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Uranyl oxo activation and functionalization by metal cation coordination**

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Correspondence and requests for materials should be addressed to P.L.A. or J.B.L. (Polly.Arnold@ed.ac.uk, Jason.Love@ed.ac.uk). X-ray crystallographic coordinates for **2thf**, **3py**, **4py**, and **5thf** have been deposited at the Cambridge Crystallographic Database, numbers 768618, 782912, 768619 and 743941.

Supplementary information:
Suplementary information is linked to the online paper at http://www.nature.com/nchem

Keywords:
bond-dissociation energies; reduction; complexes; uranium

Abstract

The oxo groups in the uranyl ion $[UO_2]^{2+}$, one of many oxo cations formed by metals from across the Periodic Table, are particularly inert, which explains the dominance of this ion in the laboratory and its persistence as an environmental contaminant. In contrast, transition metal oxo (M=O) compounds can be highly reactive and carry out difficult reactions such as the oxygenation of hydrocarbons. Here we show how the sequential addition of a lithium metal base to the uranyl ion constrained in a Pacman environment results in lithium coordination to the U=O bonds and single-electron reduction. This reaction depends on the nature and stoichiometry of the lithium reagent and suggests that competing reduction and C-H bond activation reactions are occurring.

Main text

Chemical reactions of the oxo ligands of the uranyl dication $[UO_2]^{2+}$ are rare due to the strongly covalent and linear O=U=O bonding and, as a consequence, over fifty percent of known uranium compounds incorporate this highly stable motif[1]. In contrast, the oxo groups of the transition metal congeners $[MO_2]^{2+}$ (M = Cr, Mo, W) can be highly reactive, and undergo a myriad of oxidation and oxygenation reactions with substrates as inert as hydrocarbons[2,3]. Nevertheless, reduction and oxo-functionalisation reactions of the uranyl are becoming increasingly important, particularly as there is a need to understand the chemical reactions and mechanisms that occur during the immobilisation of uranium in the environment and as a result of photoactivation of the ion, upon which it becomes a potent oxidant [4,5]. The singly reduced uranyl ion $[UO_2]^{+}$ is thought to be produced in all of these reactions and is unstable with respect to disproportionation to the uranyl dication and insoluble tetravalent uranium phases. Depending on the substrate available, different mechanisms, including unimolecular electron transfer and H-atom abstraction have been identified [6], but the instability of the pentavalent state hampers a better understanding of these process [7]. Significantly, the recent renaissance in actinide science [8] has included new anaerobic studies on uranyl reduction by reagents such as cobaltocene, $K_2(C_8H_8)$ or potassium metal [9-13], although the majority of pentavalent complexes isolated to date remain unstable with respect to disproportionation.

We reported recently a new type of chemical reaction of the uranyl ion, in which the asymmetric, macrocyclic uranyl complex **1** cleaved N-Si and C-Si bonds to form the singly reduced and oxo-silylated compound **A** (Figure 1) [14]. This transformation was initiated by the reaction between **1** and potassium bases, and DFT calculations have shown that model compounds in which K cations bond to a uranyl oxo group can undergo S_N2-type homolytic bond cleavage reactions with silanes and aminosilanes [15]. Now we report that the use of lithium bases allows the synthesis and characterisation

of a series of unique oxo-lithiated, hexa- and pentavalent uranyl complexes that adopt wedged, 'Pacman' geometries and that provide insight into the mechanism of reduction.

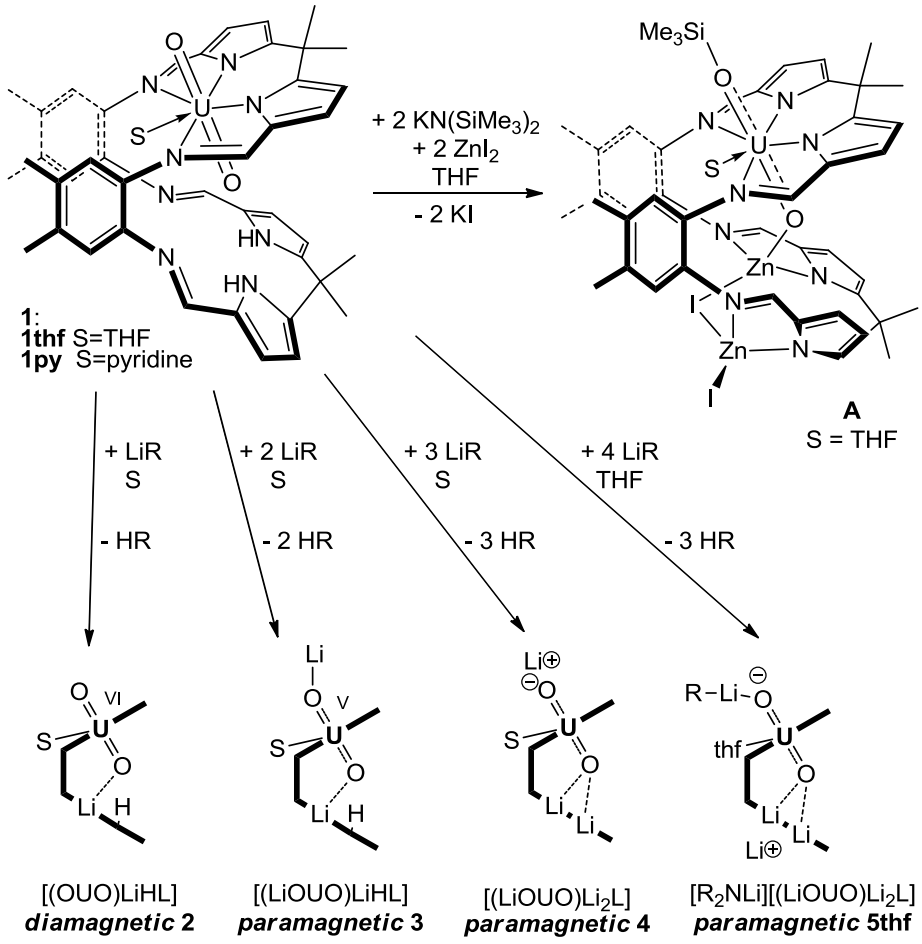

Figure 1. **Synthetic procedures to diamagnetic and paramagnetic uranyl Pacman complexes.** The reactions between the mono-uranyl complex $[UO_2(S)(H_2L)]$ **1** and one of a variety of lithium bases LiR (R = H, NH_2, N^iPr_2, $N(SiMe_3)_2$, CPh_3, C_5H_5) or $KN(SiMe_3)_2$ in the presence and absence of ZnI_2 (S = THF, pyridine) form the oxo-silylated uranyl complex **A** or mono-, doubly-, triply-, or tetra-lithiated uranyl complexes. At least two equivalents of lithium or potassium base is required to form a pentavalent uranyl complex.

Results and Discussion

Reaction of 1 with one equivalent of Li base

The addition of one equivalent of $LiN(SiMe_3)_2$ to **1thf** in THF at 25 °C generates the red-brown, diamagnetic, mono-lithiated complex, [OUO(THF){Li(THF)}(HL)] **2thf** denoted [(OUO)LiHL] **2** in

Figure 1 (L is the tetraanionic, wedge-shaped macrocycle drawn fully in Figure 1). Isolated in 51 % yield, **2thf** has been fully characterised, including by X-ray diffraction (Figure 2). This structure shows that the lithium cation is four-coordinate and bound in the bottom pocket to one imine-pyrrolide group, the *endo*-uranyl oxo, and one molecule of THF. The U1-O1 (1.794(3) Å) and U1-O2 (1.767(3) Å) bond distances are similar to other $[UO_2]^{2+}$ complexes, including **1thf**, and are commensurate with the diamagnetic nature of **2thf**. The formation of **2thf** is always accompanied by quantities of doubly- and triply-lithiated complexes but it was isolated as a pure material in small quantities by fractional crystallisation. In similar reactions in pyridine solution, the pyridine-solvated, mono-lithiated analogue, **2py** can be identified in the ^{1}H NMR spectrum but has proved difficult to isolate.

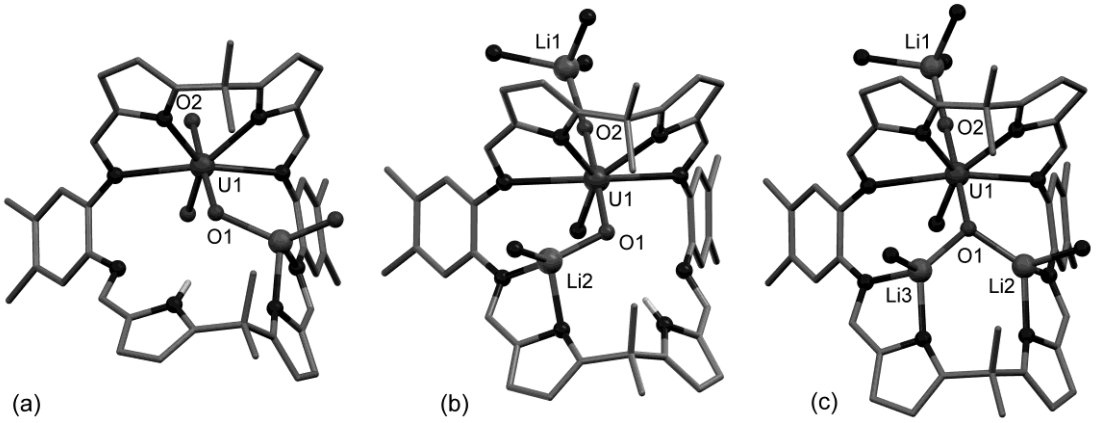

Figure 2. **X-ray crystal structure determination of mono-, doubly- and triply-lithiated uranyl complexes** (a) mono-lithiated **2thf,** (b) doubly-lithiated **3py** and (c) triply-lithiated **4py**. For clarity, hydrogen atoms, carbon atoms associated with coordinated THF or pyridine, solvents of crystallisation, and a minor disorder component of **3py** are omitted. The molecules are shown face-on. Selected bond distance (Å) and angles (º): (a) U1-O1 1.794(3); U1-O2 1.767(3); Li1-O1 2.060(11); O1-U1-O2 176.09(17); (b) U1-O1 1.834(4); U1-O2 1.879(5); Li1-O2 1.927(13); Li2-O1 1.94(2); O1-U1-O2 174.82(15); Li1-O2-U1 167.3(4); (c) U1-O1 1.894(2), U1-O2 1.859(2), O1-Li2 1.979(7), O1-Li3 1.976(7), O2-Li1 1.914(7), O1-U1-O2 174.21(10), Li1-O2-U1 169.2(3).

Reaction of 1 with two equivalents of Li base

Reactions between **1** and two equivalents of $LiN(SiMe_3)_2$ in cold pyridine or THF affords mixture of diamagnetic and paramagnetic complexes, including the majority product **4py** in pyridine (see later). However, reactions in pyridine in the presence of dihydroanthracene (DHA), which contains weak C-

H bonds (Bond Dissociation Energy (BDE) = 79 kcalmol^{-1}), leads to the preferential generation of a single paramagnetic product which is characterised as the U^V complex [(py)$_3$LiOUO(py)Li(py)(HL)] **3py**, Figure 1, viewed formally as the lithium salt of the singly reduced $[UO_2]^+$. The number and integrals of the paramagnetically-shifted resonances in the ^{1}H NMR spectrum of **3py** support an asymmetric ligand arrangement. It is likely that the most paramagnetically-shifted and broadened resonance integrating as 1H at 60.1 ppm is due to the remaining pyrrole NH. The ^{7}Li{^{1}H} NMR spectrum of **3py** displays a single resonance at 92 ppm and suggests that the Li cations are fluxional in solution. On cooling to the lowest available temperature (238 K) an additional broad new resonance at 128 ppm appears, suggesting that two Li environments are present at the low temperature limit. The asymmetric structure observed in the ^{1}H NMR spectrum is supported by a single crystal X-ray diffraction study (Figure 2) of **3py** that shows that both Li cations are four coordinate, one bound similarly to that in **2thf** *i.e.* within the cleft to the *endo*-oxo while the other coordinates to the *exo*-oxo with its tetrahedral coordination completed by three molecules of pyridine. The U1-O1 (1.834(4) Å) and U1-O2 (1.879(5) Å) bond distances are elongated substantially compared to those in diamagnetic **2thf** and support single electron reduction to $[UO_2]^+$. The FTIR spectrum of **3py** contains a weak and very broad band at 3310 cm^{-1} which could derive from a pyrrole NH, and an absorption at 709 cm^{-1} assigned to the asymmetric $[UO_2]^+$ stretch, which is weakened substantially compared to that in the U^{VI} starting material **1py** (ν U=O 908 cm^{-1}). The observation that treatment of the $[UO_2]^{2+}$ dication with a lithium *base* yields an product of single electron reduction was a great surprise due to the inertness of the uranyl dication, and the known instability of the reduced monocation $[UO_2]^+$ towards disproportionation [13,16]. The pentavalent $[UO_2]^+$ complex **3py** was also isolated from reactions between **1py** and two equivalents of LiN^{i}Pr$_2$ (LDA), LiC$_5$H$_5$, LiCPh$_3$, LiNH$_2$, or LiH in the *absence* of DHA in essentially quantitative yield. The reactions with LiNH$_2$ and LiH form initially a mixture of **4py**, **2py**, and **1py**, but on heating convert completely to **3py**. Similar reactions in THF lead to mixtures of paramagnetic products. Furthermore, reaction between [Li$_4$(L)] and [UO$_2$Cl$_2$(THF)$_3$] in pyridine generates **3py** slowly as the sole product at room temperature, a reaction that is accelerated by heating to 110 ^{o}C. The reaction between **1py** and two equivalents of LDA in pyridine is the cleanest, and furthermore, if carried out at -30 °C, a new complex with C_s symmetry (by ^{1}H NMR spectroscopy) is isolated. As with **3py**, this new complex contains a broad, paramagnetically-shifted resonance at low field, in this case at 86 ppm that integrates for 1H and is likely due to an NH or OH proton, the latter suggested by C_s symmetry. It is likely that this material is an isomer of **3py** as bulk crystallisation forms crystals of the same unit cell as **3py** and slow conversion into **3py** is observed in solution over prolonged periods at elevated temperatures.

Reaction of 1 with three or four equivalents of Li base

Reaction of **1** with three equivalents of $LiN(SiMe_3)_2$ in pyridine at 25 °C affords rapidly the triply-lithiated U^V complex $[(LiOUO)Li_2L]$ **4py**, Figure 1. A similar reaction in THF again forms mixtures of paramagnetic compounds, but the use of four equivalents of $LiN(SiMe_3)_2$ generates the stable U^V adduct $[R_2NLi][(LiOUO)Li_2L]$ **5thf**. Both **4py** and **5thf** are significantly more straightforward to isolate than the singly and doubly-lithiated complexes, and have been fully characterised, including by X-ray crystallography (see SI for **5thf**). In the X-ray structure of **4py**, all of the Li cations are 4-coordinate, Li1 interacting with the *exo*-uranyl oxo atom O2, and Li2 and Li3 bound symmetrically within the cleft and to the *endo*-oxo O1. These interactions elongate the U1-O1 (1.894(2)Å) and U1-O2 (1.859(2) Å) bond distances significantly compared to 1**thf**, and again support the presence of functionalised $[UO_2]^+$. A variable-temperature, solid state magnetic study of **5thf** (see SI) also supports the presence of a single f-electron and no further reduction to U^{IV} [17]. The FTIR spectrum of **4py** displays an absorption at 704 cm^{-1} that is assigned to the asymmetric stretch of the $[UO_2]^+$ group[5].

Reactions to probe the mechanism of formation of the pentavalent uranyl complexes

It is clear from the above data that the sequential addition of Li reagents to the uranyl complex **1** leads ultimately to single-electron reduction and Li-functionalisation of the oxo groups. The most important mechanistic step of this process is the addition of the second equivalent of Li reagent as this is the point at which reduction of U^{VI} to U^V occurs; as such, we have carried out a series of experiments to probe this transformation.

The reaction between **1py** and two equivalents of LDA in D_5-pyridine was monitored by ^1H NMR spectroscopy and generates cleanly **3py**. While the N-H resonance of the by-product amine HN^iPr_2 could not be located in the ^1H NMR spectrum, the ^2H NMR spectrum of the residues re-dissolved in H_5-pyridine shows that deuterium is incorporated at multiple sites in the ligand, and notably at 60.1 ppm (N-H) and 1.4 ppm (a *meso*-CH_3 group). The reaction between two equivalents of LiC_5H_5 and **1py** in D_5-pyridine produces **3py** cleanly and two equivalents of HC_5H_5 by integration in the ^1H NMR spectrum, with no radical-coupled products observed, and D-incorporation at 1.5 ppm, corresponding to ligand deuteriation.

In contrast, the reaction between **1py** and two equivalents of $LiN(SiMe_3)_2$ forms mixtures of paramagnetic **4py**, and diamagnetic **2py** and **1py** unless a substrate containing a weak C-H bond such as dihydroanthracene is present, upon which the formation of **3py** is favoured. The reaction between **1py** and two $LiN(SiMe_3)_2$ in D_5-pyridine in the presence of DHA was monitored by ^1H NMR spectroscopy and shows rapid and clean formation of **3py** plus, significantly, two equivalents of

$HN(SiMe_3)_2$ by integration of N-H (1.46 ppm) and $SiMe_3$ (0.08 ppm) resonances, and no $DN(SiMe_3)_2$ in the ^2H NMR spectrum. Furthermore, a stoichiometric quantity of radical-coupled 9,9',10,10'-tetrahydro-9,9'-bianthracene is seen as the dominant H-abstracted product and a small amount of anthracene [18,19]. With D_4-DHA in H_5-pyridine, the reaction is less clean with the formation of a small quantity of **4py** along with **3py**, but two equivalents of $HN(SiMe_3)_2$ are again seen in the ^1H NMR spectrum. D-incorporation into **3py** was seen in the ^2H NMR spectrum at a few resonances corresponding to ligand deuteriation, and observation of a broad resonance at 1.46 ppm suggests that a small quantity of $DN(SiMe_3)_2$ is also formed during this reaction. The reaction between **1py** and two $LiN(SiMe_3)_2$ in D_5-pyridine in the presence of xanthene, another substrate containing a weak C-H bond, gives a more complex mixture of products by ^1H NMR spectroscopy, forming **4py** (13%), **3py** (55%), **2py**+**1py** (total 28%), radical-coupled xanthene (28%) and two equivalents of $HN(SiMe_3)_2$ by integration. Interestingly, equal quantities of **3py** and radical-coupled bi-xanthene arising from H-abstraction are formed, suggesting that **4py** is formed by a different mechanism to **3py**. Indeed, the reaction of **1py** with three equivalents of $LiN(SiMe_3)_2$ in D_5-pyridine shows the sole formation of **4py** along with two equivalents of $HN(SiMe_3)_2$ and one equivalent of $DN(SiMe_3)_2$ by integration of N-H and $SiMe_3$ resonances in the ^1H NMR spectrum; the presence of $DN(SiMe_3)_2$ is supported by a resonance at 1.46 ppm in the ^2H NMR spectrum.

Plausible mechanisms that can account for the isolation of the paramagnetic, doubly- and triply-lithiated complexes **3py** and **4py** are outlined in Figure 3, and arise from the Li reagent acting either as a reductant (Path A) or a base (Path B).

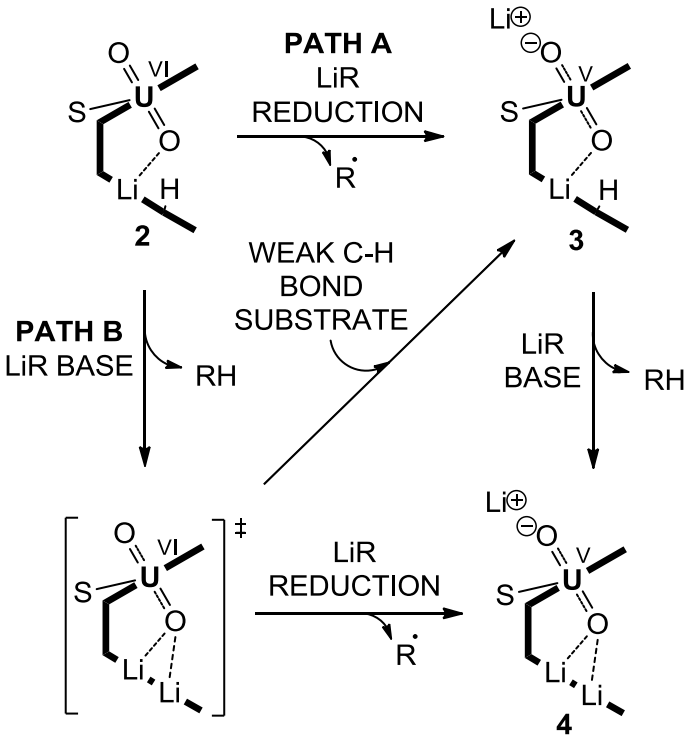

Figure 3. **Possible mechanisms that generate pentavalent uranyl $[UO_2]^+$ by reaction with a Li reagent LiR.** Two routes are proposed involving either Path A in which LiR (R = H, NH_2, N^iPr_2, $N(SiMe_3)_2$, CPh_3, C_5H_5) acts as a reducing agent or Path B in which LiR acts as a base.

The U^{VI}/U^V reduction potential of **1thf** in THF is -0.54 V (*vs*. SHE) and therefore only strongly-reducing Li reagents such as lithium alkyls and hydrides would be expected to effect the direct reduction of **1py**. However, Hayton and co-workers have shown recently that formation of an adduct between the Lewis acid $B(C_6F_5)_3$ and one of the uranyl oxo-groups in the complex $[UO_2(Acnac)_2]$ results in a 0.57 V shift of the U^{VI}/U^V couple to a more positive potential [13]. By analogy, it is therefore likely that both the singly-lithiated U^{VI} complex **2py** and the postulated doubly-deprotonated, U^{VI} intermediate $[UO_2(Li_2L)]$ are easier to reduce than **1py**. Unfortunately, we have been unable to measure with certainty the U^{VI}/U^V reduction potential of **2py** due to reaction with the electrolyte.

If it is assumed that Li cation coordination to the uranyl oxo results in a shift of the reduction potential to a more positive value it is likely that LDA (oxidation potential, E_{ox} −0.59 V vs SHE in THF/HMPA at −25 °C, HMPA = hexamethylphosphoramide) and perhaps LiC_5H_5 (E_{ox} -0.03 V vs SHE in DMSO) are capable of reducing **2py** [20,21]. The formation of two equivalents of HC_5H_5 combined with incorporation of deuterium into the ligand in the latter reaction can occur if the resulting cyclopentadienyl radical reacts with ligand C-H bonds within a radical cage complex.

In contrast however, the significantly more positive oxidation potential of $LiN(SiMe_3)_2$ (E_{ox} +0.32 V vs SHE in THF at −25 °C) [22] combined with the observation that two equivalents of $HN(SiMe_3)_2$ are produced during the reaction suggests that $LiN(SiMe_3)_2$ is acting solely as a base. The formation of the more reducing Li(DHA) carbanion (E_{ox} -0.83 V vs SHE in DMSO) during reactions in the presence of DHA is possible but unlikely as the pK_a of DHA (30.1) is significantly greater than that of $HN(SiMe_3)_2$ (25.8) and no Li(DHA) is seen in the NMR spectrum of the control reaction between DHA and $LiN(SiMe_3)_2$. The generation of triply-lithiated **4py** can be explained if it is assumed that the U^{VI}/U^{V} reduction potential of the doubly-deprotonated U^{VI} intermediate $[UO_2(Li_2L)]$ has shifted to a much more positive potential (> +0.4 V vs SHE), upon which the addition of a third equivalent of $LiN(SiMe_3)_2$ can effect reduction. This would result in the formation of $\bullet N(SiMe_3)_2$ which in D_5-pyridine would generate a mixture of $HN(SiMe_3)_2/DN(SiMe_3)_2$ in a 2:1 ratio, as is observed. The involvement of DHA or xanthene in the mechanism of formation of **3py** from **1py** is more difficult to understand, but the observation of products of H-atom abstraction suggests that cleavage of the weak (BDE < 80 $kcalmol^{-1}$) [23] C-H bond in DHA or xanthene is an important step. Significantly, the inclusion of other benzylic substrates containing stronger C-H bonds such as toluene (BDE 89 $kcalmol^{-1}$) or cyclohexene (BDE 85 $kcalmol^{-1}$) does not favour the formation of **3py** and results in the mixtures described above.

Mechanisms in which the intermediate $[U^{VI}O_2(Li_2L)]$ can cleave C-H bonds could involve the uranyl oxo-group acting in a manner similar to a transition metal, undergoing intermolecular H-atom abstraction to form a U-OH. While thermally-induced C-H bond activation by uranyl is unknown, photo-excited uranyl $[^*UO_2]^{2+}$ is known to cleave C-H bonds during the photochemical destruction of hydrocarbons. Alternatively, internal reduction could occur with the formation of a pyrrolyl radical that is sufficiently reactive to abstract a hydrogen atom from the substrate (Figure 4)[24].

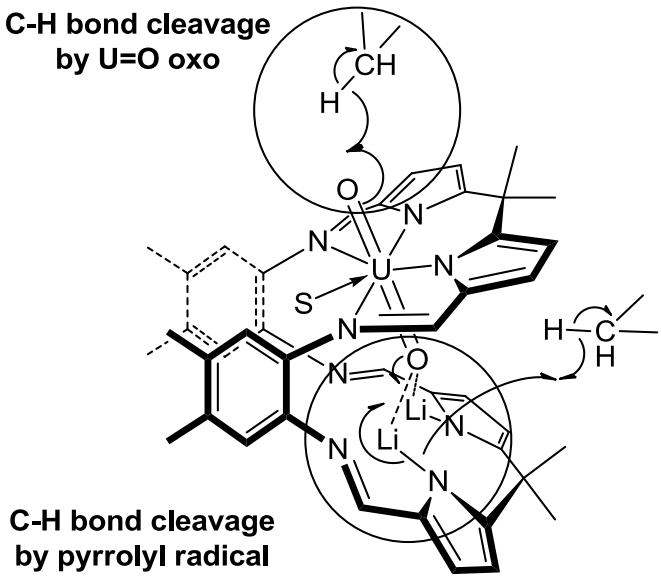

Figure 4. **Mechanistic insight into the formation of doubly-lithiated uranyl complexes.** Two mechanisms that involve C-H bond cleavage to form doubly-lithiated **3py** are postulated and involve either the uranyl oxo group, highlighted by the upper circle, or a pyrrolyl radical, highlighted by the lower circle.

In the reaction of **1py** with $LiN(SiMe_3)_2$ in the presence of D_4-DHA in H_5-pyridine, both U=O oxo and pyrrolyl radical mechanisms would be expected to result in D-incorporation in **3py**. The ^{2}H NMR spectra of these reactions show some incorporation of deuterium into ligand CH and CH_3 bonds of the macrocycle, but not clearly the expected N-H (or O-H) resonance. Furthermore, the solution structure of **3py** correlates to the solid state structure which may discriminate against an oxo-mechanism that would be expected to form a C_s-symmetric uranyl hydroxide. However, it is seen that the Li cations in **3py** exchange on the ^{7}Li NMR timescale and that intermolecular reactions between uranyl species can occur as evidenced by the conversion of mixtures of **4py**/**2py**/**1py** into **3py** at elevated temperatures. As such, we cannot rule out an oxo-based C-H bond cleavage mechanism.

A pyrrolyl radical formed through an internal reduction mechanism would result, after H-abstraction, in **3py** but its formation would necessitate a shift in the U^{VI}/U^{V} reduction potential to a value more positive than that of Li(pyrrolide) (E_{ox} +0.40 V vs SHE in DMSO). It is known that pyrrole anion radicals adopt an α-pyrrolenine tautomeric form, indicating that the radical should be able to delocalise throughout the pyrrole-imine framework; deuterium-abstraction from the substrate may then lead to D-incorporation at various sites on the macrocyclic ligand as evidenced in the ^{2}H NMR spectrum. We have also found previously that the pyrrole-imine moiety can tautomerize to azafulvene-amine on metal coordination [25]. The need for a weak C-H bond is less clear in a

mechanism involving internal reduction and formation of a pyrrolyl radical, as the reaction between Li_4L and $[UO_2Cl_2(THF)_3]$ in D_5-pyridine generates **3py** cleanly in the *absence* of DHA. However, it has been shown that rhodium-stabilised aminyl radical complexes can be isolated and react as nucleophilic radicals to abstract H-atoms from substrates such as $^nBu_3SnH$ (BDE 74 kcalmol^{-1}) and PhSH (BDE 83 kcalmol^{-1}) that contain C-H bonds weaker than in the precursor amine complex (BDE 86 kcalmol^{-1}) [26]. It is therefore plausible that a pyrrolyl radical generated through an internal reduction process is only weakly oxidising and quenched by weak C-H bonds to afford **3py**.

To further investigate these mechanisms, DFT calculations were carried out and the computed steps involved in the proposed paths A and B are found to be both kinetically and thermodynamically accessible at room temperature, Figure 5 (see SI for computational details).

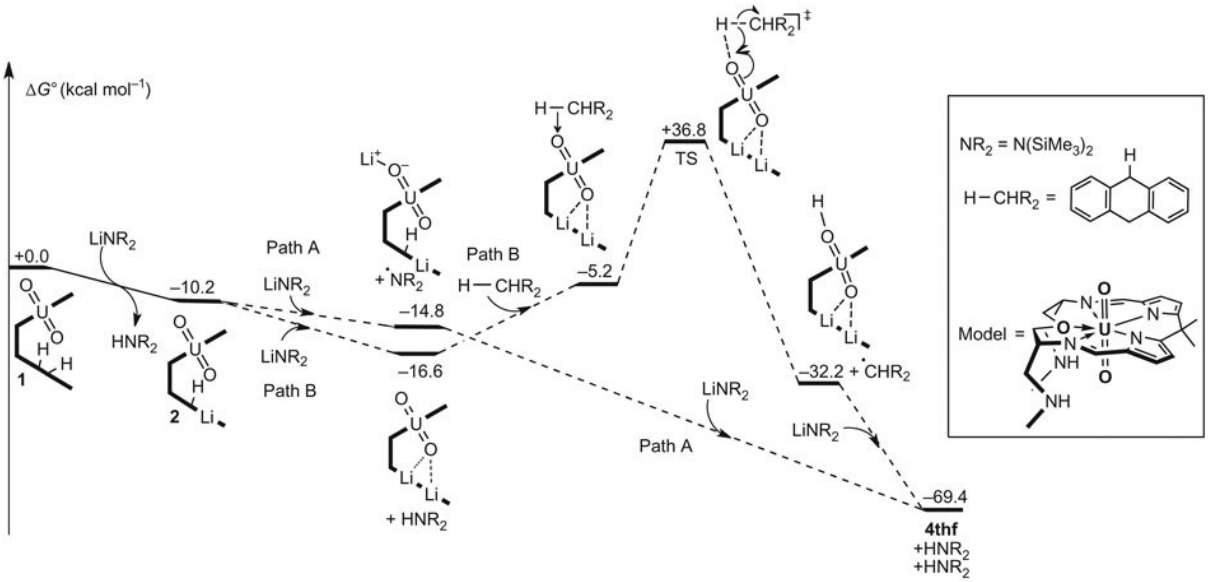

Figure 5. **Computed energy profile for the reduction and oxo-group C-H activation by a model of a Pacman uranyl complex.** The calculations show that the formation of all of the lithiated uranyl complexes is exergonic and that the transition states involving oxo-group C-H activation are thermodynamically accessible. They do not show significant differences in energy between the path A and path B mechanisms.

The reduction of **2** by $LiN(SiMe_3)_2$ (Path A) is computed to be exergonic by −14.8 kcalmol^{-1}, while the deprotonation route (Path B), is −16.6 kcalmol^{-1}; the differences in these values are too small to show any preference from a computational perspective. Of the two possible C-H abstraction possibilities shown in Figure 4, the abstraction by the oxo-group from DHA has been computed and is

found to be kinetically accessible with a barrier of 36.8 kcalmol^{-1} that is similar to that calculated for the analogous oxo silylation process [15]. Based on the geometry (the U-O bond is still short) the transition state is best described as a proton transfer between DHA and the exo-oxo group of $[UO_2]^{2+}$, with the reduction of the metal occurring immediately after the proton transfer, leading to **3**. A DFT calculation for the energetics of the alternative mechanism involving internal reduction and formation of a pyrrolyl radical (Path B) was not possible as it would not give the same product observed in the experiment and DFT cannot localise the electron. From **3**, the formation of the triply-lithiated complexes **4** is computed to be highly favourable.

Conclusions

In the reductive uranyl silylation chemistry to make **A** we proposed that the direct interaction between the activated U^{VI} complex $[UO_2(K_2L)]$ and the silyl substrate resulted in homolytic Si-N (BDE 111 kcal.mol^{-1}) or Si-C (BDE *ca.* 90 kcal.mol^{-1}) bond cleavage [14]. Similarly, the results presented in this work suggest that endogenous bonding of a lithium cation to the uranyl oxo group facilitates reduction chemistry. The sensitivity of this chemistry towards the lithium reagent implies that more than one mechanism operates during the formation of the singly-reduced uranyl complex **3**. The lithium reagents LDA, $LiNH_2$, $LiCPh_3$, LiH, or LiC_5H_5 appear to act as reductants with the release of a radical which is quenched by the ligand through H-abstraction. However, for $LiN(SiMe_3)_2$ we can eliminate this mechanism, and invoke instead H-atom abstraction by the uranyl complex, although it has not been possible to identify whether a U=O group or a ligand-centred radical in the complex cleaves the C-H bond. Unfortunately, DFT calculations have been unable to distinguish between the two mechanisms. Although the chemistry of **1** takes place in the dark, the fact that photochemically-activated uranyl dications are capable of the destruction of organic compounds by H-atom abstraction [27,28] *via* a substrate-dependent mechanism is notable in light of these results. The contrast to the silylation chemistry observed for the doubly-potassiated uranyl macrocyclic analogue suggests that the nature of the metals incorporated into the bottom pocket of the macrocycle are an important variable in expanding the scope of this reaction, and that these complexes should offer access to a wide range of new covalent bond-forming reactions of the uranyl oxo group.

Methods summary

Working under a dry, oxygen-free dinitrogen atmosphere, with reagents dissolved or suspended in aprotic solvents, and combined or isolated using cannula and glove box techniques, we first treated the hinged macrocyclic complex $[UO_2(S)(H_2L)]$, in which one compartment binds the uranyl dication

and the other still contains two pyrrolic H atoms (S = tetrahydrofuran or pyridine), with 1, 2, 3, and 4 equivalents of lithium base to afford soluble, isolable complexes in each case, containing increasing quantities of lithium cations coordinated to the uranium oxo groups. The second equivalent of base resulted in the formation of complexes in which the uranium was shown to be singly reduced. Repetition of the reaction with different bases, and in the presence of substrates with weak benzylic C-H bonds showed, by analysis of the NMR spectra, that thermal, homolytic C-H bond cleavage had occurred in the cases where a less reducing lithium base was used. All compounds were characterised by elemental analysis, FTIR spectroscopy, variable temperature magnetic moment measurements, NMR spectroscopy, and single crystal X-ray diffraction studies to confirm their identity. The authors are grateful to Prof D. Graham, Dr I. Lamour, and Prof R. E. Mulvey and Dr S. Robertson for help with obtaining the Raman spectroscopic measurements.

Competing Interests statement The authors declare that they have no competing financial interests.

Author Contributions A.-F. P. and E. H. synthesised and characterised the compounds, and solved the crystal structure data, A. Y. and L. M. carried out the DFT calculations, and S. J. P. solved and refined the disorder components for the crystal structure of **3py**. P.L.A. and J.B.L. generated and managed the project, helped characterise the compounds, analysed the data, and wrote the manuscript.

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