Reductive Silylation of $Cp^*UO_2(^{Mes}PDI^{Me})$ Promoted by Lewis Bases

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Functionalization of the uranyl moiety (UO_2^{2+}) in Cp*UO_2($^{Mes}PDI^{Me}$) (**1-PDI**) ($^{Mes}PDI^{Me}$ = 2,6-((Mes)N=CMe)$_2C_5H_3N$; Mes = 2,4,6-triphenylmethyl), which bears a reduced, monoanionic pyridine(diimine) ligand, is reported. Silylating reagents, R_3Si-X (R = Me, X = Cl, I, OTf, SPh; R = Ph, X = Cl), effectively add across the strong O=U=O bonds in the presence of the Lewis base, $OPPh_3$, generating products of the form $(R_3SiO)_2UX_2(OPPh_3)_2$ (R = Me, X = I (**2-OPPh₃**), Cl (**3-OPPh₃**), SPh (**5-OPPh₃**), OTf (**6-OPPh₃**); R = Ph, X = Cl (**4-OPPh₃**)). During this transformation, reduction to uranium(IV) occurs with loss of $(Cp^*)_2$ and $^{Mes}PDI^{Me}$, each of which acts as a one-electron source. In the reaction, the Lewis base serves to activate the silyl halide, generating a more electrophilic silyl group, as determined by ^{29}Si NMR spectroscopy, that undergoes facile transfer to the oxo groups. Complete U-O bond scission was accomplished by treating the uranium(IV) disiloxide compounds with additional silylating reagent, forming the family $(Ph_3PO)_2UX_4$. All compounds were characterized by ^1H NMR, infrared, and electronic absorption spectroscopies. X-ray crystallographic characterization was used to elucidate the structures of **2-OPPh₃, 4-OPPh₃, 5-OPPh₃,** and **6-OPPh₃**.

Introduction

Uranyl functionalization has long been a “Holy Grail” transformation for the f-block elements, as this process has important implications for environmental remediation[1] and spent fuel processing.[2] The strong uranium-oxygen multiple bonds in the $[UO_2]^{2+}$ unit, which are strengthened by the inverse *trans* influence (ITI),[3-5] are difficult to break or elaborate. An effective route that has recently been popularized is that of reductive silylation, involving silyl group transfer to the oxygen atoms, accompanied by an overall reduction of the uranium from 6+ to 4+. This process has been proven successful with uranyl in a variety of ligand environments, demonstrating its generality as a method for U-O bond cleavage. For instance, Arnold and co-workers have pioneered this idea with successful application to uranyl species ligated by large polypyrrolic ligands that wrap around the uranium center.[3, 4] Here, single-electron reduction is performed using potassium hexamethyldisilazide to generate the pentavalent, monofunctionalized unit, $[O{=}UOR]^{2+}$. Subsequent computational studies supported the importance of potassiation for activation of the uranyl *in situ*,[4, 5] whereas new findings report that Lewis acids are also effective at this.[6] Alternately, Hayton has showed the utility of this method for uranyl silylation supported by simpler acetyl-N-acetonate ligands using either an excess of Me_3SiI,[7] $HSiPh_3$ coupled with $B(C_6F_5)_3$,[8] or Ph_3SiOTf (OTf = trifluoromethanesulfonate).[9] In all cases, double functionalization is able to occur. A seminal example in this field by Ephritikhine shows complete functionalization is possible using a large excess of silylhalide absent ancillary ligands.[10]

In a recent contribution to this field, we reported the synthesis and characterization of a unique uranyl species supported by a monoanionic pyridine(diimine) ligand, Cp*UO_2($^{Mes}PDI^{Me}$) (**1-PDI**).[11] This compound has a complicated electronic structure; while formally uranium(V), spectroscopically this species is most consistent with having a hexavalent uranium ion. **1-PDI** features a bent uranyl moiety (~169°), making it particularly susceptible to functionalization using Me_3SiI, forming the *trans*-siloxide uranium(IV) species, $(Me_3SiO)_2UI_2(^{Mes}PDI^{Me})$ (**2-PDI**), by addition across the robust uranium-oxygen multiple bonds. This silylation is accompanied by a two-electron reduction of the metal, with the reducing equivalents originating from Cp*-anion as well as the radical on the $^{Mes}PDI^{Me}$ ligand, as evidenced by X-ray crystallography. Additional equivalents of Me_3SiI resulted in complete cleavage of the uranium oxygen bonds, generating tetravalent UI_4(1,4-dioxane)$_2$[12] when the reaction was performed in 1,4-dioxane solvent. This overall transformation was significant, as the uranyl functionalization and bond cleavage were performed at ambient temperature with stoichiometric quantities of silylating reagent, in contrast to previous systems.

We hypothesized that this functionalization occurred quite readily due to several factors, including 1) the activated bent uranyl moiety, 2) electrophilicity of the –$SiMe_3$ group in Me_3SiI, and 3) the ligands acting as an electron source. While little

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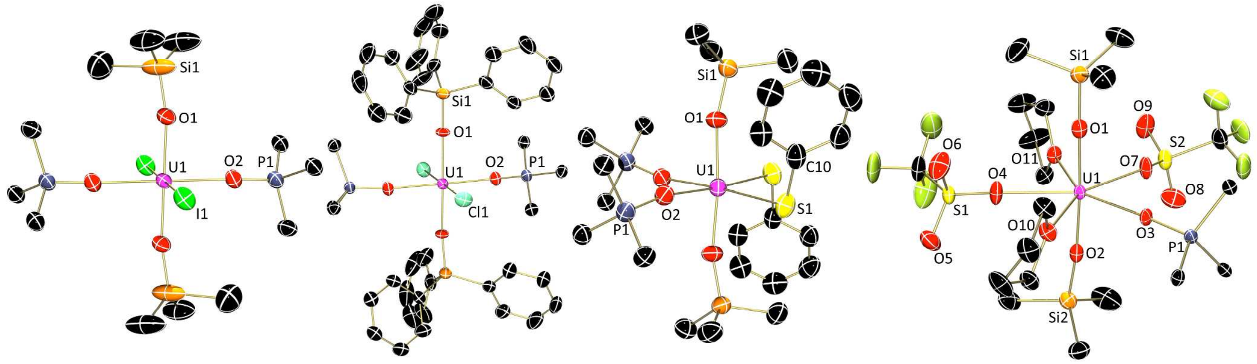


Figure 1. Molecular structures of **2-OPPh$_3$**, **4-OPPh$_3$**, **5-OPPh$_3$**, and **6-OPPh$_3$**, left to right, shown at 30% probability ellipsoids. Hydrogen atoms and co-crystallized solvent molecules have been omitted for clarity.

variation of the ligands was possible in this context, we sought a method by which to probe the effects of tuning the electrophilicity of silyl subsitutents to determine its influence on uranyl functionalization. A demonstration of this has been reported, showing that R_3Si-X reagents react with a variety of Lewis bases to generate salts (eq 1).[13] This reaction is an equilibrium that can be fine tuned through three simple modifications: 1) altering the basicity of the Lewis base, 2) changing the electronics of R-substituents, or 3) modifying the leaving group ability of X. We hypothesized that a more electrophilic silylium ion would facilitate uranyl functionalization. Herein, we report our studies aimed at expanding the scope of reagents useful for uranyl functionalization by facilitating reductive silylation using Lewis bases.

$$\mathrm{B{:}} + \mathrm{R_3Si\text{-}X} \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} [\mathrm{B\text{-}SiR_3}][\mathrm{X}] \qquad \mathbf{(1)}$$

Results and Discussion

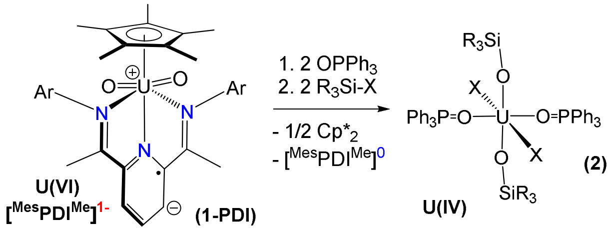
Lewis Base Assisted Reductive Silylation

An initial reaction to test our hypothesis was performed by adding the Lewis base, OPPh$_3$, to the previously reported reaction of **1-PDI** and two equivalents of Me_3SiI (eq 2). Without the Lewis base, the reaction gradually proceeds over 24 hours, and the product, $(Me_3SiO)_2UI_2(^{Mes}PDI^{Me})$ **2-PDI,** is isolated as a red solid. With the Lewis base, however, it was observed that the reaction went to completion more quickly (~4 hours) and led to the isolation of an off-white powder following work-up. Phosphine oxides, even in large excess, were not found to react with **1-PDI**.

Table 1. Structural parameters of **2-OPPh$_3$, 4-OPPh$_3$, 5-OPPh$_3$,** and **6-OPPh$_3$.**

Bond (Å) or Angle (°)	**2-OPPh$_3$** X = I	**4-OPPh$_3$** X = Cl	**5-OPPh$_3$** X = SPh	**6-OPPh$_3$** X = OTf
U-X	3.1222(7)	2.677(2)	2.7812(19)	2.430(5)
U-X	--	2.669(2)	--	2.429(5)
U-O(SiR$_3$)	2.082(6)	2.112(5)	2.113(5)	2.053(6)
	--	--	--	2.066(6)
U-O(PPh$_3$)	2.333(6)	2.285(6)	2.348(5)	2.339(4)
O-P	1.500(7)	1.527(6)	1.503(5)	1.506(4)
X-U-X	180.00	180.00	94.10(9)	141.67(17)
U-O-Si	167.4(5)	171.0(3)	162.8(4)	178.1(3)
U-O-Si				173.9(3)

^{1}H NMR spectroscopic analysis of the product revealed a paramagnetically shifted and broadened spectrum with four resonances ranging from -16.58 to 55.83 ppm. The furthest downfield resonance is an intense singlet (18H) reminiscent of that observed by Ephritikhine and co-workers. They reported that both the addition of $Me_3SiC_5R_5$ (R = H, Me) to $UO_2I_2(THF)_3$



2-OPPh$_3$: X = I; R = CH$_3$
3-OPPh$_3$: X = Cl; R = CH$_3$
4-OPPh$_3$: X = Cl; R = Ph
6-OPPh$_3$: X = OTf; R = CH$_3$

or $[UO_2Cl_2(THF)_2]_2$ and the reaction of UX_4 with $NaOSiMe_3$ gave downfield signals (reported range: 50-60 ppm) hypothesized to arise from the - $OSi(CH_3)_3$ group of a uranium(IV) siloxide.[14] Analysis of the off-white solid by infrared spectroscopy confirmed the presence of both -$SiMe_3$ and $OPPh_3$ functional groups with respective absorptions at δ_{SiCH_3} = 839 (asym) and $\upsilon_{P=O}$ = 1070 cm^{-1}. Additionally, analysis of organics extruded from the reaction mixture showed both an equivalent of $[^{Mes}PDI^{Me}]^0$ and one-half equivalent of $(C_5Me_5)_2$, analogous to that previously observed in the conversion of **1-PDI** to $(Me_3SiO)UI_3(THF)_3$, suggesting a two electron reduction of the uranyl starting material. Thus, the identity of the off-white solid was proposed to be the uranium(IV) disiloxide, $(Me_3SiO)_2UI_2(OPPh_3)_2$ (**2-OPPh$_3$**).

Confirmation of the identity of paramagnetic **2-OPPh$_3$** was achieved by X-ray diffraction analysis of single crystals obtained from a dilute toluene/*n*-pentane (1:1) solution at ambient temperature. Data refinement revealed the predicted octahedral uranium bis(iodide) (U1-I1 = 3.1222(7) Å) with both *trans*-trimethylsiloxide (U1-O1 = 2.082(6) Å) (O1-U1-I1 = 88.26(19)°) and *trans*-$OPPh_3$ (U1-O2 = 2.333(6) Å) ligands (Figure 1). Structurally, **2-OPPh$_3$** is reminiscent of $UI_2(O(CH_2)_4I)_2(OPPh_3)_2$, which was isolated as the THF-ring opened product from $UI_4(MeCN)_4$.[15]

We hypothesized the significant rate enhancement for the reductive silylation of **1-PDI** that occurs upon addition of the Lewis base was due to formation of $[Ph_3POSiMe_3][I]$ as had been previously identified. Thus, a more basic phosphine oxide should favour Si-I bond activation with a higher K_{eq}. Therefore, we screened a variety of substituted phosphine oxides for the same silylation reaction of **1-PDI** with Me_3SiI (2 equiv.) and monitored disappearance of the intense blue colour (λ_{max} = 612 nm) of the starting material. The results from these experiments show the reaction proceeds faster when a more electron donating Lewis base is used, in the order $OP(NMe_2)_3$ > $OP(p\text{-}Tol)_3$ > $OPPh_3$ > no base (Figure 2).

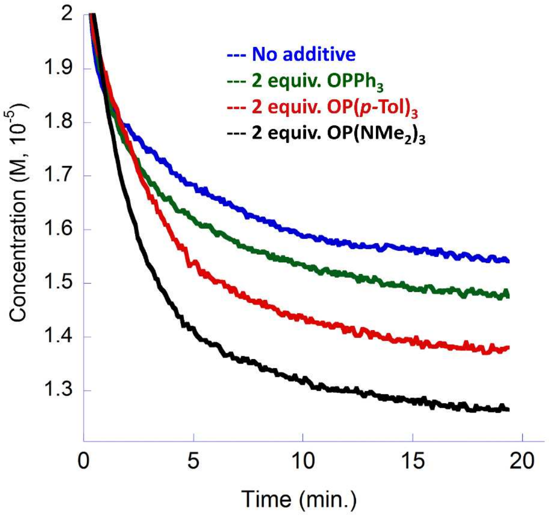


Figure 2. Competition studies (toluene, 25 °C) showing the disappearance (λ = 612 nm) of **1-PDI** during the reductive silylation reaction with various phosphine oxide derivatives.

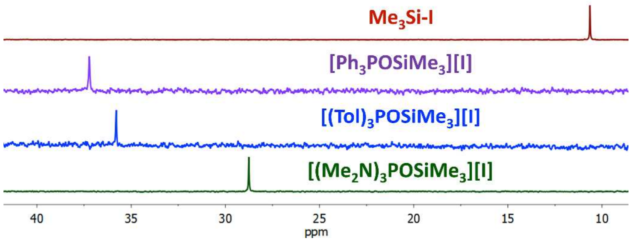


Figure 3. ^{29}Si NMR spectroscopic data (CD_2Cl_2, 25 °C), in ppm, showing the upfield trend in shifts of the silicon that track with relative electrophilicity. Me_3SiI is included as a reference value.

In order to study the relative electrophilicities of the Lewis acid-base pairs, $[R_3POSiMe_3][I]$, they were independently synthesized by the addition of the Me_3Si-I to a toluene solution of $R_3P=O$. In each case, a white powder immediately precipitated and was quantitatively collected by vacuum filtration. For each salt, the environment of the silicon atom was assessed *via* ^{29}Si NMR spectroscopy (CD_2Cl_2, 25 °C, Figure 3). It was observed that with increasing electron donation from the Lewis base (higher basicity), the ^{29}Si resonance shifts upfield accordingly. The strongly donating HMPA results in the greatest upfield shift of the salt adducts at 26.57 ppm. Not surprisingly, only a minimal shift is observed between the phenyl and *p*-tolyl analogues (Δ = 1.42 ppm). This ^{29}Si NMR trend supports that observed by Bassindale and Stout where salts of the form $[(^{R}pyr)SiMe_3][OTf]$ (^{R}pyr = substituted pyridines) and $[R_3POSiMe_3][OTf]$ (R = Ph, NMe_2) displayed increasingly upfield ^{29}Si NMR chemical shifts with increasing Lewis basicity.[13] Spialter and co-workers noted *via* Hammett plots of ^{29}Si NMR chemical shifts constructed for $(XC_6H_4)SiY_3$ (Y = F, H, OC_2H_5, CH_3, Cl) that compounds with electron-donating silyl substituents (e.g. $(XC_6H_4)SiH_3$ and $(XC_6H_4)Si(CH_3)_3$) showed upfield shifts.[16] Therefore, the trend in the upfield shift in the ^{29}Si resonance of the $[R_3POSiMe_3][I]$ salts can be attributed to increased electrophilicity of the silicon atom as R becomes more electron donating.

With a general understanding of the influence of Lewis basicity of the phosphine oxide on Me_3SiI activation, we sought to extend this to more mild silylating reagents. This would be advantageous, as previous attempts at silylation of **1-PDI** with other silanes resulted in either a) no reaction (Me_3Si-SPh, Ph_3Si-Cl, $^{i}Pr_3Si$-Cl) or b) intractable uranium products (Me_3Si-Cl, Me_3Si-OTf). Thus, the reactions of these silanes with **1-PDI** were re-examined in the presence of triphenylphosphine oxide. While HMPA is the most basic phosphine oxide, it often afforded greasy uranium products, which are more difficult to isolate.

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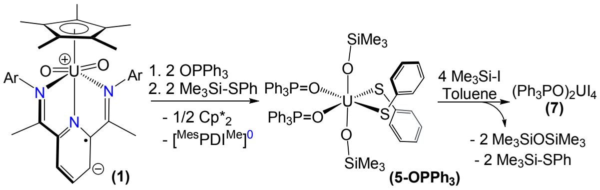
In the presence of $OPPh_3$, reductive silylation of **1-PDI** with Me_3SiCl was found to proceed to completion over four hours, affording $(Me_3SiO)_2UCl_2(OPPh_3)_2$ (**3-OPPh$_3$**), analogous to **2-OPPh$_3$**. As is typical, the presence of $(Cp^*)_2$ and neutral $[^{Mes}PDI^{Me}]^0$ were detected by ^1H NMR spectroscopy, as well as a resonance attributed to a –$OSiMe_3$ substituent (δ = 49.40 ppm). The presence of phosphine oxide ligands was confirmed by IR ($\upsilon_{P=O}$ = 1081 cm^{-1}) and ^1H NMR spectroscopies, which showed three upfield resonances (-16.76, 2.72, 4.38 ppm), similar to **2-OPPh$_3$**.

With isolation of **3-OPPh$_3$**, multiple attempts under a variety of conditions to isolate the pyridine(diimine) adduct were made to no avail, despite full consumption of Me_3SiCl. The addition of $OPPh_3$ to the reaction mixture induces the equilibrium described in eq 1, but unlike for Me_3Si-I, the inferiority of chloride as a leaving group results in only weak activation. K_{eq} was determined to be 3.8 +/- 0.3 (CD_2Cl_2, 25 °C) by ^1H NMR studies (Table S1). In the conversion of alcohols to chlorides using catalytic DMSO, Snyder suggests the reaction between DMSO and Me_3Si-Cl forms $[Me_3SiOSMe_2][Cl]$ with complete consumption of each reactant (K_{eq}>>1).[17] In that case, the increased electrophilicity of the Si in $[Me_3SiOSMe_2][Cl]$ facilitates nucleophilic attack by an alcohol.
Although a weaker activation of silylhalides by $OPPh_3$ is noted in our system as compared to the more basic DMSO, it is enough to engage the equilibrium displayed (eq 1) facilitating the reactivity of Me_3SiCl with **1-PDI** to afford **3-OPPh$_3$** in high yields and under mild conditions in short reaction times.

The reactivity of **1-PDI** was investigated with Ph_3SiCl, which is typically difficult to activate due to its poor electron-donating R-substituents that could potentially inhibit the equilibrium to form $[B\text{-}SiPh_3][Cl]$. Stirring a toluene solution of **1-PDI** with two equivalents of Ph_3SiCl over seven days did not result in any consumption of the silylhalide. Repeating the reaction with two equivalents of $OPPh_3$ resulted in gradual consumption of Ph_3SiCl with full conversion to $(Ph_3SiO)_2UCl_2(OPPh_3)_2$ (**4-OPPh$_3$**) over *ca*. five days. Following work-up, analysis of the off-white powder, **4-OPPh$_3$**, by ^1H NMR spectroscopic analysis revealed two sets of three resonances corresponding to the phenyl substituents of both –$OSiPh_3$ (furthest downfield) and $OPPh_3$ (furthest upfield).

Structural confirmation of **4-OPPh$_3$** was achieved by the analysis of single crystals obtained from a concentrated THF solution (-35 °C) by X-ray diffraction. Refinement of the data revealed an octahedral uranium dichloride (U1-Cl1 = 2.677(2); U1-Cl2 = 2.669(2) Å; Cl1-U1-Cl2 = 180.00°) species with both *trans*-triphenylsiloxide and *trans*-$OPPh_3$ (U1-O2 2.285(6) Å) ligands. The triphenylsiloxide-uranium distances in **4-OPPh$_3$** (2.112(5) Å) are significantly longer than the only other crystallographically reported uranium bis(triphenylsiloxide) complexes. Hayton and co-workers synthesized two uranium(V) complexes, $U(OSiPh_3)_2(dbm)_2(OTf)$ (dbm = *O*C(Ph)CHC(Ph)*O*) (2.005(2), 2.018(2) Å) and $[U(OSiPh_3)_2(^{Ar}acnac)_2][OTf]$ (^{Ar}acnac = ArNC(Ph)CHC(Ph)O; Ar = 3,5-$^tBu_2C_6H_3$) (2.044(2) Å), by reductive silylation of the parent uranyl species using two equivalents of Ph_3Si-OTf.[9]

With the ability of $OPPh_3$ to assist the reaction between the electron deficient silane, Ph_3Si-Cl, and **1-PDI**, we sought to determine whether a sterically bulky silane would prevent Lewis base coordination and therefore stop reactivity. Piers and co-workers observed that Lewis acid activation ($B(C_6F_5)_3$) of tertiary silanes for catalytic hydrosilylation of ketones did not proceed when $^iPr_3SiH$ was employed because the LUMO of the $^iPr_3Si\text{-}H\text{-}B(C_6F_5)_3$ adduct lies along the Si-H-B axis (accessible lobe located *trans* to the Si-H bond) and is sterically inaccessible to nucleophilic attack.[18] When the system was applied to uranyl reductive silylation, Hayton and co-workers found $^iPr_3Si$-H was also unreactive.[8] Analogously, upon reacting **1-PDI** with $^iPr_3Si$-Cl, no uranyl activation or consumption was observed in the presence of two equivalents of $OPPh_3$. Despite the potential ability of the electron donating isopropyl substituents to better stabilize silylium nature in the cation, the equilibrium in eq 1 is likely barred by the inability to perform a nucleophilic attack at Si. This also explains the lack of reactivity between **1-PDI** and $^iPr_3Si$-Cl, while its smaller counterpart, Me_3Si-Cl, reacts readily.



(3)

To investigate the generality of the Lewis base assisted uranyl reductive silylation with R_3Si-X type reagents, variation of the leaving group, X, was also examined. Reaction of **1-PDI** with two equivalents of Me_3SiSPh in the presence of two equivalents of $OPPh_3$ resulted in the gradual conversion to $(Me_3SiO)_2U(SPh)_2(OPPh_3)_2$ (**5-OPPh$_3$**), after ~2 days. Characterization of the yellow powder by ^1H NMR spectroscopy revealed seven paramagnetically shifted resonances ranging from -17.95 to 51.93 ppm. The –$OSiMe_3$ protons are furthest downfield, while again, all equatorial based ligands are shifted upfield with the *ortho* protons of the –SPh (-9.72 ppm) and -$OPPh_3$ (-17.95 ppm) affected to the greatest extent.

Structural parameters of **5-OPPh$_3$** were obtained by X-ray diffraction analysis of single crystals that precipitated from a benzene solution at room temperature. Refinement of the data revealed an octahedral uranium *trans*-bis(trimethylsiloxide) (U1-O1 = 2.113(5) Å; 174.2(3)°) complex with *cis*-phenylthiolate (94.10(9)°) and *cis*-triphenylphosphine oxide (U1-O2 = 2.348(5) Å; 86.9(3)°) ligands. The U-S distances (2.7812(19) Å) are similar to those reported for the terminal -SPh ligands in $[U(SPh)_2(\mu_2\text{-}SPh)_2(MeCN)_2]_2$ (2.813(2) Å)[19] reported by Neu and co-workers and the U1-S1-C10 bond angle (108.0(3)°) is similar to other *cis*-thiolate compounds including $Cp^*{}_2U(SCH_3)_2$ (108.1(5)°).[20]

The formation of **5-OPPh$_3$** *via* Lewis base promoted reductive silylation of **1-PDI** illustrates that halide leaving groups are not a requirement for the equilibrium in eq. 1 to be present. Hayton and co-workers have used highly reactive R_3Si-OTf (R = Ph, Me) to achieve reductive silylation of their systems.[21] The reactivity of **1-PDI** with Me_3Si-OTf was investigated to continue the silane screen and to serve as a basis for comparison. Treating a toluene solution of **1-PDI** and two equivalents of $OPPh_3$ with two equivalents of Me_3Si-OTf results in rapid quenching of the blue colour of **1-PDI** and formation of an off-white powder following workup. Investigation of the product by ^{1}H NMR spectroscopy revealed a spectrum nearly identical to **2-OPPh$_3$** with four paramagnetically broadened resonances with the furthest downfield (57.02 ppm) assigned to equivalent Me_3SiO- protons and the most upfield resonance (-16.34 ppm) assigned to the *ortho* protons of equatorially bound $OPPh_3$ ligands. Confirmation of a -OTf was confirmed by a resonance at -111.20 ppm in the ^{19}F NMR spectrum, leading to the assignment of the powder as $(Me_3SiO)_2U(OTf)_2(OPPh_3)_2$ (**6-OPPh$_3$**).

Interestingly, repeating the reaction absent $OPPh_3$ results in intractable products with full consumption of Me_3Si-OTf, consistent with its highly reactive nature. In aromatic solvents, Me_3SiOTf is known to react completely with $OPPh_3$ to form $[Ph_3POSiMe_3][OTf]$. The formation of this salt likely tempers the silane reactivity allowing for a more controlled attack of the silyl group by the UO_2^{2+} moiety. Thus, the Lewis base adducts of silyl-halides/psuedohalides can be employed to modulate the reactivity of less electrophilic (Me_3Si-Cl, Me_3Si-SPh) or highly reactive (Me_3Si-OTf) silanes.

Once again, single crystal X-ray crystallography was used to assess the structural environment around uranium. Refinement of the data obtained from crystals grown from a concentrated THF/*n*-pentane (1:1) solution revealed a seven coordinate uranium *trans*-trimethylsiloxide (176.85(17)°) complex with the equatorial plane comprised of two trifluoromethanesulfonate ligands, two THF molecules (U1-O10 = 2.480(5); U1-O11 = 2.461(4) Å), and a single $OPPh_3$ (U1-O3 = 2.339(4) Å). The U-$OSiMe_3$ distances (U1-O1 = 2.066(6); U1-O2 = 2.053(6) Å) are shorter than **2-OPPh$_3$**, and **5-OPPh$_3$**, but are similar to $(Me_3SiO)_2UI_2(2,2'\text{-bipyridyl})_2$ (2.084(4) Å).[7] The pair of η^1-OTf ligands displays long uranium-oxygen contacts (U1-O4 = 2.430(5); U1- O7 = 2.429(5) Å), but are not dissimilar to other reported uranium(IV) trifluoromethanesulfonates including $(COT)U(OTf)_2(OPPh_3)_2$ (2.382(4), 2.433(4) Å)[22] and $((^tBuO)_3SiO)_3U(OTf)(THF)_2$ (2.421(13) Å).[23] Crystallization from THF caused displacement of one $OPPh_3$ by two THF molecules; however, integration of resonances by ^{1}H NMR spectroscopy clearly indicated two $OPPh_3$ ligands per uranium in analogy to **2-OPPh$_3$** – **5-OPPh$_3$**.

As in the reductive silylation of **1-PDI**, formation of **2-OPPh$_3$** – **6-OPPh$_3$** proceeds by the reduction of uranium(VI) to uranium(IV), with electrons provided from both $[^{Mes}PDI^{Me}]^{1-}$ and Cp*-anion. The resulting six-coordinate uranium(IV) complexes show similar NMR spectroscopic characteristics, with the *trans*-siloxide protons appearing as the most downfield shifted resonances, independent of the substituents (Me, Ph). Likewise, ligands situated in the equatorial plane always display resonances in the ^{1}H NMR spectrum shifted upfield of their diamagnetic reference value regardless if they are due to the neutral $OPPh_3$ or an anionic X-ligand (Table 2). Additionally, no ^{31}P NMR signals were detected for any of the compounds reported here despite the commonality of ^{31}P NMR characterization of uranium(IV) complexes.[14, 26] We attribute this absence to extreme signal broadening, as the ^{1}H NMR signals observed are all display very large peak widths at half-height. Evans and coworkers have recently explored the utility of ^{29}Si NMR resonances of uranium complexes as they relate to uranium oxidation state.[24] Unfortunately, we were unable to detect ^{29}Si NMR resonances for complexes **2-OPPh$_3$** – **6-OPPh$_3$**, though it is unclear whether this is a result of paramagnetic broadening or if a potential signal is being obstructed by the inherent glass resonance.

The ease of the observed reductive silylation chemistry can be correlated to the silyl reagent activation by $OPPh_3$ as indicated by the equlibrium constant. In the case of Me_3SiX (X = I, OTf), complete Si-X dissociation was noted with isolation of the ion pair salts possible, and uranyl reductive silylation proceeds readily, in less than 4 hours. For Me_3SiCl and Me_3SiSPh, respective equilibrium constants of 3.8 +/- 0.3 and 1.3 +/- 0.1 were measured. In these cases, reductive silylation

Table 2. ^{1}H NMR, infrared, and electronic absorption spectroscopic data for **2-OPPh$_3$**, **3-OPPh$_3$**, **4-OPPh$_3$**, **5-OPPh$_3$**, and **6-OPPh$_3$**.

Complex	$SiMe_3$ (ppm)	*o*-$OPPh_3$ (ppm)	*m*-$OPPh_3$ (ppm)	*p*-$OPPh_3$ (ppm)	P=O stretch (cm^{-1})	λ_{max} (nm)
$(Me_3SiO)_2UI_2(OPPh_3)_2$ (**2-OPPh$_3$**)	55.83	-16.58	3.14	4.59	1070	362
$(Me_3SiO)_2UCl_2(OPPh_3)_2$ (**3-OPPh$_3$**)	49.40	-16.76	2.72	4.38	1081	328
$(Ph_3SiO)_2UCl_2(OPPh_3)_2$ (**4-OPPh$_3$**)	--	-14.15	3.59	4.72	1080	325
$(Me_3SiO)_2U(SPh)_2(OPPh_3)_2$ (**5-OPPh$_3$**)	51.93	-17.95	2.42	4.14	1082	373
$(Me_3SiO)_2U(OTf)_2(OPPh_3)_2$ (**6-OPPh$_3$**)	56.89	-16.89	3.17	4.63	1066	--

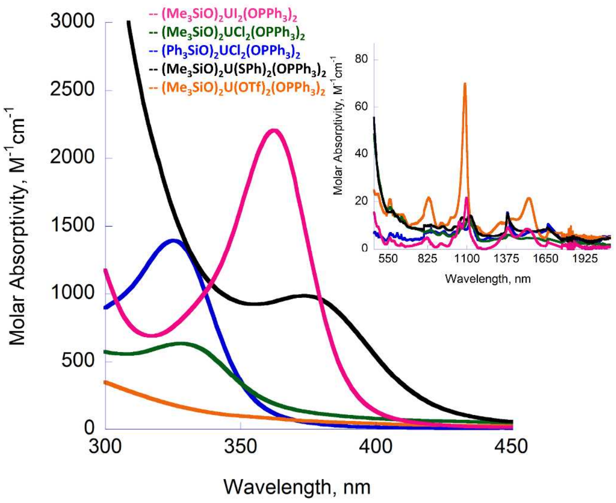


Figure 4. Electronic absorption spectra for **2-OPPh$_3$**, **3-OPPh$_3$**, **4-OPPh$_3$**, **5-OPPh$_3$**, and **6-OPPh$_3$**. Data was collected from 300-2100 nm in THF at ambient temperature.

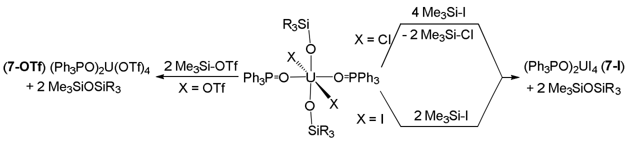
proceeds over a longer scale, requiring reaction times of 4 and 46.5 hours, respectively. For Ph_3SiCl, a weak equilibrium constant is suspected (K_{eq}<<1), and is consistent with the 115 hr reaction time required for completion of the reaction.

Vibrational spectroscopic measurements of **2-OPPh$_3$** – **6-OPPh$_3$** all display little variation in the extent of reduction of the phosphorus-oxygen double bond of the $OPPh_3$ ligands, with values ranging from 1066-1082 cm^{-1}. Their magnitude is on the order of those reported for other uranium complexes bearing OPR_3 ligands, regardless of oxidation state.[25]

Electronic absorption spectroscopic data was acquired for the entire series of compounds between 300-2100 nm, and each displays similar features. All spectra display sharp, weakly intense (ε = 5 – 70 $M^{-1}cm^{-1}$) f-f transitions throughout the near-infrared region and into the visible region, characteristic of the uranium(IV) oxidation state.[26] Light yellow **5-OPPh$_3$** displays the lowest energy absorbance (λ_{max} = 373 nm), which tails into the visible region. The other four complexes are colourless with the three halide compounds displaying strong ultraviolet features, while **6-OPPh$_3$** does not absorb in the experimental window.

Cleavage of Oxo-derived –OSiR$_3$

With the variety of examples that have now been developed to achieve the oxo-silylation of UO_2^{2+}, relatively few examples exist of the complete cleavage of the oxo derived –$OSiR_3$ substituent on reasonable scales to produce viable materials.[12, 29, 30] We have recently demonstrated from the reductive silylation of **1-PDI** that this is possible.[11] Thus, we targeted a facile, high yielding method for the formation of uranium tetra(halides) or psuedohalides from the uranium(IV) products obtained *via* Lewis base mediated reductive silylation.



Scheme 1. Cleavage of oxo derived –$OSiR_3$ substituents.

Treating a toluene slurry of **2-OPPh$_3$** with two equivalents of Me_3Si-I results in the gradual deposition of a yellow powder identified as $(Ph_3PO)_2UI_4$ (**7-I**) by ^1H NMR spectroscopy (Scheme 1).[15] Repeating the reaction in C_6D_6 confirmed the formation of Me_3Si-O-$SiMe_3$. This reaction, when performed in THF, neither produced Me_3Si-O-$SiMe_3$ nor **7-I**, but rather an oily uranium containing compound suspected to arise from THF ring opening as well as the organic byproduct, Me_3SiO-$(CH_2)_4$-I.

Thus, a general method to convert the chloride containing species, **3-OPPh$_3$** and **4-OPPh$_3$**, to **7-I** was also established. While complexes of the type $UI_{4-n}X_n$ (X = Br, Cl) exist and have been studied, their use as a viable starting material is impractical because of the facile halide exchange results in every possible halide combination.[15] Therefore, toluene slurries of each **3-OPPh$_3$** and **4-OPPh$_3$** were treated with four equivalents of Me_3Si-I, resulting in the slow deposition of insoluble **7-I**. Monitoring the reaction by ^1H NMR spectroscopy revealed the formation of two equivalents of Me_3Si-Cl as well as both Me_3Si-O-$SiMe_3$ and Me_3Si-O-$SiPh_3$ for **3-OPPh$_3$** and **4-OPPh$_3$**, respectively. The reactions to cleave the uranium-siloxide bond did not proceed when Me_3Si-Cl was employed, indicating the necessity for a strong silylating reagent for this transformation.

Finally, the trifluoromethanesulfonate species, **6-OPPh$_3$**, was converted to the tetrakis(trifluoromethanesulfonate) compound, $(Ph_3PO)_2U(OTf)_4$ (**7-OTf**), previously described by Ephritikhine and coworkers (Scheme 1).[22] Treating a colourless toluene solution of **6-OPPh$_3$** with two equivalents of Me_3Si-OTf results in an immediate colour change to mint green with expulsion of Me_3Si-O-$SiMe_3$ (^1H NMR spectroscopy, C_6D_6). Investigation of the uranium species revealed both resonances assignable to bound $OPPh_3$ (^1H, δ = 10.66 (*p*), 11.89 (*m*), 33.36 (*o*) ppm) and -OTf (^{19}F, δ = -102.65).

The formation of **7-I** and **7-OTf** from oxo-derived siloxide ligands proceeds cleanly, in high yields (72 – 98%), with minimal work-up. We surmise this general procedure should be broadly applicable to generic uranium(IV) complexes containing siloxide ligands for the production of useful homoleptic tetra(halide) starting materials.

Experimental

General Considerations All air- and moisture-sensitive manipulations were performed using standard Schlenk techniques or in an MBraun inert atmosphere drybox with an atmosphere of purified nitrogen. The MBraun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen as well as two −35 °C freezers for cooling samples and crystallizations. Solvents for sensitive manipulations were dried and deoxygenated using literature procedures with a Seca solvent purification system.[27] Benzene-d_6 was purchased from Cambridge Isotope Laboratories, dried with molecular sieves and sodium, and degassed by three freeze–pump–thaw cycles while $CDCl_3$ and CD_2Cl_2 were distilled from CaH_2. Me_3Si-I, Me_3Si-OTf, Me_3Si-SPh, Ph_3Si-Cl, $^iPr_3Si$-Cl, and $OPPh_3$ were used as received from Sigma-Aldrich. Me_3Si-Cl and HMPA were distilled from CaH_2. **1-PDI**[11] and OP(*p*-Tol)$_3$[28] were synthesized according to literature procedures.

^{1}H NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 299.992 MHz. All chemical shifts are reported relative to the peak for $SiMe_4$, using ^{1}H (residual) chemical shifts of the solvent as a secondary standard. The spectra for paramagnetic molecules were obtained by using an acquisition time of 0.5 s, thus the peak widths reported have an error of ±2 Hz. For paramagnetic molecules, the ^{1}H NMR data are reported with the chemical shift, followed by the peak width at half height in Hertz, the integration value, and, where possible, the peak assignment. ^{31}P spectra were recorded on a Varian Inova 300 spectrometer operating at 121.423 MHz and chemical shifts are reported relative to 85% H_3PO_4. ^{29}Si spectra were recorded on a Bruker AV-III-500-HD spectrometer operating at 99.38 MHz with an approximate 30-degree observe pulse, acquisition time of 0.8 sec., and a relaxation time of 6 sec. Elemental analyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ. Electronic absorption measurements were recorded at 294 K in sealed 1 cm quartz cuvettes with a Jasco V-6700 spectrophotometer.

Single crystals suitable for X-ray diffraction were coated with poly(isobutylene) oil in a glovebox and quickly transferred to the goniometer head of a Rigaku Rapid II image plate diffractometer equipped with a MicroMax002+ high intensity copper X-ray source with confocal optics and examined with Cu Kα radiation (λ = 1.54184 Å). The data were collected at 200(1) K.

Synthesis of $(Me_3SiO)_2UI_2(OPPh_3)_2$ (2-OPPh$_3$) A 20 mL scintillation vial was charged with (0.100 g, 0.125 mmol) Cp*UO$_2$(^{Mes}PDI^{Me}) (**1-PDI**) and 10 mL of toluene. Triphenylphosphine oxide (0.070 g, 0.252 mmol) was added and stirred for 5 min. *Via* microsyringe, Me_3SiI (0.035 mL, 0.245 mmol) was added resulting in a gradual colour change from blue to purple to purple/red. After 4 hr, volatiles were removed *in vacuo*. The crude mixture was washed with *n*-pentane (3 x 10 mL) and the washings set aside. The remaining light red solid was recrystallized from dilute THF layered with pentane (-35 °C) to afford off-white powder (0.126 g, 0.103 mmol, 82%) assigned as $(Me_3SiO)_2UI_2(OPPh_3)_2$ (**2-OPPh$_3$**). Single, X-ray quality crystals were obtained from a dilute toluene/*n*-pentane (1:1) solution at room temperature. Elemental analysis of $C_{42}H_{48}O_4Si_2P_2I_2U$: Calculated, C, 41.12; H, 3.95; N, 0.00. Found, C, 41.17; H, 3.95; N, <0.02. ^{1}H NMR ($CDCl_3$, 25 °C) δ = -16.58 (91, 12H, *o*-Ph-C*H*), 3.14 (44, 12H, *m*-Ph-C*H*), 4.59 (38, 6H, *p*-Ph-C*H*), 55.83 (111, 18H, Si(C*H*$_3$)$_3$). IR: $\delta_{(SiCH3\ sym)}$ = 1245 cm^{-1}; $\upsilon_{(P=O)}$ = 1070 cm^{-1}; $\delta_{(SiCH3\ asym)}$ = 839 cm^{-1}. UV-Vis: λ_{max} = 362 nm, ε = 2205 M^{-1}cm^{-1}. The solvent from the pentane washings was removed *in vacuo* to afford a slurry from which $(C_5Me_5)_2$ and ^{Mes}PDI^{Me} were identified by ^{1}H NMR spectroscopy.

Synthesis of $(Me_3SiO)_2UCl_2(OPPh_3)_2$ (3-OPPh$_3$) A 20 mL scintillation vial was charged with (0.121 g, 0.151 mmol) Cp*UO$_2$(^{Mes}PDI^{Me}) (**1-PDI**) and 10 mL of toluene. Triphenylphosphine oxide (0.084 g, 0.302 mmol) was added and stirred for 5 min. *Via* microsyringe, chlorotrimethylsilane (0.039 mL, 0.307 mmol) was added resulting in a gradual colour change from blue to purple over 30 min. After 4 hr, volatiles were removed *in vacuo*. The crude mixture was washed with *n*-pentane (3 x 15 mL) and the washings set aside. The remaining solid was recrystallized from a concentrated THF solution layered with *n*-pentane (-35 °C) to afford off-white powder (0.081 g, 0.078 mmol) assigned as $(Me_3SiO)_2UCl_2(OPPh_3)_2$ (**3-OPPh$_3$**). Further recrystallization of the mother liquor afforded an additional 0.072 g of off-white powder (0.153 g total, 0.147 mmol, 97%). Elemental analysis of $C_{42}H_{48}O_4Si_2P_2Cl_2U$: Calculated, C, 48.31; H, 4.64; N, 0.00. Found, C, 48.46; H, 4.72; N, <0.02. ^{1}H NMR (C_6D_6, 25 °C) δ = -16.76 (308, 12H, *o*-TPPO-C*H*), 2.72 (251, 12H, *m*-TPPO-C*H*), 4.38 (222, 6H, *p*-TPPO-C*H*), 49.40 (561, 18H, C*H*$_3$). IR: $\delta_{(SiCH3\ sym)}$ = 1243 cm^{-1}; $\upsilon_{(P=O)}$ = 1081 cm^{-1}; $\delta_{(SiCH3\ asym)}$ = 836 cm^{-1}. UV-Vis: λ_{max} = 328 nm, ε = 635 M^{-1}cm^{-1}. The solvent from the pentane washings was removed *in vacuo* to afford a slurry from which $(C_5Me_5)_2$ and ^{Mes}PDI^{Me} were identified by ^{1}H NMR spectroscopy.

Synthesis of $(Ph_3SiO)_2UCl_2(OPPh_3)_2$ (4-OPPh$_3$) A 20 mL scintillation vial was charged with (0.200 g, 0.249 mmol) Cp*UO$_2$(^{Mes}PDI^{Me}) (**1-PDI**) and 10 mL of toluene. Triphenylphosphine oxide (0.138 g, 0.496 mmol) was added and stirred for 5 min. Chlorotriphenylsilane (0.147 g, 0.499 mmol) was added and stirred for 115 hr resulting in a gradual colour change from blue to purple. Volatiles were removed *in vacuo*. The crude mixture was washed with *n*-pentane (5 x 10 mL) and the washings set aside. The remaining solid was washed with benzene (10 mL) to afford off-white powder upon drying (0.171 g, 0.145 mmol, 58%) assigned as $(Ph_3SiO)_2UCl_2(OPPh_3)_2$ (**4-OPPh$_3$**). Single, X-ray quality crystals were obtained from a concentrated tetrahydrofuran solution at -35 °C. Elemental analysis of $C_{72}H_{60}O_4Si_2P_2Cl_2U$: Calculated, C, 61.05; H, 4.28; N, 0.00. Found, C, 60.99; H, 4.03; N, <0.02. ^{1}H NMR ($CDCl_3$, 25 °C) δ = -14.15 (32, 12H, *o*-TPPO-C*H*), 3.59 (20, 12H, *m*-TPPO-C*H*), 4.72 (38, 6H, *p*-TPPO-C*H*), 11.83 (17, 6H, *p*-SiPh$_3$-C*H*), 12.55 (18, 12H, *m*-SiPh$_3$-C*H*), 41.19 (23, 12H, *o*-SiPh$_3$-C*H*). IR: $\upsilon_{(P=O)}$ = 1080 cm^{-1}. UV-Vis: λ_{max} = 325 nm, ε = 1,396 M^{-1}cm^{-1}. The solvent from the pentane washings was removed *in vacuo* to afford a slurry from which $(C_5Me_5)_2$ and ^{Mes}PDI^{Me} were identified by ^{1}H NMR spectroscopy.

Synthesis of $(Me_3SiO)_2U(SPh)_2(OPPh_3)_2$ (5-OPPh$_3$) A 20 mL scintillation vial was charged with (0.200 g, 0.249 mmol) Cp*UO$_2$(^{Mes}PDI^{Me}) (**1-PDI**) and 10 mL of toluene. Triphenylphosphine oxide (0.138 g, 0.496 mmol) was added and stirred for 5 min. Trimethyl(phenylthio)silane (0.094 mL, 0.496 mmol) was added *via* microsyringe resulting in a gradual colour change from blue to dark purple. After 46.5 hr, volatiles were removed *in vacuo*. The crude mixture was washed with *n*-pentane (5 x 10 mL) until the washing ran clear and the washings set aside. The remaining solid was recrystallized from a THF solution layered with an equal amount of *n*-pentane (-35 °C) to afford light yellow block shaped crystals (0.080 g) assigned as $(Me_3SiO)_2U(SPh)_2(OPPh_3)_2$ (**5-OPPh$_3$**). Subsequent recrystallization of the mother liquor afforded an additional 0.115 g (0.195 g total, 0.161 mmol, 65%) of $(Me_3SiO)_2U(SPh)_2(OPPh_3)_2$ as yellow powder. Single, X-ray quality crystals were obtained from a concentrated benzene solution stored at room temperature. Elemental analysis of $C_{54}H_{58}O_4Si_2P_2S_2U$: Calculated, C, 53.64; H, 4.84; N, 0.00. Found, C, 53.81; H, 4.79; N, <0.02. ^{1}H NMR (C_6D_6, 25 °C) δ = -17.95 (54, 12H, *o*-TPPO-C*H*), -9.72 (35, 4H, *o*-SPh-C*H*), 2.42 (27, 12H, *m*-TPPO-C*H*), 4.14 (26, 6H, *p*-TPPO-C*H*), 5.07 (24, 4H, *m*-SPh-C*H*), 6.12 (25, 2H, *p*-SPh-C*H*), 51.93 (77, 18H, C*H*$_3$). IR: $\delta_{(SiCH3\ sym)}$ = 1243 cm^{-1}; $\upsilon_{(P=O)}$ = 1082 cm^{-1}; $\delta_{(SiCH3\ asym)}$ = 835 cm^{-1}. UV-Vis: λ_{max} = 373 nm, ε = 986 M^{-1}cm^{-1}. The solvent from the pentane washings was removed *in vacuo* to afford a slurry from which $(C_5Me_5)_2$ and ^{Mes}PDI^{Me} were identified by ^{1}H NMR spectroscopy.

Synthesis of $(Me_3SiO)_2U(OTf)_2(OPPh_3)_2$ (6-OPPh$_3$) A 20 mL scintillation vial was charged with (0.200 g, 0.249 mmol) Cp*UO$_2$(^{Mes}PDI^{Me}) (**1-PDI**) and 10 mL of toluene. Triphenylphosphine oxide (0.139 g, 0.499 mmol) was added and stirred for 5 min. *Via* microsyringe, trimethylsilyl trifluoromethanesulfonate (0.090 mL, 0.497 mmol) was added resulting in a gradual colour change from blue to purple over *ca.* 15 min. After 4 hr, volatiles were removed *in vacuo*. The crude mixture was washed with *n*-pentane (3 x 10 mL) and the washings set aside. The remaining solid was recrystallized from a saturated THF solution layered with *n*-pentane (-35 °C) to afford off-white powder with a slight hint of green (0.151 g) assigned as $(Me_3SiO)_2U(OTf)_2(OPPh_3)_2$ (**6-OPPh$_3$**). Further recrystallization of the mother liquor afforded an additional 0.062 g (0.213 g total, 0.168 mmol, 79 %). Single, X-ray quality crystals were obtained from a concentrated tetrahydrofuran/*n*-pentane (1:1) solution at -35 °C. Elemental analysis of $C_{44}H_{48}O_{10}Si_2P_2S_2F_6U$: Calculated, C, 41.57; H, 3.81; N, 0.00. Found, C, 41.43; H, 3.53; N, <0.02. ^{1}H NMR (C_6D_6, 25 °C) δ = -16.34 (40, 12H, *o*-TPPO-C*H*), 2.64 (25, 12H, *m*-TPPO-C*H*), 3.87 (25, 6H, *p*-TPPO-C*H*), 57.05 (45, 18H, C*H*$_3$). ^{19}F NMR (C_6D_6, 25 °C) δ = -111.20 (s, 6F, C*F*$_3$). IR: $\upsilon_{(SO3\ asym)}$ = 1333 cm^{-1}; $\delta_{(SiCH3\ sym)}$ = 1241 cm^{-1}; $\upsilon_{(CF3\ sym)}$ = 1236 cm^{-1}; $\upsilon_{(CF3\ asym)}$ = 1124 cm^{-1}; $\upsilon_{(P=O)}$ = 1066 cm^{-1}; $\upsilon_{(SO3\ sym)}$ = 1017 cm^{-1}; $\delta_{(SiCH3\ asym)}$ = 864 cm^{-1}; $\delta_{(CF3\ sym)}$ = 748 cm^{-1}; $\delta_{(SO3\ sym)}$ = 636 cm^{-1}; $\delta_{(CF3\ asym)}$ = 584 cm^{-1}; $\delta_{(SO3\ asym)}$ = 539 cm^{-1}. The solvent from the pentane washings was removed *in vacuo* to afford a slurry from which $(C_5Me_5)_2$ and ^{Mes}PDI^{Me} were identified by ^{1}H NMR spectroscopy.

Lewis Base Competition Experiments by UV-Vis From stock toluene solutions, Me_3SiI and Lewis base (1.25 x 10^{-7} moles each) were added to a 3 mL screw-top cuvette equipped with an injectable septum. The mixture was diluted with toluene to 3.00 mL and mixed for 30 min. At the spectrometer, **1-PDI** (6.25 x 10^{-8} moles, toluene stock solution) was injected into the cuvette. The cuvette was shaken violently for 3 sec prior to data collection.

General Synthesis of $(Ph_3PO)_2UI_4$ (7-I) from $(R_3SiO)_2UX_2(OPPh_3)_2$ From **2-OPPh$_3$**: A 20 mL scintillation vial was charged with **2-OPPh$_3$** (0.100 g, 0.082 mmol) and 5 mL of toluene. To the stirring slurry, Me_3SiI (0.023 mL, 0.162 mmol) was added *via* microsyringe resulting in a gradual colour change to a yellow suspension from off-white (Note: for X = Cl, four equivalents of Me_3SiI were used). After 4 hr, the volatiles were removed *in vacuo*. The resulting solid was washed with *n*-pentane to afford yellow powder (0.102 g, 0.078 mmol, 96%) identified as $(Ph_3PO)_2UI_4$. Yields from **3-OPPh$_3$**, 72%; **4-OPPh$_3$**, 98%; **5-OPPh$_3$**, 74%.

Synthesis of $(Ph_3PO)_2U(OTf)_4$ (7-OTf) A 20 mL scintillation vial was chaged with **6-OPPh$_3$** (0.100 g, 0.079 mmol) and 5 mL of toluene. While stirring, Me_3SiI (0.029 mL, 0.160 mmol) was added *via* microsyringe resulting in a rapid colour change from colourless to mint green. After 30 min, volatiles were removed *in vacuo*. The resulting solid was washed with *n*-pentane to afford light green powder (0.098 g, 0.070 mmol, 90%) assigned as $(Ph_3PO)_2U(OTf)_4$. ^{1}H NMR (C_6D_6, 25 °C) δ = 10.69 (t, *J* = 5.4, 6H, *p*-TPPO-C*H*), 11.91 (19, 12H, *m*-TPPO-C*H*), 33.30 (70, 12H, *o*-TPPO-C*H*). ^{19}F NMR (C_6D_6, 25 °C) δ = -102.65 (s, 12F, C*F*$_3$). IR: $\upsilon_{(asym\ SO3)}$ = 1349 cm^{-1}; $\upsilon_{(asym\ CF3)}$ = 1121 cm^{-1}; $\upsilon_{(P=O)}$ = 1063 cm^{-1}; $\delta_{(sym\ CF3)}$ = 729 cm^{-1}; $\delta_{(sym\ SO3)}$ = 634 cm^{-1}; $\delta_{(asym\ CF3)}$ = 590 cm^{-1}; $\delta_{(asym\ SO3)}$ = 539 cm^{-1}.

Formation of 7-I and 7-OTf *via* NMR experiments A J-Young NMR tube was charged with $(R_3SiO)_2UX_2(OPPh_3)_2$ and 0.75 mL C_6D_6. To the slurry, Me_3SiI (for X = I, 2 eq; X = Cl, 4 eq) or Me_3Si-OTf (for X = OTf) was added *via* microsyringe. The slurry in the tube was shaken for fifteen minutes and the ^{1}H NMR spectrum obtained.

Conclusions

In summary, the studies presented demonstrate that uranyl functionalization, which has typically been a challenging transformation due to the high uranium-oxygen multiple bond strength, can be facilitated by Lewis bases. The substituted phosphine oxides used here are commercially available and operationally simple to use, serving to activate less reactive silylating reagents towards nucleophilic attack by uranyl oxo ligands, thus broadening the scope of the family of reagents that can be used. This is evidenced by the fact that Me_3Si-SPh, Me_3SiCl, and Ph_3SiCl, which are effective in our Lewis base promoted system, have not been demonstrated previously to be successful for stoichiometric uranyl functionalization. In some cases, we have also demonstrated that phosphine oxides can mediate highly reactive silanes, thus directing their reactivity toward the desired goal. During the course of the silylation reaction, reduction of the central uranium from 6+ to 4+ occurs, with both the ^{Mes}PDI^{Me} and Cp* ligands serving as electron sources. Once addition across the strongly bonded O=U=O unit has been accomplished, the weaker U-O single bonds can now be easily cleaved with the stoichiometric addition of Me_3SiI.

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Notes and references

1. J. Li, K. Zhu, J. Shang, D. Wang, Z. Nie, R. Guo, C. Liu, Z. Wang, X. Li and J. Liu, *Separation Science and Technology*, 2012, **47**, 1507.

2. M. Amme, T. Wiss, H. Thiele, P. Boulet and H. Lang, *J. Nucl. Mater.*, 2005, **341**, 209.

3. P. L. Arnold, D. Patel, C. Wilson and J. B. Love, *Nature*, 2008, **451**, 315.

4. A. Yahia, P. L. Arnold, J. B. Love and L. Maron, *Chem. Commun.*, 2009, 2402.

5. A. Yahia, P. L. Arnold, J. B. Love and L. Maron, *Chem.--Eur. J.*, 2010, **16**, 4881.

6. P. L. Arnold, A.-F. Pecharman, R. M. Lord, G. M. Jones, E. Hollis, G. S. Nichol, L. Maron, J. Fang, T. Davin and J. B. Love, *Inorg. Chem.*, 2015, **54**, 3702.

7. J. L. Brown, C. C. Mokhtarzadeh, J. M. Lever, G. Wu and T. W. Hayton, *Inorg. Chem.*, 2011, **50**, 5105.

8. D. D. Schnaars, G. Wu and T. W. Hayton, *Inorg. Chem.*, 2011, **50**, 4695.

9. E. A. Pedrick, G. Wu and T. W. Hayton, *Inorg. Chem.*, 2014, **53**, 12237.

10. J.-C. Berthet, G. Siffredi, P. Thuery and M. Ephritikhine, *Eur. J. Inorg. Chem.*, 2007, 4017.

11. J. J. Kiernicki, D. P. Cladis, P. E. Fanwick, M. Zeller and S. C. Bart, *J. Am. Chem. Soc.*, 2015, **137**, 11115.

12. M. J. Monreal, R. K. Thomson, T. Cantat, N. E. Travia, B. L. Scott and J. L. Kiplinger, *Organometallics*, 2011, **30**, 2031.

13. A. R. Bassindale and T. Stout, *Tetrahedron Lett.*, 1985, **26**, 3403.

14. J.-C. Berthet, G. Siffredi, P. Thuery and M. Ephritikhine, *Dalton Trans.*, 2009, 3478.

15. L. R. Avens, D. M. Barnhart, C. J. Burns and S. D. McKee, *Inorg. Chem.*, 1996, **35**, 537.

16. C. R. Ernst, L. Spialter, G. R. Buell and D. L. Wilhite, *J. Am. Chem. Soc.*, 1974, **96**, 5375.

17. D. C. Snyder, *J. Org. Chem.*, 1995, **60**, 2638.

18. D. J. Parks, J. M. Blackwell and W. E. Piers, *J. Org. Chem.*, 2000, **65**, 3090.

19. A. J. Gaunt, B. L. Scott and M. P. Neu, *Inorg. Chem.*, 2006, **45**, 7401.

20. C. Lescop, T. Arliguie, M. Lance, M. Nierlich and M. Ephritikhine, *J. Organomet. Chem.*, 1999, **580**, 137.

21. E. A. Pedrick, G. Wu and T. W. Hayton, *Inorg. Chem.*, 2015, **54**, 7038.

22. J. C. Berthet, M. Nierlich and M. Ephritikhine, *Eur. J. Inorg. Chem.*, 2002, **2002**, 850.

23. C. Camp, V. Mougel, J. Pecaut, L. Maron and M. Mazzanti, *Chem. - Eur. J.*, 2013, **19**, 17528.

24. C. J. Windorff and W. J. Evans, *Organometallics*, 2014, **33**, 3786.

25. P. Gans and B. C. Smith, *J. Chem. Soc.* , 1964, 4172.

26. I. Castro-Rodriguez and K. Meyer, *Chem. Commun.*, 2006, 1353.

27. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.

28. Y. Hasegawa, T. Ohkubo, T. Nakanishi, A. Kobayashi, M. Kato, T. Seki, H. Ito and K. Fushimi, *Eur. J. Inorg. Chem.*, 2013, **2013**, 5911.