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Breaking C–O Bonds with Uranium: Uranyl Complexes as Selective Catalysts in the Hydrosilylation of Aldehydes

Louis Monsigny, Pierre Thuéry, Jean-Claude Berthet* and Thibault Cantat*.

NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette, France

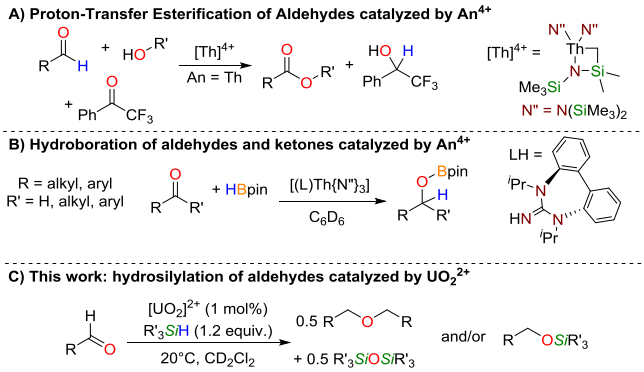
ABSTRACT: *We report herein the possibility to perform the hydrosilylation of carbonyls, using actinide complexes as catalysts. While complexes of the uranyl ion $[UO_2]^{2+}$ have been poorly considered in catalysis, we show the potentialities of the Lewis acid $[UO_2(OTf)_2]$ (**1**) in the catalytic hydrosilylation of a series of aldehydes. $[UO_2(OTf)_2]$ proved a very active catalyst affording distinct reduction products depending on the nature of the reductant. With Et_3SiH, a number of aliphatic and aromatic aldehydes are reduced into symmetric ethers, while $^iPr_3SiH$ yielded silylated alcohols. Studies of the reaction mechanism led to the isolation of aldehyde/uranyl complexes, $[UO_2(OTf)_2(4\text{-}Me_2N\text{-}PhCHO)_3]$, $[UO_2(\mu\text{-}\kappa^2\text{-}OTf)_2(PhCHO)]_n$ and $[UO_2(\mu\text{-}\kappa^2\text{-}OTf)(OTf)_2(PhCHO)_2]_2$ which have been fully characterized by NMR, IR and single crystal X-ray diffraction.*

KEYWORDS*: Homogenous catalysis, Uranium, Uranyl, Hydrosilylation, Reduction, Aldehydes, Mechanisms.*

Actinides have aroused considerable fundamental researches to better understand their fascinating chemical and physical properties. The last decades have witnessed a profuse literature of the chemistry of the 5f-elements revealing unprecedented structures and reactivities including the isolation of new coordination motifs or unusual activation of small molecules (such as N_2, CO or CO_2).[1] Translating these chemical features in the realm of catalysis remains shy and catalytic applications have been mainly achieved with the organometallic An^{4+} species (Th, U) for the hydroamination, hydrosilylation and polymerization of alkenes and alkynes.[1b, 2] The transformation of oxygenated compounds with actinide catalysts represents a difficult task, as the strength of actinide-oxygen bonds may preclude efficient catalytic turnover.[1d, 3] Nonetheless, the group of Eisen recently challenged this vision by unveiling the ability of some uranium(IV) and thorium(IV) complexes to promote the catalytic dimerization of aldehydes (Tishchenko reaction).[4] These authors thus paved the way to developments in this field, substantiated by the subsequent reports of key examples of hydroalkoxylation,[5] addition of alcohols on heterocumulene,[6] ring opening polymerization of epoxides[7] and esters[8] and dehydration of amides.[9]

The reduction of oxygenated substrates, involving the cleavage of C–O and/or C=O bonds, is of fundamental importance, for instance in the conversion of carbonyl or bio-based substrates[10] and CO_2.[11] The utilization of actinide based catalysts in this area is extremely rare, as the metal ion must cope with the strength of the An-O bonds and tolerate the reductant.[12] Eisen *et al.* showed that aldehydes could undergo esterification reactions in the presence of alcohols, in the presence of α,α,α,trifluoro-benzophenone as a sacrificial hydride acceptor (**Erreur ! Source du renvoi introuvable.**, A).[13] In this example, the thorium(IV) complex favors a hydrogen transfer that formally results in the reduction of α,α,α,trifluoro-benzophenone. Very recently the same group reported the first catalytic reduction of carbonyl compounds (aldehydes and ketones) with hydroboranes (R_2BH), in the presence of thorium complexes able to generate reactive [Th]-H species as catalytically active intermediates, thereby unlocking new opportunities in catalysis with actinides (**Erreur ! Source du renvoi introuvable.**, B).[12a]

In contrast to hydroboranes, hydrosilanes (R_3SiH) have never been used for the reduction of carbonyl or heterocumulene compounds with actinide catalysts. Hydrosilanes are milder reductants compared to hydroboranes[14] or diboranes[15]. Yet, the slight polarization of the Si-H bond offers appealing advantages for the development of selective reduction processes in organic chemistry,[10,11] the valorization of biomass,[16] and the recycling of plastics.[17]



Scheme 1. Exhaustive overview of the catalytic reduction of oxygenated compounds using actinide complexes.

These recent successes in catalytic reduction chemistry have been achieved with An^{4+} (An=U, Th) organometallic complexes, and the catalysts are in consequence sensitive to air and moisture. In contrast, the uranyl cation $[UO_2]^{2+}$ is the most abundant form of uranium in the environment and it is ubiquitous in the nuclear industry. Although the use of uranyl in reductive transformations would be novel and attractive, it also poses significant questions:

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indeed, a handful of reports describe the reduction of $[UO_2]^{2+}$ species into U(V) or U(IV) compounds by hydrosilanes in the presence of the Lewis acid ($B(C_6F_5)_3$)[18] or a catalytic quantity of bases (MX = $KNSiMe_3$, KO^tBu, *etc*).[15a] These findings prompted us to investigate, in anhydrous conditions, the potentialities of uranyl species as catalysts in the reductive hydrosilylation of carbonyls.

The reduction of benzaldehyde (**2**) with a uranyl catalyst and a hydrosilane was initially investigated as a model reaction (Eqn (1)). Because $[\{UO_2Cl_2(THF)\}_2]_2$ is an efficient pre-catalyst for the ring opening polymerization of epoxides,[7] it was first tested with a 2.5 mol% charge for the hydrosilylation of **2** with 1.2 equivalent of triethylsilane (Et_3SiH), at room temperature in dichloromethane (Table 1, entry 1). Poorly soluble in dichloromethane, the dimeric complex dissolved upon addition of excess **2** to give a clear yellow solution, but proved inactive. In similar conditions, the iodide analogue $[\{UO_2I_2(THF)\}_3]$ (5 mol%) displayed a weak activity with a low conversion of **2** into the symmetric ether $PhCH_2OCH_2Ph$ (**2a),** obtained in *ca* 23% yield within 19 h (Table 1, entry 2).

Such reductive etherification of aldehyde has been reported with various Lewis acid such as Me_3SiX (X = I[19], OTf), Fe(III)[20], $M(OTf)_3$ (M = In[21], Sc, Bi, Ga, Al[22]), $M(OTf)_2$ (M= Cu[23], Zn[24]) as well as several Sb(III)[25] and Sb(V)[26] compounds.[27] Several reports describe the reductive coupling of aldehydes and ketones to ethers with organosilicon reagents in the presence of Lewis acid activators.

The high Lewis acidity of metal triflates has been extensively used in recent years in a number of organic transformations since they enhance reactivity of substrates through electrophilic activation.[28] Accordingly, we tested a stronger Lewis acid, *e.g.* uranyl triflate $[UO_2(OTf)_2]$ (**1**), in the hydrosilylation of **2**. Yellow complex **1** is quite soluble in polar organic solvents, such as THF (which undergoes rapid polymerization), pyridine and acetonitrile, but is insoluble in toluene and dichloromethane. Addition of 1.2 equiv. Et_3SiH to a slurry of complex **1** in toluene or CH_2Cl_2 did not induce solubilization of **1** or its reaction at 20 or 65 °C. However, addition of benzaldehyde (**2**) to 1 mol% of catalyst **1** at room temperature led to an immediate clear yellow solution. ^1H NMR monitoring of the reaction showed the quantitative conversion of benzaldehyde, within 1 hour, into ether **2a** and the siloxane $Et_3SiOSiEt_3$ (Table 1, entry 3). Interestingly, a somewhat different outcome was observed when an excess Et_3SiH (> 4 equiv.) was used, since ether **2a** along with the silylated alcohol $PhCH_2OSiEt_3$ (**2b**) were formed in a ~75:25 ratio (Table 1, entry 4).

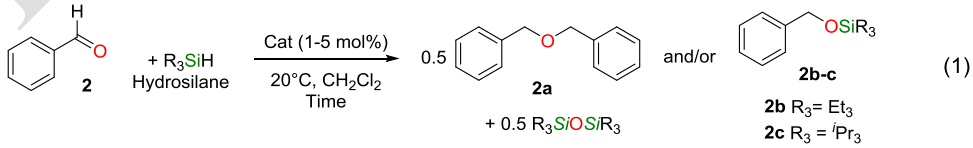
To probe the influence of the nature of the hydrosilane on the reduction of **2**, different reagents were used. Phenyldimethylsilane ($PhMe_2SiH$) and triphenylsilane (Ph_3SiH) behaved similarly to Et_3SiH affording **2a** quantitatively, although a longer reaction time (6 h) was necessary with Ph_3SiH (Table 1, entries 5 and 6). The use of the sterically hindered $^iPr_3SiH$ induced a considerable change with the selective formation of the silylated alcohol $PhCH_2OSi^iPr_3$ (**2c**) in nearly quantitative yield within 12 h (Table 1, entry 7).

The reductive etherification of aldehydes proved general and a number of benzaldehyde derivatives were successfully transformed into the corresponding dibenzylethers **3-10** in excellent yields, ranging from 83 to 99% (

). Depending on the nature of the substituents, the reactions required 0.5-10 h at room temperature to go to completion, with the release of $Et_3SiOSiEt_3$ as by-product. More precisely, *p*-substituted benzaldehydes **3-7**, featuring electron withdrawing (EW) halogen atoms (Cl, Br, I) or electron donating alkyl (ED) groups (Me, ^{t}Bu) were readily reduced into the symmetrical ethers **3a-7a** (

). Surprisingly, the increased steric congestion in **9** – possessing an *ortho*-methyl group – or in the anthracene derivative **8** did not affect the rate of the reaction. Importantly, ketone groups were tolerated and the hydrosilylation of 4-acetylbenzaldehdye **10** led chemoselectively to ether **10a** with excellent yields and a longer reaction time (10 h). This selectivity was confirmed with the absence of reaction with ketones (acetophenone or benzophenone). Furthermore, the carboxylic functionality in *ortho* position of **11** was maintained upon hydrosilylation of the formyl moiety with 2.4 equiv. of Et_3SiH and 1 mol% of uranyl **1**, and it led to an intramolecular cyclization to phthalide **11a**. Benzaldehyde derivatives with EW para-substituents (CN or NO_2) afforded, after long reaction times (12 and 24 h, respectively), a 1:1 mixture of ether **12a** and silyl ether **12b** or only the silylated alcohol **13b**, respectively. While no reaction was observed with *p*-dimethylaminobenzaldehyde (**15**), *p*-methoxybenzaldehyde led to a complex mixture of deoxygenated and Friedel-Craft products. Pyridine-, furan-, and thiophene-2-carboxaldehyde derivatives were also found unreactive, a trend that may be related to a deleterious chelation of the catalyst by the substrate.

Table 1: Optimization of the hydrosilylation of benzaldehyde (**2**), catalyzed by uranyl(VI) complexes

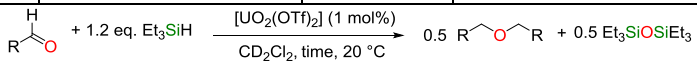


(1)

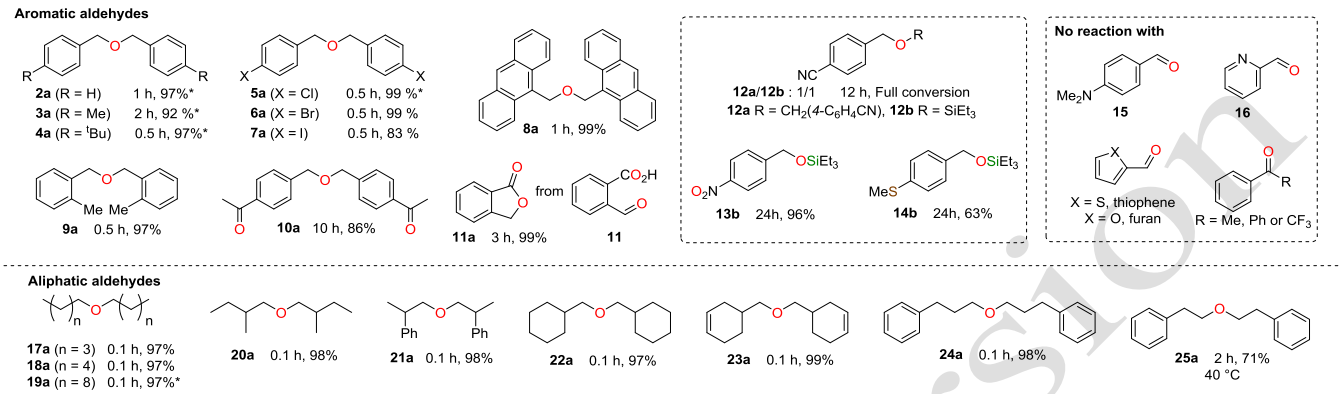
Entry	Cat (mol%)	Hydrosilane (n eq.)	Time	Conversion (%)	2a (%)	2b-c (%)
1	$[\{UO_2Cl_2(THF)\}_2]$ (5)	Et_3SiH (1.2)	24 h	< 5%	-	-
2	$[\{UO_2I_2(THF)\}_3]$ (5)	Et_3SiH (1.2)	19 h	39 %	23%	13%
3	$[UO_2(OTf)_2]$ **1** (1)	Et_3SiH (1.2)	1 h	> 99%	> 99%	-
4	**1** (1)	Et_3SiH (4)	1 h	> 99%	73%	24%
5	**1** (1)	$PhMe_2SiH$ (1.2)	1 h	> 99%	> 99%	-

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6	**1** (1)	Ph_3SiH (1.2)	6 h	> 99%	> 99%	-
7	**1** (1)	$^{i}Pr_3SiH$ (1.2)	12 h	> 99%	-	**2c** > 99%
8	-	Et_3SiH (1.2)	24 h	0%	-	-



(2)



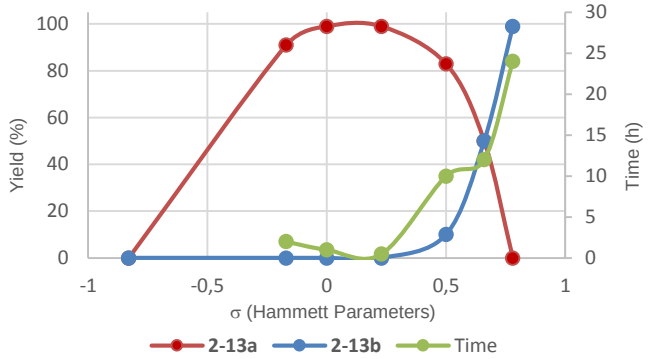
Scheme 2. Scope of the catalytic reductive etherification of aromatic and aliphatic aldehydes with Et_3SiH and $[UO_2(OTf)_2]$ (**1**). Reaction conditions: aldehyde (0.2 mmol); 0.24 mmol Et_3SiH; CD_2Cl_2 (0.4 mL; 0.5 M). Yields determined by ^1H NMR using mesitylene (10 mL) as an internal standard. *Yields of isolated products from scaled-up experiments (2 mmol scale).

The divergent selectivities in these reactions can be tentatively explained by considering the Hammett σ parameters of the substituents.[29] (Scheme 3) For strong ED groups, characterized by negative σ constants (NMe_2, –0.83), no reaction occurs. The formation of symmetric ethers is favored for σ constants in the range -0.3 to 0.5. More electron deficient substrates, characterized by higher σ constants, require longer reaction times and exhibit a different selectivity, with the formation of silylated alcohols $ArCH_2OSiR_3$ being facilitated.

The behavior of the *p*-MeS-benzaldehyde ($\sigma_{para}(SMe) = \sigma(H) = 0.00$) is intriguing. Instead of the expected dibenzylether derivative **14a**, only **14b** was obtained, albeit with a low 63 % yield, after 24 h. This result may suggest a peculiar influence of sulfur although thioethers are weak ligands for the hard uranium(VI) ion.

The formation of ethers RCH_2OCH_2R or silylethers RCH_2OSiR_3 from aromatic and aliphatic aldehydes has been previously reported with $Zn(OTf)_2$ in the presence of TMDS (TMDS = tetramethyldisiloxane) or Et_3SiH, and the selectivity strongly correlated to the electron–donating or electron–withdrawing properties of the aldehyde substituents.[24] Similar results have been observed with $Cu(OTf)_2$ and this catalyst was also able to reduce ketones into the corresponding symmetrical ether and carboxylic acids into the corresponding alcohols.[23] Altogether, these observations may suggest that the uranyl cation can follow catalytic paths similar to Lewis acids based on the transition metals.

In the presence of Lewis acidic complexes, a common side reaction of *aliphatic* aldehydes is the homo-aldol condensation, relying on the keto-enol tautomerism catalyzed by Lewis acids such as lanthanide triflates. [28a, 30] Gratifyingly, in the conditions of eqn. 2, the aliphatic aldehydes **17-24** were rapidly converted into the corresponding ethers **17a-24a** in excellent yields (97 - 99% in 0.1 h) without any side-product observed. Aldol condensation only occurred at elevated temperature (> 70 °C) with longer reaction time (>2 h, see SI). Linear aldehydes **17-19** as well as branched aliphatic aldehydes **20-22** displayed a similar reactivity with respect to the uranyl catalyzed hydrosilylation. It is noteworthy that the double bond in cyclohexene **23** was left untouched. α,β-unsaturated aldehydes



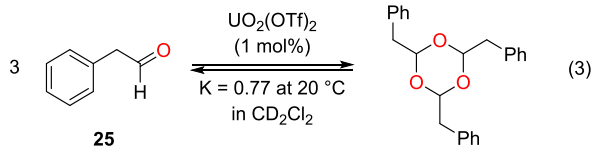
Scheme 3. Correlation of the yields of ethers **2-13a** (red line) and silylated alcohols **2-13b** (blue line) and reaction time (green line) of the reaction of hydrosilylation of aldehydes 4-R-PhCHO (R = NMe_2, Me, H, Cl, MeC(O), CN, NO_2) with the Hammett parameters

led to a rapid degradation of the starting materials as observed with 1-cyclohexene-1-carboxaldehyde and cinnamaldehyde. In contrast, hydrocinnamaldehyde was efficiently reduced to **24a** at room temperature, while the reductive etherification of phenylacetaldehyde (**25**) required a longer reaction time and a smooth heating to 40 °C. ^1H and ^{13}C NMR monitoring of the later catalytic run showed well separated resonances assignable to free aldehyde **25** and its trimeric form $(PhCH_2CHO)_3$ which are in equilibrium (K(20 °C) = 0.77, Eqn. 3, Scheme 4). Formation of the trioxane is catalyzed by

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uranyl **1**, as observed in a subsequent experiment by mixing only uranyl triflate and **25** in CD_2Cl_2. While the trioxane is favored at low temperatures, moderate heating at 40 °C gave back the genuine aldehyde **25** which can then be reduced into the ether **25a**.

The thermodynamic parameters measured for the equilibrium depicted in eqn. (3) revealed an exothermic (ΔH = −54 ± 0.3 kJ/mol) and entropically unfavorable reaction (ΔS = −184.6 ± 1.2 J/K.mol) with an overall reaction free energy of ΔG = +84.2 J/mol at 20 °C (see SI). The cyclotrimerisation of **25** is reminiscent of the cyclisation of methanal (CH_2O) to 1,3,5-trioxane. Such a reactivity has been widely reported with different Lewis acids (incl. Ru,[31] Me_3SiCl,[32] $InCl_3$,[33] $FeCl_3$,[34] etc[35]). If the other aldehydes with α-hydrogen atoms are left untouched by **1** in CH_2Cl_2, in neat condition they were transformed into the corresponding 1,3,5-trioxanes which often solidified in the flask.

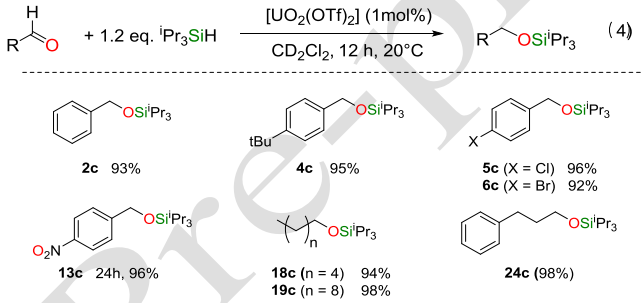


(3)

Scheme 4: Equilibrium reaction between phenylacetaldehyde and its trioxane form catalyzed by uranyl complex **1** in CD_2Cl_2

Thus, in presence of uranyl catalyst **1**, the aldehydes **21, 22, 24, 25**, rapidly stiffened as white solid trimers within 10 min-30 min while compounds **17, 18** gave colorless oils. These trioxanes have been readily isolated in quantitative yields (see SI).

Replacing Et_3SiH with $^iPr_3SiH$ considerably altered the course of the reaction and aromatic and aliphatic aldehydes were transformed into the corresponding silylated alcohols (Eqn (4)). The reaction required 12 h to reach completion in CH_2Cl_2, and showed quantitative conversions, excellent selectivity and yields (92-98%) (Scheme 5).



(4)

Scheme 5. Reduction of aldehydes into silylated alcohols catalyzed by $[UO_2(OTf)_2]$ in presence of $^iPr_3SiH$.Quantitative conversion for all the reactions. Yields determined by ^1H NMR using mesitylene (10 µL) as internal standard.

In order to gain insights into the mechanism of this reaction and to better apprehend the role of the uranyl catalyst, kinetic measurements were carried out by ^1H NMR for the reductive coupling of *p*-MePhCHO with Et_3SiH (see ESI for details). These investigations revealed a complex rate law for the reaction presented in Eqn. 5. with a third order for the catalyst, a first order in hydrosilane and an inverse $^3/_2$ order in aldehyde.

$$\frac{\partial p}{\partial t} = k \times \frac{[\mathbf{1}]^3 \times [hydrosilane]^1}{[aldehyde]^{3/2}} \qquad (5)$$

The activation energy (Ea), the enthalpy ($\Delta H^{\ddagger}$), and the entropy ($\Delta S^{\ddagger}$) of activation for the rate-determining step were found to be 11.4 ± 0.40 kcal/mol, 10.8 ± 0.5 kcal/mol, and -43.2 ± 0.5 eu, respectively. ($\Delta G^{\ddagger}$ = 23.7 ± o.6 kcal/mol). The high negative entropy values would indicate a highly ordered transition state at the rate-determining step (RDS). Studies of the isotopic effect by using deuterated hydrosilanes yielded a KIE value of 2.3 ± 0.1, revealing that the H atom transfer was involved in the RDS. A secondary kinetic isotope effect (SDKIE) of 0.90 was determined for Et_3SiH with the deuterated substrate PhCDO. This low value (< 1) is indicative of a purely ionic mechanism, excluding a radical pathway.[36]

The inverse kinetic order observed for the aldehyde underlines a progressive deactivation of the catalyst with increasing concentrations of aldehyde, likely by saturation of the coordination sphere of uranium which may impede an access to the metal center for the reductant or a decreased Lewis acidity on the U^{VI} cation. Such interpretation is supported by the acceleration noted in the hydrosilylation of bulky aldehydes derivatives (0.5 h for *p*-^{t}Bu or *o*-Me-compounds **4** and **9** *vs* 2 h for *p*-MePhCHO (**3**)), which may favor the occurrence of unsaturated uranium centers. Influence of the triflate ion is also notable. Thus addition of 1 eq. [^{n}Bu$_4$N]OTf proved deleterious with a dramatic decrease of the rate of the reaction which is reflected by a kinetic constant k_{obs} of $6.0.10^{-6}$ $M.s^{-1}$ while it is $2.5.10^{-5}$ $M.s^{-1}$ without [^{n}Bu$_4$N]OTf.

In order to better apprehend the mechanism of Eqns 2 and 4, we turned our attention on the uranium species that might be formed when complex **1** is treated with either hydrosilanes or aldehydes, or under the catalytic conditions.

The insolubility of $[UO_2(OTf)_2]$ in CD_2Cl_2 disfavors the observation by ^1H NMR of a possible contact between Et_3SiH and the amphoteric uranyl complex.[37] However, when suspended in neat $PhSiH_3$, a stronger reductant than Et_3SiH, the yellow powder of **1** turned green after 1h at 100°C. Addition of pyridine gave an immediate orange solution upon which slow addition of pentane afforded green crystals of the hexanuclear U(IV) oxide cluster $[U_6O_8(OTf)_8(py)_{10}]$ previously obtained from reduction of uranyl.[38] The reduction of **1** into uranium(IV) is reminiscent of the instability of uranyl borohydride compounds, which likely results from H_2 loss from putative uranyl hydride intermediates.[39]

While complexation of uranium ions with ketones has given rise to numerous studies related to nuclear fuel reprocessing, similar investigations with aldehydes are rare. Only two species, *e.g.* the uranyl(VI) $[UO_2(\kappa^2\text{-CSAL})(\kappa^1\text{-CSAL})(DMSO)_2]$ (CSAL-H = 3,5-dichloro-2-hydroxybenzaldehyde)[40] and $[UO_2(\kappa^2\text{-ALAC})_2(H_2O)]$ (ALAC-H = 2-dimethylacetal-4-chloro-2-hydroxybenzaldehyde) compounds have been crystallographically characterized.[41] It is noteworthy that the ALAC and CSAL ligands are derivatives of salicylaldehyde (2-hydroxybenzaldehyde), for which the coordination of the formyl moiety to uranium is facilitated by a chelation effect ensured by bonding of the phenoxide group.

In presence of a series of aldehydes reported in

, suspension of **1** in CH_2Cl_2 immediately gave clear yellow to orange solutions. Most attempts at crystallization failed, but crystals suitable for X-ray diffraction were grown with ben-

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zaldehyde (**2**) and *p*-Me_2NPhCHO (**16**), by slow diffusion of pentane into a CH_2Cl_2 solution of **1** with a large excess of ligand.

Yellow crystals of the polymer $[UO_2(\mu\text{-}\kappa^2\text{-OTf})_2(PhCHO)]_n$ (**26**) (Figure 1) and the dimer $[UO_2(\mu\text{-}\kappa^2\text{-OTf})(\kappa^1\text{-OTf})(PhCHO)_2]_2$ (**27**) (Figure 2 and 3) were obtained from distinct batches prepared under the same conditions.[42] Attempts at isolation of powdery samples of the uranyl(VI) compound, by precipitation from a mixture of **1** with 10 equiv. of **2**, gave a dry product formulated as $[UO_2(OTf)_2(PhCHO)_2]$ (according to NMR and elemental analyses) in 74% yield. The ^{1}H NMR spectra in CH_2Cl_2-d_2 revealed a thin CHO signal at δ = 10.1 slightly shifted downfield in comparison with that of free benzaldehyde **2** (10.0 ppm).

With *p*-Me_2NPhCHO, dark-orange crystals of the monometallic complex $[UO_2(\kappa^1\text{-OTf})_2(Me_2N\text{-PhCHO})_3]$ (**28**) were readily collected (Figure 3). Dried powder samples have the same formula and displayed a ^{1}H NMR signal at δ = 10.31 for the CHO group and a singlet at δ = 3.24 for the Me_2N group (*vs* δ = 9.70 and δ = 3.07 for the free aldehyde **15**).

The three structures evidence that the aldehydes are weak ligands for the $[UO_2]^{2+}$ ion as triflate bridges are sometimes maintained and not displaced towards the formation of cationic species as in $[UO_2(OPPh_3)_4][OTf]_2$.[43] Moreover, the monomeric form of **28** confirms the stronger coordinating ability of the more electron rich *p*-Me_2NPhCHO, compared to benzaldehyde.

Complexes **26** and **27** both display an inversion center located at the center of the U_2S_2 square entity. The three complexes display the usual pentagonal-bipyramidal uranium coordination environment with the equatorial plane, defined by the uranium atom and five oxygen

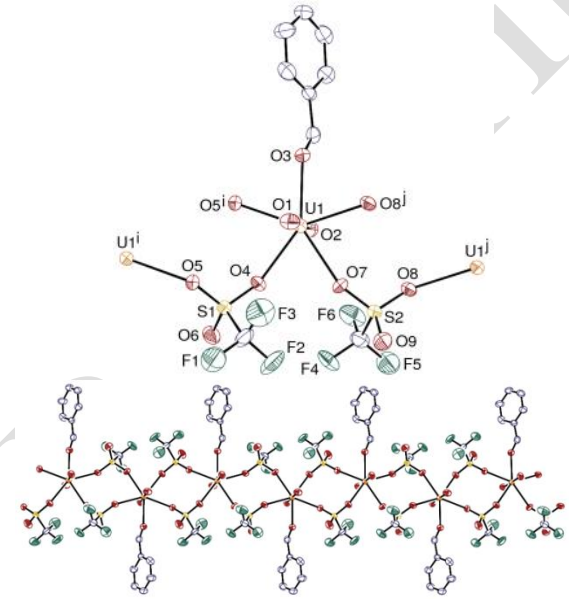


Figure. 1 Views of complex **26** with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity. Symmetry codes: i = 2 – *x*, –*y*, –*z*; j = 1 – *x*, 1 – *y*, –*z*.

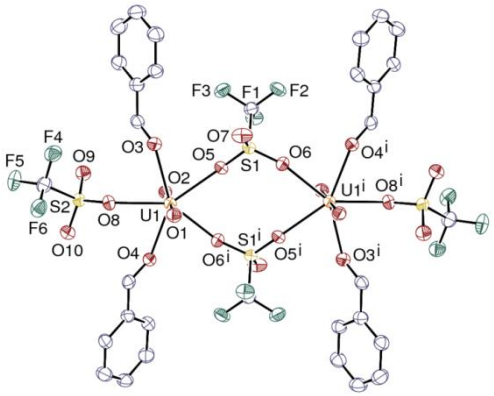


Figure. 2 View of complex **27** with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity. Symmetry code: i = 2 – *x*, 2 – *y*, 2 – *z*.

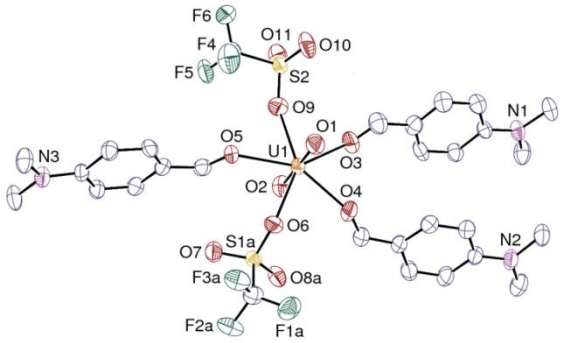


Figure 3 View of complex **28** with 40% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

donors of the aldehyde and triflate ligands, perpendicular to the linear UO_2 moiety (O–U–O > 178.6°). To our knowledge, **26** is the first $[UO_2(OTf)_2]$ species with a polymeric structure. Connections between the neighboring uranyl entities in **26** and **27** are ensured by bidentate bridging triflate anions and these compounds are unique uranyl species with (κ^2-μ-OTf) ligands. The U–O(uranyl), U–O(aldehyde) and U–OTf (bridging bidentate and monodentate) distances in **26**, **27** and **28** are unexceptional, with mean values of 1.743(4) / 1.762(1) / 1.748(5) Å, 2.391(4) / 2.413(2) / 2.403(9) Å and 2.410 (1) / 2.38(2) / 2.397(3) Å, respectively. These values can be compared to the mean values of 2.410(1) Å for the monodentate triflates in $[UO_2(\kappa^1\text{-OTf})_2(THF)_3]$ and 2.45(2) Å for the U-O(ArCH=O) bond length in $[UO_2(ALAC)_2(H_2O)]$ and in $[UO_2(CSAL)_2(DMSO)_2]$. Finally, the C=O bond lengths in **28** of 1.196(7), 1.235(7) and 1.269(7) Å can be compared to that in the free aldehyde **15** (1.204(2) Å).[44] The N-C(aromatic) bond lengths are slightly shorter in complex **28** than in the free aldehyde (1.338(7) (twice) and 1.340(6) Å vs 1.366(2) Å) which seems to confirm the existence of a charge transfer of the ligand **15** to the metal center.

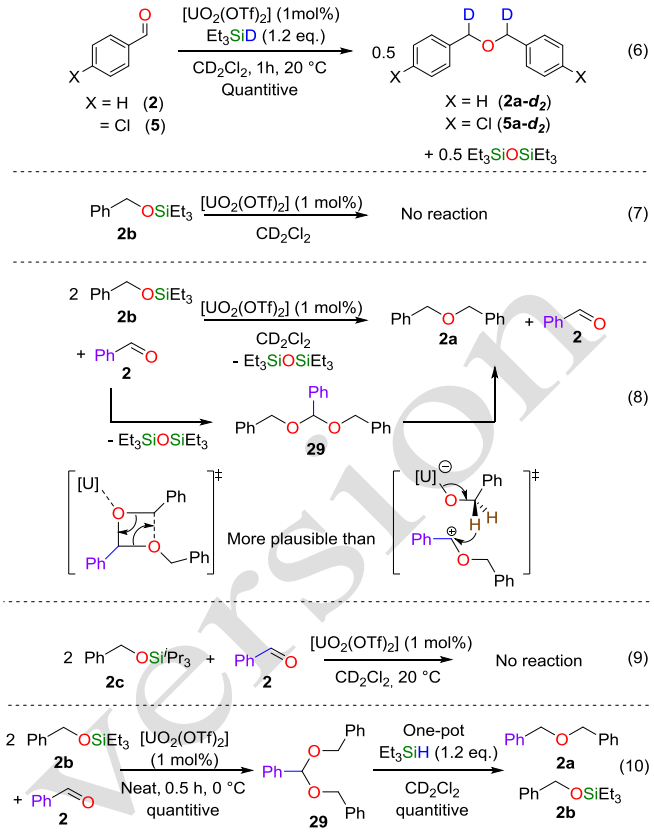
To gain further information on how the catalytic hydrosilylation proceeds (Eqns. 2 and 4), stoichiometric reactions from isolated uranyl species, labeling experiments, and concomitant addition of a 1:1 mixture of an aldehyde and the derived silylated alcohol were carried out (Eqns 6-10, Scheme

6). When reacted with a stoichiometric amount of Et_3SiH (1 equiv.) in dichloromethane, complex **27** did not afford any observable intermediate, and only the dibenzyl ether **2a** was produced quantitatively (with respect to Et_3SiH) along with siloxane.

Catalytic hydrosilylation of **2** and *p*-chlorobenzaldehyde **5** with Et_3SiD and 1 mol% **1** evidenced, in both cases, the quantitative formation of the corresponding deuterated dibenzylether **2a-*d*$_2$** and **5a-*d*$_2$** formed within 1 h (Scheme 6, Eqn 6). $^{13}C\{^1H\}$ NMR spectra revealed clearly the presence of a single deuterium atom on each methylene moiety (δ_{CHD} = 71.8 ppm and δ_{CHD} = 71.6 ppm, respectively with the same $^3J_{C-D}$ = 21.5 Hz values). This result confirms a net transfer of the hydride group from silicon to the aldehyde.

In the catalytic formation of ethers (Eqn 2), silylated alcohols were systematically observed in low quantities (1-5%), whatever the nature of the hydrosilane (Et_3SiH, $PhMe_2SiH$ and Ph_3SiH), before they were fully consumed by the end of the reaction. To evaluate their potential role as intermediates in the formation of ethers, $PhCH_2OSiEt_3$ (**2b)** was added to **1** (1 mol%) in CH_2Cl_2 (Scheme 6, Eqn 7). Although no reaction occurred, addition of 1 equiv. benzaldehyde led to the rapid and incomplete formation of the benzaldehyde dibenzyl acetal **(29**), in ca. 50 % yield, and $Et_3SiOSiEt_3$ as byproduct (Scheme 6, Eqn 8). Compound **29** was not observed in the catalytic experiments with hydrosilanes but its formation in Eqn 8 was shown unambiguously by NMR.[45] From this mixture, **29** slowly degraded into the corresponding ether **2a** and benzaldehyde **2** within 1 week. To understand this evolution, a labeling experiment with PhCDO was performed, which unveiled a σ-bonds metathesis of **29** catalyzed by the uranium complex. A 1,3-H shift pathway is unlikely, as PhCHO was absent (Scheme 6, see SI).

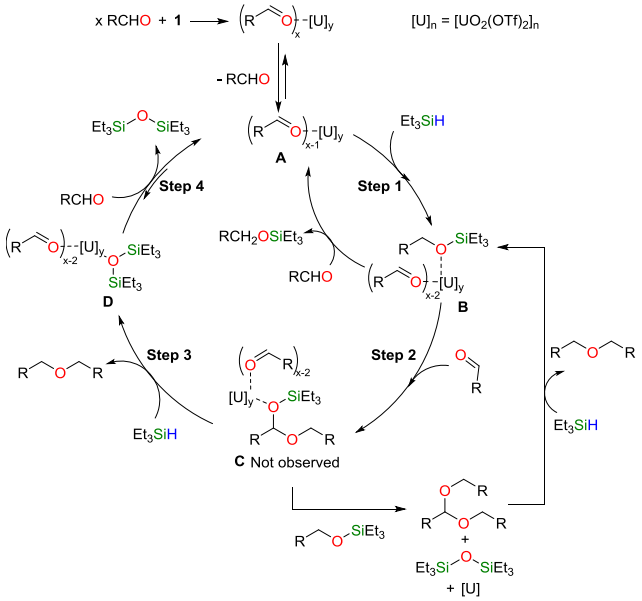
As depicted in Eqn 9, replacing the silyl ether $PhCH_2OSiEt_3$ with its sterically congested analogue $PhCH_2OSi^iPr_3$ **2c** prevented the reaction, and **2a** was not detected after one week at 20 °C. At last, cleavage of **29** into the ether **2a** is considerably accelerated in presence of the reductant: treatment of **29** with a mixture of Et_3SiH (1.2 equiv.) and **1** (1 mol%) at 20°C, led within minutes to the ether **2a** and the silylated alcohol **2b** (Scheme 6, eqn 10). These two important points evidence the key role of acetal intermediates, such as **29**, in the reductive coupling of aldehydes into symmetric ethers.



Scheme 6: Reaction of silylated benzyl alcohol **2b** and **2c** with benzaldehyde and deuterium labeling experiments

Based on the above experiments and kinetic results, a plausible mechanism is proposed in Scheme 7, for the uranyl-catalyzed hydrosilylation of aldehydes. At the onset, the insoluble polymeric uranyl triflate is coordinated by the aldehydes to yield soluble oligomeric adducts $[UO_2(OTf)_2(aldehyde)_n]_y$, likely engaged in equilibria, as reflected in the distinct structures of **26** and **27**. The active uranyl catalyst **A** is expected to be unsaturated to enter in the catalytic cycle. The first step of the cycle is the hydrosilylation of the aldehyde RCHO to the silylated alcohol RCH_2OSiR_3. The latter reacts with a molecule of aldehyde to give the transient silylated acetal complex **C** (step 2) which was not detected. Hydrosilylation of the coordinated acetal affords the desired ether $(RCH_2)_2O$ and the by-product $(Et_3Si)_2O$, while catalyst **A** is regenerated (steps 3 and 4). Complex **C** can also react with RCH_2OSiR_3 to provide the acetal analogue of **29** which, as seen in Eqn 8, is readily transformed into the symmetric ether and the silylated alcohol. This mechanism highlights the key role of acetal intermediates.

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Scheme 7: Plausible mechanism of the uranyl catalyzed reductive coupling of aldehydes into ethers

In conclusion, treatment of uranyl(VI) triflate **1** in the presence of hydrosilanes induced the reduction of C=O bonds in a large range of aromatic and aliphatic aldehydes. Symmetric ethers and silylated alcohols could be selectively obtained, depending on the nature of the hydrosilane. With $PhMe_2SiH$, Ph_3SiH and Et_3SiH, reductive coupling of the aldehydes into the symmetric ethers was observed, while the choice of a more sterically congested hydrosilane, *e.g.* $^{i}Pr_3SiH$, leads to the silylated alcohol $RCH_2OSi^{i}Pr_3$ in excellent yield.

This work provides a new and rare example of a catalytic transformation of oxygen-containing molecules with the highly oxophilic actinide ions. Above all, it shows the first use of an actinide complex to carry out catalytic hydrosilylation of C=O bonds and clearly evidences that high oxidation state species derived from the ubiquitous uranyl(VI) ion are stable and able to carry out reduction reactions in presence of reducing agents. Despite the uranyl ion contains oxidizing U=O bonds, reduction of the C=O group and C–O bond cleavage are possible without compromising the integrity of the uranyl moiety.

AUTHOR INFORMATION

Corresponding Author

* E-mail: jean-claude.berthet@cea.fr; thibault.cantat@cea.fr; Fax: +33 1 6908 6640; Tel: +33 1 6908 4338
† NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette, France.

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ASSOCIATED CONTENT

The following files are available free of charge. Supplementary equations, detailed descriptions of experimental methods, kinetic and mechanism studies are provided in the Supporting Information.

Accession Codes

CCDC 1904787−1904789 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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42. These compounds were always contaminated with a few green crystals of a hexanuclear U(IV) oxide cluster with a central $[U_6O_4(OH)_4(OTf)_7(PhCO_2)_5(PhCHO)_5]$ core, the crystal structure of which could not be refined in a completely satisfying manner due to considerable disorder..

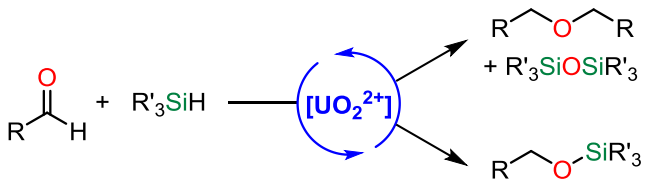
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