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Control of oxo-group functionalization and reduction of the uranyl ion

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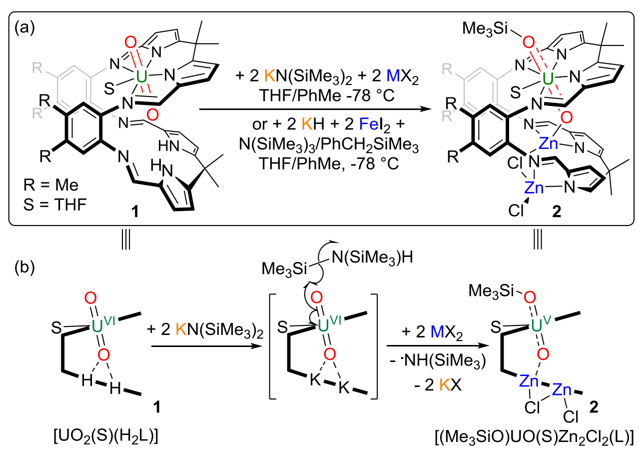
ABSTRACT: Uranyl complexes of a large, compartmental N_8-macrocycle adopt a rigid, 'Pacman' geometry that stabilizes the U^V oxidation state and promotes chemistry at a single uranyl oxo group. We present here new and straightforward routes to singly reduced and oxo-silylated uranyl Pacman complexes and propose mechanisms that account for the product formation, and the by-product distributions that are formed using alternative reagents. Uranyl(VI) Pacman complexes in which one oxo group is functionalized by a single metal cation are activated towards single-electron reduction. As such, the addition of a second equivalent of a Lewis acidic metal complex such as MgN''_2 (N'' = $N(SiMe_3)_2$) forms a uranyl(V) complex in which both oxo groups are Mg functionalized as a result of Mg-N bond homolysis. In contrast, reactions with the less Lewis acidic complex [Zn(N'')Cl] favor the formation of weaker U-O-Zn dative interactions, leading to reductive silylation of the uranyl oxo group in preference to metalation. Spectroscopic, crystallographic, and computational analysis of these reactions and of oxo-metalated products isolated by other routes has allowed us to propose mechanisms that account for pathways to metalation or silylation of the *exo*-oxo group.

Introduction

Metal oxo group reactivity is an active area of research as both mono- and poly-oxo transition metal complexes are widely used by industry and enzymes in catalytic transformations of hydrocarbons and other key chemicals.[1] In contrast, the uranyl dication, the prevalent, stable, and persistent form of uranium in nature, is characterized by remarkably low Lewis base reactivity of the oxo groups and its two very strong, linear and covalent, uranium oxo bonds.[2] A better understanding of actinide oxo group reactivity is important because the heavier and more radioactive neptunium and plutonium fission products in civil nuclear waste also form actinyl $[AnO_2]^{n+}$ ions but with f^1 and f^2 configurations, and exhibit greater oxo basicity. [3] Furthermore, the $[UO_2]^+$ ion is implicated as an important but unstable intermediate in the reduction processes found in environmental uranium immobilization through disproportionation to uranyl(VI) and insoluble U^{IV} oxides.[4]



Scheme 1 (a) reductive silylation of the uranyl ion constrained in a Pacman-shaped macrocyclic ligand, (b) mechanism proposed at the time for the reductive silylation.

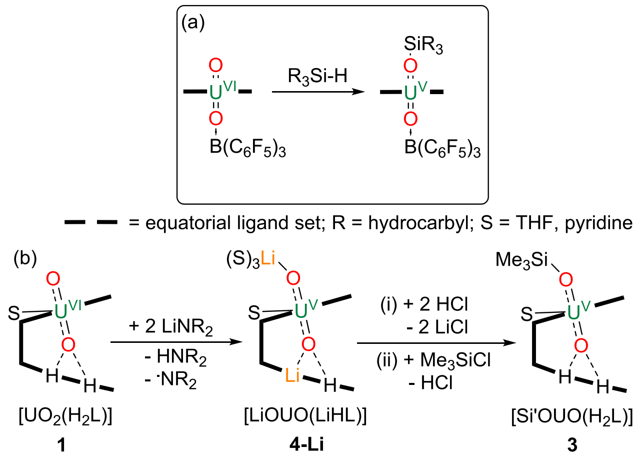
We reported the first covalent bond forming reaction at a uranyl oxo-group in the form of an O-Si bond, using a macrocyclic Pacman-shaped ligand to restrict uranyl ion reactivity to a single oxo group.[5] Treatment of the asymmetric uranyl-Pacman complex $[UO_2(H_2L)]$ **1** shown in Scheme 1a with a potassium silylamido base, KN" (N" = $N(SiMe_3)_2$) and a transition metal dihalide in a one-pot reaction resulted in rare, one-electron uranyl reduction and oxo-group silylation, i.e. a reductive silylation reaction to give **2**. Experimental and computational data suggested that the Group 1 base was key to this reaction and we proposed that the oxo group reactivity was enhanced by coordination of Lewis acidic metals while the complexation of the transition metal ions provided the stabilization necessary to isolate the silylated complexes (Scheme 1).[5-6] Sarsfield first showed that Lewis acidic boranes could bind to the uranyl oxo group;[7] since then, work by Hayton and us has shown that this coordination of Lewis acids to one uranyl oxo group can make the reduction potential of the uranyl(VI) ion more favorable by up to 0.6 V. Hayton showed the uranyl complex $UO_2(^{Ar}acnac)_2$ could be rendered reducible by the silane $HSiR_3$ if oxo-activated by the strong Lewis acid $B(C_6F_5)_3$ (Scheme 2a; $^{Ar}acnac$ = ArNC(Ph)CHC(Ph)O; Ar = 3,5-$Bu^t{}_2C_6H_3$).[2,5,8] We have observed a similar effect on the U^{VI} to U^{V} redox potential upon coordination of Li cations in the spontaneous reduction and C-H bond cleavage chemistry that affords the uranyl(V) Pacman complexes $[(S)_3LiOUO(S)Li(S)(HL)]$ **4-Li** (Scheme 2b; S = THF, py).[9] The large difference in size, and thus softness, or Lewis acidity, of the Group I metal cations is well documented to allow different modes of reactivity in their bases.[10] For comparison, the coordination of a single, softer 3d transition metal cation does not confer the same oxidizing power to uranyl(VI) in $[UO_2(S)M(S)(L)]$ **1-M**, (M = Mn, Fe, Co, Zn; S = THF).[8a,9,11]

We have undertaken a series of reactions to determine the roles of the Group 1 and transition metal salts in the reductive silylation reaction. Herein, we present new routes to the originally reported, oxo-silylated complexes, show how the choice of added metal reagent allows the control of uranyl-oxo group metalation or silylation, and propose a generalized mechanism, supported by computational modeling, to account for the oxo-functionalization process.

Results and Discussion

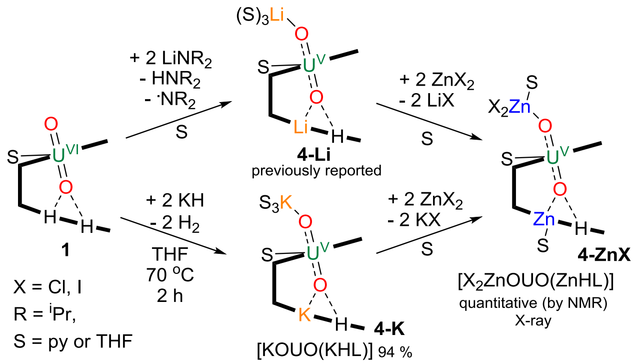
Reductive metalation of uranyl complexes with MX reagents (M = Li, K; X = N", $N(^iPr)_2$, H)

We have previously shown that the reactions of the uranyl(VI) Pacman complex **1** with one equivalent of LiN" or $TM(N")_2$ (N" = $N(SiMe_3)_2$; TM = Mn, Fe, Co, Zn) afford simple protonolysis products, i.e. uranyl(VI) products in which the metal substitutes the pyrrole NH group(s) in the bottom macrocyclic pocket, and the *endo*-oxo group behaves as a simple donor to the metal.[9,11a] The uranyl *endo*-oxo group is slightly lengthened in these complexes, but no redox processes were seen. We have also shown how reaction of **1** with two equivalents of a reducing base, namely LDA (lithium di*iso*propylamide) results in the quantitative formation of the uranyl(V) complex $[(py)_3LiOUO(py)Li(py)(HL)]$ **4-Li** (Scheme 2b).[9]



Scheme 2 Lewis-acid assisted reduction of the uranyl dication.

The potassium congener of **4-Li**, $[(py)_3KOUO(py)K(py)(HL)]$ **4-K** is also isolable as a dark red solid in 94 % yield from the reaction of **1** with two equivalents of potassium hydride at elevated temperature (Scheme 3). The ^1H NMR spectrum of **4-K** shows a new paramagnetic compound of C_s symmetry and not the expected C_1 symmetry seen in **4-Li**,[9] and the Mg and Zn analogues (see below). This is presumably because the ionic radius of the potassium cation is considerably larger than that of Zn^{2+} or Li^+ (138 pm for 6-coordinate K^+, 0.74 for Zn^{2+}, 0.76 for Li^+) and therefore coordinates more symmetrically in the lower Pacman compartment. The most contact-shifted paramagnetic resonance at 90 ppm is assigned to the pyrrole NH, and suggests a hydrogen-bonding interaction with the uranyl(V) *endo*-oxo group. The FTIR spectrum contains a broad band at 3417 cm^{-1} which corresponds to the pyrrole NH, and two bands for the UO stretches at 808 and 736 cm^{-1}; these are weakened in comparison to the UO stretches in the starting material and in the expected range for $[UO_2]^+$.[8b,12] While, **4-K** is sufficiently stable to be isolated as a powder from a rapid synthesis from KH (hot THF, two hours), reactions carried out at low temperatures over prolonged periods with KH or KN" at -78 °C or at ambient temperature produced uranyl(VI) hydroxide or oxo complexes.[13]



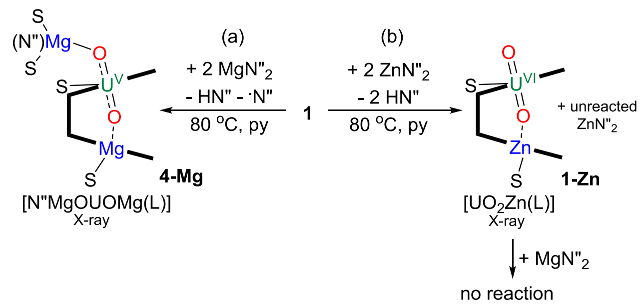
Scheme 3 Routes to the uranyl(V) complexes 4-M (M = Li, K) and their conversion to doubly metallated complexes [(S)X_2ZnOUO(S)Zn(S)(HL)] 4-ZnX (X = Cl, I, S = py, THF).

Both **4-Li** and **4-K** react with two equivalents of ZnX_2 to afford doubly metallated complexes (Scheme 3). The one-pot reaction between one equivalent of **4-Li** and two equivalents of ZnI_2 or $ZnCl_2$ in pyridine at room temperature for 16 h results in a color change from brown-yellow to dark red. Work-up affords [(py)X_2ZnOUO(py)Zn(py)(HL)] **4-ZnX** as brown solids in good yields (X = I, 76 % with 2 LiI incorporated, X = Cl, quantitative by ^{1}H NMR spectroscopy) and the reactions proceed similarly in THF solution. The reaction of **4-K** and two equivalents of ZnI_2 in THF over 16 h affords a red-brown suspension and work-up of the THF-soluble fraction affords [(THF)I_2ZnOUO(THF)Zn(THF)(HL)] **4-ZnI** in high yield (85 %).

It is clear from the ^{1}H NMR spectra that the complexes **4-ZnX** are similar, paramagnetic, adopt a Pacman structure, and are of C_1 symmetry (Fig. 2). In **4-ZnI**, the most contact-shifted paramagnetic resonance is at 58.4 ppm and is assigned to the pyrrole NH. The analogous NH resonance for the THF solvate of **4-ZnI** is at 65.8 ppm. The FTIR spectrum of the pyridine solvate contains one broad band at 3329 cm^{-1} corresponding to the presence of a pyrrole NH (*cf.* 3373 cm^{-1} in **1**) and two U-O stretches at 873 and 697 cm^{-1} (*cf.* 908 cm^{-1} in **1**).[8b,12] The molecular structure of **4-ZnI** is presented and discussed below and the chloride and other solvated adducts are in the Supporting Information SI4. Importantly, none of these metallated uranyl(V) complexes react with silylamines (see Supporting Information for details).

Reductive metalation of uranyl complexes with M(N")$_2$ reagents (M = Mg, Zn)

The stability of the oxo-metallated complexes described in Scheme 3 suggests that for oxo-group silylation to occur there is a requirement for the silyl group to be in the coordination sphere of the reacting metals. It is instructive to compare silylamido complexes of metals of different Lewis acidity and metal-nitrogen bond strengths, since the softer transition metal silylamido complexes (e.g. Fe, Zn) react to give oxo-silylated rather than oxo-metallated products.[5,14] Accordingly, reactions between **1** and two equivalents of MgN"$_2$ and ZnN"$_2$ were studied (Scheme 4). The two M^{II} cations are the same size, and if coordinated by the oxo group will provide a proximal Me_3SiN group. Presumably the oxo can form a stronger donor bond to the Mg than the Zn reagent.



Scheme 4 Contrasting reactions of the uranyl(VI) Pacman complex with metal silylamides of different Lewis acidity: (a) with MgN"$_2$ to give the reduction product [N"MgOUO(MgL)]; (b) with ZnN"$_2$ to give the substitution product [UO_2Zn(L)].

Reaction of **1** with two equivalents of MgN"$_2$ yields the singly reduced, metallated uranyl(V) complex [$(py)_2$(N")MgOUO(THF)Mg(py)(L)] **4-Mg** (Scheme 4a). Single crystals of **4-Mg** were analyzed by X-ray diffraction (Figure 2). This reaction occurs under forcing conditions and presumably involves the thermal homolysis of the Mg-N bond which provides a reducing electron for the $U^{VI/V}$ reduction, releasing an aminyl radical (which can abstract an H atom from solvent to give the HN" by-product). We have previously exploited a similar process to generate a reducing electron from the redox-inactive rare earth complexes LnN"$_3$ in reactions with **1** to afford the $5f^1$-$4f^n$ Ln-reduced uranyl complexes **[UO_2Ln(L)]$_2$**.[15] In contrast, reaction of **1** with two equivalents of ZnN"$_2$ yields exclusively the uranyl(VI) mono-metallated product [UO_2(py)Zn(py)(L)][11c] **1-Zn** and unreacted ZnN"$_2$ even after boiling the solution at 80 °C for 16 h (Scheme 4b). Further heating results in decomposition to many unidentifiable products, whilst heating pre-formed **1-Zn** with one equivalent of MgN"$_2$ in d_5-pyridine (80 °C) also gave no reaction, Scheme 4. These results show that the zinc ion has only a weak coordination to the *exo*-oxo, and that symmetrical *endo*-oxo zinc ion coordination in **1-Zn** is insufficiently activating to enable uranyl(VI) reduction by M-N homolysis.

Probably it is a combination of a greater activation of the UO_2 group in the putative **1-Mg** by Mg, and a stronger coordination of the *exo*-oxo group to the second Mg that favors metallation to form **4-Mg** (BDE Mg-O = 394, BDE Zn-O = 284 kJ.mol^{-1}).[16] The Zn-N" bond is stronger than the Mg-N" bond,[17,18] and the Zn-N bond is stronger than the N-Si bond (BDE(Zn-N) = 565, BDE(N-Si) = 439, BDE(O-Si) = 798 kJ.mol^{-1});[16] further factors that would suggest a metallation product for Mg, and a silylation product for softer metal silylamides such as those of Zn^{II}.

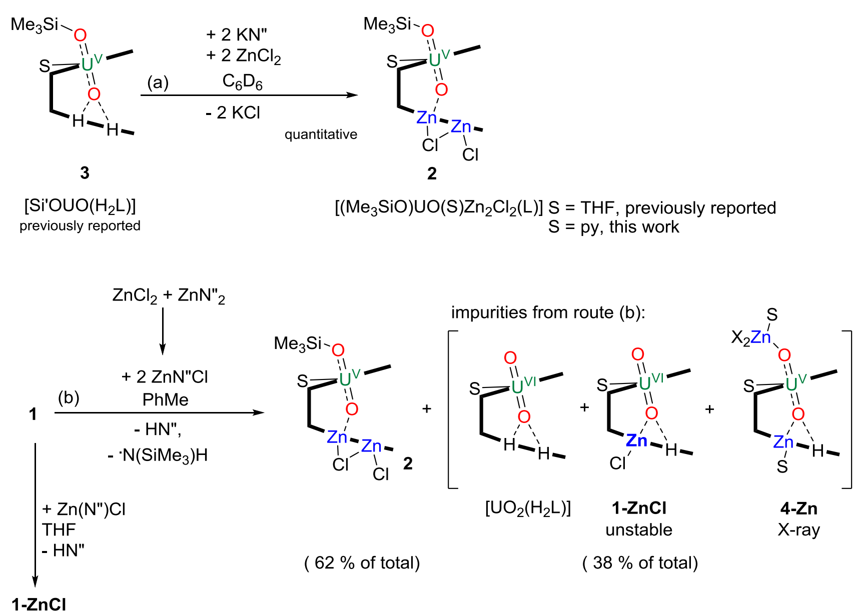
Alternative routes to oxo-silylated uranyl(V) complexes

Samples of **1** were reacted with two equivalents of potassium base, in an effort to isolate the paramagnetic U^V intermediate formed prior to zincation, but no stable product could be isolated, in agreement with the results of potassiation shown in Scheme 3. However, two new, simpler routes to **2** have now been identified and are shown in Scheme 5 and described below.

a: Synthesis *via* prior oxo-silylation. We have recently shown that the protonated uranyl(V) complex [HOUO(py)(H_2L)] reacts with Me_3SiCl to afford the thermally robust, oxo-silylated U^V complex [(Me_3SiO)UO(S)(H_2L)] **3** (S = py,[19] THF, this work, see Supporting Information). Treatment of **3** with two equivalents of KN" at room temperature results in the disappearance of the IR absorption for the pyrrole NH, the formation of two equivalents of HN", and a complex we assign tentatively as [(Me_3SiO)UO(S)K_2(S)$_n$(L)] (S = THF, py) **[Si'OUO(K_2L)]**. This complex reacts *in situ* with two equivalents of $ZnCl_2$, precipitating KCl and forming quantitatively (as ascertained by NMR spectroscopy) the target silylated uranyl(V) complex **2** (S = THF,[5] py, this work). The single crystal X-ray structure of the new pyridine solvate of **2**, [(Me_3SiO)UO(py)Zn_2Cl_2(L)] is shown in Figure 2.

b: Synthesis by reaction with the mixed-ligand reagent [Zn(N")Cl]. Considering that a metal-bound silylamido group proximal to the uranyl oxo might provide an efficient route to silylation, the zinc compound [Zn(N")Cl] was made with rigorous exclusion of Group 1 salts by combining equimolar $ZnCl_2$ and $ZnN"_2$ in arene solvent at room temperature, Scheme 6. The resulting colorless solid analyses as [Zn(N")Cl], is benzene-soluble, and displays a single resonance in the ^{1}H NMR spectrum at 0.2 ppm. Assuming that this material would be subject to a Schlenk-type equilibrium, a solution of **1** and two equivalents of freshly prepared [Zn(N")Cl] was boiled in toluene for 24 h, producing a brown suspension (Scheme 5b). The desired product **2** was isolated from the toluene-soluble fraction in 62 % yield. Analysis of single crystals grown from a saturated d_6-benzene solution confirms that it is isostructural (save for the identity of the coordinated solvent) with that originally reported for **2**.

The latter route (b) is of particular interest since it involves a single reagent that affords both uranyl ion reduction and silylation of the oxo group. Investigation of the remainder of the reaction products (the other 38 % of the material) by NMR spectroscopy shows the byproducts to be the uranyl(VI) adduct [UO_2(S)ZnCl(HL)] **1-ZnCl**, the uranyl(V) complex **4-Zn**, and **1** in a 7:2:1 ratio. However, the ratio of **1** to **1-ZnCl**



Scheme 5 Alternative routes to the uranyl(V) oxo-silylated complex 2: (a) through prior oxo-silylation; (b) through the reaction with the mixed-ligand reagent [Zn(N")Cl].

may well not represent the actual mixture formed in the reaction as solutions of **1-ZnCl** decompose upon storage or solvent evaporation to **1** and unidentified Zn-containing complexes. Complex **1-ZnCl** was made quantitatively in an independent reaction between **1** and one equivalent of Zn(N")Cl in THF (after trituration of the reaction mixture with pyridine, in which the two complexes do not react), and has been characterized by NMR spectroscopy. The ^{1}H NMR spectrum shows a single pyrrole N-H hydrogen in the lower macrocycle pocket, and the formation of $HN(SiMe_3)_2$ (see Supporting Information). On numerous occasions, single crystals suitable for X-ray diffraction were obtained from THF or pyridine solutions of **1-ZnCl**, and always identified as the uranyl complex **1**, and in one case, $ZnCl_2(py)_2$, giving clear evidence for the instability of **1-ZnCl**

A comparison of the behaviors of $[UO_2(py)ZnCl(HL)]$ **1-ZnCl** and the symmetrical $[UO_2(py)Zn(py)(L)]$ **1-Zn** is also pertinent: no reaction is observed between **1-Zn** and Zn(N")Cl in pyridine at 80 °C for 12 h, demonstrating the greater activation provided by the asymmetrically coordinated ZnCl ion in the bottom macrocyclic pocket.

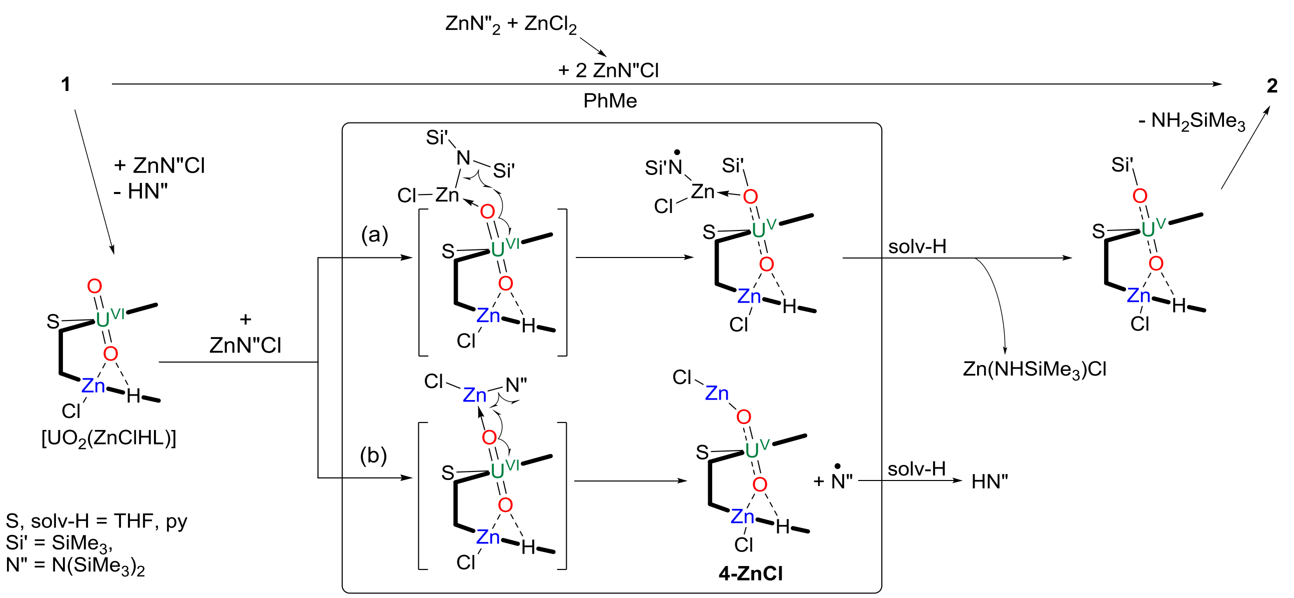
Proposed mechanisms for the reactions for silylation or metalation of the uranyl oxo groups

The silylation of the uranyl oxo group only occurs under certain conditions, and remains one of the few covalent bond forming processes observed yet for the uranyl ion, hence the mechanism is of interest. We propose that the key step to enable oxo-silylation is the generation of an intermediate that favors N-Si over M-N bond homolysis within an oxo-coordinated M-N-SiR_3 group. The suggested mechanism for reductive oxo silylation which is consistent with the experimental data is shown in Scheme 6, path (a).

As described above, mono-metallated uranyl Pacman complexes are easier to reduce and their oxo groups are better donors to other metal cations at the more accessible *exo*-oxo group. This is particularly so when the metal ion in the bottom macrocyclic pocket is more electropositive, or coordinated to just one pyrrolide ion, allowing a stronger interaction with the *endo*–oxo group. Thus, once ZnCl bonds to the *endo*-oxo, coordination of the second silylamide-containing metal complex by the *exo*-oxo group is more facile.

The compound [Zn(N")Cl] appears particularly well-suited to both oxo activation and silyl delivery, and avoids the solution instability problems associated with the labile alkali metal complexes.[9] The Zn-N bond in the reagent [Zn(N")Cl] is relatively covalent, so the N-Si bond of the coordinated metal silylamide group is more susceptible to homolysis. The resulting motif (Scheme 6, path a) is set up to form a strong O-Si bond as the U^{VI} center is reduced to U^{V}, and a zinc-stabilized, N-centered (aminyl) radical Zn-N•$(SiMe_3)$,[20] the latter abstracting a H atom from solvent to form $Zn(NHSiMe_3)Cl$. A final metalation of the bottom pocket (the second pyrrole NH) by the $Zn(NHSiMe_3)Cl$ by-product installs the second ZnCl group, releasing the volatile amine H_2NSiMe_3 and forming **2**.

If the second metal reagent contains a homolysable metal-ligand bond, pathway (b) in Scheme 6 is followed, giving the uranyl(V) doubly metallated products **4** that are minor products in the [Zn(N")Cl] reactions. Here, Zn-N bond homolysis provides the reduc-



Scheme 6 Proposed mechanistic steps for uranyl oxo group metalation or silylation

ing electron and forms a U^{V}-O-M motif, releasing the highly reactive •N" aminyl radical to abstract H from solvent. Control reactions (see Supporting Information) show that once formed, the doubly metalated uranyl(V) complexes **4** do not react with simple aminosilanes.

Pathway b dominates when [Zn(N")Cl] is replaced by much more electropositive metal silylamido complexes, e.g. of Li, K, Mg, Ln. The contrasting behaviors of MgN''_2 and ZnN''_2 (Scheme 4) and that of the lanthanide LnN''_3 (to form uranyl(V) $[UO_2Ln(S)(L)]_2$) and d-block TMN''_2 (to form uranyl(VI) **1-TM**) reported by us, also underline this.[15,21] The zincated 'by-products' **4-Zn** can be made cleanly, but only from pre-reduced uranyl(V) complexes. The ionic radii of four-coordinate Li, Mg, and Zn cations are extremely similar: 0.73 pm (Li^{I}), 0.72 pm (Mg^{II}) and 0.74 pm (Zn^{II}), ruling out a sterically-induced mechanism, and the bottom macrocyclic cavity can clearly flex somewhat to strengthen the oxo-interaction to the single ZnCl ion in **1-ZnCl** compared with **1-Zn** that is insufficiently activated.[22] The Zn^{II} ion coordinated by one chloride and one pyrrolide group is presumably also more Lewis acidic than that coordinated by two N-ligands. Amido M-N bond strengths are not known for these simple homoleptic complexes but there is no evidence that the late transition metals have weaker M-N bonds in their amido complexes.[23]

Clearly, the silylation path is driven by formation of the strong O-Si bond and is enhanced when the alternative O-M bond is less strong. This bond strength has enabled a few other instances of uranyl silylation by simple electrophiles. We showed that oligomeric clusters that combined uranyl(V) and uranyl(VI) dioxo ions in the Pacman framework could be cleaved with Me_3SiCl to release the U^{VI} ion and the $SiMe_3$-capped $[(Me_3SiOUO)_2(L)]$.[14] Hayton showed that Me_3SiI reacts with $UO_2(^{Ar}acnac)_2$ ($^{Ar}acnac$ = ArNC(Ph)CHC(Ph)O; Ar = 3,5-$Bu^t_2C_6H_3$) to afford $U^{V}(O\text{-}SiMe_3)_2(^{Ar}acnac)(I)_2$ with the reduction here deriving from loss of the iodide radical I•.[8b] Whilst not explicitly described as an oxo-group silylation, Berthet has shown that UO_2Cl_2 reacts with Me_3SiCl exhaustively in MeCN to form $UCl_4(NCMe)_3$ and $Me_3SiOSiMe_3$, a reaction in which multiple U=O-$SiMe_3$ functionalization steps are inherent.[24]

Computational analysis of the mechanisms proposed for silylation vs metalation of the oxo groups

Two different calculated reaction profiles

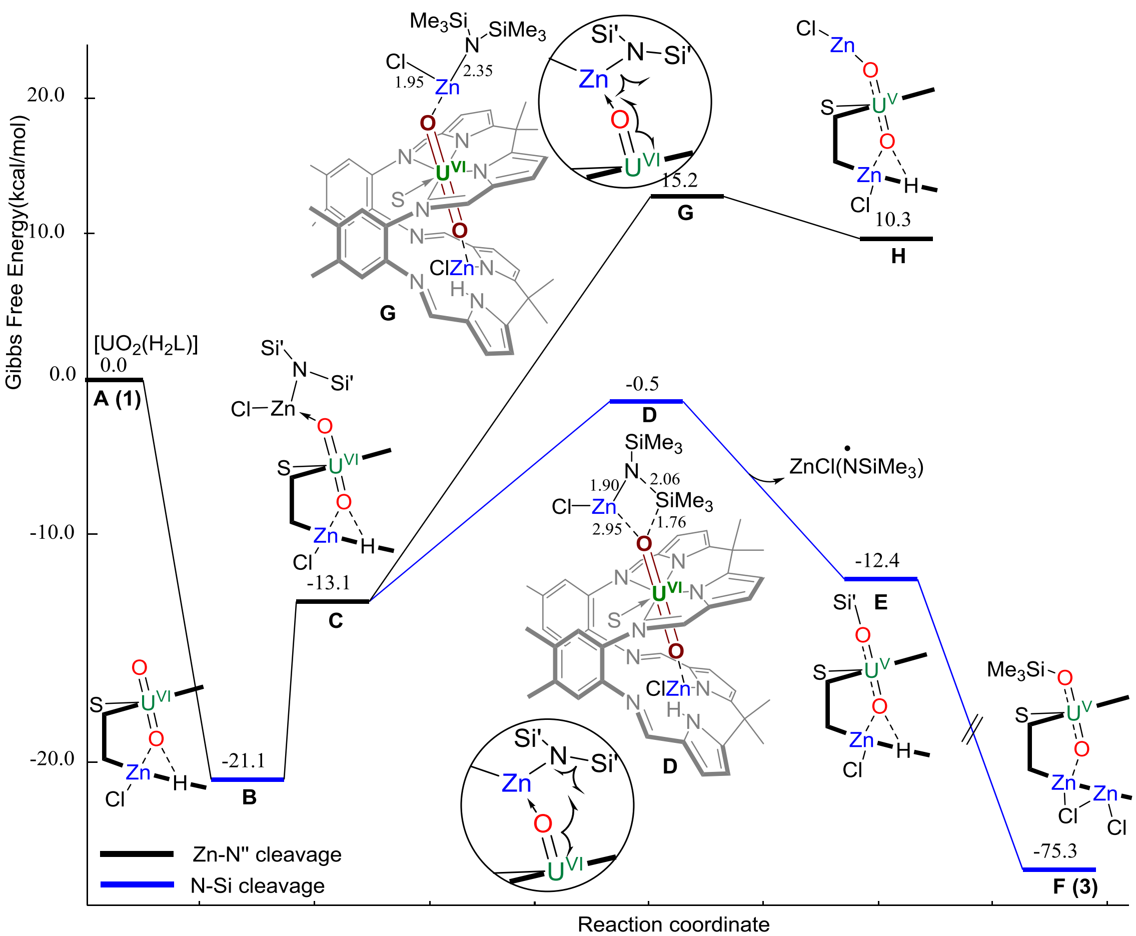


Figure 1 Computed free energy pathway (kcal/mol) for two competing reactions of 1 with [Zn(N")Cl] that can result in either uranyl oxo-group silylation or metalation.

(DFT/B3PW91) are combined in Figure 1 that show the two possibilities available for reaction of **1** (**A** in the calculations) with two equivalents of [Zn(N")Cl] to form silylated or metallated products. The numbers below each bar correspond to the calculated intermediates and transition states, with the calculated Gibbs free energies displayed above. The first step forms the uranyl(VI) mono-zincated complex $[UO_2(S)ZnCl(HL)]$ **1-ZnCl** (**B** in the calculation) which then reacts with a second [Zn(N")Cl] to form an adduct which can either reduce and functionalize the uranyl oxo by homolytic cleavage of an N-Si bond (blue path, lower) or by cleavage of a Zn-N bond (black path, upper). The oxo-silylated route (in blue), through the intermediate **D**, is lower in energy by 15.7 kcal/mol than the Zn-N bond homolysis pathway that forms the *exo*-oxo metallated by-product (intermediate **G**). The silylated products **E** and **F** on the blue path are also significantly lower in energy for the Zn reactions. These calculations agree with our experimental findings, and full reaction schemes and structures of the calculated intermediates are included in the Supporting Information SI. Additional calculations that compare the reactions of the uranyl(VI) complex **B** with either [Zn(N")Cl] or $ZnN"_2$ show that *exo*-oxo coordination of $ZnN"_2$ is strongly disfavored (the activation barrier to the analogue of **G** formed from $ZnN"_2$ is 42.7 kcal/mol, see Supporting Information), again agreeing with our experimental findings (Scheme 4b) that no reduction is observed when this poorly-coordinating Zn reagent is used.

Single crystal X-ray structures of representative complexes

In the solid state **4-Zn** and **4-Mg** are essentially isostructural, and are shown in Figure 2. In all exam-

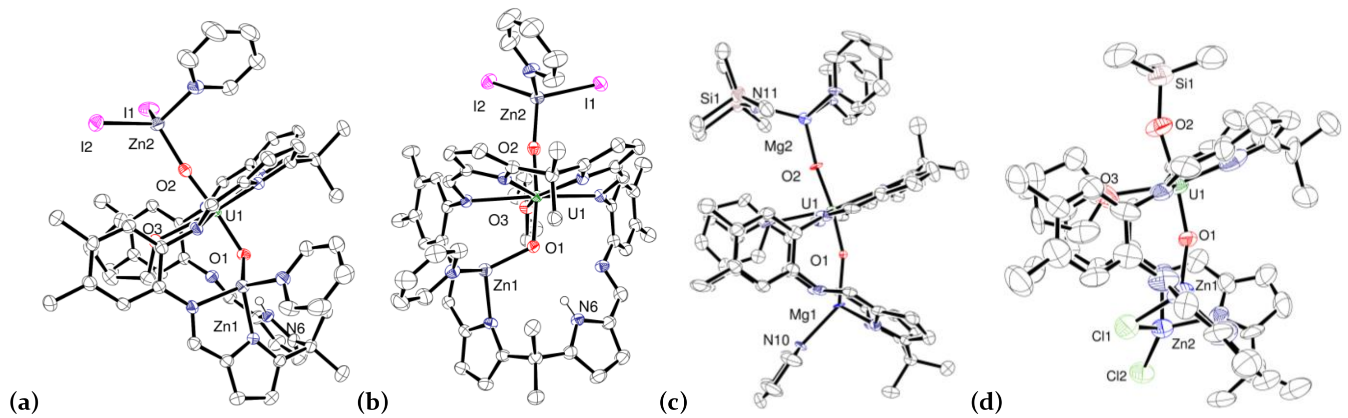


Figure 2 Solid state structures of $[(py)I_2ZnOUO(THF)Zn(py)(HL)]$ 4-ZnI **showing side (a) and front view (b), of the amido analogue** $[(py)_2(N")MgOUO(py)Mg(py)(L)]$ 4-Mg **showing side view (c), and the complex** $[(Me_3SiO)UO(THF)Zn_2Cl_2(L)]$**, which is isostructural with the other members of the family** $[(Me_3SiO)UO(S)(M_2X_2L)]$ **M = Fe, Zn, X = Cl/I, S = THF, py (d). For clarity, hydrogen atoms, except the pyrrole NH, and lattice molecules of solvent are omitted (displacement ellipsoids drawn at 50 % probability).**

Table 1: Selected bond distance (Å) and angles (°) for $[(py)I_2ZnOUO(THF)Zn(py)(HL)]$ **4-ZnI,** $[(py)Cl_2ZnOUO(py)Zn(py)(HL)]$ **4-ZnCl,** $[(py)_2(N")MgOUO(py)Mg(py)(L)]$ **4-Mg, and** $[(Me_3SiO)UO(THF)Zn_2Cl_2(L)]$ **2a**

$(py)I_2ZnOUO(THF)Zn(py)(HL)$ **4-ZnI**		$(py)Cl_2ZnOUO(py)Zn(py)(HL)$ **4-ZnCl**		$(py)_2(N")MgOUO(py)Mg(py)(L)$ **4-Mg**		$(Me_3SiO)UO(THF)$ **2**	
Bond	**Distance(Å) /angle (°)**	**Bond**	**Distance(Å) /angle (°)**	**Bond**	**Distance(Å) /angle (°)**	**Bond**	**Distanc /angle (**
U1-O1 endo	1.908(3)	U1-O1	1.934(2)	U1-O1	1.846(10)	U1-O1	1.840(10
U1-O2 exo	1.879(3)	U1-O2	1.887(3)	U1-O2	1.867(12)	U1-O2	1.993(11)
U1-O3	2.473(3)	U1-N9	2.586(3)	U1-N9	2.597(17)	U1-N9	2.411(14)
O1-Zn1	1.965(3)	O1-Zn1	1.962(2)	O1-Mg1	2.037(12)	O1-Zn1	1.957(11)
O2-Zn2	1.988(3)	O2-Zn2	1.989(3)	O2-Mg2	1.966(13)	O1···Zn2	3.815
O1···N6	3.178	O1···N7	3.068			O2···Si1	1.697(12)
O1-U1-O2	173.03(13)	O1-U1-O2	170.47(13)	O1-U1-O2	172.6(5)	O1-U1-O2	172.9(5)
Zn1-O1-U1	118.92(15)	Zn1-O1-U1	119.51(13)	Mg1-O1-U1	162.1(6)	Zn1-O1-U1	149.6(7)
Zn2-O2-U1	172.27(19)	Zn2-O2-U1	172.99(15)	Mg2-O2-U1	172.9(8)		

ples, the uranyl has significantly elongated U-O bonds compared to the uranyl(VI) starting materials but remains linear with multiple U-O bonding evident; each U center is five-coordinate in the equatorial plane. The Zn/Mg centers adopt pseudo-tetrahedral geometries in each structure. The endo uranyl U-O bond length is always longer than the exo U-O bond length in a given complex; even where the lower pyrrole groups remain protonated, a hydrogen-bonding interaction with the endo-oxo group is suggested. Table 1 contains selected distances and angles for comparison, with full discussions of the crystal structures in the Supplementary information SI. The structure of the chloride analogue of **2**, $[(Me_3SiO)UO(THF)Zn_2Cl_2(L)]$ has been determined (that previously reported contained mixed Cl and I occupancy in the halide site), and the bond distances and angles are the same within standard uncertainties as those previously reported by us.

Conclusions

The coordination of strongly Lewis acidic metals into the endogenous cavity of the uranyl(VI) Pacman macrocycle, such as in $[UO_2Li(HL)]$, $[UO_2Mg(L)]$, $[UO_2ZnCl(HL)]$, and $[UO_2Ln(L)]_2$, results in a direct interaction to the endo-oxo group, enhancing the basicity of the exo-oxo group and the oxidizing power of the uranyl(VI) ion. Similar complexes derived from transition metal cations TM^{2+} such as $[UO_2TM(L)]$ (TM = Mn, Fe, Co, Zn) are much more inert.

Significantly, a second equivalent of a Lewis acidic metal salt can promote reductive metalation or silylation of the oxo group. While the bis(amido) ZnN''_2 complex is insufficiently Lewis acidic for oxo-binding to result in reductive functionalisation, the Lewis acidic MgN''_2 forms a strong U-O_{exo}-Mg dative interaction that favors homolytic Mg-N bond cleavage, with concomitant reduction of U^{VI} to U^{V} and formation of a U-O-Mg bond. The 'Goldilocks' reagent for reductive silylation is [Zn(N")Cl], which is a weaker Lewis acid than MgN''_2 but sterically less hindered than ZnN''_2. This allows the formation of a weak U-Oexo-Zn dative interaction which favors homolytic N-Si cleavage, strong O-Si bond formation, and reduction. The release of a Zn-stabilized aminyl radical by-product and subsequent incorporation of the remaining equivalent of Zn^{II} allows a new and straightforward, single-reagent route to reductively silylated uranyl complexes such as $[(Me_3SiO)UO(THF)Zn_2Cl_2(L)]$ **2**. In addition to DFT calculations, a range of complexes have been prepared that support the proposed mechanisms.

The new one-pot route to oxo-silylation from a single metal silylamide precursor, and an understanding of the factors that promote uranyl oxo-functionalization should open up many new opportunities for alternative oxo-functionalization chemistry, and the incorporation of metals salts of greater relevance to the minerals that contact uranyl salts in the environment.

Experimental Details

All synthetic work described was conducted with rigorous exclusion of air and water by Schlenk, vacuum line, and glovebox techniques. Full general details, further synthetic data, analyses, and control reactions are contained in the supplementary information. The syntheses of $[H_4L]$,[25] $[UO_2(N'')_2(THF)_2]$ ($N'' = N(SiMe_3)_2$),[26] $[UO_2(THF)(H_2L)]$,[5] $[UO_2\{N(SiMe_3)_2\}(py)_2]$,[14] MgN''_2,[27] ZnN''_2,[28] and $[UO_2(py)(H_2L)]$,[15] are reported in the literature.

$[UO_2(py)Zn(py)(L)]$ 1-Zn

A Schlenk was charged with $[UO_2(py)(H_2L)]$ (496 mg, 0.493 mmol), one equivalent of $Zn\{N(SiMe_3)_2\}_2$ (190 mg, 0.493 mmol), a magnetic stirrer bar, and sufficient pyridine to dissolve the reagents at 20 °C (40 mL). The brown solution then stirred at room temperature for 3 weeks before the removal of volatiles. The resulting brown residue was washed with toluene (50 mL) and hexane (10 mL) and dried under vacuum for 1 h affording $[UO_2(py)Zn(py)(L)]$ **1-Zn** as a brown solid, (410 mg, 72 %). The X-ray structure of the THF-solvate has been previously communicated to the CSD.[11c]

^{1}H NMR (d_5-pyridine): δ_H: 9.42 (s, 2H, imine), 8.11 (s, 2H, imine), 7.26 (d, 2H, J = 7 Hz, pyrrole), 6.65 (d, 2H, J = 7 Hz, pyrrole), 6.56 (d, 2H, aryl), 6.49 (d, 2H, J = 7 Hz, pyrrole) 6.40 (s, 2H, aryl), 6.28 (d, 2H, pyrrole), 2.11 (s, 6H, aryl-methyl), 1.93 (s, 3H, *meso*-methyl), 1.87 (s, 6H, aryl-methyl), 1.63 (s, 3H, *meso*-methyl), 1.55 (s, 3H, *meso*-methyl), 1.41 (s, 3H, *meso*-methyl). Analysis. Found. C, 54.29; H, 4.32; N, 11.96 %. $C_{52}H_{50}N_{10}O_2ZnU$ requires C, 54.29; H, 4.38; N, 12.18 %. FTIR (cm^{-1}). U=O_{asym} 899 cm^{-1}.

Oxo-metalated complexes

$[(THF)I_2ZnOUO(THF)Zn(THF)(HL)]$ 4-ZnI

To a mixture of $[(py)_3LiOUO(py)Li(py)(HL)]$ **4-Li** (207 mg, 0.17 mmol) and ZnI_2 (2 equiv, 112.51 mg, 0.35 mmol) in a Schlenk tube was added pyridine (10 mL). The solution was stirred for 16 h, the volatiles were removed then the solid was washed with toluene (3 x 5 mL) to afford $[(py)I_2ZnOUO(py)Zn(py)(HL)]$ **4-ZnI** with 2 LiI incorporated as a brown solid in 76 %, 189 mg. When the reaction was repeated in the presence of $N(SiMe_3)_3$, no consumption of $N(SiMe_3)_3$ was observed.

Analysis. Found: C, 39.44; H, 3.86; N, 8.92 %. $C_{62}H_{61}I_4Li_2N_{12}O_2UZn_2$ requires C, 39.26; H, 3.24; N, 8.86 %. ^{1}H NMR (d_5-pyridine): δ_H 58.43 (s, 1H), 29.29 (s, 3H), 12.52 (s, 1H), 11.60 (s, 1H), 10.31 (s, 3H), 8.06 (s, 1H), 5.33 (s, 1H), 5.04 (s, 3H), 2.50 (s, 3H), 1.43 (s, 1H), 0.47 (s, 1H), 0.34 (s, 1H), 0.03 (s, 1H), −0.35 (s, 3H), −1.75 (s, 3H), −2.05 (s, 3H), −2.21 (s, 1H), −2.65 (s, 1H), −2.96 (s, 1H), −2.96 (s, 1H), −3.46 (s, 1H), −4.80 (s, 1H), −6.32 (s, 1H), −4.99 (s, 1H), −5.81 (s, 1H), −6.32 (s, 3H), −14.45 (s, 1H) ppm. ^{7}Li{^{1}H} NMR (d_5-pyridine): δ_{Li} 5.0 ppm. IR (Nujol, cm^{-1}): ν 3329(NH). Orange single crystals suitable for X-ray diffraction studies were grown from a saturated solution of THF with a few drops of C_6D_6 at room temperature.

[UO_2(py)Mg(py)(L)] 1-Mg

A Schlenk was charged with [UO_2(py)(H_2L)] (134 mg, 0.134 mmol), one equivalent of Mg(N")$_2$ (65 mg, 0.134 mmol), a magnetic stirrer bar, and sufficient pyridine to dissolve the reagents at 20 °C (15 mL). The brown solution then stirred at room temperature for 2 days before the removal of volatiles. The resultant brown residue was then washed with toluene (10 mL) and hexane (5 mL) and dried under vacuum for 1 h affording [UO_2(py)Mg(py)(L)] **1-Mg** as a brown solid. (64 mg, 44 %).

^{1}H NMR (d_5-pyridine): δ_H: 9.44 (s, 2H, imine), 7.91 (s, 2H, imine), 8.10 (s, 3H, *meso*-methyl), 7.24 (d, 2H, J = 7 Hz, pyrrole), 6.74 (d, 2H, J = 7 Hz, pyrrole), 6.54 (d, 2H, aryl), 6.42 (d, 2H, J = 7 Hz, pyrrole) 6.38 (s, 2H, aryl), 6.28 (d, 2H, pyrrole), 2.14 (s, 6H, aryl-methyl), 1.93 (s, 3H, *meso*-methyl), 1.91 (s, 6H, aryl-methyl), 1.83 (s, 3H, *meso*-methyl), 1.71 (s, 3H, *meso*-methyl), 1.22 (s, 3H, *meso*-methyl). FTIR (cm^{-1}). U= O_{asym} 899 cm^{-1}.

[(py)$_2$N"MgOUO(py)Mg(py)(L)] 4-Mg

An ampoule was charged with [UO_2(py)(H_2L)] (196 mg, 0.195 mmol), two equivalents of Mg(N")$_2$ (191 mg, 0.390 mmol), a magnetic stirrer bar, and 40 mL pyridine. The brown solution was heated to 80 °C for 3 d. The brown solid that formed was isolated by filtration and dried under vacuum to afford [(py)$_2$N"MgOUO(py)Mg(py)(L)] **4-Mg** as a brown solid in 58 % yield (163 mg). Single crystals were grown from a d_5-pyridine solution of the complex at room temperature.

^{1}H NMR (d_5-pyridine): δ_H: 10.56 (s, 2H), 9.73 (s, 2H), 8.10 (s, 3H, *meso*-methyl), 7.00 (s, 3H, *meso*-methyl), 5.24 (s, 2H), 4.90 (s, 18H, N(Si*Me*$_3$)$_2$), -0.59 (s, 3H, *meso*-methyl), -0.63 (s, 2H), -1.01 (s, 6H, aryl-methyl), -1.81(s, 3H, *meso*-methyl), -5.04 (s, 3H, *meso*-methyl), -5.18 (s, 2H), -6.48 (s, 2H). Resonances integrating to 2H are imine, pyrrolic and aryl two of which are obscured by the solvent.

Reactions of 1-Zn with ZnN"$_2$, and with [Zn(N")Cl]

A solution of [UO_2(py)Zn(py)(L)] (35 mg, 0.030 mmol) in d_5-pyridine (0.7 mL) and ZnN"$_2$ (12 mg, 0.030 mmol, 2 equiv) was heated at 80 °C for 12 h during which no reaction was observed. Repetition of the reaction in THF afforded the same result.

Reaction of 1 with [Zn(N")Cl]: attempt to synthesize [UO_2(py)ZnCl(HL)] 1-ZnCl

A mixture of powdered [UO_2(THF)(H_2L)] (26.5 mg, 0.024 mmol) and ZnN($SiMe_3$)$_2$Cl (6.4 mg, 0.025mmol) were dissolved in in d_5-pyridine (0.7 mL). No change in the resonances of **1** was observed by ^{1}H NMR spectroscopy even after 72 hours standing, but the chemical shifts for the Zn(N")Cl (^{1}H and ^{29}Si) are shifted, suggesting some form of association with **1**. The solution was concentrated to near-dryness, and redissolved in d_8-THF (0.5 mL). After 24 h standing, the ^{1}H NMR spectrum of this solution contains a single set of ligand resonances assigned as **1-ZnCl**, alongside residual HN" (Figure SI 7).

Complex **1-ZnCl** is unstable when stored as a THF solution, even at low temperatures, and concentration and/or storage of solutions have yielded single crystals of [UO_2(py)(H_2L)][THF]$_2$ on multiple occasions (identified in each case by X-ray diffraction on single crystals).

Oxo-silylated complexes

Preparation of [Zn(N")Cl]

To a mixture of $ZnCl_2$ (105.8 mg, 0.77 mmol) and ZnN"$_2$ (300 mg, 0.77 mmol) was added toluene (10 mL). The suspension was stirred at room temperature until gelation occurred. The volatiles were removed under reduced pressure to afford [Zn(N")Cl] as a colorless solid (400 mg). ^{1}H NMR (C_6D_6): δ_H 0.2 ppm.

[(Me_3SiO)UO(THF)Zn_2Cl_2L] 2

To a mixture of **1** (50 mg, 0.048mmol) and [Zn(N")Cl] (25.5 mg, 0.097 mmol) was added toluene (5 mL) and the solution was heated at 110 °C for 24 h. The suspension was filtered and the filtrate was dried under vacuum to afford the known compound **2** as a brown solid in 62 % yield (38.4 mg). Red block crystals of [(Me_3SiO)UO(THF)Zn_2Cl_2(L)] suitable for X-ray diffraction studies were grown from a saturated C_6D_6 solution at room temperature. Analysis. Found: C, 46.30; H, 4.50; N, 8.72 %. $C_{49}H_{57}Cl_2N_8O_3SiZn_2U$ requires C, 46.19; H, 4.52; N, 8.80 %.

Supporting Information. Detailed synthetic and computational data. CCDC numbers for the X-ray structures are CCDC 985559-985563 and 1050693.

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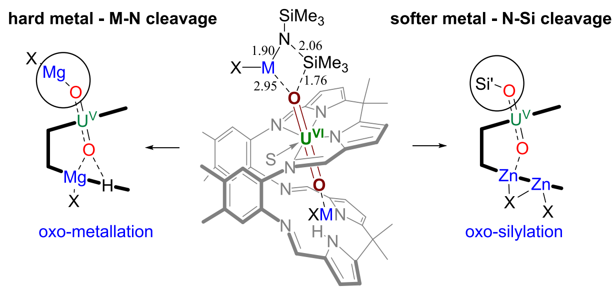
SYNOPSIS TOC (Word Style "SN_Synopsis_TOC").



Uranyl(VI) complexes of a constraining, Pacman-shaped aza macrocycle in which one oxo group is functionalized by a single metal cation are activated towards single-electron reduction. New and straightforward routes to singly reduced and oxo-silylated U(V) uranyl Pacman complexes, combined with computational analyses allow us to propose mechanisms that account for the different products formed, oxo-metallated or oxo-silylated, depending on the Lewis acidity of the metal complex used.