complexes.

Introduction

The chemistry of *N*-alkyl, -aryl or -silyl substituted triamidoamine (Tren) ligands, Fig. 1, is well known, given their significance as supporting ligands for intermediates for ceramic materials and semiconductors, biomimetic models, extraction agents, superbases and homogeneous catalysts.[1] In particular, transition metal–Tren complexes, of which a search of the Cambridge Structural Database returns ~400 results,[2] are significant as they are able to capture otherwise reactive moieties, as demonstrated by the wide array of examples of Tren-complexes featuring multiple bonds between a metal ion and a main group donor atom.[3]

Terminal metal–carbon double and triple bonds have been stabilised in the form of tantalum alkylidene and tungsten carbyne complexes featuring Tren frameworks (**I** and **II**, Fig. 2).[4] Multiply-bonded transition metal–nitrogen fragments have been the focus of much attention due to their biological significance. In particular, it has been shown that a number of parent or substituted imides, nitrides, diazenides and hydrazenides can all be accessed; of note was the landmark report of the first molecular catalytic reduction of dinitrogen to ammonia employing sterically demanding Tren-derivatives in complexes of molybdenum(III) in which dinitrogen adducts are implicated (*e.g.* **III**, Fig. 2).[5] A handful of Tren–transition metal complexes featuring multiply bound heavier pnictides in the form of phosphinidenes, phosphidos, arsenidos and stibidos have been reported (**IV–VII**, Fig. 2), demonstrating the versatility of Tren at

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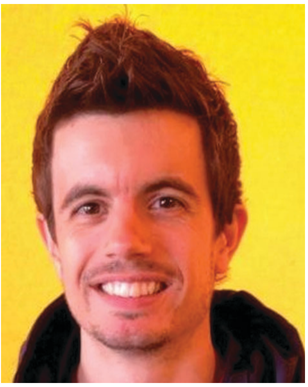


Benedict M. Gardner

Ben Gardner completed his MSci and PhD degrees at the University of Nottingham, UK, the latter in 2012 under the supervision of Steve Liddle, where he investigated the organometallic chemistry of uranium supported by sterically demanding Tren ligands. He has since been undertaking post-doctoral research with Steve Liddle investigating low-valent uranium activation chemistry of small molecules. He has 14 publications to date.

Stephen T. Liddle

Steve Liddle obtained his BSc (Hons) in 1997 and PhD in 2000 from Newcastle University. After post-doctoral fellowships at the Universities of Edinburgh, Newcastle, and Nottingham, he took up a Royal Society University Research Fellowship at Nottingham where he is currently a Professor of Inorganic Chemistry. His research interests include metal–ligand multiple bonding, metal–metal bonds, small molecule activation, and single molecule magnetism of the f-block elements, with a particular focus on uranium. He has published over 140 papers, reviews, and book chapters to date.

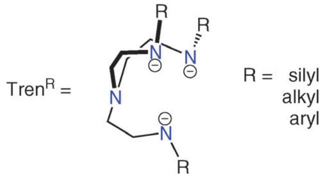


Fig. 1 The generic Tren–ligand framework.

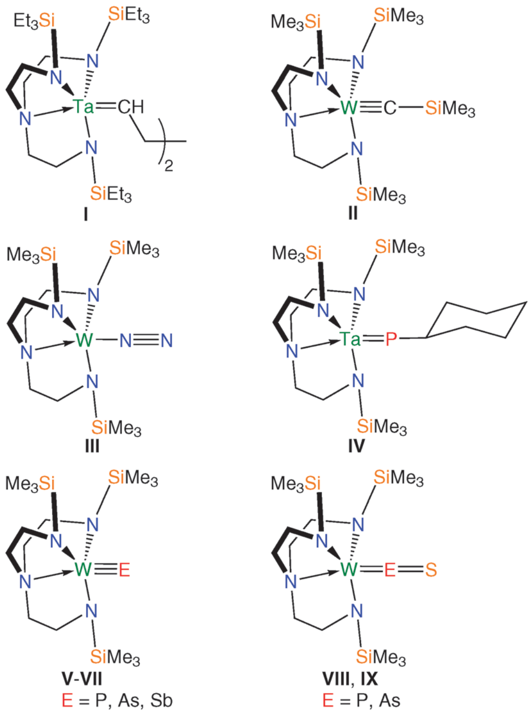


Fig. 2 Selected examples of Tren–transition metal complexes supporting novel linkages.

stabilising unusual and reactive multiply-charged main group ligands.[5k,7] Such systems have established routes to metal-bound main group fragments and terminal Tren–transition metal–pnitctide/chalcogenide complexes featuring M═O/Se/Te/PS/AsS multiple bonds (*e.g.* **VIII**, **IX**, Fig. 2) that would otherwise be challenging to directly construct.[4b,5k,6]

Reports of Tren–uranium compounds have demonstrated that the [U(Tren^R)] fragment is robust, stabilising reactive functionalities yet permitting further reactivity in the auxiliary coordination sphere. The chemical reactivity profile of Tren–uranium compounds complements structurally related uranium tris(pyrrolyl-α-methyl)amine[7] and uranium polyaryloxide or polyamide systems, which are increasingly well explored.[8–10] As this *Feature Article* will describe, the use of Tren ligands can lead to novel types of reactivity at uranium, ascribed to a combination of the chelate effect, facial coordination of the ligating atoms and tuneable steric demands *via* variation of the amido substituents.[11] Furthermore, it is becoming apparent that the tertiary amine centre of Tren can play a role in the electronic stabilisation of multiply bonded main group donor atoms that reside *trans* to the amine centre.

This *Feature Article* will systematically guide the reader through the Tren–uranium chemistry published in the primary scientific literature with an emphasis on structurally characterised compounds. It is organised firstly by common precursor compounds, then by the group number of the principal donor atom in the ligand under consideration that is coordinated to uranium, then small molecule activation chemistry before lastly covering uranium–transition metal systems (sub-organised by group number). The field of Tren–uranium chemistry can justifiably be described as burgeoning simply by the diverse array of fragments from across the p- and d-block that Tren^R–uranium has been shown to stabilise in recent years.

Tren–uranium precursor complexes

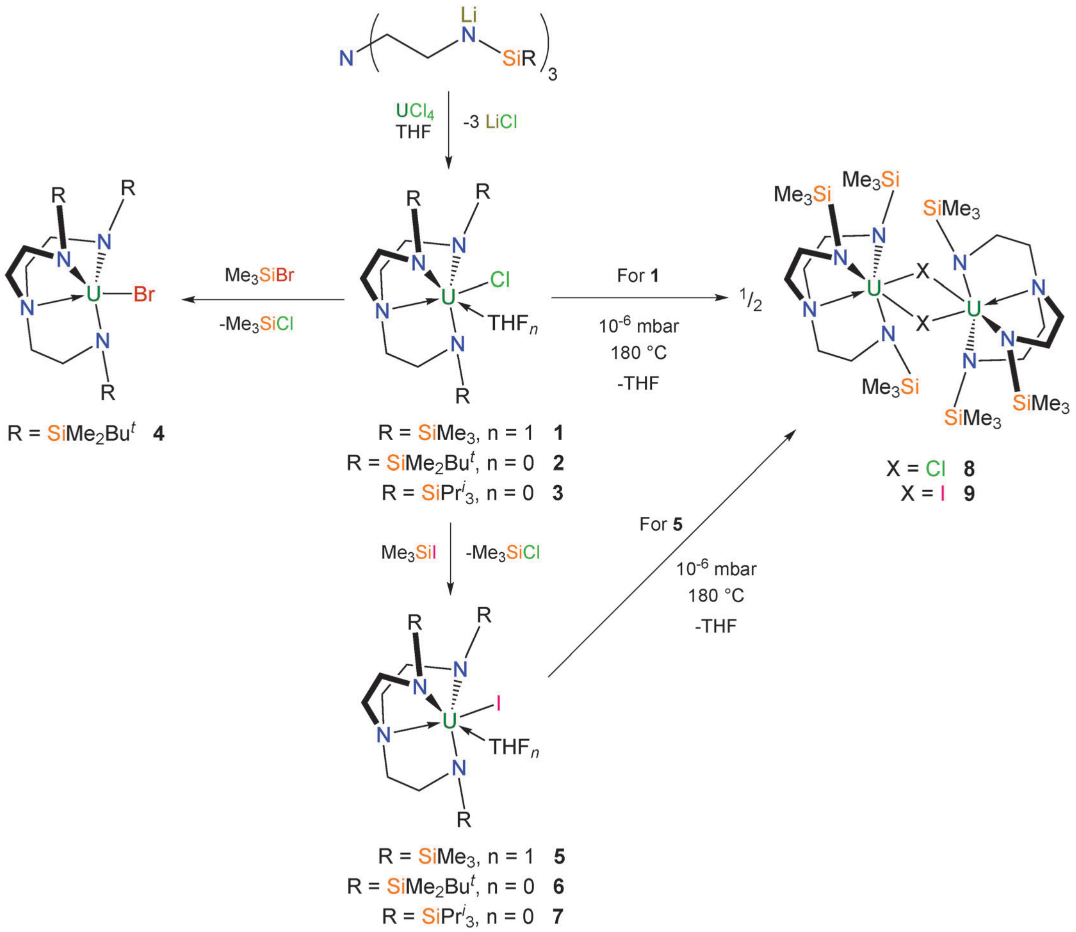
Halide derivatives

The Tren ligand is conveniently introduced into the coordination sphere of uranium *via* salt metathesis of uranium tetrachloride with the appropriate trilithiated Tren proligand, [Li_3Tren^R].[5b,12] This gives the pale green Tren–uranium(IV) chloride complexes **1–3** (Scheme 1).[12b,13] Conversion of **2** into the dark green bromo congener **4** can be achieved by treatment with Me_3SiBr,[13b] and the pale green iodo complexes **5–7** analogously with Me_3SiI.[13b,14] Complexes **1–6** are all structurally characterised, and are mononuclear in the solid state. Tren^{TMS}–uranium(IV) halide complexes **1** and **5** crystallise as THF solvates with one molecule of coordinated THF per uranium that can be removed by sublimation (180 °C, 10^{-6} mbar) to afford yellow **8** and **9**, respectively, each of which exhibit dimeric solid state structures with bridging halide centres.[15]

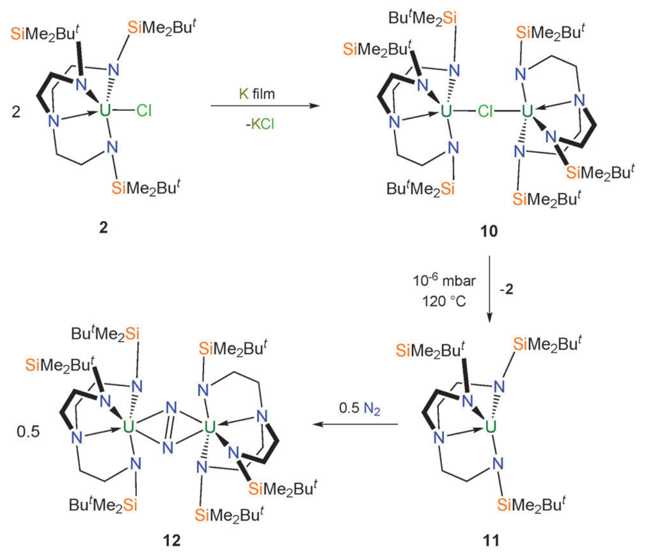
Uranium(III) derivatives

Reduction of **2** over a potassium mirror affords the dark purple mixed-valent uranium(III/IV) bridging chloride complex [{U(Tren^{DMBS})}$_2$(μ-Cl)] (**10**) (Scheme 2),[16] as determined by a single crystal X-ray diffraction (XRD) experiment. Careful sublimation of **10** at 120 °C and 10^{-6} mbar affords a dark purple solid characterised as the trivalent complex [U(Tren^{DMBS})] (**11**), and if heated up to 180 °C pale green **3** is recovered. It has also been shown that **11** can be independently prepared from **6** by reduction over a potassium mirror.[17]

Very early on the potential novelty of Tren–uranium complexes was highlighted by the observation that freeze–thaw degassed solutions of **11** placed under an atmosphere of dinitrogen change colour from purple to red. The identity of the new complex was confirmed by a structural determination, performed on dark red crystals grown from pentane, to be the novel side-on bridging dinitrogen complex [{U(Tren^{DMBS})}$_2$(μ-η^2:η^2-N_2)] (**12**), which was the first f-block dinitrogen complex.[18] Inspection of the characterisation data for **12** initially suggested a U^{III}–N_2–U^{III} bonding picture with no increase in valency for the uranium centres and a neutral N_2 ligand; however, with advances in computational and spectroscopic techniques it was later suggested that in fact the solid state data for **12** were somewhat misleading and a more likely bonding situation is that of a reduced N_2 unit coordinated to



Scheme 1 Synthesis of **1–9**.



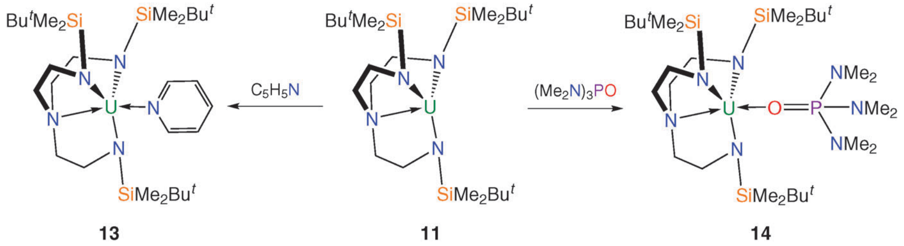
Scheme 2 Synthesis of **10–12**.

uranium(IV) centres consistent with U → N_2 backbonding.[18,19] This has since been supported by additional examples of diuranium–dinitrogen complexes that have been characterised by Raman spectroscopy, which is regarded as the best probe of the dinitrogen unit and thus uranium oxidation state in this context.[20]

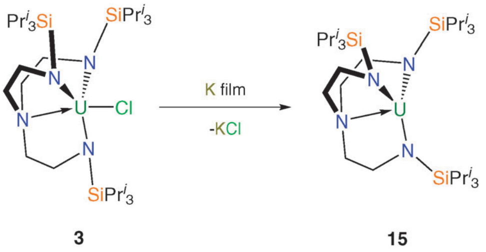
Treatment of trivalent **11** with neutral Lewis bases such as pyridine and hexamethylphosphoramide [$(Me_2N)_3PO$, HMPA] produces colour changes from purple to orange and black, respectively, affording [U(Tren^{DMBS})(C_5H_5N)] (**13**) and [U(Tren^{DMBS})-{OP(NMe_2)$_3$}] (**14**), Scheme 3. The molecular structure of **14** was confirmed by a single crystal XRD study, and although **13** was not structurally characterised, its analytical data support its proposed formulation.[17]

The HMPA molecule in **14** coordinates through the oxygen atom; the NMR and absorption spectra for **13** and **14** are typical of uranium(III) species. Given the extreme sensitivity to air and moisture of **11**, and indeed its highly reactive nature generally as exemplified by the formation of **12**, a significant increase in stability was observed for the adducts **13** and **14**.

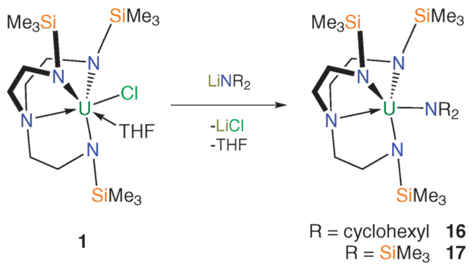
Analogously to **11**, [U(Tren^{TIPS})] (**15**) was prepared in a straightforward manner from potassium reduction of **3** (Scheme 4) although notably the reduction proceeds cleanly to completion from U(IV) to U(III) without the formation of mixed valent species.[12b] Surprisingly given the expected coordinative unsaturation, the solid state structure of **15** has been shown not to feature any U···HC agostic interactions and reveals a well-defined axial steric 'pocket'. In contrast to **11**, there is no evidence that **15** reacts with dinitrogen,



Scheme 3 Synthesis of **13** and **14**.



Scheme 4 Synthesis of **15**.



Scheme 5 Synthesis of **16** and **17**.

presumably because the steric bulk of the $\mathrm{Tren^{TIPS}}$ precludes side-on binding of dinitrogen.

Amide derivatives

Tren–uranium amide complexes have found utility as precursors to a range of novel Tren–uranium complexes, usually as protonolysis reagents. Treatment of **1** with one equivalent of lithium dicyclohexylamide or lithium bis(trimethylsilyl)amide afforded – after workup and recrystallisation from hexane – yellow crystals of solvent-free $[\mathrm{U(Tren^{TMS})(NR_2)}]$ (R = cyclohexyl, **16**; R = $\mathrm{SiMe_3}$, **17**), Scheme 5.[15b] Single-crystal XRD studies confirmed the molecular structures of **16** and **17**, which were found to be as expected with the $\mathrm{NR_2}$ units adopting trigonal planar geometries suggesting likely π-base character.

Tren–uranium – group 13 derivatives

Borate derivatives

The single example of a Tren–uranium tetrahydroborato derivative was reported in 1995.[21] It was prepared in THF by treatment of the corresponding uranium(IV) chloride, **8**, with one equivalent of lithium tetrahydroborate per uranium and crystallised from pentane. A single crystal XRD study determined the structure to be $[\mathrm{U(Tren^{TMS})\{(\mu\text{-}H)_3BH\}(THF)}]$ (**18**), Fig. 3, which includes a coordinated molecule of THF. Whilst the hydride atoms of the tetrahydroborate ligand were not located by the diffraction experiment, the assignment of the $(\mu\text{-H})_3\mathrm{BH}$ coordination mode is supported by the U–B distance of 2.68(2) Å and IR data.

Tetraarylborate complexes can be more desirable borate synthetic precursors than tetrahydroborates in view of the reduced capacity for coordination of the aryl units to the uranium centre relative to borohydrides; the former are out-competed by Lewis bases such as THF and therefore should be removed more easily than the latter. Since it is known that Tren–uranium halide complexes do not react with tetraarylborate sources such as $\mathrm{KBPh_4}$, amine or alkane elimination methodologies have been employed to access Tren–uranium tetraarylborates.[15b] Either of the two $\mathrm{Tren^{TMS}}$–uranium(IV) amide complexes $[\mathrm{U(Tren^{TMS})(NR_2)}]$ (R = cyclohexyl, trimethylsilyl)[15b] can be treated with $[\mathrm{Et_3NH}][\mathrm{BPh_4}]$ to afford, after work up, the target separated ion pair complex $[\mathrm{U(Tren^{TMS})(THF)_2}][\mathrm{BPh_4}]$ (**19**) as a free-flowing green powder from hexanes in 95% yield (Scheme 6).

A single crystal XRD experiment was conducted on a yellow-green crystal of **19** grown from toluene, which confirmed it to be a separated ion pair complex, with no contacts between the cation and anion, incorporating two molecules of coordinated THF. The cationic nature of the uranium-containing fragment in **19** is supported by inspection of the $\mathrm{U–N_{amide}}$ bond lengths; the mean $\mathrm{U–N_{amide}}$ distance of 2.238(3) Å compares to the mean $\mathrm{U–N_{amide}}$ distance of 2.253(8) Å in **5**[14a] and is consistent with the cationic nature of the $\mathrm{Tren^{TMS}}$–uranium(IV) fragment.

Due to the potential for the tetraphenylborate anion to engage in side reactions[22] the more robust $[\mathrm{BAr^f_4}]^-$ $[\mathrm{Ar^f} = 3,5\text{-}(\mathrm{CF_3})_2\text{–}\mathrm{C_6H_3}]$ anion was investigated as an alternative non-coordinating anion *via* the target complex $[\mathrm{U(Tren^{TMS})(THF)_2}][\mathrm{BAr^f_4}]$. Analogously to **19**, treatment of the amides with $[\mathrm{Et_3NH}][\mathrm{BAr^f_4}]$ in THF (Scheme 6) afforded an oily yellow-brown product to which was added one equivalent of **1**, in the anticipation that a coordinated THF molecule would be displaced and the second uranium centre would bind

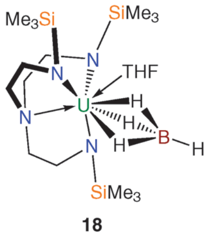
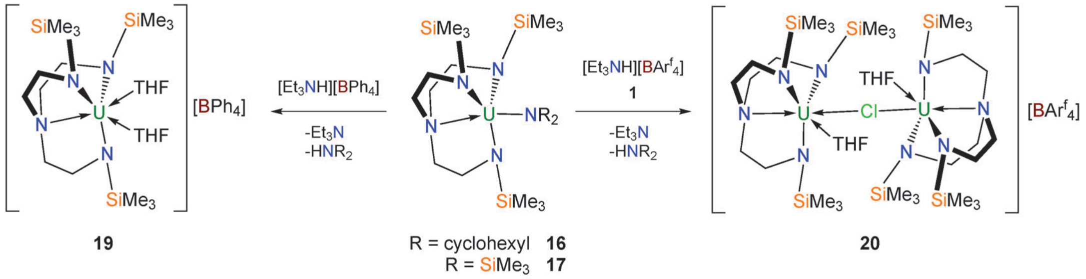


Fig. 3 Molecular structure of **18**.



Scheme 6 Synthesis of **19** and **20**. $Ar^f = 3,5-(CF_3)_2-C_6H_3$.

via a bridging chloride to give an isolable complex. Accordingly the cationic separated ion pair complex $[\{U(Tren^{TMS})(THF)\}_2(\mu\text{-Cl})][BAr^f_4]$ (**20**) was isolated as pale green crystals, confirmed by a structural determination.[15b] The dinuclear uranium(IV) cationic component consists of two essentially identical $[U(Tren^{TMS})(THF)]^+$ units bridged by a chloride anion whose U–Cl bond distances are not equivalent [2.887(2) and 2.918(2) Å], which suggests that the chloride is not equally associated with the uranium centres.

Tren–uranium tetraphenylborate complexes were targeted *via* alkyl precursors, namely $[U\{N(CH_2CH_2NSiMe_2Bu^t)_2(CH_2CH_2NSiMeBu^tCH_2)\}]$[23] (**21**) and $[U\{N(CH_2CH_2NSiPr^i_3)_2(CH_2CH_2NSiPr^i_2C[H]MeCH_2)\}]$ (**22**).[24] Treatment of **21** and **22** with $[Et_3NH][BPh_4]$ yielded the cationic complexes $[(Tren^{DMBS})U(MeCN)_2][BPh_4]$ (**23**) and $[(Tren^{TIPS})U(THF)][BPh_4]$ (**24**), after addition of donor solvents respectively, as a pale green solids in near-quantitative yield (Scheme 7).

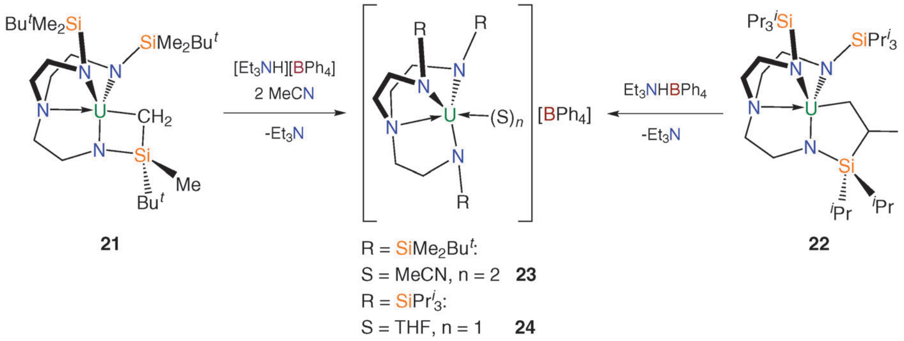
Following work-up, the green-brown solid produced from the reaction of $[U\{N(CH_2CH_2NSiMe_2Bu^t)_2(CH_2CH_2NSiMeBu^tCH_2)\}]$, **21**, with triethylammonium tetraphenylborate appeared to be consistent with the formation of "$[U(Tren^{DMBS})(THF)][BPh_4]$" by inspection of its ^1H NMR spectrum, but persistent impurities precluded any further analysis and slowly cooled saturated solutions of this solid in THF afforded oily material. However, dissolution in a toluene–acetonitrile mix resulted in the formation of a yellow-brown solution which upon cooling yielded green-brown crystals suitable for a single crystal X-ray diffraction study, revealing the bis(acetonitrile) complex **23**. The solid state structure of **23** consists of a $[U(Tren^{DMBS})(NCMe)_2]^+$ cation exhibiting the expected contraction of the U–N bond distances [$U–N_{amide}$ 2.220(6) Å (av.), $U–N_{amine}$ 2.577(6) Å and $U–N_{nitrile}$ 2.595(7) Å (av.)] relative to many comparable neutral Tren–uranium systems. The structure of **23** also features a non-coordinated tetraphenylborate anion.[25]

The solid state structure of **24** could not be ascertained by XRD due its oily nature, however it could be deduced from the ^1H NMR spectrum and the elemental microanalysis data for **24** that one molecule of coordinated THF is present in the complex and there is no evidence of any contacts to the uranium centre from the tetraphenylborate anion.[24]

Gallyl derivatives

In 2009 the isolation and characterisation of the first actinide–group 13 complex to exhibit both σ- and π-components in the metal–metal bond was reported.[13a,26] Prepared from an equimolar mixture of **1** and $[K\{Ga(NArCH)_2\}(TMEDA)]$ ($Ar = 2,6\text{-}^iPr_2\text{–}C_6H_3$; $TMEDA = Me_2NCH_2CH_2NMe_2$)[27] in THF, the target Tren–uranium(IV) gallyl complex $[U(Tren^{TMS})\{Ga(NArCH)_2\}(THF)]$ (**25**), Fig. 4, was characterised by a single crystal XRD study that revealed two crystallographically independent molecules of **25** in the asymmetric unit, each with slightly different U–Ga bond lengths [3.221(2) and 3.298(2) Å].

Both U–Ga bond distances are slightly longer than the sum of the covalent radii of U and Ga (3.18 Å),[28] which may be a consequence of the high steric demands of the gallyl and $Tren^{TMS}$ components. Although undoubtedly a weak and highly polarised U–Ga bond, a DFT study of a closely related model complex revealed not only a σ-interaction but also a π-component to the uranium–gallium bond; the latter interaction is characterised by donation of nitrogen lone pairs into the vacant gallyl p-orbital



Scheme 7 Synthesis of **23** and **24**.

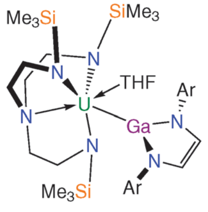


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Fig. 4 Molecular structure of **25**.

with subsequent donation to uranium. Additionally, **25** represents a model for the as yet unknown isolobal [U(IV)–CO$^{-\bullet}$] fragment.

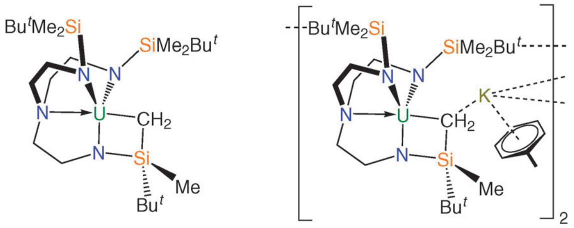
Tren–uranium – group 14 complexes

Alkyl, acetylide, and cyclometallate derivatives

The monomeric metallacyclic uranium(IV) alkyl complex [U{N(CH$_2$CH$_2$NSiMe$_2$Bu^t)$_2$(CH$_2$CH$_2$NSiMeBu^{t}CH$_2$)}] (**21**), Fig. 5,[23,29] was initially prepared by treatment of **2** with a range of lithium, potassium, magnesium and zinc alkyls in pentane to give brown solutions from which extremely air-sensitive orange-brown crystals of **21** could be isolated. However, optimum yields (*ca.* 70%) were later obtained by the reaction of the iodide derivative **6** with stoichiometric quantities of diethylzinc, neopentyllithium or benzylpotassium in toluene. The molecular structure of **21** was determined by a single crystal XRD experiment, which revealed a U–C bond, which at 2.752(11) Å is amongst the longest U–C σ-bonds reported and this is probably a consequence of its incorporation within a highly strained four-membered [U–N–Si–C] metallacyclic ring.

The attempted reduction of **6** in toluene by a potassium film unexpectedly afforded the bimetallic metallacyclic anion [{(K[η^6-C$_6$H$_5$Me])(U[N{CH$_2$CH$_2$NSiMe$_2$Bu^t}$_2${CH$_2$CH$_2$NSiMeBu^{t}CH$_2$}])}$_2$] (**26**), Fig. 5, which was remarkable as **6** is routinely reduced to trivalent **11** by a potassium film in pentane.[18a] The solid state structure of **26** reveals two metallacyclic anions bridged by two K cations, related to one another by a crystallographic centre of inversion. Each potassium ion is bound by a toluene ligand that coordinates in an η^6 fashion and the metallacyclic U–C distance of 2.575(10) Å is significantly shorter than that observed in **21** but remains at the upper end of known U–C bond distances. It was proposed that **26** was formed *via* the *in situ* potassium reduction of **21**, which itself is produced within the reaction mixture from small quantities of benzylpotassium (that form by the reaction of the K film with toluene solvent) reacting with the starting material **6**.

Metallacycle **21** reacts with a variety of acetylenes to afford mono-, di- and trimetallic Tren$^{\mathrm{DMBS}}$–uranium(IV) acetylide complexes (Scheme 8). Complex **21** reacts with stoichiometric quantities of the acetylenes HCCX (X = H, Ph, *p*-tolyl) to afford the respective mononuclear acetylide complexes [U(Tren$^{\mathrm{DMBS}}$)(C$_2$X)] [X = H (**27**), Ph (**28**), *p*-tolyl (**29**)], although structural characterisation is lacking for **27**.[23,30] It was stated in one publication[30] that **28** could not be prepared from **2** and LiCCPh as initially reported[23] – with the lithium 'ate' complex [U(Tren$^{\mathrm{DMBS}}$)(C$_2$Ph)$_2$(μ-Li)(THF)] being the only isolable product – instead a 1 : 1 mixture of **21** and phenylacetylene was required to synthesise **28**. The U–C–C bond angles in



21 26

Fig. 5 Structures of **21** and **26**.

28 and **29** of 160.9(4) and 156.4(6)°, respectively, are significantly more acute than the reported range for structurally characterised terminal f-element alkynyls (170–176°), which was ascribed to a geometric distortion to maximise U–C π-interactions.

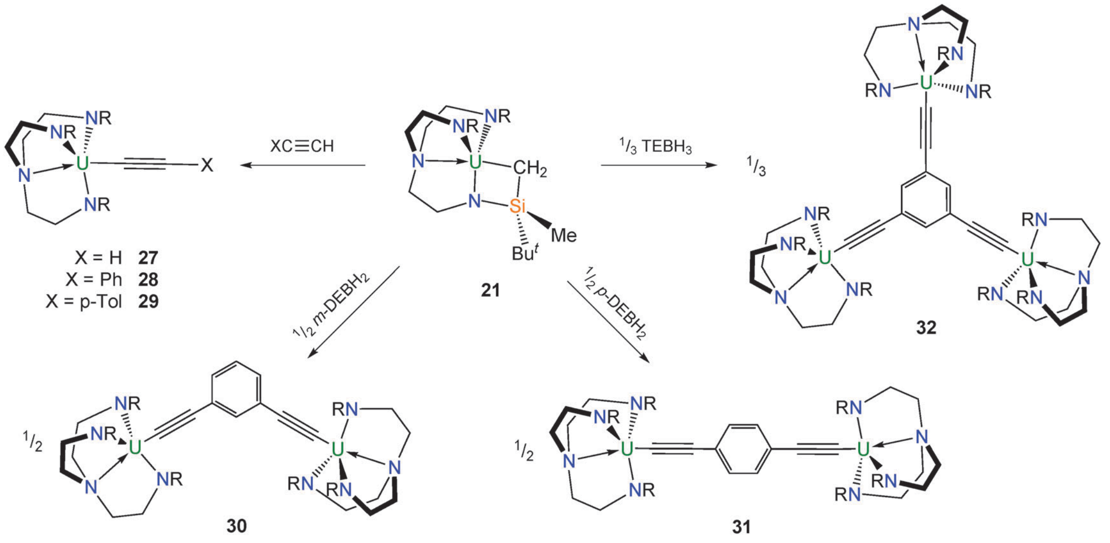
Treatment of **21** with *meta-* and *para*-diethynylbenzene as well as triethynylbenzene in the appropriate stoichiometry afforded the bright green Tren–uranium arylacetylides [{U(Tren$^{\mathrm{DMBS}}$)}$_2$-(μ-κ^2-1,3-(C$_2$)$_2$–C$_6$H$_4$)] (**30**), [{U(Tren$^{\mathrm{DMBS}}$)}$_2$(μ-κ^2-1,4-(C$_2$)$_2$–C$_6$H$_4$)] (**31**) and [{U(Tren$^{\mathrm{DMBS}}$)}$_3$(μ-κ^3-1,3,5-(C$_2$)$_3$–C$_6$H$_3$)] (**32**), respectively (Scheme 8).[30] X-ray structural studies on **30–32** confirmed the individual cluster connectivities, however in the case of **32** a full analysis was precluded by poor data quality. A detailed magnetometric analysis of all three of the polynuclear compounds identified magnetic singlet ground states at low temperature, although these data were suggestive of weak ferromagnetic communication between the uranium centres in **30–32**.

Further reactivity of **21** was disclosed in reports[23,29] that metallacyclic **21** undergoes an acid–base reaction with pyridine, affording the Tren$^{\mathrm{DMBS}}$–uranium(IV) pyridyl complex **33**, Scheme 9. Complex **33** was structurally characterised and confirmed the pyridyl unit to be bound in a planar η^2 coordination mode.

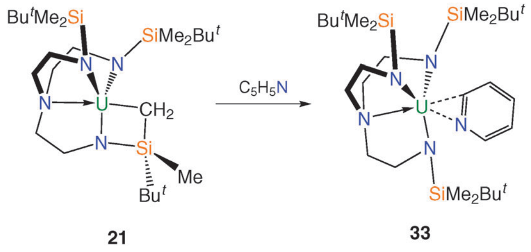
Given the documented ability for metalated alkyl groups in uranium complexes to undergo facile deuteration in solution,[10f] a d_8-toluene solution of **21** was exposed to D$_2$ at room temperature, Scheme 10. It was reported that under these conditions over a period of a few hours deuteration of all SiMe$_2$ groups as well as the metallacyclic CH$_2$ unit was observed. *tert*-Butyl CH$_3$ groups and methylene CH$_2$ groups were not deuterated, ascribed to the absence of α-Si atoms for these units.[29]

Subsequently, cyclometallation chemistry at uranium has been explored using the less sterically demanding Tren$^{\mathrm{TMS}}$ ligand system.[22] Treating **5** with benzylpotassium was anticipated to give the Tren$^{\mathrm{TMS}}$–uranium(IV) 'tuck-in' metallacycle "[U{N(CH$_2$-CH$_2$NSiMe$_3$)$_2$(CH$_2$CH$_2$NSiMe$_2$CH$_2$)}(THF)]" both by analogy to **21** and with reference to the wider literature.[10f,23] A green toluene solution of **5** reacts with KCH$_2$Ph to give a dark yellow turbid suspension, suggesting KI elimination. Following work-up, yellow crystals were isolated from hexanes and a single crystal XRD study revealed them to be the unusual dinuclear tuck-in-tuck-over tuck-over Tren$^{\mathrm{TMS}}$–uranium(IV) dialkyl complex [U{N(CH$_2$CH$_2$NSiMe$_3$)-(CH$_2$CH$_2$NSiMe$_2$CH$_2$)$_2$}U(Tren$^{\mathrm{TMS}}$)] (**34**), Scheme 11.

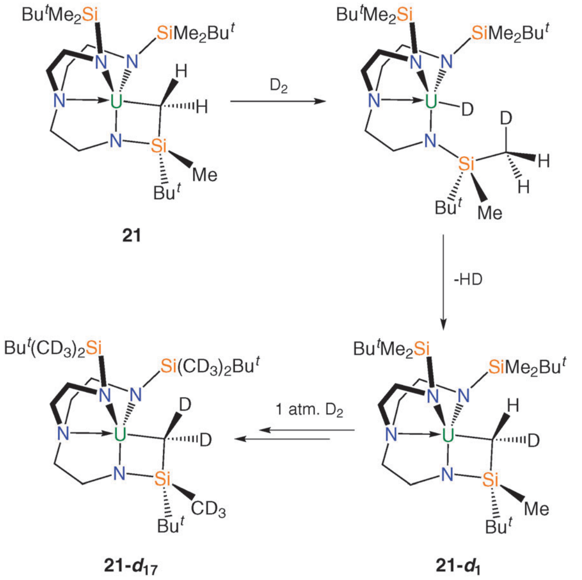
The molecular structure of **34** is bimetallic and consists of two uranium(IV) units in a tuck-in-tuck-over tuck-over triamidedialkyl–triamide coordination mode, which was unprecedented for Tren ligands. Two four-membered metallacycles are formed – [U–N–Si–C]



Scheme 8 Synthesis of **27–32**. R = $SiMe_2Bu^t$; *m*-$DEBH_2$ = 1,3-diethynylbenzene; *p*-$DEBH_2$ = 1,4-diethynylbenzene; $TEBH_3$ = 1,3,5-triethynylbenzene.



Scheme 9 Synthesis of **33**.



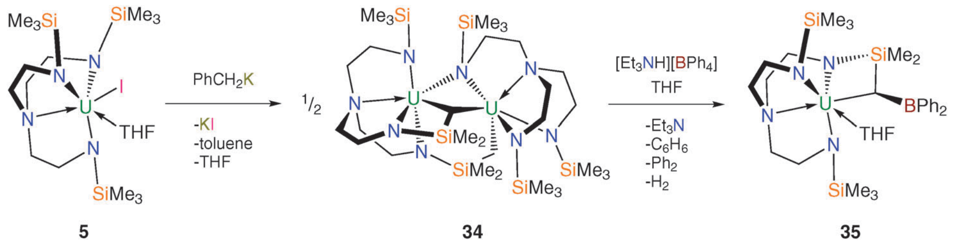
Scheme 10 Selective H/D exchange process for **21**.

and [U–N–U–C] – that feature markedly different bite angles [67.13(13)° and 81.89(12)°, respectively] reflecting the difference between the constituents and their relative location within the structure.

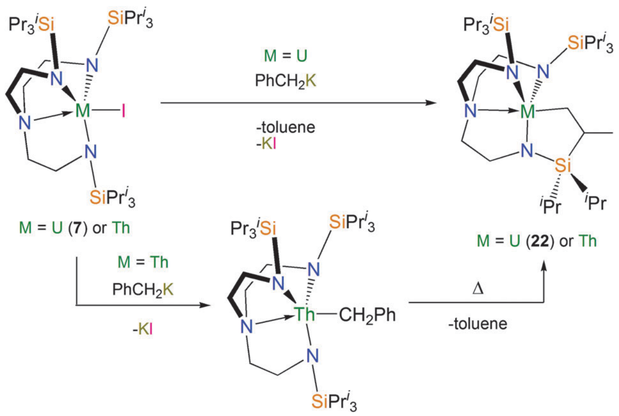
The synthesis of the anticipated separated ion pair $Tren^{TMS}$–uranium(IV) complex $[U(Tren^{TMS})(THF)_2][BPh_4]$ (**19**) was attempted by treatment of **34** with one molar equivalent per U of $[Et_3NH][BPh_4]$ in THF. However the molecular structure of the uranium-containing product was determined to be the mononuclear BPh_2-functionalised metallacyclic tuck-in $Tren^{TMS}$–uranium(IV) complex $[U\{N(CH_2CH_2NSiMe_3)_2(CH_2CH_2NSiMe_2C[H]BPh_2)\}(THF)]$ (**35**), Scheme 11. The boron centre is trigonal planar and the B–C_{alkyl} bond distance of 1.493(11) Å is short inferring partial multiple B–C bond character, which was supported by a DFT study that revealed a B–C Mayer bond order of 1.33, consistent with the presence of a B–C π-bond which is perturbed by the polarising uranium centre. The reaction between **34** and $[Et_3NH][BPh_4]$ was monitored using variable temperature ^1H NMR spectroscopy and GC-MS, which revealed the presence of hydrogen, benzene and biphenyl as identifiable products of the reaction. The isolation of **35** represents the first example of double dearylation of BPh_4^- in a molecular context, adding to the debate against the use of this anion in homogeneous catalysts.[22]

Cyclometallation chemistry has been explored with the sterically encumbered $Tren^{TIPS}$ ligand in the context of divergent reactivity patterns for Tren–uranium(IV) and thorium(IV) systems.[31] Whilst **7**, upon treatment with KCH_2Ph, affords the orange-red cyclometallated Tren–uranium complex $[U\{N(CH_2CH_2NSiPr^i_3)_2(CH_2CH_2NSiPr^i_2C[H]MeCH_2)\}]$ (**22**) at temperatures well below ambient, the equivalent reaction with the colourless thorium(IV) analogue $[Th(Tren^{TIPS})(I)]$ gives a colourless, isolable η^1-benzyl complex. This benzyl requires heating to afford the thoracyclic analogue of **22**, Scheme 12.

The origin of the inversion of the above reactivity trend was investigated by a DFT study. This showed that the greater f-orbital participation for uranium compared to thorium facilitates the σ-bond metathesis transition state. For thorium the transition state is more ionic and so the benzyl intermediate can be isolated experimentally, whereas no such benzyl complex was



Scheme 11 Synthesis of **34** and **35**.



Scheme 12 Synthesis of **22**.

observed for the uranium case, even when probed using low-temperature ^{1}H NMR spectroscopy.

Ylide derivatives

The synthesis of terminal actinide alkylidene complexes remains a major synthetic target despite extensive investigations into phosphorus ylide complexes with significant U–C multiple bond character.[9d,32] Given the synthetic accessibility of, for instance, a tantalum alkylidene using methylene trimethylphosphorane, such a complex was targeted utilising the Tren^{DMBS} ligand scaffold. It was reported[17] that the addition of CH_2PMe_3 to a purple solution of **11** afforded a dark green solution from which a dark green solid was isolated. The analytical data supported the proposed formulation of the Tren–uranium methylene(trimethylphosphorane) complex [U(Tren^{DMBS})(CH_2PMe_3)] (**36a**), Fig. 6, although it lacks structural characterisation. The electronic absorption spectrum of **36a** is strongly suggestive of a CH_2PMe_3 adduct of uranium(III).

During attempts to structurally characterise **36a** a small sample of dark green crystals was isolated and shown by X-ray diffraction to be the uranium(IV) methylene(trimethylphosphorane) hydroxide complex **36b**, Fig. 6. Due to the low yield additional analytical data are unavailable, however the structure of **36b** does have some unusual structural features, namely the highly extended U–C distance [2.706(12) Å], which is comparable to that found in the highly strained metallacycle **21**, and the presence of the first terminal U–OH linkage.

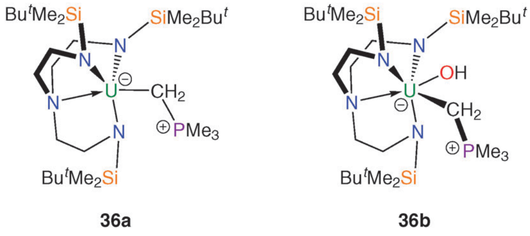


Fig. 6 Structures of **36a** and **36b**.

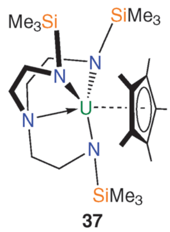


Fig. 7 Structure of **37**.

Cyclopentadienyl derivatives

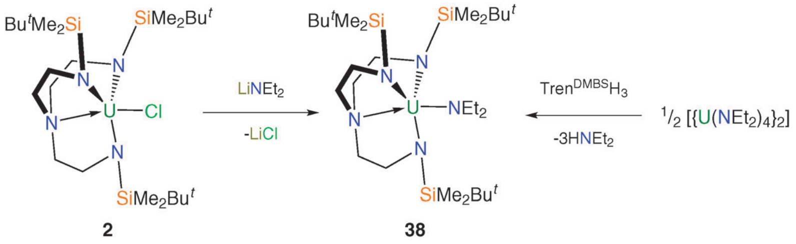
Cyclopentadienyl (Cp) complexes of uranium are well known but only one Tren–uranium–Cp derivative has been structurally characterised.[21] [U(Tren^{TMS})(η^5-C_5Me_5)] (**37**), Fig. 7, was prepared from [Na(C_5Me_5)] and half a molar equivalent of **8**. The product **37** was purified by sublimation and a single crystal XRD experiment confirmed the anticipated structure, with the $C_5Me_5^-$ ring exhibiting the expected η^5 coordination mode. The room-temperature ^{1}H NMR spectrum of **37** is indicative of average C_{3v} molecular symmetry, but it was stated that the ground-state geometry would be close to that in the solid state structure.

Tren–uranium – group 15 complexes

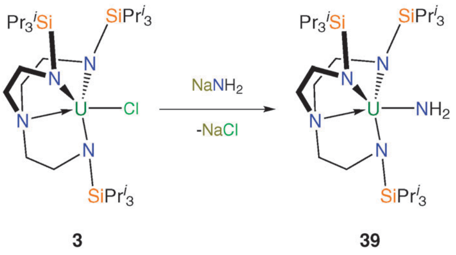
Amide derivatives

The synthesis of [U(Tren^{DMBS})(NEt_2)] (**38**) demonstrates how alternative methodologies can be employed to access Tren–uranium amide complexes.[13b] The diethylamide complex **38** is prepared from either **2** or [{U(NEt_2)$_4$}$_2$] as the source of uranium (Scheme 13). The solid state structure of **38** was obtained *via* an XRD experiment, which revealed a monomeric complex with the overall structural features typical for Tren–uranium(IV) complexes and it is similar to complexes **16** and **17**.

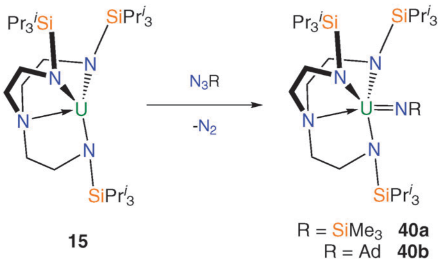
Following its previously reported inadvertent production in varying yields,[14b] it was shown that the parent terminal amide complex [U(Tren^{TIPS})(NH_2)] (**39**) can be prepared in high yield on multi-gram scales. Compound **39** represents an attractive



Scheme 13 Synthesis of **38**.



Scheme 14 Synthesis of **39**.



Scheme 15 Synthesis of **40a** and **40b**.

precursor from which to target U–N multiple bonds *via* subsequent deprotonation methods, bearing in mind the successful isolation of a terminal molybdenum carbide complex [Mo(C){N(R)Ar}$_3$]-[K(benzo15C5)$_2$] [R = C(CD$_3$)$_2$CH$_3$, Ar = C$_6$H$_3$Me$_2$-3,5], from a methylidyne precursor by deprotonation and alkali metal sequestration.[33] The parent amide **39** was synthesised by salt elimination from the reaction of **3** with NaNH$_2$ in THF (Scheme 14). A single crystal XRD study performed on a yellow crystal of **39** revealed a monomeric structure with a terminal U–NH$_2$ bond distance of 2.228(4) Å, which is closely comparable to the only other structurally characterised example of a U–NH$_2$ linkage [2.194(5) Å (av.)].[34]

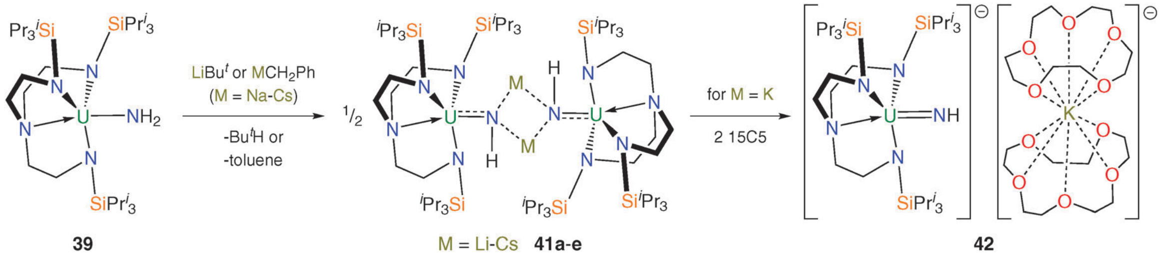
Imido derivatives

The first report of a Tren–uranium imido complex came in 2002 when it was demonstrated that dark purple trivalent complex **11** reacts with trimethylsilylazide, Me$_3$SiN$_3$, with a colour change to dark red and evolution of gas.[17] Although the characterisation data for the isolated product supported the formulation as [U(Tren^{DMBS})(NSiMe$_3$)] – the imido product of a two-electron oxidation at uranium – no corroborative structural data are available. Along similar lines, dark purple **15** was shown to react with Me$_3$SiN$_3$ or AdN$_3$ (Ad = 1-adamantyl) evolving nitrogen gas to afford, after work-up and crystallisation, red-brown and dark brown crystals, respectively, of the terminal Tren–uranium(V) imidos [U(Tren^{TIPS})(NSiMe$_3$)] (**40a**) and [U(Tren^{TIPS})(NAd)] (**40b**), Scheme 15.[14b]

Single crystal XRD experiments confirmed the expected structures of the two products. The terminal uranium(V) imido complexes **40a** and **40b** are the product of two-electron oxidations at uranium, facilitated by nitrogen evolution, and the U═N$_{imido}$ bond distances of 1.954(3) and 1.946(13) Å for **40a** and **40b**, respectively, are typical of terminal uranium(V) imido complexes.[9d,35] Complex **40a** could be viewed as a nitride precursor since the polarised Me$_3$Si–N bond could in theory be cleaved to generate a nitride, however attempts to this end were not successful.

Until very recently there were no reports of f-element terminal *parent* imido linkages (L$_n$M═NH), presumably due to the requirement for significant kinetic stabilisation at the metal centre, usually conferred by large R groups installed on the imido nitrogen; for metals toward the bottom of the periodic table this issue would be compounded by their large ionic radii and would certainly be at its most acute for actinide centres. Deprotonation of the parent amide **39** with LiBu^t or MCH$_2$Ph (M = Na, K, Rb, Cs) affords the dimeric alkali metal-bridged uranium(V) imido complexes [{U(Tren^{TIPS})(μ-NH)(μ-M)}$_2$] [M = Li–Cs (**41a–e**)] as pale-pink crystalline solids after workup and crystallisation, Scheme 16.[36] The molecular structures of **41a–e** were determined by single crystal XRD, which revealed in each case dimeric structures constructed around a centrosymmetric M$_2$N$_2$ four-membered ring. The uranium–imido bonds in **41a–e** span the range 2.042(3) to 2.135(3) Å and are significantly shorter than the U–NH$_2$ bond length of 2.228(4) Å in **39**, reflecting the build-up of imido character of **41a–e** compared with the amide character of **39**.

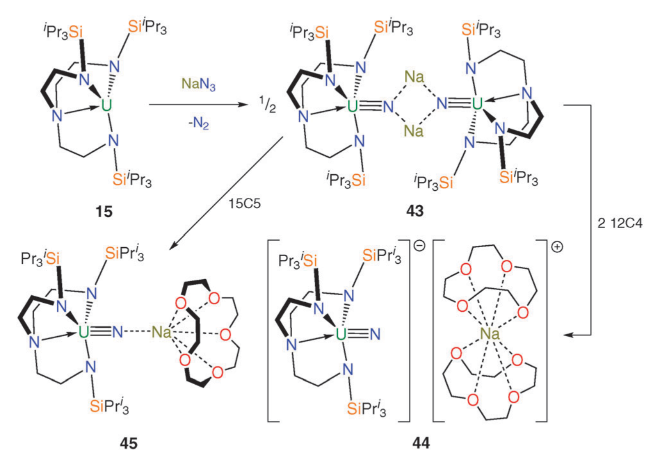
Treatment of **41c** with 2 equivalents of 15-crown-5 ether (15C5) and stirring of the resulting oil in hexanes affords a brown solid. The solid-state structure of [U(Tren^{TIPS})(NH)]-[K(15C5)$_2$] (**42**) was determined by single crystal XRD, which confirmed the separated ion pair (SIP) formulation. The U–N$_{imido}$ bond length in **42** was found to be comparable to those in **41a–e** at 2.034(3) Å, though this was attributed to the anionic nature of [U(Tren^{TIPS})(NH)]$^-$ partially offsetting the expected U–N$_{imido}$ bond contraction upon abstraction of an alkali metal from the bridging imido to give a terminal U═NH unit. Theoretical studies of the near-linear U═N–H group [172(3)°] in **42** show the presence of a threefold $\sigma^2\pi^4$ bonding combination, supporting the assertion that **42** represents a protected nitride given that the proton bound to the imide nitrogen may in principle be removable.



Scheme 16 Synthesis of **41a–e** and **42**.

Nitride derivatives

Until 2012, an isolable molecule under ambient conditions containing the uranium nitride linkage as a terminal unit had evaded all attempts to prepare it for decades even though it represents a fundamental synthetic target for the study of metal–ligand multiple bonding and f-orbital participation. Previous reports of terminal uranium nitride species were restricted to elegant matrix isolation studies or mass spectrometric observations;[11b] molecular uranium nitride complexes prepared under ambient conditions included polymetallic compounds with bridging nitride units, covalently-bound nitridoboranes, or transient species that undergo C–H insertion reactions with ancillary ligands under photolytic conditions.[11b] The key advance came with the report of a terminal uranium nitride supported by the bulky Tren^{TIPS} ligand framework.[12b] Trivalent **15** undergoes a two-electron oxidation upon treatment with sodium azide to afford the dimeric, sodium-bridged Tren–uranium(V) nitride complex [{U(Tren^{TIPS})(μ-N)(μ-Na)}$_2$] (**43**). Subsequent addition of two equivalents of 12-crown-4 ether (12C4) per sodium affords the terminal SIP uranium nitride [U(Tren^{TIPS})(N)][Na(12C4)$_2$] (**44**), or one equivalent of 15-crown-5 ether (15C5) per sodium produces the capped nitride [U(Tren^{TIPS})(μ-N)(μ-Na)(15C5)][14b] (**45**), Scheme 17. The success of this approach to give **44** rests on the combination of the sterically demanding Tren ligand preventing the nitride from bridging to another uranium centre, stabilisation of the nitride during installation by the sodium, but straightforward abstraction of the sodium ion due to its ionic bonding to the nitride and appropriate size-matching to a crown ether.

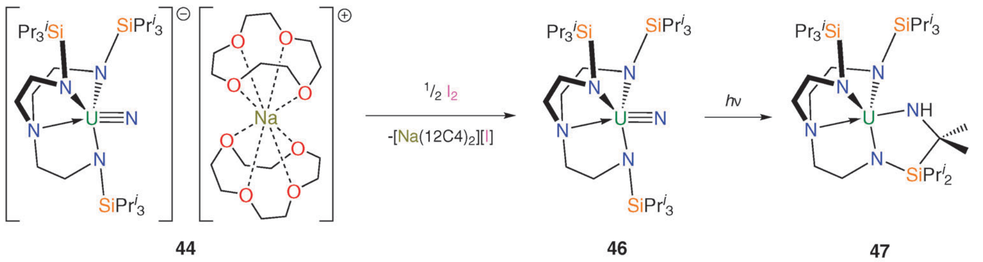


Scheme 17 Synthesis of **43–45**.

Single crystal XRD experiments confirmed the molecular structures of **43**, **44** and **45**, and revealed very short U–N$_{nitride}$ bond distances of 1.883(4), 1.825(15) and 1.810(5) Å, respectively, with the latter two being indistinguishable but as expected showing a moderate contraction of *ca.* 0.06 Å relative to **43** either upon complete encapsulation of the alkali metal and removal from the nitride centre or upon removal of one sodium per nitride and inclusion of a capping 15C5. This contraction was ascribed to the removal of polarising Na$^+$ cations from the nitride atom resulting in a higher charge density for the terminal or Na-capped nitride centres in **44** and **45**, respectively, relative to the disodium-bridged **43**. Upon formation of **43**, it is postulated that the coordinated alkali metal centres help to stabilise the high charge density on the nitride moieties, minimising deleterious side reactions, despite the likely weak nature of the sodium–nitride interactions in **43**. Electronic absorption spectroscopy and variable temperature magnetometric measurements support the assignment of the +5 oxidation state for uranium in **43–45**. A computational study revealed the expected threefold $\sigma^2\pi^4$ molecular orbital description of the U$\equiv$N triple bonds with Mayer bond orders of 2.21, 2.91 and 2.45 for the uranium–nitride linkages in **43**, **44** and **45**, respectively, reflecting the effect of the number of coordinated sodium ions located on the nitride centre in each case. For **44**, the molecular orbitals representing the U–N σ bond are higher in energy than those representing the π interactions and this is the same as for the uranyl dication, but the reverse of what would be expected based on observations in U═C and U═N double bonds. This can be explained by considering an antibonding interaction at short U–N distances between the σ-orientated N 2p$_z$ orbital and the annular lobes of the U 6d and 5f orbitals (with the U$\equiv$N bond orientated along the *z*-axis).[12b]

The terminal nitride **44** reacts with excess water in the presence of three equivalents of the reductant cobaltocene, CoCp$_2$, to produce ammonia confirming the existence of a basic nitride unit. Additionally, **44** was shown to react with Me$_3$SiCl producing the Tren–uranium(V) imido complex [U(Tren^{TIPS})(NSiMe$_3$)] (**40a**), eliminating [Na(12C4)$_2$][Cl], thus demonstrating nucleophilic character.[12b]

Attempts to oxidise **43** with mild oxidants such as AgPF$_6$ resulted in decomposition to, for instance, [U(Tren^{TIPS})(F)], but that when **44** was treated with half a molar equivalent of iodine, I$_2$, elimination of [Na(12C4)$_2$][I] was observed, Scheme 18, and red crystals of the uranium(VI)–nitrido complex [U(Tren^{TIPS})(N)] (**46**) were isolated.[14b]



Scheme 18 Preparation of **46** and **47**.

The uranium(VI)–nitride bond length in **46** was crystallographically determined to be 1.799(7) Å, which is statistically invariant to the U–N$_{nitride}$ bonds in **44** and **45** and this feature is attributed to the removal of a non-bonding 5f electron upon oxidation; the very short uranium–N$_{amine}$ distance [2.465(5) Å] is ascribed to a consequence of the inverse-*trans*-influence.[37] Thus, as mentioned in the introduction, the amine may play a vital electronic role in the successful isolation of these terminal uranium nitrides by providing stabilisation to *trans* multiply bonded ligands. FTIR and NMR spectroscopic data also supported the formulation of a diamagnetic 5f^0 uranium(VI) nitride. DFT studies on **46** again reveal a $\sigma^2\pi^4$ U≡N threefold bonding manifold and a Mayer bond order of 2.92 for the uranium–nitride linkage, which is all but identical to that for **44** (2.91) and underlines the minor effect on the U≡N interaction upon removal of the non-bonding 5f electron. Surprisingly, a topological analysis of the electron density for the terminal uranium–nitride linkages in **44** and **46** suggested a comparable degree of covalency to terminal group 6 nitrides.

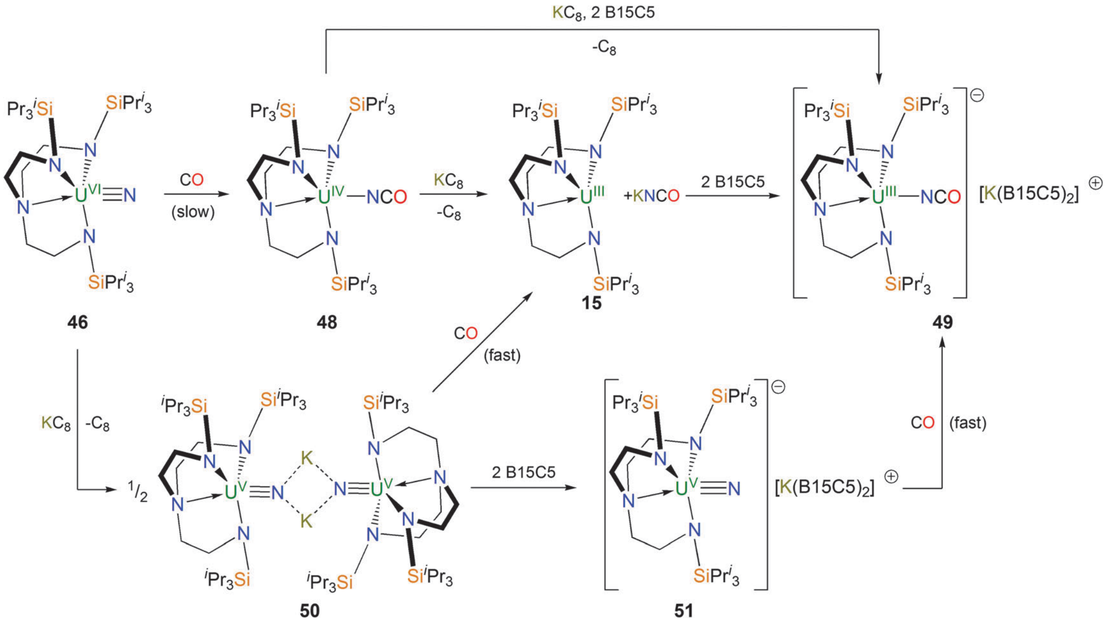
Photolysis for *ca.* twenty minutes or exposure to sunlight for several days of toluene solutions of **46** resulted in C–H activation and insertion of the nitride into an isopropyl C–H bond to afford the secondary amide [U{(N[H]CMe$_2$SiPr$^i_2$NCH$_2$CH$_2$)N(CH$_2$CH$_2$N-SiPr$^i_3$)$_2$}] (**47**), Scheme 18, underlining the highly reactive nature of the uranium(VI) nitride species under photolytic conditions. What is noticeable about the observed reaction chemistry of **44** and **46** is that despite the removal of a formally non-bonding 5f electron upon oxidation of **44** to **46**, which is suggested by the X-ray and theoretical data not to have much of an impact on the bonding, the relative photochemical reactivity of **44** and **46** are profoundly different. Under photolytic conditions **44** does not decompose whereas **46** does, which can be attributed to the more oxidising nature of uranium(VI) compared to (V) since the mechanism of this photochemical C–H activation requires reduction of uranium. However, under normal conditions **44** is generally more reactive than **46** which suggests a weaker uranium–nitride linkage in the former compared to the latter.

The reactivity of Tren–uranium nitrides towards CO has been investigated,[38] owing to its ambiphilicity, industrial and environmental significance, and also that carbonylation of transition metal nitride complexes is rare.[39] As shown in Scheme 19, the red Tren–uranium(VI) nitride **46** undergoes reductive carbonylation when treated with carbon monoxide to afford green crystals of the Tren–uranium(IV) cyanate complex [U(Tren^{TIPS})(NCO)] (**48**), which mirrors reactivity seen for a handful of transition metal nitrides.[39] The solid state structure of **48** is unremarkable, and features a virtually linear U–NCO unit [U–N–C = 173° (av.)]. The outcome of a reduction of **48** with KC$_8$ is dependent on the reaction conditions although a nitride product – arising from reductive decarbonylation – is never isolated. In the absence of crown ethers, the reaction of **48** with KC$_8$ results in the extrusion of KNCO and trivalent **15** is isolated from the reaction; however when two equivalents of benzo-15C5 are present, the uranium(III) cyanate SIP complex [U(Tren^{TIPS})(NCO)][K(B15C5)$_2$] (**49**) is isolated as dark green crystals. In contrast to **48**, the U–NCO unit in **49** is bent [U–N–C = 138° (av.)] in the solid state, likely by virtue of the attenuation of U–N$_{cyanate}$ π-interactions due to the increased electron density on the U(III) centre in **49** relative to the U(IV) centre in **48**.

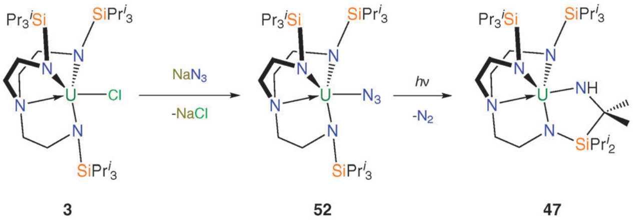
The bridging uranium(V) nitride [{U(Tren^{TIPS})(μ-N)(μ-K)}$_2$] (**50**) also undergoes similar reductive carbonylation chemistry under an atmosphere of CO, affording **15** and KNCO. The SIP nitride complex [U(Tren^{TIPS})(N)][K(B15C5)$_2$] (**51**) was prepared from **50** by treatment with 2 equivalents of benzo-15C5 and reacted with CO to afford **49**. Both the reductive carbonylation reactions of **50** to produce **15** and KNCO as well as that of **51** to produce **49** were observed to proceed much more rapidly than that of **46** affording **48**, which underscores the divergent reactivity for these uranium(V) and uranium(VI) nitrides. This discrepancy was examined by a DFT investigation, and it was found that in either case the reaction can be described as nucleophilic attack of the nitride to the incoming CO molecule in a [2+1]-cycloaddition reaction and the difference in observed rates can be explained by U–CO pre-coordination. The barrier to the transition state is higher in the case of the uranium(VI) species due to the smaller size of uranium(VI) relative to uranium(V), which requires the CO molecule to approach closer to the metal atom; a process that is energetically costly.

Photochemistry of azide, diazomethane, and isocyano derivatives

Metal azide complexes are known to be attractive precursors to nitride complexes as they can undergo photolytic denitrification to afford a nitride compound that is the product of a two-electron oxidation.[39b,c] No isolable uranium nitride complex has been accessed in this manner, although the photochemical conversion of uranium(IV) azides into C–H bond activated products, likely *via* a uranium(VI) nitride intermediate, has been studied.[40] This methodology was tested using Tren^{TIPS}, whereby the azide precursor [U(Tren^{TIPS})(N$_3$)] (**52**) was synthesised *via* salt metathesis from **3** and sodium azide, Scheme 20.[14b]



Scheme 19 Synthesis of **48–51**. B15C5 = benzo-15-crown-5.



Scheme 20 Synthesis and photolysis of **52** to give **47**.

The solid state structure of **52** was confirmed by a single crystal XRD experiment, which revealed a monomeric Tren–uranium(IV) azide. No reaction was observed when a toluene solution of **52** was heated and extended reaction times result in quantitative decomposition. Photolysis of **52** in toluene results in C–H activation to afford the secondary amide **47**, which suggested that a transient uranium(VI) nitride could have been formed but decomposed under the harsh photolytic conditions required to promote N_2 evolution; a rationale supported by the observed photolytic activation of **46** (see Scheme 18).

Metal–diazomethane ($L_nM–CR_2N_2$) complexes represent attractive precursors for metal alkylidene species.[41] Additionally, reports of organometallic actinide photochemistry are exceedingly rare in contrast to that for the d-block,[42] although they suggest that f-block-diazoalkane reactivity trends are different to those for the transition metals. In an attempt to access a Tren–uranium alkylidene of the form "[U(Tren^{DMBS})(CHSiMe$_3$)]", it was reported that a dark purple pentane solution of **11** reacted with Me_3SiCHN_2 to afford a dark red solution, but no evolution of gas was observed.[17] Dark red crystals formulated as the uranium hydrazido complex [U(Tren^{DMBS}){$N_2CH(SiMe_3)$}] (**53**) were isolated, however no structural data were provided, although the identity of **53** was supported by its EI-mass spectrum and ^1H NMR spectrum. No evidence of the target alkylidene complex was obtained after refluxing a d_6-benzene solution of **53** or irradiation with ultraviolet light.

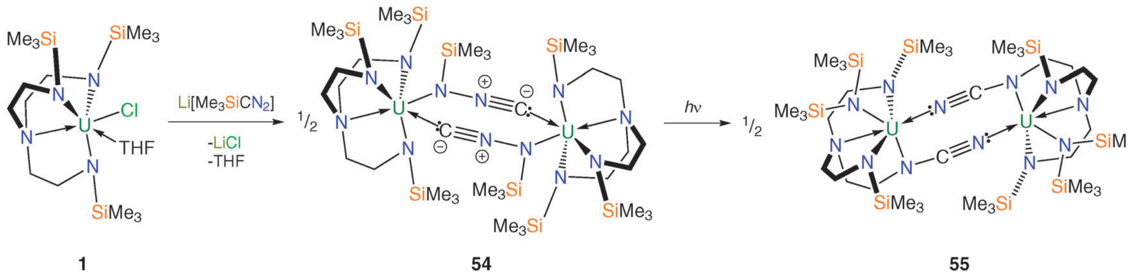
A more recent report utilised Tren^{TMS} to access a novel isocyano(trimethylsilyl)amide complex **54** *via* salt elimination using Me_3SiCN_2Li (obtained from the lithiation of Me_3SiCHN_2 with *n*-butyllithium), Scheme 21.[43] Crystallographic refinement of N-bound *versus* C-bound disorder models for the $SiMe_3$ group in the N($SiMe_3$)NC unit led to the assignment of the *N*-silyl isomer exclusively.

Given the documented reactivity of diazomethane derivatives, a toluene solution of **54** was heated at 110 °C for three days. However, even after this time no reaction was observed and heating the solution to higher temperatures eventually resulted in the quantitative decomposition of **54** and the formation of unidentifiable products. Photolysis of a toluene solution of **54** at room temperature, however, resulted in a gradual colour change of the solution from green-yellow to brown. The molecular structure of the photolysis product **55** was determined by an XRD experiment is illustrated in Scheme 21.

With the assumption that [LiC(N_2)SiMe$_3$] has a C-bound trimethylsilyl group, as is preferred thermodynamically over the N-bound form,[44] a 1,3-silyl shift from C to N is required during the formation of **54**. The production of **55** is less straightforward, requiring N–Si and N–N bonds to be broken and C–N and N–Si bonds to be formed. The photolytic transformation of **54** to **55**, involving multiple bond-cleavage and -capture, is not thermally accessible and was without precedent in diazoalkane chemistry.

Phosphinidene derivatives

Reports of terminal metal phosphinidene complexes, $L_nM{=}PR$, remain rare relative to those for metal imides, carbenes and alkylidenes. In 2014, it was shown that the parent phosphide



Scheme 21 Synthesis of **54** and **55**.

could be installed onto a Tren^{TIPS}–uranium(IV) fragment to afford the first PH_2^- complex of uranium (Scheme 22).[24] Yellow [U(Tren^{TIPS})(PH_2)] (**56**) was structurally characterised and features a U–P bond distance of 2.883(2) Å which is slightly longer than comparable reported complexes such as in [U(C_5Me_5)$_2${P($SiMe_3$)$_2$}(Cl)] [U–P = 2.789(4) Å].[45]

When **56** is treated with benzylpotassium and 2,2,2-cryptand, the bridging phosphinidiide [U(Tren^{TIPS})(μ-PH)(μ-K)(2,2,2-cryptand)] (**57**) was isolated as black crystals. A single crystal XRD study demonstrated a contracted U═PH distance of 2.661(2) Å relative to **56** and revealed that the potassium ion is coordinated by the P atom and by the cryptand, although the long P–K distance of 3.575(2) Å suggests the P–K interaction should be regarded as weak.

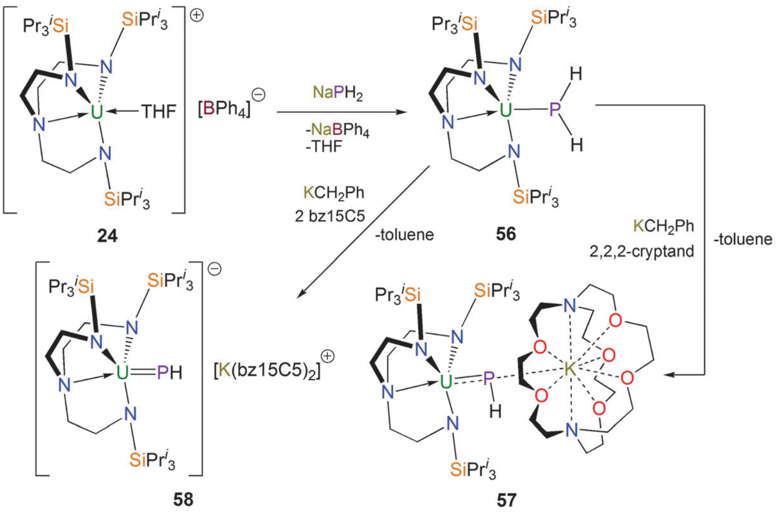
Treatment of **56** with KCH_2Ph and two equivalents of benzo-15-crown-5 ether (benzo-15C5) furnished the uranium(IV) terminal parent phosphinidene complex [U(Tren^{TIPS})(PH)] [K(benzo-15C5)$_2$] (**58**) as black crystals. Complex **58** was structurally authenticated by a single crystal XRD study revealing a U═P distance of 2.613(2) Å, which is around 0.05 Å shorter than the U═P distance in **57**, representing the first metal-stabilised terminal parent phosphinidene. The sum of the double bond covalent radii of U and P is 2.36 Å, so the U═P distance in **58** lies midway between the sum of the covalent single and double bond radii values and within the range of the few reported uranium phosphinidene and phosphinidiide complexes – 2.562(3) Å in [U(η^5-C_5Me_5)$_2$($OPMe_3$)-(P-2,4,6-$Bu^t_3C_6H_2$)][46] and 2.743(1) Å in [{U(η^5-C_5Me_5)$_2$(OMe)}$_2$-(μ-PH)].[47] Compound **58** has a calculated Mayer bond index of 1.92, which is as expected and Natural Bond Orbital (NBO) analysis identifies σ- and π-bonding interactions in the U═P double bond.

Tren–uranium – group 16 complexes

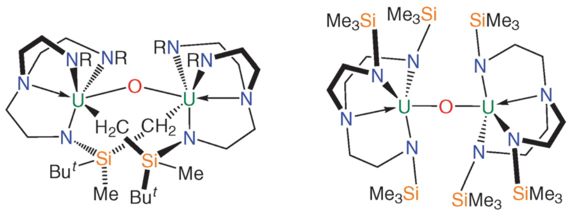
Oxo derivatives

The ubiquity of the uranyl ion $[UO_2]^{2+}$ within aqueous and non-aqueous uranium chemistry imparts particular significance to the study of oxo complexes.[48] The prerequisite facial coordination mode and steric constraint of the axial coordination environment of Tren complexes has meant that Tren–uranium frameworks have proven attractive targets towards the isolation of novel uranium O-atom containing compounds as well as the elusive *cis*-uranyl fragment.[49]

During attempts to grow crystals of trivalent **11** suitable for an XRD experiment, a small quantity of black crystals were isolated, and a structural characterisation determined the structure to be the bimetallic bridging oxo complex [{U(N[$CH_2CH_2NSiBu^tMe_2$]$_2$-[μ-$NSiMeBu^tCH_2$])}$_2$(μ-O)] (**59**), Fig. 8.[23] Complex **59** is dinuclear and features two metalated methylsilyl groups and a bridging oxo unit, each of which bridge the two uranium centres. Formally, the



Scheme 22 Synthesis of **56–58**. B15C5 = benzo-15-crown-5.

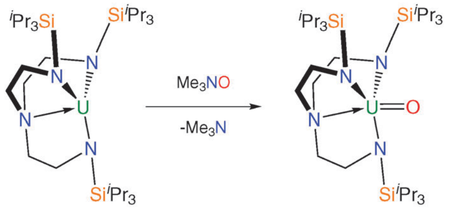


59 **60**

Fig. 8 Structures of **59** and **60**. R = $SiMe_2Bu^t$.

uranium centres in **59** can be assigned as uranium(V) based on charge balance arguments, as the U–N bond distances in **59** are not normally diagnostic of +4 or +5 oxidation states of uranium due to the predominantly ionic bonding regime. No further characterisation data are available to confirm the assignment. Compound **59** is believed to have formed *via* the ingress of air into a solution of **11** leading to oxo-abstraction.

In the course of efforts to synthesise molecular heterobimetallic complexes featuring unsupported U–Mn bonds, it was reported that $[KMnCp_2]$ reacted with $[U(Tren^{TMS})(THF)_2][BPh_4]$ (**19**) under a variety of conditions to eliminate $KBPh_4$ and $MnCp_2$, which were separated. From the remaining material, a crop of yellow plates was isolated and identified as the bridging oxo complex $[\{U(Tren^{TMS})\}_2(\mu\text{-}O)]$ (**60**), Fig. 8.[15b] The uranium(IV) centres in **60** are bridged by an oxo group that exhibits a linear geometry by virtue of its position on a crystallographic centre of inversion. Complex **60** is considered the product of oxo abstraction, the origin of which is ascribed to coordinated or bulk THF solvent and it was proposed that, following salt elimination, a putative $[U(Tren^{TMS})(MnCp_2)]$ complex is formed, but that this decomposes *via* homolytic bond cleavage yielding $MnCp_2$ and, ultimately, **60**. The tetravalent bridging oxo complex $[\{U(Tren^{DMBS})\}_2(\mu\text{-}O)]$ has also been reported[17] and spectroscopically characterised but no structural data are not available.



15 **61**

Scheme 23 Synthesis of **61**.

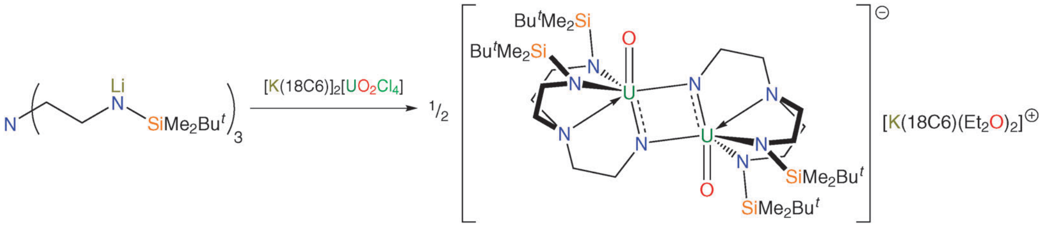
The trivalent complex **15** was treated with the oxo atom transfer reagent trimethylamine-*N*-oxide, Me_3NO, Scheme 23, which afforded the pentavalent Tren–uranium oxo complex $[U(Tren^{TIPS})(O)]$ (**61**) as red crystals *via* a formal two-electron oxidation process.[50] In the single crystal XRD structure $U\text{–}N_{amine}$ bond distance is highly contracted at 2.482(6) Å, which is ascribed to the inverse *trans* influence of the oxo ligand as is the case for **46**. Although EPR silent, **61** displays complex magnetic behaviour and it was determined *via* a raft of variable temperature SQUID (Superconducting Quantum Interference Device) measurements that it exhibits single molecule magnetism (slow relaxation of the molecular magnetisation). Complex **61** was the first monometallic uranium(V) single molecule magnet, the origin of which was ascribed to the strong axial ligand field in **61** giving rise to a large magnetic anisotropy. Whilst the energy barrier of this complex to relaxation of the magnetization breaks no records at 15.3 cm^{-1} (22 K), it does exhibit slow relaxation up to a blocking temperature of 3.5 K and at scanning frequencies as low as 10 Hz which suggests this is fertile territory with respect to discovering novel magnetic phenomena.[51]

In pursuit of the elusive *cis*-uranyl fragment, use of the Tren framework has been studied due to the geometric constraints imposed by the face-capping nature of this chelating ligand.[52] A yellow suspension of the uranyl chloride complex $[K(18\text{-}crown\text{-}6)]_2[UO_2Cl_4]$ was treated with the ligand transfer reagent $[Li_3Tren^{DMBS}]$ in THF. Following workup and crystallisation from diethyl ether, red crystals were isolated and subjected to an X-ray structural determination. The molecular structure was found to be the mixed-valent uranium(V/VI) oxo-imido dimer $[U(O)\{\mu\text{-}NCH_2CH_2N(CH_2CH_2NSiBu^tMe_2)_2\}]_2[K(18C6)(Et_2O)_2]$ (**62**), Scheme 24.

The generation of **62** results from the activation of both the uranyl fragment and the Tren ligand, with nominal loss of one O atom and one silyl group per molecule of starting material as well as a one electron reduction overall since the product is U(V/VI). Inspection of the structural parameters supports the mixed-valence formulation, with notably long U=O and U=N bonds arising from electron-rich uranium centres, with the conclusion that the extra electron is delocalised around the two imido fragments.

Alkoxide derivatives

Several neutral and anionic Tren–uranium(IV) alkoxides and aryloxides are known. $[U(Tren^{TMS})(OR)]$ [R = Bu^t, **63a**; $t\text{-}C_4F_9$,



62

Scheme 24 Synthesis of **62**.

63b; Ph, **63c**; 2,6-Bu^t_2-4-Me-C_6H_2, **63d**] and [U($Tren^{TMS}$)(OR)(OR′)(μ-Li)(thf)] [R, R′ = Bu^t, **63e**; R = Bu^t, R′ = OPh, **63f**; R, R′ = OPh, **63g**] were synthesised from **1** and the appropriate lithium alkoxide or aryloxide in the requisite stoichiometry.[21,23,53] The reactions to produce **63** proceed straightforwardly and the characterisation data supported their proposed formulations, however structural authentication was only obtained for **63a**, **63b** and **63e**. The attempted oxidation of the anionic ‘ate’ complexes **63e–g** with ferrocenium hexafluorophosphate [$FeCp_2$][PF_6] afforded brown solids assumed to be [U($Tren^{TMS}$)(OR)(OR′)] on the basis of NMR, IR and microanalysis data, but again no structural data are available to support their pentavalent assignments.

Small molecule activation

Reductive homologation of carbon monoxide

Given the documented ability for the $Tren^{TIPS}$–uranium(III) complex **15** to activate azide (N_3^-) and form a bridging nitride complex,[12b] the reductive capacity of other Tren–uranium(III) complexes with varying steric demands has been investigated; this may highlight contrasting reactivities such as the reactivity of dinitrogen with **11** to give **12** but no such reactivity with **15**. It has been demonstrated that the $Tren^{DMBS}$–uranium(III) complex **11** can reductively homologate CO under ambient conditions to selectively produce the diuranium(IV)–ethynediolate complex [{U($Tren^{DMBS}$)}$_2$(μ-η^1:η^1-OCCO)] **64**, Scheme 25,[54a] which in uranium chemistry is generally a rare transformation for CO effected by only a handful of complexes.[10a,54b] Upon thermolysis, **64** undergoes Si–N bond insertion and oxo-abstraction affording **65**, which is in contrast to the only other reported example of uranium-coordinated ethynediolate reactivity where an ethynediolate inserts into a ligand C–H bond.[10a] The insertion product **65** is afforded quantitatively, which emphasises the silicophilic nature of the $(C_2O_2)^{2-}$ unit in **64**.

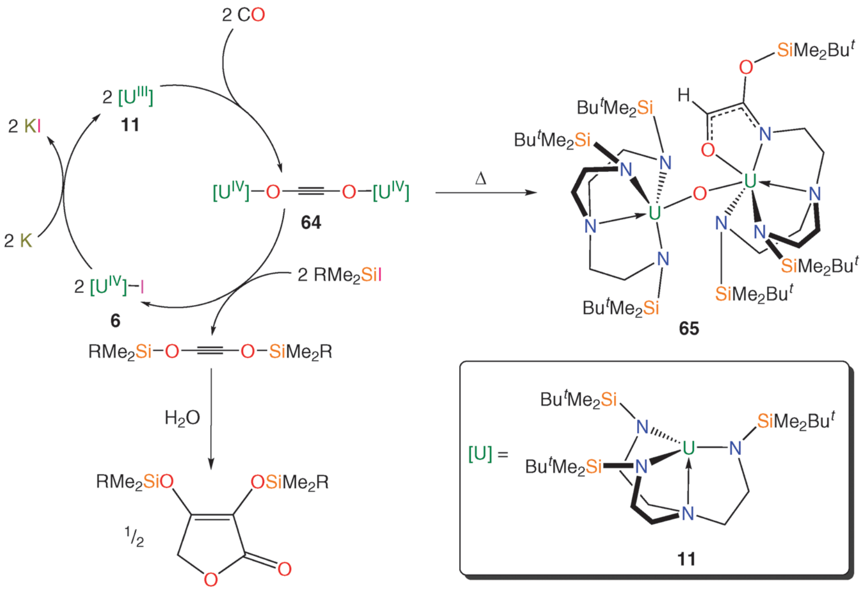
Treatment of **64** with RMe_2SiI liberated the functionalised acetylenes “$(RMe_2SiOC)_2$” (R = Me, Ph) in high yield alongside **6**, which can be recycled and re-used, closing the synthetic cycle *via* reduction with potassium to regenerate **11**. A DFT study suggested that the pre-organised nature of the $Tren^{DMBS}$–uranium unit may be important to this uniquely straightforward liberation chemistry, probably arising from the minimal ligand reorganisation energies required and which may have significant application in the design of future catalytic cycles for CO activation. The C_2-bis(ether)acetylenes that are produced undergo conversion to C_4-furanones upon treatment with water, both of which are precursors to industrially relevant diols and furans.

Tren–uranium–metal bonds

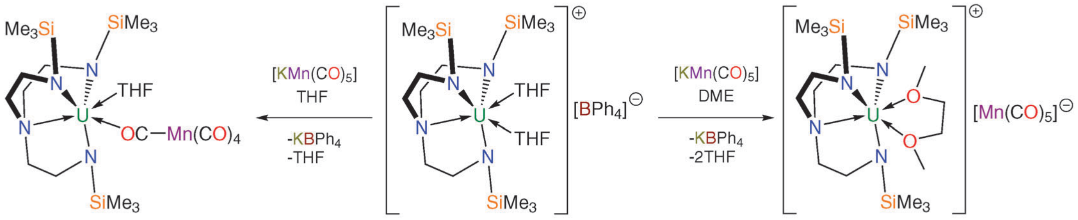
Manganese isocarbonylate derivatives

Due to its widespread utility in the construction of p-block – and transition metal – manganese linkages the pentacarbonylmanganese fragment [$Mn(CO)_5$] has been utilised in attempts to access elusive unsupported U–Mn bonded complexes.[15b] It transpired that none of the manganese carbonylate compounds discussed below contain U–Mn bonds, but they are included here because they illustrate important lessons in the drive to isolate uranium–metal bonds. Treatment of the SIP complex [U($Tren^{TMS}$)$(THF)_2$][BPh_4] (**19**) with [$KMn(CO)_5$] in THF or DME (DME = 1,2-dimethoxyethane) affords the manganese carbonylate complexes [U($Tren^{TMS}$)(THF)(μ-OC){$Mn(CO)_4$}] (**66**) or [U($Tren^{TMS}$)(DME)][$Mn(CO)_5$] (**67**), respectively (Scheme 26) with no evidence for the formation of U–Mn bonds.

Both **66** and **67** were structurally characterised, revealing the $[Mn(CO)_5]^-$ unit to be directly coordinated to the uranium(IV) centre in **66** but displaced by the chelating DME molecule in **67**. The Mn centre in **66** adopts a distorted square pyramidal



Scheme 25 Synthetic cycle for the reductive homologation and functionalisation of CO and thermolysis of **64** to **65**. R = Me, Ph; Cp* = η^5-C_5Me_5.



66 **19** **67**

Scheme 26 Synthesis of **66** and **67**.

geometry whereas that in **67** assumes an axially elongated, trigonal bipyramidal geometry by virtue of the solvent separated ion pair formulation for the latter.

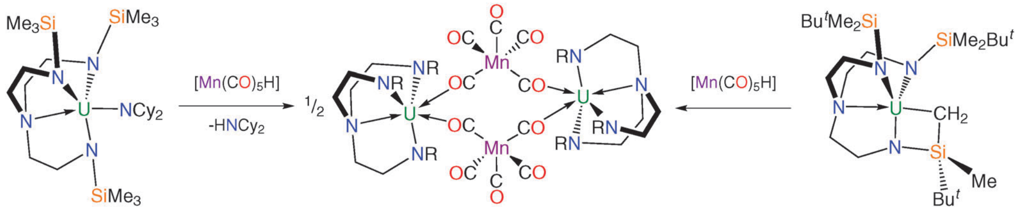
Attempts to access U–Mn bonded species by avoiding coordinating solvents, for instance *via* amine or alkane elimination methods produced diuranium doubly-bridging complexes, even when the more sterically encumbered Tren^{DMBS} ligand is employed to disfavour such oligomerisation. When treated with manganese pentacarbonyl hydride, [Mn(CO)$_5$H], [U(Tren^{TMS})(NCy$_2$)] (**16**) and [U{N(CH$_2$CH$_2$NSiMe$_2$Bu^t)$_2$(CH$_2$CH$_2$NSiMeBu^{t}CH$_2$)}] (**21**) undergo amine and alkane elimination, respectively, to afford [{U(Tren^{TMS})(μ-OC)$_2$Mn(CO)$_3$}$_2$] (**68**) or [{U(Tren^{DMBS})(μ-OC)$_2$-Mn(CO)$_3$}$_2$] (**69**), in each case (Scheme 27).

Both complexes were structurally characterised and exhibited very similar structural features with minor differences ascribed to the greater steric demands of Tren^{DMBS} relative to Tren^{TMS}. IR data for the two complexes revealed the expected isocarbonyl stretching bands at 1731 and 1734 cm^{-1} for **68** and **69**, respectively.

Rhenocene derivatives

The aforementioned uranium–manganese complexes underscore the difficulties in isolating metal–metal bonds when carbonyl groups are present since *via* backbonding carbonyls can carry an appreciable charge and make them better donors to uranium than the manganese centres. As an alternative to carbonyl-containing anionic manganese fragments, construction of a U–Mn bond featuring the bis(η^5-cyclopentadienyl)manganese (manganocene) anion was attempted as the absence of carbonyl co-ligands should circumvent the problem of isocarbonyl formation. However, as shown in Fig. 8, [KMnCp$_2$] reacts with [U(Tren^{TMS})(THF)$_2$][BPh$_4$] (**19**) under a variety of conditions to produce the bridging oxo complex [{U(Tren^{TMS})}$_2$(μ-O)] (**60**).[15b] As a result, the rhenium analogue of the manganocene anion, [ReCp$_2$]$^-$, has been targeted construct Tren–uranium–metal bonds as it was anticipated that U–Re bonds should be more stable than U–Mn bonds on the basis of improved Re 5d orbital overlap with the U valence orbitals relative to that for 3d manganese. Accordingly, it has been found that both salt- and alkane-elimination methods can be used to access unsupported U–Re complexes, either *via* the reaction of **5** with pale yellow [KReCp$_2$] or **21** with yellow rhenocene hydride, [ReCp$_2$H], to produce the dark red complexes [U(Tren^{TMS})(ReCp$_2$)] (**70**) or [U(Tren^{DMBS})(ReCp$_2$)] (**71**), respectively (Scheme 28).[14a,55]

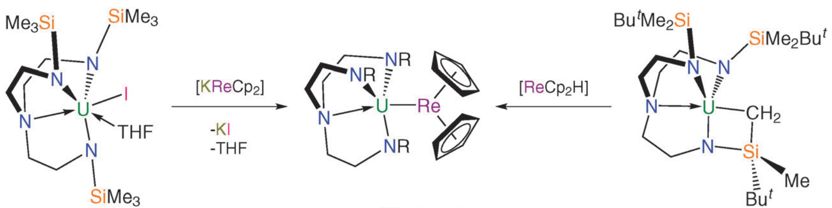
The heterobimetallic complex **70** was the first structurally authenticated uranium–transition metal bond, with a U–Re



16 **21**

R = SiMe$_3$ **68**
R = SiMe$_2$Bu^t **69**

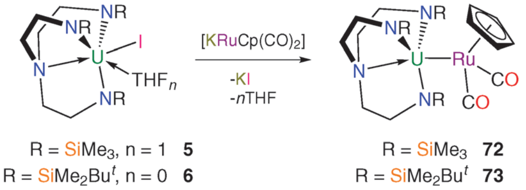
Scheme 27 Synthesis of **68** and **69**.



5 **21**

R = SiMe$_3$ **70**
R = SiMe$_2$Bu^t **71**

Scheme 28 Synthesis of **70** and **71**.



Scheme 29 Synthesis of **72** and **73**.

bond distance of 3.0475(4) Å, *ca.* 0.42 Å shorter than the sum of the covalent radii of uranium and rhenium (3.47 Å).[28] Complex **71** could not be prepared by salt elimination, presumably due to the increased steric bulk of the Tren^{DMBS} ligand, so was accessed *via* the treatment of the alkyl complex **21** with rhenocene hydride. Complex **71** was characterised by single crystal XRD, revealing a U–Re bond of 3.0479(6) Å, which is virtually identical to the U–Re bond length in **70**. DFT analysis of **70** and **71** describes the bonding as polarised-covalent, notably with σ- and very weak π-bonding components in the U–Re bonding interactions.[55a]

Cyclopentadienyl ruthenium dicarbonyl derivatives

Analogously to **70** and **71**, and to earlier reports of [Th(η^5-C_5Me_5)(I){RuCp(CO)$_2$}] and [LuCp$_2$(THF){RuCp(CO)$_2$}],[56] Tren–uranium–ruthenium complexes were targeted using the [RuCp(CO)$_2$]$^-$ anion, the heavier congener of the ubiquitous [FeCp(CO)$_2$]$^-$ fragment. Complexes **5** and **6** both react with [KRuCp(CO)$_2$] to afford orange crystals suitable for single crystal XRD studies, which confirmed the anticipated bimetallic structures of [U(Tren^{TMS}){RuCp(CO)$_2$}] (**72**) and [U(Tren^{DMBS})-{RuCp(CO)$_2$}] (**73**), Scheme 29.[57]

Heterobimetallic complexes **72** and **73** were the first structurally authenticated examples of uranium–ruthenium bonds, with U–Ru bond distances of 3.0925(3) and 3.0739(2) Å, respectively. Similarly to **70** and **71**, the uranium–metal bonds in **72** and **73** are approximately 0.33 and 0.35 Å shorter than the sum of the covalent radii of uranium and ruthenium (3.42 Å),[28] respectively, although unlike **71**, **73** could be prepared *via* salt elimination. The U–Ru bond length of 3.0739(2) Å in **73** is very slightly shorter than that in **72**, which was surprising considering the increased steric demands of Tren^{DMBS} relative to Tren^{TMS}. A theoretical study of **72** and **73** suggested that the bonding is predominantly electrostatic in nature.[57]

Summary & conclusions

This *Feature Article* provides an up-to-date account of the diverse array of Tren–uranium chemistry presented in the scientific literature. It is now clear that the marriage of uranium with triamidoamine ligands is a profitable one, Fig. 9. The Tren ligand certainly imparts kinetic and thermodynamic stability, by virtue of being a quadridentate ligand and forming relatively strong uranium–amide bonds. There is mounting evidence that the trialkylamine, which often resides *trans* to a novel ligand, is implicated in electronic stabilisation of such linkages by the inverse-*trans*-influence. The steric variation of the *N*-R groups is also key, not only in terms of optimising the crystallinity of target complexes, but also by controlling the coordination environment at uranium. When the SiMe$_3$ group is used, solvent may coordinate to uranium, however moving to the bulky SiPr$^i_3$ group generally precludes solvent coordination and generates a well-defined pocket to stabilise reactive groups. Perhaps the clearest demonstration of the effect of the steric bulk of the *N*-R groups is in reactivity studies; **11** reacts with dinitrogen and carbon monoxide, whereas the much bulkier **15** does not, but in contrast **15** has so far proven to be the only triamidoamine uranium complex capable of stabilising a terminal nitride linkage. Tren ligands are also capable of stabilising uranium over all commonly accessible oxidation states (III–VI), which is important for reactivity in stoichiometric and catalytic transformations as well as stabilising reactive ligand fragments. Lastly, Tren uranium complexes have been shown to exhibit single molecule magnetism, which exploits the strong axial crystal field that results from an axial amine-multiply bonded ligand combination; given the single molecule magnetism of uranium is burgeoning this holds promise. Although the complexes described herein are highly air and moisture sensitive, the straightforward ability to control the steric and electronic properties of Tren–uranium fragments by variation of the *N*-substituents holds much promise for future endeavours. It is therefore likely that Tren–uranium chemistry will continue to deliver exciting developments in the future.

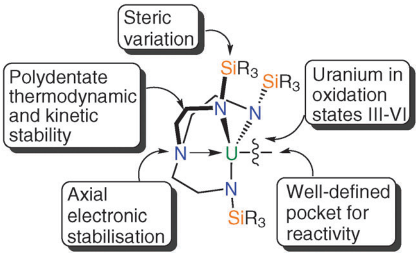


Fig. 9 Summary of design features of uranium triamidoamine complexes.

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