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Introduction

The redox chemistry of uranium is dominated by single electron transfer reactions,¹ but examples of U(III) to U(V) electron transfer oxidations are increasingly observed.^{1a,2a-i} Notably, dinitrogen reduction to a hydrazido ligand by a diuranium(III) complex was recently reported to involve a two-electron transfer from each metal centre.³ Single centre U(IV)/U(VI) two-electron transfer reactions have also been reported with oxidative atom transfer agents.⁴ Redox reactivity of uranium compounds involving the transfer of more than two electrons has so far only been achieved by combining the uranium centre with redox active ligands capable of storing electrons and rendering them available to oxidising agents.^{5,6} Notably, several uranium-redox active ligand systems have been reported to effect the four-electron reductive cleavage of azobenzene.^{5c,d,h,6b,c,7-11} In particular, uranium(III)/(IV)-redox active ligand systems such as hydride,^{5e,7} tetraphenylborate,^{5d,8} bridging arene,⁹ bipyridine,^{6c} phosphinidene,¹⁰ and metallacyclopene¹¹ complexes reduce azobenzene to yield U(VI) bis(imido) complexes. Some of these

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Single metal four-electron reduction by U(II) and masked "U(II)" compounds†

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The redox chemistry of uranium is dominated by single electron transfer reactions while single metal four-electron transfers remain unknown in f-element chemistry. Here we show that the oxo bridged diuranium(III) complex $[K(2.2.2\text{-cryptand})_2\{((Me_3Si)_2N)_3U\}_2(\mu\text{-O})]$, **1**, effects the two-electron reduction of diphenylacetylene and the four-electron reduction of azobenzene through a masked U(II) intermediate affording a stable metallacyclopene complex of uranium(IV), $[K(2.2.2\text{-cryptand})][U(\eta^2\text{-C}_2Ph_2)\{N(SiMe_3)_2\}_3]$, **3**, and a bis(imido)uranium(VI) complex $[K(2.2.2\text{-cryptand})][U(NPh)_2\{N(SiMe_3)_2\}_3]$, **4**, respectively. The same reactivity is observed for the previously reported U(II) complex $[K(2.2.2\text{-cryptand})][U\{N(SiMe_3)_2\}_3]$, **2**. Computational studies indicate that the four-electron reduction of azobenzene occurs at a single U(II) centre *via* two consecutive two-electron transfers and involves the formation of a U(IV) hydrazide intermediate. The isolation of the *cis*-hydrazide intermediate $[K(2.2.2\text{-cryptand})][U(N_2Ph_2)\{N(SiMe_3)_2\}_3]$, **5**, corroborated the mechanism proposed for the formation of the U(VI) bis(imido) complex. The reduction of azobenzene by U(II) provided the first example of a "clear-cut" single metal four-electron transfer in f-element chemistry.

complexes also effect the multielectron reduction of alkynes to yield uranium metallacycles.^{5d,6c,7,9,10a,11a,b} The redox active ligands either remain bound to the metal during the electron transfer^{5h} or are expelled as byproducts.^{5c-e,6b-d,9}

The four-electron reductive cleavage of azobenzene was first achieved by C. Burns by using multiple equivalents of the U(III) complex $[(C_5Me_5)_2U^{III}Cl(NaCl)]$ to yield a mixture of U(VI) bis(imido) and U(IV) species.¹² The proposed mechanism involves two-electron transfer processes and the comproportionation of a U(V) intermediate, but the possibility of a U(II) intermediate cannot be completely ruled out. Complete cleavage of azobenzene by a single metal centre has so far been reported only for W(II),¹³ and four-electron transfer by a single metal centre remains unknown in f-element chemistry.

Uranium(II) compounds could potentially effect four-electron transfer, but only very few examples of uranium in the +2 oxidation state have been reported so far¹⁴ and their reactivity remains practically unexplored.¹⁵ Indeed, the very low redox potential of the isolated U(II) complexes renders it difficult to control their reactivity, which can result in competitive one electron transfer reactions rather than multielectron transfer reactions.^{10b} Conversely, complexes associating uranium in the +3 or +4 oxidation state to redox active ligands have proven effective in performing multielectron transfer reactions with a wide variety of substrates.⁵

Recently, we reported the synthesis of the diuranium(III) oxo complex $[K(2.2.2\text{-cryptand})_2\{((Me_3Si)_2N)_3U\}_2(\mu\text{-O})]$, **1** (ref. 16) and showed that complex **1** provides a convenient precursor for



studying the reactivity of U(II). Indeed, when complex **1** is reacted with N-heterocycles, it releases a “U(II)” synthon that effects one- or two-electron reductions depending on the N-heterocycle.¹⁶ We also found that the isolated U(II) complex [K(2.2.2-cryptand)][U{N(SiMe₃)₂}₃], **2**, previously reported by the Evans group^{14f} showed similar behaviour but its reactivity turned out to be more complicated to control due to its low stability in solution.

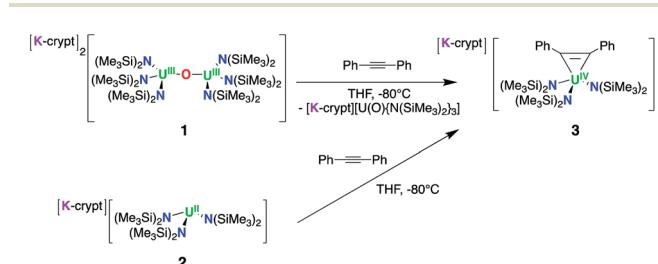
Here we report the reactivity of complexes **1** and **2** with diphenylacetylene and azobenzene. Complex **1** effects the two-electron reduction of diphenylacetylene to yield a stable uranium metallacyclopene complex through the delivery of a masked U(II). A similar reactivity is also observed for the U(II) complex [K(2.2.2-cryptand)][U{N(SiMe₃)₂}₃], **2**.

Moreover, we show that both the masked U(II) in **1** and the U(II) complex **2** reductively cleave azobenzene to yield a U(VI) bis(imido) complex, providing the first example of a “clear-cut” single metal four-electron reduction process in f-element chemistry. Computational studies show that in both cases the reaction proceeds at a single metal centre through the formation of a U(IV) hydrazido intermediate that could also be isolated at -40 °C.

Results and discussion

Synthesis and structural characterisation

The diuranium(III) oxo complex [K(2.2.2-cryptand)][$\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{U}_2(\mu\text{-O})$], **1** (ref. 16) reacts immediately with 1 equiv. of diphenylacetylene at -80 °C in THF. The ¹H NMR spectrum at -80 °C showed full conversion of complex **1** and the appearance of signals corresponding to the previously reported U(IV) oxo complex, [K(2.2.2-cryptand)][U(O){N(SiMe₃)₂}₃]. After removal of the U(IV) oxo complex, the metallacyclopene complex [K(2.2.2-cryptand)][U($\eta^2\text{-C}_2\text{Ph}_2$){N(SiMe₃)₂}₃], **3**, was isolated in 25% yield (Scheme 1). The conversion, as measured by ¹H NMR (using TMS₂O as internal standard), is >65%, and the low yield is due to the partial solubility of **3** in toluene used to remove the U(IV) oxo by-product. The products of the reaction are consistent with the release of a “U(II)” synthon and a U(IV) oxo complex upon addition of diphenylacetylene. A closely related U(II) “disproportionation reaction” to afford a U(IV) species and a “U(II)” synthon was reported in an early study by Marks and co-workers for the trinuclear U(III) complex {U(C₅Me₅)₂(μ -Cl)}₃ upon reaction with diphenylacetylene.^{5b}



Scheme 1 Reactivity of **1** and **2** with diphenylacetylene yielding the metallacyclopene complex **3**.

To further corroborate that complex **1** releases a “U(II)” synthon upon reaction with diphenylacetylene, we also explored the reactivity of the previously reported U(II) complex [K(2.2.2-cryptand)][U{N(SiMe₃)₂}₃], **2**.^{14f} Because, in our hands, previous attempts to carry out reactivity studies on isolated complex **2** had resulted in intractable mixtures of compounds,¹⁶ the reactivity was performed on THF solutions of **2** generated *in situ* at -80 °C, as previously described,^{14f} by reduction of [U{N(SiMe₃)₂}₃]¹⁷ with KC₈ in presence of 2.2.2-cryptand. The reaction of *in situ* generated **2** with 1 equiv. of diphenylacetylene also produced complex **3** in an isolated yield of 37%.

¹H NMR studies showed that complex **3** is stable in solid state and in solution at -40 °C but decomposes slowly in THF solution at room temperature.

In the solid-state structure of complex **3**, as determined by X-ray diffraction studies (Fig. 1), the uranium centre is bound by three anionic N(SiMe₃)₂ ligands and a bidentate dianionic PhCCPh. The C-C bond length of 1.342(5) Å is similar to those found in the three reported uranium metallacyclopene complexes (1.338(11) Å to 1.341(3) Å)^{10a,11b,18} and is in line with a double bond (1.331 Å). The U-C bond lengths of 2.345(3) Å and 2.352(3) Å and the value of the C1-U1-C2 angle of 33.22(11)° are comparable to those reported in the uranium metallacyclopene complexes (U-C = 2.303(3) to 2.350(9) Å), and C1-U1-C2 = (33.3(3)°, 33.7(1)°). Overall, the structural parameters are consistent with the assignment of **3** as a U(IV) metallacyclopene complex.

Actinide metallacyclopene compounds have shown interesting reactivity with heterounsaturated molecules but remain rare and essentially limited to cyclopentadienyl derivatives.^{10a,11b,19} Notably, the first example of a stable uranium metallacyclopene, the cyclopentadienyl derivative [$(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2\text{SiMe}_3)_2$]⁺, was isolated only recently.^{11b} Thus, the reactions of **1** and **2** with diphenylacetylene provide access to a new class of uranium metallacyclopene complexes.

In view of the observed ability of complexes **1** and **2** to effect multielectron transfer, we decided to investigate the reduction

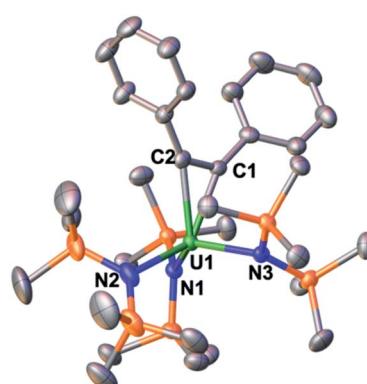
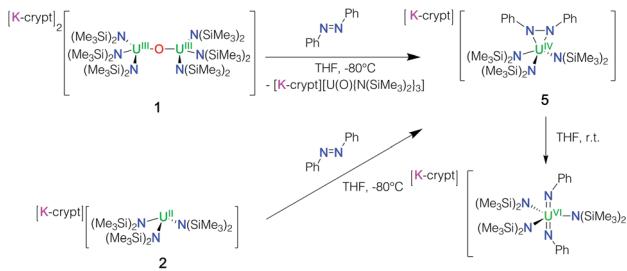


Fig. 1 Molecular structure of the [U($\eta^2\text{-C}_2\text{Ph}_2$){N(SiMe₃)₂}₃]⁻ component of **3**. Hydrogen atoms and the [K(2.2.2-cryptand)]⁺ counterion were omitted for clarity. Selected bond lengths (Å) and angles (°): U1-(Namide)avg 2.34(2), U1-C1 2.345(3), U1-C2 2.352(3), C1-C2 1.342(5), C1-U1-C2 33.22(11).





Scheme 2 Reactivity of **1** and **2** with azobenzene yielding the bis(imido) complex **4** through the hydrazido intermediate complex **5**.

of azobenzene, a potential four-electron oxidising agent. Upon addition of a red THF solution of azobenzene to dark purple crystals of complex **1** at $-80\text{ }^\circ\text{C}$, the solution immediately turned dark brown and the signals assigned to the terminal oxo complex $[\text{K}(2.2.2\text{-cryptand})][\text{U(O)}\{\text{N}(\text{SiMe}_3)_2\}_3]$ were observed in the ^1H NMR spectrum. After raising the temperature to $25\text{ }^\circ\text{C}$, the ^1H NMR spectrum showed additional signals at 6.97, 5.51, 5.44, and 0.46 ppm, assigned to the trans bis(imido) complex $[\text{K}(2.2.2\text{-cryptand})][\text{U(NPh)}_2\{\text{N}(\text{SiMe}_3)_2\}_3]$, **4** (Scheme 2). Single crystals of **4** were grown by slow diffusion of hexane at $-40\text{ }^\circ\text{C}$ into a concentrated THF solution. Washing with toluene removed the terminal U(IV) oxo complex $[\text{K}(2.2.2\text{-cryptand})][\text{U(O)}\{\text{N}(\text{SiMe}_3)_2\}_3]$ and allowed the isolation of clean complex **4** in 69% yield. Thus, following addition of azobenzene to **1**, the products of the reaction are consistent with the release of a U(IV) oxo and a “U(II)” synthon. The “U(II)” synthon effects the four-electron reduction of azobenzene to yield the bis(imido) complex.

Furthermore, the reaction at $-80\text{ }^\circ\text{C}$ of the freshly *in situ* prepared U(II) complex **2** with azobenzene also led to the isolation of the four-electron reduction product, the bis(imido) complex **4** in 37% yield. These results confirm that complex **1**

reacts as a U(II) synthon and that both complexes **1** and **2** are able to effect a single-metal four-electron reduction.

In the solid-state structure of **4** (Fig. 2), the uranium centre is five-coordinate and bound by three anionic $\text{N}(\text{SiMe}_3)_2$ ligands and two dianionic imido ligands with a trigonal bipyramidal geometry. The $\text{U}-\text{N}_{\text{imido}}$ bond lengths of $1.929(8)\text{ \AA}$ and $1.935(8)\text{ \AA}$ are similar to those reported in other U(VI) trans bis(imido) complexes ($1.840(4)$ to $1.992(5)\text{ \AA}$).^{5*a*,12*b*,20} In addition, the mean $\text{U}-\text{N}_{\text{amide}}$ bond length of $2.34(2)\text{ \AA}$ is close to the one reported for the analogous uranyl complex, $[\text{K}(2.2.2\text{-cryptand})][\text{U(O)}_2\{-\text{N}(\text{SiMe}_3)_2\}_3]$ ($2.323(2)\text{ \AA}$).²¹ The $\text{U}=\text{N}-\text{Ph}$ angles ($162.5(6)$ and $165.0(6)^\circ$) deviate significantly from linearity as found in other bis(imido) U(VI) complexes^{12*b*,22} and suggest partial localization of the pi lone pair on the imido nitrogen (supported by the bonding analysis in ESI†). *Trans* bis(imido) U(VI) complexes have attracted considerable interest in uranium chemistry because of their fundamental insight in the study of U-L multiple bonds, their isoelectronic structure with the ubiquitous uranyl(VI) cation and their potential application in small molecule activation and catalysis.^{1*a*,5*a*,20,23}

Complete cleavage of azobenzene by uranium(III) compounds was achieved in the past by using several equivalents of the U(III) complex^{2*b*,12*a*} or by coupling the U(III) centres to redox active ligands.^{5*a*,5*d*} The mononuclear U(III) complexes $[(\text{C}_5\text{Me}_5)_2\text{U}][(\mu\text{-Ph})_2\text{BPh}_2]$ ^{5*d*} and $[(\text{C}_5\text{Me}_5)_3\text{U}]^{5*d*}$ and the dinuclear complexes $\{[(\text{C}_5\text{Me}_5)_2\text{U}]_2(\mu\text{-C}_6\text{H}_6)\}^{24}$ and $\{(\text{C}_5\text{Me}_5)\text{U}[\mu\text{-C}_5\text{Me}_3(\text{CH}_2)_2](\mu\text{-H})_2\text{U}(\text{C}_5\text{Me}_5)_2$ (ref. 5*a*) were reported to effect the cleavage of 1 or 2 equiv. of azobenzene by transferring four or eight electrons, respectively. In these systems, it was suggested that the multielectron reductive chemistry proceeded by combining metal-centred three-electron U(III)/U(VI) transfers and ligand based one-electron transfers. Alternatively, the reduction of azobenzene by complexes **1** and **2** proceeds *via* an unprecedented U(II)/U(VI) four-electron transfer that, so far, was only observed in transition metal chemistry.

Uranium(IV) hydrazido complexes have long been invoked as intermediates in the four-electron reduction of azobenzene.^{2*h*,4*a*,12*a*} Recently, a U(IV) hydrazido species was isolated from the reaction of a U(III)-benzyl complex supported by bulky hydrotris(3,5-dimethylpyrazolyl)borate ligands with azobenzene, but further reduction of the N-N bond to yield the U(VI) bis(imido) species was not observed even at high temperature.^{6*b*}

In order to gain more insight into the mechanism of the four-electron reduction of azobenzene by complexes **1** and **2**, we performed computational studies (see the following section) and pursued the isolation of the probable intermediates by conducting crystallisation experiments at low temperature. X-ray quality crystals of the two-electron reduction intermediate $[\text{K}(2.2.2\text{-cryptand})][\text{U}(\text{N}_2\text{Ph}_2)\{\text{N}(\text{SiMe}_3)_2\}_3]$, **5**, could be isolated from the reaction mixture of **1** and **2** with azobenzene in THF by slow diffusion of hexane at $-40\text{ }^\circ\text{C}$. When the THF solution of **5** is left at room temperature, the complex immediately starts to convert into the U(VI) bis(imido) **4** and after 2 h is completely converted into **4**.

In the solid-state structure of **5** (Fig. 3), the uranium centre is five coordinate and bound by three $\text{N}(\text{SiMe}_3)_2$ ligands and one

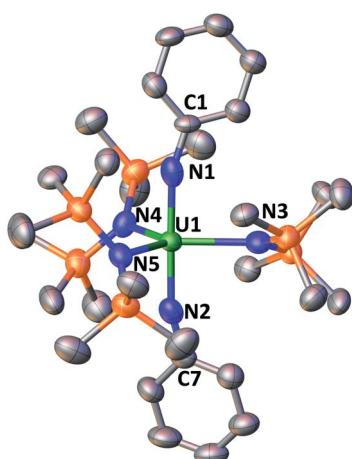


Fig. 2 Molecular structure of the $[\text{U}(\text{NPh})_2\{\text{N}(\text{SiMe}_3)_2\}_3]^-$ component of **4**. Hydrogen atoms and the $[\text{K}(2.2.2\text{-cryptand})]^+$ counterion have been omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): $\text{U1}-\text{(N}_{\text{amide}}\text{)}_{\text{avg}} 2.34(2)$, $\text{U1}-\text{N1} 1.929(8)$, $\text{U1}-\text{N2} 1.935(8)$, $\text{N1}-\text{U1}-\text{N2} 178.8(3)$, $\text{N1}-\text{U1}-\text{(N}_{\text{amide}}\text{)}_{\text{avg}} 89.6(5)$, $\text{N2}-\text{U1}-\text{(N}_{\text{amide}}\text{)}_{\text{avg}} 90.5(9)$.



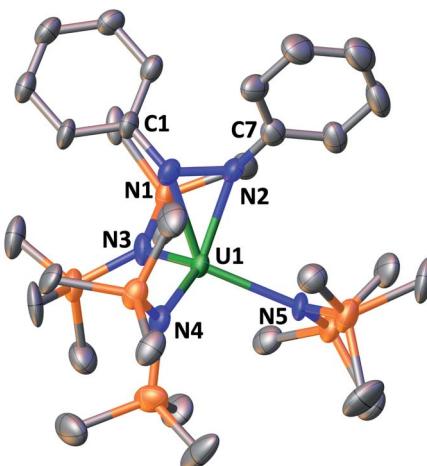


Fig. 3 Molecular structure of the $[\text{U}(\text{N}_2\text{Ph}_2)\{\text{N}(\text{SiMe}_3)_2\}_3]^-$ component of 5. Hydrogen atoms and the $[\text{K}(2.2.2\text{-cryptand})]^+$ counterion have been omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): $\text{U1}-\langle \text{N}_{\text{amide}} \rangle_{\text{avg}}$ 2.34(2), $\text{U1}-\text{N}1$ 2.271(14), $\text{U1}-\text{N}2$ 2.229(13), $\text{N}1-\text{N}2$ 1.43(2), $\text{N}1-\text{U1}-\text{N}2$ 37.1(5).

bidentate $\text{N}_2\text{Ph}_2^{2-}$ ligand. A significant elongation of the diazo moiety ($\text{N}-\text{N} = 1.43(2) \text{\AA}$) is observed with respect to neutral *cis*-azobenzene (1.251\AA) and can be compared to that found in lanthanide complexes²⁵ of the $\text{N}_2\text{Ph}_2^{2-}$ ligand and in the only other reported $\text{U}(\text{iv})$ *cis*-hydrazido complex ($\text{N}-\text{N} = 1.440(3) \text{\AA}$).^{6b} The $\text{N}-\text{N}$ elongation is also larger than what is found in mono-reduced azobenzene ($1.331(17) \text{\AA}$)²⁶ and in the $\text{U}(\text{v})$ complex $[(\text{SiMe}_2\text{NPh})_3\text{-tacn}]\text{U}(\eta^2\text{-N}_2\text{Ph}_2)]$ ($1.353(4) \text{\AA}$) containing a singly reduced azobenzene.²⁷ Furthermore, the U-N hydrazido bond lengths of 2.271(14) and 2.229(13) \AA are similar to those observed in the previously reported $\text{U}(\text{iv})$ *cis*-hydrazide complex ($2.2254(15) \text{\AA}$).^{6b}

The isolation, at low temperature, of complex 5 which readily transforms into the bis(imido) 4 at room temperature provides final evidence for the mechanism involving a step-wise four-electron $\text{U}(\text{ii})/\text{U}(\text{vi})$ redox process at a single metal centre.

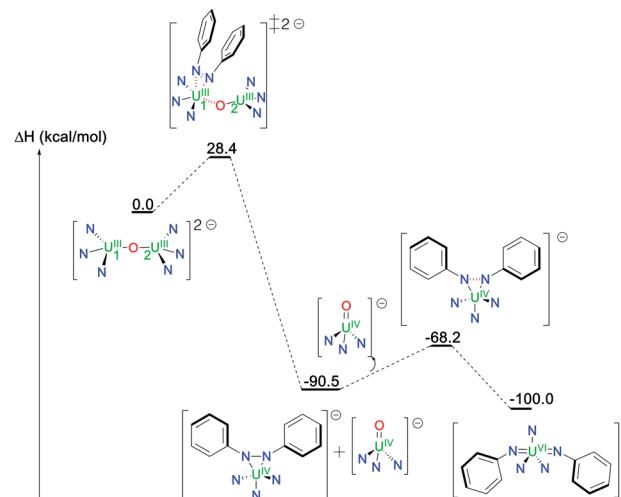


Fig. 5 Computed enthalpy profile (in kcal mol^{-1}) for the formation of 4 from the reaction of complex 1 with azobenzene.

Computational studies

The mechanism of the reaction of 2 with azobenzene was further investigated by computational methods (DFT, B3PW91 functional) and shows that the reduction proceeds through a $\text{U}(\text{iv})$ intermediate where the two-electron reduced azobenzene, ($\text{N}_2\text{Ph}_2^{2-}$), binds the metal centre in a bidentate fashion (Fig. 4). The associated barrier of $20.3 \text{ kcal mol}^{-1}$ is in line with a kinetically accessible reaction. The final $\text{U}(\text{vi})$ imido complex is then formed in an exothermic process ($9.5 \text{ kcal mol}^{-1}$ from the $\text{U}(\text{iv})$ intermediate) *via* the transfer of two additional electrons in a kinetically favourable process ($22.3 \text{ kcal mol}^{-1}$).

Addition of azobenzene to 1 also results in a two-electron reduction that yields the same $\text{U}(\text{iv})$ intermediate and the $\text{U}(\text{iv})$ terminal oxo complex whose formations are exothermic by $90.5 \text{ kcal mol}^{-1}$ (Fig. 5). The unpaired spin density in the $\text{U}(\text{iv})/(\text{N}_2\text{Ph}_2^{2-})$ intermediate (2.2) as well as the HOMO of the system (see Fig. S13 in ESI†) highlight the two electrons reduction of the azobenzene ligand. The final $\text{U}(\text{vi})$ bis(imido) complex is also in this case formed in an exothermic process ($9.5 \text{ kcal mol}^{-1}$ from the $\text{U}(\text{iv})$ intermediate) *via* the transfer of two additional electrons in a kinetically favourable process ($22.3 \text{ kcal mol}^{-1}$).

Conclusions

In conclusion, we showed that the addition of diphenylacetylene and azobenzene to 1, results in the cleavage of a $\text{U}-\text{O}$ bond, release of a $\text{U}(\text{iv})$ oxo complex and two-electron and four-electron reduction, respectively, of the substrate by a putative $\text{U}(\text{ii})$ intermediate. The previously reported $\text{U}(\text{ii})$ complex 2 showed the same reactivity, providing the first example of a two-electron oxidative-addition reaction across the $\text{U}(\text{ii}/\text{iv})$ redox couple. Computational studies indicate that the four-electron reduction of azobenzene occurs at a single $\text{U}(\text{ii})$ centre *via* two consecutive two-electron transfer reactions and

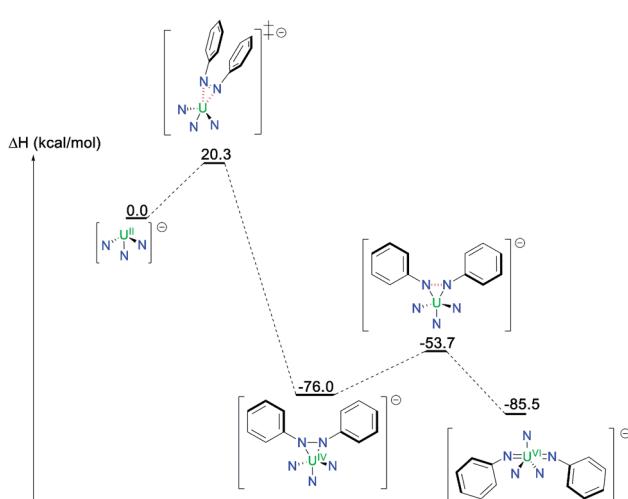


Fig. 4 Computed enthalpy profile (in kcal mol^{-1}) for the formation of 4 from the reaction of complex 2 with azobenzene.



involves the formation of a U(IV) hydrazide intermediate. The isolation of the *cis*-hydrazide intermediate **5** corroborated the mechanism proposed for the formation of the U(VI) bis(imido) complex **4**. The reduction of azobenzene by U(II) provided the first example of a “clear-cut” single metal four-electron transfer in f-elements chemistry.

Author contributions

D. K. M. carried out the synthetic experiments; D. K. M. and C. T. P. analysed the experimental data; R. S. carried out the X-ray single crystal structure analyses; I. D. and L. M. carried out and analysed the computational data. M. M. originated the central idea, coordinated the work, and analysed the experimental data. M. M., D. K. M. and C. T. P. wrote the manuscript with input from all co-authors.

Conflicts of interest

There are no conflicts to declare.

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