Evidence for single metal two electron oxidative addition and reductive elimination at uranium

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Reversible single-metal two-electron oxidative addition and reductive elimination are common fundamental reactions for transition metals that underpin major catalytic transformations. However, these reactions have never been observed together in the f-block because these metals exhibit irreversible one- or multi-electron oxidation or reduction reactions. Here we report that azobenzene oxidises sterically and electronically unsaturated uranium(III) complexes to afford a uranium(V)-imido complex in a reaction that satisfies all criteria of a single-metal two-electron oxidative addition. Thermolysis of this complex promotes extrusion of azobenzene, where H-/D-isotopic labelling finds no isotopomer cross-over and the non-reactivity of a nitrene-trap suggests that nitrenes are not generated and thus a reductive elimination has occurred. Though not optimally balanced in this case, this work presents evidence that classical d-block redox chemistry can be performed reversibly by f-block metals, and that uranium can thus mimic elementary transition metal reactivity, which may lead to the discovery of new f-block catalysis.
Redox chemistry is a defining feature of transition metal (d-block) chemistry. Within this realm, oxidative addition, first discovered over 50 years ago, is a fundamentally important and elementary transformation. Two types of oxidative addition are known, involving either two single-electron oxidations, involving two metal centres (MLn, Ln = ancillary ligands) or a binuclear complex (Fig. 1a), or the more classical single-metal two-electron reaction (Fig. 1b). In order to define these reactions, a number of criteria are applied to classify them, where for the former oxidative addition reaction of type (a), the oxidation state (OS), valence electron (VE) and coordination number (CN) all increase by one, the d-electron count (dn) decreases by one, and new covalent M–A and M–B bonds are made at different metal centres. In the latter oxidative addition reaction of type (b), the O.S., V.E., and C.N. all increase by two, the d6 count becomes d6−2, and two new covalent M–A and M–B bonds are made at the same metal centre. Of the two types of oxidative addition reaction, which describe the overall reaction with no mechanistic implications, the latter is the most important type, and the reverse reaction is defined as reductive elimination; together, these two principal reaction types constitute the key steps that underpin most catalytic reactions. With notable main group exceptions such as Grignard (and heavier group 2 congeners) formation (e.g., Mg0 + RX → RMgII)X−3 and oxidative additions/reductive eliminations involving group 13–15 elements, this mode of reactivity generally remains the preserve of transition metals.

In contrast, the physicochemical properties of the f-block metals render them generally unable to support classical oxidative addition and reductive elimination reactions because the lanthanides and actinides cannot typically access two electron metal-based redox couples, though irreversible Grignard type reactions (e.g., M2+ + RI → RMII)1; M = Eu, Yb, Sm, R = Me, Et, Ph21, which are oxidative additions overall, are known; their reactivity is instead usually defined by single-electron transfers and σ-bond metathesis chemistries that exploit their highly electropositive and polarising natures. Indeed, f-block catalysts can be highly active in σ-bond metathesis reactions22, but despite decades of f-block research there are no examples of any lanthanide or actinide complexes that perform pure, classical oxidative addition and reductive elimination reactions. It should be noted that in recent years some spectacular uranium-mediated multi-electron transfer reactions have been reported23,24, but these utilise metal-ligand redox cooperativity and even when an oxidative addition or reductive elimination is observed it is irreversible and/or does not fit the above definitions.25,26. If reversible oxidative addition and reductive eliminations could be established for any f-block complex, this would demonstrate transition metal-like reactivity and that these elements might be harnessed in new types of catalysis.

When contemplating introducing classical oxidative addition and reductive elimination reactions to f-block chemistry, a number of factors need to be addressed. Heavier elements are more likely to react since their VE are less tightly bound than in lighter elements. An electron rich, low OS metal will be more oxidisable. Hard σ-donor ligands will favour oxidative addition since they stabilise the resulting higher OS of the metal. Relatively small, sterically undemanding ligands and a large metal will favour oxidative addition, as the coordination sphere of the metal will not be overcrowded. Strong M–A and M–B bonds and a weak A–B bond will favour oxidative addition, but those bond energetics are often finely balanced, resulting in oxidative addition and reductive elimination being viewed as a reversible process, Fig. 1b. With these considerations noted, we concluded that uranium, well known to exhibit variable OSs, represents a promising f-block metal with which to target oxidative addition and reductive elimination since its properties compare favourably with the above criteria. However, although examples of oxidative addition-type behaviour of substrates by uranium, which are distinct to two-electron oxidations of uranium to give terminal mono-oxo and -imido ligands, are known or proposed, they are limited to examples that do not conform to the classical definition. For example, cooperative multi-metallic redox transformations (Type (a) in Fig. 1) utilising multiple single-electron uranium redox couples [U(III) → U(IV) or U(V) → U(VI)], where one new covalent uranium-ligand bond per uranium centre is formed are known.30–36. Non-innocent ligands can provide multi-electron reservoirs with apparent oxidation and one or two new uranium-ligand covalent bonds are formed but the formal uranium OS is unchanged in reactant and product37–39, or a combination of uranium and non-innocent ligand reductive reactions can occur.40–43 The electron paramagnetic resonance (EPR) data in one study suggest possible oxidative addition of water to uranium(III)44. Where reductive elimination is concerned, few examples exist. For instance, biphenyl is known to eliminate from [UO2Ph2] to give UO2.45. Elimination of oxidatively coupled dibenzyl from tetrabenzyl uranium following addition of a non-innocent diazabutadiene (DAB) ligand has been reported, but the formal OS of uranium remains (IV) in the reactant and product and the benzyl electrons reduce the DAB ligand and not uranium.46. H-H and C-H formal reductive eliminations can generate a masked form of [U(C5Me5)2H]2, but the formal OS of uranium remains (IV) in reactant and product.47. Lastly, bimetallic reductive elimination of dihydrogen from uranium hydrides, exploiting multiple single-electron U(IV) to U(III) redox couples, is known [reverse of Type (a) in Fig. 1]48,49. Thus, noting catalytic reduction of azides50 and reversible bimetallic one-electron, per uranium(III) ion, addition-elimination reactions of pyrazine51 that do not fit the definitions above, an f-block system exhibiting reversible classical oxidative addition and reductive elimination is yet to be realised.

Here, we report evidence for bona fide oxidative addition and reductive elimination reaction at an f-block centre. We exploited a reactive, sterically open and electronically unsaturated uranium (III) trimide complex that supports a reversible two-electron metal-centred U(III)–U(IV) redox couple. This oxidative addition-reductive elimination couple is not well-balanced, but it suggests that the idea that f-block elements can support such reactivity is valid and could form the basis for new catalytic cycles supported

![Fig. 1](https://example.com/f1.png)

**Fig. 1** Principal types of oxidative addition reaction observed with d-block metals. a Two single-electron oxidations of an A–B bond of a substrate at either transition metal centres (M) or a binuclear complex resulting in changes of +1 to the oxidation state (OS), valence electron (VE) and coordination number (CN) of the metals and a reduction of d-electrons by one. b Classical two-electron oxidative addition, the reverse of which is reductive elimination, of an A–B bond with a single transition metal centre, resulting in changes of +2 to the metal OS, VE, CN, and a reduction of d-electrons by two.
Fig. 2 Synthesis and reactivity of 3. Reduction of 1 by different routes involving either reduction in the presence of stabilising polyamines to give 2.tmeda or 2.pmdeta, which react with azobenzene or D10-labelled azobenzene to give 3, or a one-pot approach via 2. Thermolysis of 3 extrudes azobenzenes by a concerted process to presumably regenerate 2, but the latter decomposes under thermolytic conditions. Ar = 3,5-Me2C6H3.

Results

Precursor synthesis and the oxidative addition product. We previously reported that reduction of the uranium(IV) triamide complex [U(TsXy)(Cl)(THF)] [1, TsXy = H(SiMe2NAr)H] or a one-pot approach via 2. Thermolysis of 3 extrudes azobenzenes by a concerted process to presumably regenerate 2, but the latter decomposes under thermolytic conditions. Ar = 3,5-Me2C6H3.

by elementary reactions that are usually restricted to transition metals.

Fig. 3 Molecular structure of [U(TsXy)(tmeda)] (2.tmeda) at 120 K with 40% probability ellipsoids. Hydrogen atoms and minor disorder components are omitted for clarity. Selected distances: U1-N1 2.307(8), U1-N2 2.310(9), U1-N3 2.320(7), U1-N4 2.771(8), U1-N4A 2.760 (7) Å.
3 in 47% yield (Fig. 2). In order to confirm the synthesis of 3, we also prepared it independently from the aforementioned arene complex $[[\text{U(Ts}^\text{Xy})]_2(\mu-\eta^6-\eta^6-\text{C}_6\text{H}_5\text{Me})]$ with concomitant elimination of toluene, but in reduced 29% crystalline yield. This latter reaction is reminiscent of the reaction of the diuranium arene inverted sandwich complex $[\text{K}_2\text{I}]\{[\text{U(NCMes-But)}_3(\mu-\eta^6-\eta^6-\text{NPh})]_2\}$ with azobenzene which afforded the uranium(V)-imido dimer $[[\text{U}(\text{NCMesBut})_3(\mu-\eta^6-\eta^6-\text{NPh})]_2]$.

Solid state structures. The solid-state structures of 2-tmeda and 2-pmdeta were determined by single crystal X-ray diffraction and are illustrated in Figs. 3 and 4 with selected bond lengths (See Supplementary Tables 1 and 2). The uranium(III) centres are coordinated to the tridentate Ts$^\text{Xy}$ ligand through the three amide donor atoms leaving the remaining coordination hemispheres to be completed by the di- and tridentate polyamine ligands. The striking feature of the structures of 2-tmeda and 2-pmdeta is that if they are considered without the stabilising amine then the coordination sphere of the uranium(III) ion would clearly be extraordinarily exposed since the Ts$^\text{Xy}$ ligand barely occupies a hemisphere of coordination space at uranium, which nicely accounts for the high reactivity of 2. The U–N$\text{amido}$ distances span the range 2.307(8)–2.394(6) Å for 2-tmeda and 2-pmdeta, which considering their five- and six-coordinate uranium(III) ions compares very well to the U–N$\text{amido}$ distance of 2.320(4) Å in three-coordinate $[\text{U}[\text{N}(\text{SiMe}_3)_2]]$ this is consistent with the uranium(III) formulations of 2-tmeda and 2-pmdeta, and this range compares well to the U–N distances in pentavalent $[[\text{U(Ts}^\text{Xy})]_2(\mu-\eta^6-\eta^6-\text{C}_6\text{H}_5\text{Me})]$ and $[[\text{U(NCMesBu)}_3(\mu-\eta^6-\eta^6-\text{NPh})]_2]$ which is consistent with a uranium(V) formulation. The bridging U–N$\text{amido}$ distances of 2.208(4) and 2.210(4) Å are essentially indistinguishable from the U–N$\text{amido}$ distances reflecting their bridging nature; for comparison, uranium(V) terminal imido bond lengths tend to be ~1.95 Å.

The electronic absorption spectrum of 3 was confirmed by single crystal X-ray diffraction and is illustrated in Fig. 5 (for the isosstructural D$^{10}$-analogue prepared using D$^{10}$-PhNNPh see Supplementary Fig. 5). The salient feature of 3 is its dimeric centrosymmetric formulation with bridging imido groups to give five-coordinate uranium centres. The U–N$\text{amido}$ distances in 3 span the range 2.205(4)–2.228(4) Å, which is ~0.15 Å shorter than the corresponding distances in 2-tmeda and 2-pmdeta and this range compares well to the U–N distances in pentavalent $[[\text{U(Ts}^\text{Xy})]_2(\mu-\eta^6-\eta^6-\text{C}_6\text{H}_5\text{Me})]$ and $[[\text{U(NCMesBu)}_3(\mu-\eta^6-\eta^6-\text{NPh})]_2]$ which is consistent with a uranium(V) formulation. The bridging U–N$\text{amido}$ distances of 2.208(4) and 2.210(4) Å are essentially indistinguishable from the U–N$\text{amido}$ distances reflecting their bridging nature; for comparison, uranium(V) terminal imido bond lengths tend to be ~1.95 Å.

Both imido phenyl rings are orientated perpendicular to the uranium–uranium vector, so neither of the imido centres can be considered to be doubly-bonded to one uranium and dative-bound to the other uranium centre, which is consistent with the symmetrical nature of the U$_2$N$_2$ four-membered ring.

Characterisation data. In order to probe the formal OSs of uranium in 2-tmeda, 2-pmdeta, and 3, and hence unambiguously confirm the occurrence of classical oxidative addition, we examined their ultraviolet/visible/near-infrared (UV/Vis/NIR) electronic absorption and EPR spectra, and magnetic properties (Supplementary Figs. 6–14). The electronic absorption spectrum of 3 in toluene exhibits broad absorptions at 6570, 7650, and 9815 cm$^{-1}$ ($\varepsilon = 40–70 \text{ M}^{-1}\text{ cm}^{-1}$) in the NIR region, which are characteristic of Laporte forbidden 5$f\rightarrow 5$f transitions for uranium(V) from the $^2\text{F}_{5/2}$ ground state to the $^2\text{F}_{7/2}$ excited state electronic manifold, and a strong ligand to metal charge transfer (LMCT) band which talls in from the UV-region to ~10,000 cm$^{-1}$. The electronic absorption spectrum of 2-tmeda and 2-pmdeta in toluene are distinct from that of 3, but also exhibit Laporte forbidden 5$f\rightarrow 5$f transitions in the NIR region

Fig. 4 Molecular structure of $[[\text{U(Ts}^\text{Xy})(\text{pmdeta})]]$ (2-pmdeta) at 120 K with 40% probability ellipsoids. Hydrogen atoms and minor disorder components are omitted for clarity. Selected distances: 2-pmdeta - U1-N1 2.373(5), U1-N2 2.394(6), U1-N3 2.355(5), U1-N4 2.831(7), U1-N5 2.866(7), U1-N6 2.899(6) Å.

Fig. 5 Molecular structure of $[[\text{U(Ts}^\text{Xy})(\mu-\text{NPh})]]$ (3) at 90 K with 40% probability ellipsoids. Hydrogen atoms and minor disorder components are omitted for clarity. 3-D$_{10}$ is isostuctural to 3. Selected distances: 3-U1-N1 2.221(4), U1-N2 2.228(4), U1-N3 2.205(4), U1-N4 2.208(4), U1-N4A 2.210(4) Å.
Reductive elimination studies. While initially attempting to isolate pure crystalline 3, we noticed that when we placed 3 under dynamic vacuum and gentle heat to remove residual solvent from washing during work-up an orange material slowly began to extrude from 3. The rate of extrusion can be moderately increased by heating 3 to >100 °C under sublimation conditions, but it is kinetically hindered by the crystalline nature of isolated 3 even when finely-ground. Collection of the orange material and analysis by NMR spectroscopy revealed it to be azobenzene, which was confirmed by comparison of its NMR spectra to those of an authentic sample from a commercial supplier and by a peak at m/z = 181 ([PhNPhN−H]+) in the negative mode electrospray ionisation mass spectrum of this material (Supplementary Figs. 15–19). In order to confirm this result, we isolated 3 by washing the crystalline material with dry pentane and drying under a nitrogen flow, then took this material and heated it in a sublimation tube, after confirming purity by NMR spectroscopy and elemental analysis, with an identical result.

Uranium(III) is strongly reducing and uranium(V) is strongly oxidising, and it would appear that 3 is close enough to the cusp of this redox couple so that the initial oxidative addition reaction that produces 3 can be reversed by reductive elimination when thermally instigated. This view is supported by the fact that treatment of 3 with sources of H+, e.g., water, results in decomposition and the liberation of PhNH2, as assayed by 1H NMR spectroscopy, with no PhNPh detected under those conditions.

The extrusion of PhNPh from 3 suggests that a concerted reductive elimination is occurring, but monometallic and/or nitrene mechanisms would compromise the claim of reductive elimination from 3. Therefore, we prepared 3-D10 using D10–PhNPh and thermolysed a homogenous 50:50 mixture of 3 and 3-D10; if a concerted reductive elimination mechanism operates pure H10–PhNPh and D10–PhNPh would be obtained but if monometallic intermediates or nitrenes are generated then H2/D2–PhNPh would be formed as well as H10–PhNPh and D10–PhNPh. Experimentally, we find that only H10–PhNPh and D10–PhNPh are formed (Supplementary Figs. 20 and 21), as evidenced by electrospray ionisation mass spectrometry (Supplementary Fig. 22), which shows peaks at m/z 183 ([PhNPhNPhH]+) and 193 ([D10–PhNPhH]+) in positive ion mode, but the m/z 188 peak for ([H2/D2–PhNPhH]+) is absent (Fig. 7). Further, when Ph3C=CH2, an established nitrene trapping agent (Z- or E-Ph(H)C=CH(H)Ph are too volatile), is mixed into the reductive elimination mixture no aziridine products that would be expected from nitrene generation are observed, and only PhNPh is isolated again.

Mechanistic studies. Oxidative addition describes the overall reaction and has no mechanistic implications. However, to be
considered a true oxidative addition the reactions of 2.tmeda and 2.pmdeta should not proceed via a terminal uranium-imide monomer. In order to probe this aspect, since in situ probing of this reaction by NMR or optical spectroscopies were not practicable, we modelled the reaction computationally since DFT reaction profile calculations have proven their ability to reliably describe the redox activity of f-element molecules; we provide ΔH and ΔG data, and note that the latter presents essentially the same picture as the former, but use the former in our discussions since the latter introduces errors from the way ΔS is calculated within the harmonic approximation (See Supplementary Tables 3–15).

At the B3PW91 level of theory, we examined the formal four-electron reduction of PhNNPh in the presence of 2, with the polyamine ligands omitted from the calculations for computational efficacy (Fig. 8). Overall, the reaction of two equivalents of 2 with PhNNPh to give 3 is found to be highly favoured enthalpically (−42.1 kcal mol\(^{-1}\) overall), where the complete cleavage and reduction of the PhNNPh is readily apparent along with oxidation of each uranium from +3 to +5 OSs as evidenced by excellent agreement of key metrical bond length data (Supplementary Fig. 23). Initially, one electron reduction of azobenzene, induced by coordination to uranium is found to be exothermic by 25.7 kcal mol\(^{-1}\). The formal OS of the uranium ion in this species is IV, which is apparent from the 0.08 Å elongation of the N–N distance of the azobenzene with respect to the computed distance of 1.257 Å for free azobenzene in the gas-phase, and we note that N=N distances span the range ~1.10–1.25 Å in crystallographically authenticated examples of free-azobenzene\(^{34}\). The elongated N–N distance is within the range of experimentally determined mono-reduced azobenzenes in f-element chemistry\(^{63–66}\), and the spin density is also commensurate with the uranium(IV) assignment (Supplementary Fig. 24). It should be noted that the coordinated azobenzene radical is now somewhat distorted with respect to the free molecule, but still maintains its trans configuration. Isomerisation of the coordinated azobenzene to obtain a cis conformer affords an energetically more stable intermediate, int-B, being −37.5 kcal mol\(^{-1}\) with respect to 2. Surprisingly, examination of the spin density distribution reveals a broken symmetry state, with two α-spin electrons located on the uranium ion and one β-spin diffused onto the azobenzene fragment. Interestingly, an intermediate with minor geometry variations that is extremely close in energy could be located, which corresponds to the intermediate int-C. In the latter, the N–N distance is 1.41 Å, which is in the region of doubly reduced azobenzenes (See Supplementary Fig. 25)\(^{64–66}\). Hence, these two distinct intermediates are very close in energy, and can be viewed as the two limiting forms of the intermediate that would have strong multi-reference character and we note that this presents a similar spin density picture to that found in ytterbium intermediate-valence compound\(^{67}\). Inspection of the molecular orbitals of int-C reveals an intriguing bonding situation; specifically, its singly occupied molecular orbital principally represents overlap between a general setting \(m = 2\) type 5f orbital with the N–N π*-orbital of the azobenzene (Fig. 9). Fascinatingly, four lobes from the 5f orbital overlap with the four lobes of the aforementioned π*-orbital in a δ-type bonding motif. It should be noted that the same bonding situation is found in int-B.

The formation of a terminal uranium(V)-imido monomer complex, int-D, was investigated. This reaction is slightly endothermic compared to int-B and int-C (4.6 and 3.3 kcal mol\(^{-1}\), respectively) so that these two complexes could in principle be in equilibrium. However, the coordination of a second molecule of 2 to \([\text{U(Ts}^{\text{V}})\left(\text{cis}^2\text{-PhNNPh}\right)]\) and subsequent two-electron reduction, yielding the final bis-imido bimetallic complex 3, is
exothermic by a further 5.9 kcal mol\(^{-1}\). On the basis of those data it is difficult to ensure that the overall four-electron reduction is direct and not involving formation of two terminal imido complexes by two two-electron reductions that subsequently dimerise. However, given the sterically wide-open coordination sphere of uranium with a \(\text{Ts}^{\text{XY}}\)-ligand set a terminal imido complex would certainly react with unsaturated substrates. Therefore, we examined reactions of 2.tmeda and 2.pmdeta with PhNNPh in the presence of alkynes and also the addition of alkynes to already prepared and isolated 3. If a terminal imido complex were ever to exist as an intermediate, then it would undergo a \([2 + 2]\)-cycloaddition to yield a metallacyclobutadiene-type complex formation. However, a range of alkynes (\(\text{MeC} = \text{CMe}, \text{PhC} = \text{CPh}, \text{BuC} = \text{CCH}, \text{Me}_{2}\text{SiC} = \text{CCH}\)) are found experimentally to not react, and even the polar and thus reactive \(\text{Bu} = \text{C} = \text{P}\) does not react where it has previously been found to be much more reactive than \(\text{PhC} = \text{CPh}\).58–71 These observations, however, are in agreement with the calculated reaction profile (see Supplementary Fig. 26), which for \(\text{MeC} = \text{CMe}\) as an exemplar reveals that the hypothetical product of a \([2 + 2]\)-cycloaddition between \([\text{U}(\text{Ts}^{\text{XY}})(\text{NPh})]\) and \(\text{MeC} = \text{CMe}\) exhibits an activation barrier of 12.3 kcal mol\(^{-1}\) uphill and is thus disfavoured though in principle is accessible under experimental conditions. We note that the energy of the final \([2 + 2]\)-cycloaddition product for \(\text{MeC} = \text{CMe}\) is 15.2 kcal mol\(^{-1}\) lower than the experimentally observed outcome of 3, and so is thermodynamically favoured yet not observed. Furthermore, we tested reactions also with \(\text{Bu} = \text{CN}, \text{Bu} = \text{NCO}\) and \(\text{PhNCO}\) and find no evidence of any reactivity. Lastly, we tested the reactivity of 2.tmeda with one equivalent of \(\text{PhN}_{2}\) in an attempt to prepare \([\text{U}(\text{Ts}^{\text{XY}})(\text{NPh})(\text{tmeda})]\), but we find no evidence for the formation of this monomeric imido complex and in fact isolate only \([\text{U}(\text{Ts}^{\text{XY}})](\mu - \text{n}^6\text{n}^6\text{C}_6\text{H}_5\text{Me})\). This suggests, in-line with calculations, that the monomeric imido version of 3 is thermodynamically high-lying and does not play a role in this chemistry. The combined lack of experimental evidence for the monomer-route reaction that is consistent with the computationally derived reaction profile thus rules out the monometallic reduction route for the direct four-electron reduction of PhNNPh, and suggests that 2, 2.tmeda, and 2.pmdeta react by an oxidative addition route with PhNNPh.

Discussion

Although interpretation of the reaction that affords 3 is convoluted by the fact that a dimeric formulation is observed, it is instructive to analyse the fundamental characteristics of this transformation. As unequivocally demonstrated by the combined structural, spectroscopic and magnetic characterisation data, each uranium centre has been formally oxidised by two units (i.e., (III) in 2 to (V) in 3), the valence \(5f^0\) count is now \(5f^{n-2}\) (e.g., \(5f^3\) in 2 to \(5f^1\) in 3), the metal valence count per uranium centre has increased by two (i.e., 9 in 2 to 11 in 3 discounting any \(\pi\)-bonding as is normal practice), and two new covalently bound ligand bonds have been installed in the coordination sphere of each uranium centre in 3. Although 3 is dinuclear, from the perspective of each individual ion the transformation is clear-cut and since oxidative addition describes an overall transformation the reaction that produces 3 is thus a genuine, clear-cut oxidative addition, since it satisfies all the criteria for this reaction. This oxidative addition reaction is unique in actinide chemistry and contrasts to the previous multi-metal electron redox transformations described above.25–43 There are few examples of low valent uranium complexes reacting with diazobenzene, and where documented the resulting di-imido complexes derived from a uranium(II) equivalent in a four-electron transformation,42, cooperative uranium and non-innocent multi-electron redox couples involving charge loaded amines,26,32,73–74 or no cleavage of the \(\text{N}=\text{N}\) bond occurs to give \([\text{U}(\text{N} = \text{N})_3]\) species where the diazobenzene retains a \(\text{N}=\text{N}\) bond and is formulated as a radical anion:53 the latter is analogous to reactions of certain iridium complexes with dioxygen, where an \(\text{O}=\text{O}\) bond is retained and thus those reactions are not oxidative addition.74 Further, alternative mechanisms that would invalidate a claim of oxidative addition are found to be unfeasible by experimentally supported computational reaction profiles.

Where reductive elimination is concerned, isotopic labelling studies suggest that this reaction is concerted since only isotopically pure \(\text{H}_2\text{O}^-\) and \(\text{D}_2\text{O}^-\text{PhNNPh}\) compounds are formed and no isotopic cross-over products are observed. Furthermore, an established nitrene trap produces no aziridine products when reactions are spiked, which suggests that nitrenes are not generated that itself is consistent with a concerted reductive elimination. Thus, even though the uranium by-product of the reductive elimination step remains inherently unknown, since the reaction mixture becomes an intractable mixture of products due to the thermal regime, all the experimental and computational evidence are internally consistent and uniformly point to a reductive elimination reaction since no other reaction could credibly account for the reformation of diazobenzene.

The evidence we have assembled for reversible oxidative addition and reductive elimination chemistry of 2, 2.tmeda, 2.pmdeta and 3 advances the concept that these principal reaction types, which are key to classifying and understanding reactivity that has been prevalent and widely exploited in transition metal catalysis for over half a century, are feasible in f-block chemistry. This suggests that uranium can chemically mimic the d-block even though it is an actinide element. The question then arises as to why this system exhibits such reversible reactivity. This will certainly require further investigations, but some observations can be summarised at this juncture. The coordination of the \(\text{Ts}^{\text{XY}}\) ligand is quite open, which will allow substrates to enter and exit the coordination sphere of uranium straightforwardly. The ligand overall is quite rigid, so there would be anticipated to be minimal ligand-reorganisation energy that might be otherwise expected for a metal changing OS.75 Despite the overall ligand rigidity, we note that because the N-aryl groups are planar and ‘two-dimensional’ the nitrogen centres can easily rotate from trigonal-planar to -pyramidal geometries, as found in 3; they are thus in principle able to modulate their \(\pi\)-donor ability as required to meet the ligand donor requirements of the uranium ion as it shuttles from III to V OSs. Lastly, there are no other donor atoms in the \(\text{Ts}^{\text{XY}}\) ligand set other than the three amides to strongly favour metal high OSs compared to, for example, Tren ligands where the additional amine-anchor clearly stabilises high OS metal complexes and conversely destabilises low OS metal complexes.

The system reported here is clearly not optimised. However, the fact our combined experimental and computational evidence suggest that it can execute oxidative addition and be coerced into reductive elimination, with a substrate with a thermolytic disruption enthalpy of 93 kcal mol\(^{-1}\), validates the notion that with suitable ancillary ligands uranium catalysis that exploits elementary oxidative addition and reductive elimination pathways centred on a uranium(III/V)-redox couple may well be achievable. With optimised supporting ligands that better-balance the redox couple the prospect that this could therefore form the basis of new catalytic cycles in f-block chemistry, for example the production of aniline derivatives, becomes realistic.

Methods

General. Experiments were carried out under a dry, oxygen-free dinitrogen atmosphere using Schlenk-line and glove-box techniques. All solvents and reagents
were rigorously dried and deoxygenated before use. Compounds were variously characterised by elemental analyses, NMR, FTIR, EPR, and UV/Vis/NIR electronic spectroscopy and with Evans and SQUID magnetometric methods, single crystal X-ray diffraction studies, and DFT calculations. Further details are available in Supplementary Methods.

**Preparation of \([\text{U(TsXy)}_2(\text{p-mdeta})]\) (2.tmeda).** A solution of TMEDA (0.69 g, 4.0 mmol) in hexanes (15 ml) was added to a cold (–78 °C) stirring mixture of 1 (1.78 g, 2.0 mmol) and KC8 (0.3 g, 2.2 mmol). The stirring mixture was allowed to warm to room temperature slowly over 16 h. After this time, the purple solution was separated from the red dark purple precipitate by filtration through a fritted Schlenk, and the solids washed with hexanes (3 × 5 ml), combined extracts reduced to dryness in vacuo to yield a purple solid. Recrystallisation of the solids from hot hexanes yielded pure 2.tmeda as purple crystals. Purple block shaped crystals of 2.tmeda suitable for X-ray diffraction studies were grown by storage of a saturated hexanes solution of 2.tmeda at room temperature over 16 h. Yield: 0.60 g, 33%. Anal. Calc.: for C46H64N11Si7U: C, 44.22; H, 6.37; N, 7.29. Found: C, 44.74; H, 3.79; N, 7.17. FTIR (KBr): 3077 cm⁻¹ (vCH), 3057 cm⁻¹ (vCH), 2925 cm⁻¹ (vCH), 2857 cm⁻¹ (vCH), 1729 cm⁻¹ (vC=O), 1470 cm⁻¹ (vC=C), 1375 cm⁻¹ (vC–N), 1269 cm⁻¹ (vC–N), 1002 cm⁻¹ (vC–O).

**Preparation of \([\text{U(TsXy)}_2(\text{p-mdeta})]\) (2.pmdeta).** A solution of PMDETA (0.69 g, 4.0 mmol) in hexanes (15 ml) was added to a cold (–78 °C) stirring mixture of 1 (1.78 g, 2.0 mmol) and KC8 (0.3 g, 2.2 mmol). The mixture was allowed to warm to room temperature slowly over 16 h. After this time, the purple solution was separated from the black precipitate by filtration through a fritted Schlenk, and the solids washed with hot hexanes (3 × 5 ml), and the volatiles were removed under reduced pressure. Brown dark purple crystalline solids. Recrystallisation of the solid from hot hexanes yields pure 2.pmdeta as dark violet crystals (1.07 g, 56%). FTIR (KBr): 3095 cm⁻¹ (vCH), 3079 cm⁻¹ (vCH), 2959 cm⁻¹ (vCH), 2855 cm⁻¹ (vCH), 1728 cm⁻¹ (vC=O), 1472 cm⁻¹ (vC=C), 1367 cm⁻¹ (vC–N), 1264 cm⁻¹ (vC–N), 1004 cm⁻¹ (vC–O).

**Preparation of \([\text{U(TsXy)}_2(\text{p-mdeta})]\) (2.pmdeta).** A method: Hexanes (2 ml) were added to a cold (–78 °C) stirring mixture of 2.tmeda or 2.pmdeta (0.9 mmol) and azobenzene (0.08 g, 0.5 mmol) in an ampoule. The resultant mixture was allowed to warm to room temperature over 16 h. After this time, the mixture was heated and filtered while hot and the liquor was allowed to cool to room temperature and stored at room temperature for 16 h to yield crystals of 3. The solid residue was recrystallised from hot toluene (3 ml), filtered and allowed to cool to room temperature and stored at room temperature for 16 h also yielding crystals of 3. Both sets of crystals were isolated by filtration and dried by the passage of N2 over the surface. Yield (crystalline combined): 0.37 g, 47 %. Anal. Calculated for C46H78N11Si7U: C, 52.96; H, 5.96; N, 6.47; U, 9.49. Found: C, 53.30; H, 5.90; N, 6.47; U, 9.46. FTIR v/cm⁻¹ (Nujol): 3015 (1611), 2932 (1553), 2929 (1530), 2921 (1520), 2855 (1498), 2850 (1488), 2786 (1446), 2769 (1445), 2633 (1419), 2143 (1301), 1721 (1295), 1106 (1075), 1003 (977), 972 (945), 894 (853), 828 (812), 774 (740), 704 (671), 600, 587, 519, 500, 485, 456, 432, 417, 405, 386, 372, 350, 330, 318, 306, 295, 284, 273, 264, 253, 242, 231, 219, 208, 198, 187, 176, 165, 154, 143, 132, 121, 110, 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 5, 4, 3, 2, 1 cm⁻¹. Magnetic moment (Evans method, CD2Cl2): μeff = 2.79 μB.

**Preparation of \([\text{U(TsXy)}_2(\text{p-mdeta})]\) (2.pmdeta).** A method: Hexanes (2 ml) were added to a cold (–78 °C) stirring mixture of 1 (1.78 g, 2.0 mmol) and KC8 (0.3 g, 2.2 mmol). The mixture was allowed to warm to room temperature slowly over 16 h. After this time, the purple solution was separated from the black precipitate by filtration through a fritted Schlenk, and the solids washed with hot hexanes (3 × 5 ml), and the volatiles were removed under reduced pressure. Brown dark purple crystalline solids. Recrystallisation of the solid from hot hexanes yields pure 2.pmdeta as dark violet crystals (1.07 g, 56%). FTIR (KBr): 3095 cm⁻¹ (vCH), 3079 cm⁻¹ (vCH), 2959 cm⁻¹ (vCH), 2855 cm⁻¹ (vCH), 1728 cm⁻¹ (vC=O), 1472 cm⁻¹ (vC=C), 1367 cm⁻¹ (vC–N), 1264 cm⁻¹ (vC–N), 1004 cm⁻¹ (vC–O).

**Preparation of \([\text{U(TsXy)}_2(\text{p-mdeta})]\) (2.pmdeta).** A method: Hexanes (2 ml) were added to a cold (–78 °C) stirring mixture of 2.tmeda or 2.pmdeta (0.9 mmol) and azobenzene (0.08 g, 0.5 mmol) in an ampoule. The resultant mixture was allowed to warm to room temperature over 16 h. After this time, the hexanes (2 ml) were added to the residual solids and the mixture was heated and filtered while hot. Toluene (2 ml) was added to the residue and was heated and filtered whilst hot. Both solutions were stored at room temperature for 16 h and crystals of 3 were deposited in both. The crystals were isolated by filtration and dried by the passage of N2 over them. Yield (crystalline combined): 0.22 g, 29%. Further removal of solvent in vacuo was not achievable as 3 decomposes upon exposure to dynamic vacuum, but we note that 3 is thermally stable. Brown block shaped crystals of 3 suitable for X-ray diffraction studies were grown by storage of a saturated toluene solution of 3 at –30 °C over 16 h.

**Preparation of \([\text{U(TsXy)}_2(\text{p-mdeta})]\) (2.pmdeta).** A method: Hexanes (3 ml) were added to a cold (–78 °C) stirring mixture of \([\{\text{U(TsXy)}_2(\text{p-mdeta})]\] (0.83 g, 0.5 mmol) and azobenzene (0.09 g, 0.5 mmol) in an ampoule. The resultant mixture was allowed to warm to room temperature over 16 h. After this time, the mixture was heated and filtered while hot and the liquor was allowed to cool to room temperature and stored at room temperature for 16 h to yield crystals of 3. The solid residue was recrystallised from hot toluene, filtered and allowed to cool to room temperature and stored at room temperature for 16 h also yields crystals of 3. Both sets of crystals were isolated by filtration and dried by the passage of N2 over the surface. Yield (crystalline combined): 0.29 g, 47 %. Further removal of solvent in vacuo was not achievable as 3 decomposes upon exposure to dynamic vacuum. Brown block shaped crystals of 3 suitable for X-ray diffraction studies were grown by storage of a saturated toluene solution of 3 at room temperature over 16 h.

**Preparation of \([\text{U(TsXy)}_2(\text{p-mdeta})]\) (2.pmdeta).** A method: Hexanes (3 ml) were added to a cold (–78 °C) stirring mixture of 1 (0.89 g, 1.0 mmol), KC8 (0.14 g, 1.0 mmol) and azobenzene (0.09 g, 0.5 mmol) in an ampoule. The resultant mixture was allowed to warm to room temperature over 16 h. After this time, the mixture was heated and filtered while hot and the liquor was allowed to cool to room temperature and stored at room temperature for 16 h.

**Data availability.** The X-ray crystallographic coordinates for structures reported in this Article have been deposited at the Cambridge Crystallographic Data Centre.
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Author contributions
B.M.G., D.P., and E.L.: Conducted the synthetic work and analysed the data. C.E.K. and L.M.: Conducted and analysed the reaction profile calculations. F.T. and E.J.L.M.: Conducted and analysed the EPR and magnetic measurements. A.I.W.: Conducted crystallographic refinements. S.T.L.: Originated the central idea, supervised the work, analysed the data, and wrote the manuscript with input from all the authors.

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