Reactivity of $UI_4(OEt_2)_2$ with phenols: probing the chemistry of the U–I bond⁺

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Solutions of $UI_4(OEt_2)_2$ in Et₂O were found to deposit orange crystals of $[H(OEt_2)_2][UI_3(OEt_2)]$ (1) upon standing at room temperature. The proton in the cation of 1 most likely originates from the surface of the glass vial in which the solution was stored. Reactions of $UI_4(OEt_2)_2$ with 1 equiv. of ArOH in toluene, followed by addition of THF, provides $UI_3(OAr)(THF)_x$ (Ar = Ph, x = 3, 2; Ar = 2,6-Ph₂C₆H₃, x = 2, 3). UI₄(OEt₂)₂ also reacts with 2 equiv. of ArOH (Ar = Ph, 4-'BuC₆H₄, 2,6-Me₂C₆H₃, C₆F₅) in toluene, followed by addition of THF, to generate $UI_2(OC_6H_5)_2(THF)_3$ (4), $UI_2(O-4-'BuC_6H_4)_2(THF)_3$ (5), $UI_2(O-2,6-Me_2C_6H_3)_2(THF)_3$ (6) and $UI_2(OC_6F_5)_2(THF)_3$ (7), in moderate yields. Complete conversion to the products requires the use of a dynamic vacuum to remove the HI generated upon addition of the phenol.

Introduction

The lack of a commercially available uranium halide, the typical starting point for most organometallic uranium chemistry, requires that any uranium halide or pseudo-halide synthon be synthesized 'in-house'. The most popular access point for synthetic U(IV) chemistry is undoubtedly UCl₄, which is simple to prepare and can be isolated in good yields.^{1,2} However, the ability of the chloride ligands to readily form "ate" complexes³⁻¹¹ has made the discovery of a simple, high-yielding route to its bromo or iodo congeners of considerable interest.^{12,13} In this regard, the recent development of two low-temperature and high-yielding routes to $UI_4(OEt_2)_2$,^{14,15} is potentially of great benefit to the synthetic actinide community.

The development of a new synthon can have a major impact in an area. This is well illustrated by the synthesis of $UI_3(THF)_{4}$,¹⁶ which spurred a major expansion of U(III) chemistry,¹⁷ as this reagent has several advantages, including ease of preparation and high solubility in organic solvents, over the previous alternative, UCl_3 .¹⁸⁻²¹ It is possible that $UI_4(OEt_2)_2$, which is also easy to prepare and soluble in Et_2O and toluene, will have a similar impact. However, its utility for synthesis can not be adequately judged until preliminary reactivity studies are completed.

In this contribution, we report the first reactivity study of this new, and potentially important, U(IV) synthon. Here, we present the synthesis of several uranium(IV) phenoxide complexes by direct protonation of a U–I bond in UI₄(OEt₂)₂ with a variety of phenols. This method negates the need to first generate the alkali metal salt of the phenol, as required in previous syntheses of uranium phenoxides.^{11,22-24} It also eliminates the possibility of forming "ate" complexes, which are normally undesirable. While iodide ligands are less likely than other halides to form "ate" complexes, a few iodide "ate" complexes are known for the highly electropositive f elements.^{4,25-28}

Results

 $UI_4(OEt_2)_2$ is stable indefinitely in the solid state at -25 °C, however it slowly decomposes at room temperature to an intractable tan powder. When allowed to stand at room temperature, cherryred Et_2O solutions of $UI_4(OEt_2)_2$ turn orange over the course of 24 h, concomitant with the deposition of orange needles. An X-ray crystallographic analysis of this material has shown it to be $[H(OEt_2)_2][UI_5(OEt_2)]$ (1) (Fig. 1), the result of HI addition to $UI_4(OEt_2)_2$. Complex 1 crystallizes in the orthorhombic space group Pnna and consists of discrete cation-anion pairs. The [UI₅(OEt₂)]⁻ anion exhibits octahedral coordination around the uranium(IV) center with bond angles of I2–U1–I2* = $178.70(5)^{\circ}$ and I3–U1–I3* = $174.14(7)^{\circ}$. The U–I bond lengths in 1 range from 2.964(2)-2.998(1) Å, while the U1-O1 bond length is 2.43(1) Å. The cation portion of the complex consists of a proton coordinated to two diethyl ether molecules. The proton could not be observed in the electron density map, but the distance between



Fig. 1 ORTEP diagram of $[H(OEt_2)_2][UI_5(OEt_2)]$ (1) with 50% probability ellipsoids being shown. Selected bond lengths (Å) and angles (°): U1–I1 = 2.964(2), U1–I2 = 2.998(1), U1–I3 = 2.984(1), U1–O1 = 2.43(1), I1–U1–I2 = 90.65(3), I1–U1–I3 = 92.93(3), I1–U1–O1 = 180.0, I2–U1–I3 = 90.71(3), I2–U1–I2* = 178.70(5), I2–U1–O1 = 89.35(3), I3–U1–I3* = 174.14(7), I3–U1–O1 = 87.07(3).

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the two oxygen atoms (O2–O3 = 2.48 Å), is comparable to the O-O distances observed for this cation in previous examples.²⁹⁻³² The formulation of complex 1 as a uranium(v) iodide was also considered. However, we believe this possibility is unlikely, in part because UI₅ is unknown.³³ In addition, the U–I bond lengths in 1 match well with that reported for UI₄(OEt₂)₂ (U–I = 2.964(1) Å).¹⁴

The formation of 1 from $UI_4(OEt_2)_2$ most likely occurs via protonation of a U-I bond by a hydroxyl group on the glass surface, generating a molecule of HI. The HI can then react with an intact molecule of $UI_4(OEt_2)_2$ to generate complex 1 (eqn (1)). To demonstrate the involvement of glass in the formation of 1, a solution of UI₄(OEt₂)₂ was partitioned into two vials, one glass and one PTFE, and both vials were stored at room temperature. After 48 h, the solution in the glass vial contained orange needles and an orange solution consistent with the formation of 1, whereas the solution in the PTFE vial was unchanged (as confirmed by ¹H NMR spectroscopy). Attempts to further characterize complex 1 were complicated by its low solubility in non-coordinating solvents and its reactivity with donor solvents, such as THF and MeCN.



Given the striking reactivity of $UI_4(OEt_2)_2$ with glass, we have explored the reactivity of this complex with other protic substrates. For instance, addition of 1 equiv. of phenol to a cherry-red toluene solution of $UI_4(OEt_2)_2$ results in a colour change to orange. Upon application of a dynamic vacuum this solution becomes cloudy. The addition of excess THF, and recrystallization from toluene-hexanes provides air- and moisture-sensitive green crystals of $UI_3(OC_6H_5)(THF)_3$ (2) in a 41% yield (Scheme 1). Similarly, reaction of $UI_4(OEt_2)_2$ with 2,6-Ph₂C₆H₃OH under identical conditions provides UI₃(O-2,6-Ph₂C₆H₃)(THF)₂ (3), also in a moderate yield.





The ¹H NMR spectra of 2 and 3 are both consistent with the incorporation of the aryl alcohol. For instance, the ¹H NMR spectrum of 2 in C_6D_6 exhibits signals at 76.9 ppm, 39.2 ppm and 28.1 ppm, assignable to the ortho, meta, and para hydrogen nuclei of the phenyl ring, respectively; while the signals attributable to the THF ligands are observed at -18.1 ppm and -27.3 ppm as broad singlets.

Single crystals of 2 suitable for X-ray diffraction analysis were grown from toluene-hexanes solutions stored at -25 °C for several days. Complex 2 crystallizes in the orthorhombic space group Pbca



as the toluene solvate, $2 \cdot C_7 H_8$. Its solid-state molecular structure is shown in Fig. 2. Complex 2 exhibits a pentagonal bipyramidal geometry in the solid-state, with the phenoxide ligand and one iodide ligand occupying the axial sites. The U-O(phenoxide) bond length is 2.01(1) Å, while the U1–O1–C1 bond angle is 172(1)°. The U–I bond distances (av. U–I = 3.08 Å) are typical of other U(IV) iodides,³⁴ while the U–O(THF) bond lengths (av. 2.43 Å) are also similar to other tetrahydrofuran complexes of uranium.24,35



Fig. 2 ORTEP diagram of UI₃(OC₆H₅)(THF)₃ (2·C₇H₈) with 50% probability ellipsoids being shown. Selected bond lengths (Å) and angles (°): U1-O1 = 2.01(1), U1-O2 = 2.47(1), U1-O3 = 2.42(1), U1-O4 = 2.41(1), U1-OU1-I1 = 3.018(2), U1-I2 = 3.108(2), U1-I3 = 3.099(2), U1-O1-C1 =172(1), O1-U1-I1 179.0(4).

Single crystals of 3 were grown from toluene-hexanes, where it crystallizes in the monoclinic space group C2/c (Fig. 3). In contrast to 2, complex 3 exhibits an octahedral structure in the solid state. Presumably, the extra steric bulk of the 2,6diphenylphenoxide precludes the coordination of three THF ligands to the uranium center. Like 2, complex 3 exhibits a short



Fig. 3 ORTEP diagram of $UI_3(O-2,6-Ph_2C_6H_3)(THF)_2$ (3) with 50% probability ellipsoids being shown. Selected bond lengths (Å) and angles (°): U1–O1 = 2.088(7), U1–O2 = 2.378(6), U1–O3 = 2.382(6), U1–I1 = 3.013(1), U1-I2 = 3.021(1), U1-I3 = 3.014(1), U1-O1-C1 = 170.9(6),O1-U1-I3 = 178.2(2).

U–O(phenoxide) distance (U1–O1 = 2.088(7) Å) and a nearly linear U1–O1–C1 angle (170.9(6)°). It also exhibits comparable U–I (av. 3.02 Å) and U–O(THF) distances (U1–O2 = 2.378(6) Å and U1–O3 = 2.382(6) Å).

The exchange of two iodide ligands in $UI_4(OEt_2)_2$ by protonation is also possible. For instance, addition of 2 equiv. of phenol to a toluene solution of $UI_4(OEt_2)_2$, followed by application of a dynamic vacuum, and addition of excess THF, results in the formation of $UI_2(OC_6H_5)_2(THF)_3$ (4) in a 67% yield (Scheme 1). Several other uranium(IV) bis(phenoxide) complexes can be synthesized in an identical manner. Thus, $UI_2(O-4-'BuC_6H_4)_2(THF)_3$ (5), $UI_2(O 2,6-Me_2C_6H_3)_2(THF)_3$ (6), and $UI_2(OC_6F_5)_2(THF)_3$ (7) can also be isolated in moderate yields (Scheme 1). Again, the application of a dynamic vacuum is essential for driving the reaction to completion.

Complexes **4–7** can also be isolated by addition of 2 equiv. of NEt₃ to the reaction mixture, negating the requirement of a dynamic vacuum. However, when synthesized in this manner the uranium complexes are invariably contaminated with [NEt₃H]I, and the resulting yields are much lower. In addition, the comproportionation reaction of complex **4** with UI₄(OEt₂)₂ in CD₂Cl₂ quickly yields complex **2**. Attempts to make U(OPh)₃I and U(OPh)₄ by reacting UI₄(OEt₂)₂ with 3 and 4 equiv. of phenol, respectively, yield only complex **4** in both cases.

The ¹H NMR spectra for compounds **4**, **5**, **6**, and **7** are consistent with the proposed formulations. For instance, the ¹H NMR spectrum of **4** in C₆D₆ exhibits signals at 93.8 ppm, 46.8 ppm and 33.4 ppm, assignable to the *ortho*, *meta*, and *para* hydrogen nuclei of the phenyl ring, respectively. These chemical shifts are similar to those observed for **2**. The ¹H NMR spectra for **5** and **6** also exhibited paramagnetically-shifted resonances for the protons on the phenoxide ligands, while for complex **7** the ¹⁹F{¹H} NMR spectrum in C₆D₆ contains three singlets at –33.8 ppm, –71.6 ppm and –86.5 ppm, corresponding to the *ortho*, *meta*, and *para* fluorine nuclei, respectively.

Complex **5** crystallizes in the orthorhombic space group *Pbca*, while complex **6** crystallizes in the monoclinic space group *C2/c*, as the THF solvate **6**·2THF, and **7** crystallizes in the monoclinic space group *P2*₁/*c*, as the THF solvate $7 \cdot \frac{1}{2}$ THF. The solid-state molecular structures for **5**, **6**·2THF, and $7 \cdot \frac{1}{2}$ THF are shown in Fig. 4, 5 and 6, respectively. Selected bond length and angles for **5**, **6**·2THF and $7 \cdot \frac{1}{2}$ THF can be found in Table 1. All three of these compounds adopt similar distorted pentagonal bipyramidal geometries, with the two phenoxide ligands exhibiting a *trans* disposition.



Fig. 4 ORTEP diagram of $UI_2(O-4-'BuC_6H_4)_2(THF)_3$ (5) with 50% probability ellipsoids being shown.



Fig. 5 ORTEP diagram of $UI_2(O-2,6-Me_2C_6H_3)_2(THF)_3$ (6-2THF) with 50% probability ellipsoids being shown.

The U–O(phenoxide) bond lengths for **5**, **6**·2THF and **7**· $\frac{1}{2}$ THF are nearly identical. For instance, complex **5** exhibits U– O(phenoxide) bond lengths of 2.051(8) Å and 2.084(8) Å, complex **6** exhibits a U–O(phenoxide) bond length of 2.092(8) Å, and in complex **7** the U–O(phenoxide) bond lengths are 2.114(7) Å and 2.125(6) Å. In addition, the U–O–C bond angles of the phenoxide ligands are nearly linear. For example, in complex **5** the U–O–C angles are U1–O1–C1 = 176.9(8)° and U1–O2– C11 = 166.1(8)°. These metrical parameters are similar to other U(IV) phenoxide complexes.^{35,36} For instance, UI₂(OAr)₂(THF) (Ar = 2,6-'Bu₂C₆H₃) exhibits U–O(phenoxide) bond lengths of

Table 1 Selected bond lengths (Å) and angles (°) for 5, 6.2THF and $7 \cdot \frac{1}{2}$ THF

5		6·2THF		$7 \cdot \frac{1}{2}$ THF	$7 \cdot \frac{1}{2}$ THF	
U1–I1	3.145(1)	U1–I1	3.1326(8)	U1–I1	3.0918(9)	
U1–I2	3.143(1)			U1–I2	3.0914(9)	
U101	2.051(8)	U1-O1	2.092(8)	U1–O1	2.114(7)	
U1–O2	2.084(8)			U1–O2	2.125(6)	
U1–O3	2.443(9)	U1–O2	2.521(7)	U1–O3	2.449(6)	
U1–O4	2.47(1)			U1–O4	2.486(6)	
U1–O5	2.499(9)	U1–O3	2.47(1)	U1–O5	2.398(6)	
O1-U1-O2	173.5(3)	O1–U1–O1*	168.2(4)	O1–U1–O2	174.4(2)	
U1-01-C1	176.9(8)	U1-O1-C1	176.8(6)	U1-O1-C1	176.0(6)	
U1O12C11	166.2(8)			U1-O2-C7	173.8(6)	



Fig. 6 ORTEP diagram of $UI_2(OC_6F_5)_2(THF)_3$ (7. $\frac{1}{2}THF$) with 50% probability ellipsoids being shown.

2.073(9) Å and 2.080(8) Å, and U-O–C bond angles of 172.6(8)° and 166.2(8)°, 35 while the U–O bond length in U(OAr)_4 is 2.135(4) Å. 36

Given the similarity of the U-O(phenoxide) bond lengths in 5, 6.2THF and 7. $\frac{1}{2}$ THF, we are unable to draw any conclusions from the crystallographic data about variation in the phenoxide bonding interaction as a function of the arvl ring. However, the absorption spectra for complexes 4, 6 and 7 do exhibit changes depending on the aryl ring substituents. In Et₂O, these compounds produce similar UV-vis spectra (Fig. 7). In particular, complex 7 $(Ar = C_6 F_5)$ exhibits a well-defined peak at 362 nm ($\varepsilon = 4200$ L mol⁻¹ cm⁻¹). Notably, this feature is successively red-shifted as the phenoxide ligand becomes more electron donating.³⁷ For instance, this peak is observed at 369 nm ($\varepsilon = 3260 \text{ L mol}^{-1} \text{ cm}^{-1}$) and 378 nm $(\varepsilon = 4430 \text{ L mol}^{-1} \text{ cm}^{-1})$ for complexes 4 (Ar = Ph) and 6 (Ar = 2,6-Me₂C₆H₃), respectively. Complex 5 (Ar = $4^{-t}BuC_6H_4$) does not follow this trend: its absorption is observed at 370 nm ($\varepsilon =$ 4230 L mol⁻¹ cm⁻¹), but based on pK_a it should be closer to that observed for 6.



Fig. 7 Absorption spectra of 4 (0.19 mM), 5 (0.20 mM), 6 (0.22 mM), and 7 (0.24 mM). All spectra recorded in Et_2O .

Given the similarity of the bands observed for complexes 4–7 with those observed for $UI_4(OEt_2)_2$ (both in terms of location and intensity), we attribute these features to an iodide–metal LMCT.¹⁴ A similar feature in $UI_2(O'Pr)_2(HO'Pr)_x$ was also assigned to

iodide-metal charge transfer.³⁸ The observed red-shift can be rationalized by invoking a larger crystal field splitting upon coordination of increasingly electron rich phenoxide ligands. This subsequently raises the energy of the metal-based orbitals involved in the LMCT.

Discussion

Both theoretical and experimental thermochemical data shows that U-I bonds are amongst the weakest bonds known for uranium,³⁹⁻⁴¹ while U-O bonds are amongst the strongest.^{39,42,43} The reactivity observed for $UI_4(OEt_2)_2$ can be explained within this context as the reaction is driven by the formation of a strong U–O bond, which can overcome the unfavourable pK_a of HI. A similar protonation is also observed during the reaction of uranium metal with iodine in isopropanol. This reaction results in the isolation of [UI₂(O^{*i*}Pr)₂(HO^{*i*}Pr)₂]₂, which is presumably formed via a solvated UI₄ complex.³⁸ In addition, UI₄(THF)_x (generated in situ) is known to rapidly ring-open THF, producing $UI_2(OCH_2CH_2CH_2CH_2I)_2(THF)_x$, again demonstrating the sensitivity of the U-I bond and the oxophilicity of the uranium center.44 Several other UI₄ complexes have also been reported, but they do not exhibit such reactive U-I bonds. Typically these complexes contain better donor ligands, such as MeCN or PhCN, 12,13,45-50 suggesting that the electron poor uranium center in $UI_4(OEt_2)_2$ also plays a role in the U-I bond reactivity. Interestingly, UI₄(MeCN)₄ has been previously used to make uranium aryloxides, including $U(OAr)_4$ and $U(OAr)_2I_2(THF)$ (Ar = 2,6-'Bu₂C₆H₃),¹¹ but these syntheses follow the traditional metathetical protocol.

The increased stability of $UI_4(OEt_2)_2$ solutions when stored in PTFE strongly suggests that glass is the source of the proton in the hydronium counterion of complex **1**. This type of reactivity is rare, but not unprecedented. Several f element complexes are known to react with glass. For instance, $[(C_5Me_5)_2Ln][(\mu-Ph)_2BPh_2]$ (where Ln = La, Ce, and Pr) can abstract an oxygen from the glass surface, generating $[(C_5Me_5)_2Ln]_2(\mu-O).^{51}$

The dynamic vacuum required to synthesize complexes 2–7 (Scheme 1) is probably necessary to remove HI from the reaction mixture. This synthetic method reduces the possibility of forming "ate" complexes during metathesis, an often unwanted reaction pathway that is common for the f elements.^{4,5,8,11} There are several previous examples in transition metal chemistry,⁵² and the actinides,^{38,53} of direct protonation of a metal-halide bond to form a metal alkoxide and HX.

Summary

 $UI_4(OEt_2)_2$ has proven to be an incredibly reactive U(IV) synthon as shown by its ability to deprotonate glass to form $[H(OEt_2)_2][UI_5(OEt_2)]$. We have demonstrated that this potent reactivity can be productively harnessed through our syntheses of $UI_3(OAr)(THF)_x$ (Ar = Ph, x = 3; Ar = 2,6-Ph₂C₆H₃, x = 2) and $UI_2(OAr)_2(THF)_3$ (Ar = Ph, 4-'Bu-C₆H₄, 2,6-Me₂C₆H₃, C₆F₅) directly from $UI_4(OEt_2)_2$ and ArOH. This procedure eliminates the requirement of first making the alkali metal salt of the phenol. It also simplifies the reaction work-up, as no salt byproduct is generated. This represents a potential advantage that $UI_4(OEt_2)_2$ has over other U(IV) halides. It is likely that $UI_4(OEt_2)_2$ will be an

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extremely useful reagent for future synthetic studies with uranium, and we are continuing to explore the reactivity of this complex.

Experimental

General

All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions either under high vacuum or an atmosphere of nitrogen or argon. THF, hexanes, diethyl ether and toluene were dried by passage over activated molecular sieves using a Vacuum Atmospheres solvent purification system. C_6D_6 and CD_2Cl_2 were dried over activated 4 Å and 3 Å molecular sieves respectively for 24 h before use. Uranium metal was obtained from Los Alamos National Laboratory, and $UI_4(OEt_2)_2$ was prepared using the published procedure.¹⁴ All other reagents were obtained from commercial sources and used as received.

NMR spectra were recorded on a Varian INOVA 400 spectrometer. ¹H NMR spectra are referenced to external SiMe₄ using the residual protio solvent peaks as internal standards. ¹⁹F NMR spectra were referenced to external 0.05% α , α , α -trifluorotoluene in C₆D₆. UV-vis experiments were performed on a JASCO V-570 UV-Vis-NIR spectrometer. Elemental analyses were performed by Desert Analytics in Tucson, AZ or the Microanalytical Laboratory at UC Berkeley.

[H(OEt₂)₂][UI₅(OEt₂)] (1). A 20 mL glass vial was charged with a magnetic stir bar, UI₄(OEt₂)₂ (102 mg, 0.11 mmol), and Et₂O (7 mL). The resulting cherry-red solution was filtered through a column of Celite supported on glass wool (0.5 cm \times 2 cm). The filtrate was stored at room temperature for several days producing an orange solution and an orange crystalline solid. The solid was isolated and dried *in vacuo* to provide orange crystals of 1 (19.6 mg, 16% yield). Complex 1 has proven to be insoluble in non-coordinating solvents, such as Et₂O, toluene and CH₂Cl₂, limiting the amount of characterization data that could be collected. Anal. calcd for UI₅O₃C₁₂H₃₁: C 13.15, H 2.85. Found: C 11.10, H 2.52. Crystals of 1 turn opaque when dried *in vacuo*.

Complexes 2–7 were synthesized similarly and only the synthesis of complex 2 will be described in detail.

UI₃(OC₆H₅)(THF)₃ (2). A 20 mL glass vial was charged with a magnetic stir bar, UI₄(OEt₂)₂ (32.7 mg, 0.037 mmol), and toluene (2 mL). Addition of phenol (3.6 mg, 0.038 mmol) to the cherry red solution resulted in a colour change to orange. The volume of the solution was reduced *in vacuo* to 0.5 mL and then diluted with toluene (1 mL), resulting in a cloudy orange solution. THF (0.2 mL) was then added, and the resulting yellow solution was filtered though a Celite column supported on glass wool (0.5 cm × 2 cm). The filtrate was layered with hexanes (3 mL) and stored at -25 °C for 96 h resulting in the deposition of green crystals (13.9 mg, 41% yield). Anal. calcd for UI₃O₄C₁₈H₂₉: C 23.29, H 3.15. Found: C 22.94, H 3.05. ¹H NMR (400 MHz, 25 °C, C₆D₆): δ 76.87 (s, 2H, *ortho* CH), 39.15 (s, 2H, *meta* CH), 28.06 (s, 1H, *para* CH), -18.11 (s, 12H, β-THF), -27.29 (s, 12H, α-THF).

 $UI_3(O-2,6-Ph_2C_6H_3)(THF)_2$ (3). The synthesis required $UI_4(OEt_2)_2$ (31.0 mg, 0.035 mmol) and 2,6-diphenylphenol (8.5 mg, 0.035 mmol) in toluene (2 mL). Total yield: 19.0 mg, 54%. Anal. calcd for $UI_3O_3C_{26}H_{29}$: C 30.97, H 2.90. Found: C

30.52, H 2.85. ¹H NMR (400 MHz, 25 °C, C₆D₆): δ 40.26 (s, 2H, *meta* CH), 33.82 (s, 4H, *ortho* CH), 27.79 (t, 1H, $J_{CH} = 7.4$ Hz, *para* CH), -5.09 (s, 4H, *meta* CH), -17.51 (s, 8H, β-THF), -58.80 (s, 8H, α-THF). The resonance attributable to the 2 *para* hydrogen atoms of the aryloxide was not found.

UI₂(OC₆H₅)₂(THF)₃ (4). The synthesis required UI₄(OEt₂)₂ (30.0 mg, 0.034 mmol), and phenol (6.3 mg, 0.067 mmol) in toluene (3 mL). Total yield: 20.1 mg, 67% yield. Crystals of 4 turn opaque and pale green-yellow when dried *in vacuo*. Anal. calcd for UI₂O₅C₂₄H₃₄: C 32.23, H 3.83. Anal. calcd for UI₂O₄C₂₀H₂₆ (*i.e.* UI₂(OC₆H₅)₂(THF)₂): C 29.21, H 3.19. Found: C 28.77, H 3.27. ¹H NMR (400 MHz, 25 °C, C₆D₆): δ 93.80 (s, 4H, *ortho* CH), 46.75 (s, 4H, *meta* CH), 33.35 (s, 2H, *para* CH), -21.76 (s, 12H, β-THF), -28.25 (s, 12H, α-THF). UV-vis (Et₂O, 0.19 × 10⁻³ M): 303 nm (sh, ε = 4840 L mol⁻¹ cm⁻¹), 369 nm (ε = 3260 L mol⁻¹ cm⁻¹).

UI₂(**O**-4-'**BuC**₆**H**₄)₂(**THF**)₃ (5). The synthesis required UI₄(OEt₂)₂ (30.0 mg, 0.034 mmol) and 4-*tert*-butylphenol (10.1 mg, 0.067 mmol) in toluene (2 mL). Total yield: 11.1 mg, 33% yield. Crystals of **5** turn opaque and pink when dried *in vacuo*. Anal. calcd for UI₂O₅C₃₂H₅₀: C 38.18, H 5.01. Anal. calcd for UI₂O₃C₂₄H₃₄ (*i.e.* UI₂(O-4-'BuC₆H₄)₂(THF)): C 33.43, H 3.97. Found: C 33.13, H 3.95. ¹H NMR (400 MHz, 25 °C, C₆D₆): *δ* 93.15 (s, 4H, *ortho* CH), 47.58 (s, 4H, *meta* CH), 17.54 (s, 18H, 'Bu), -27.05 (s, 12H, β-THF), -35.92 (s, 12H, α-THF). UV-vis (Et₂O, 0.20 × 10⁻³ M): 300 nm (sh, ε = 7080 L mol⁻¹ cm⁻¹), 370 nm (ε = 4230 L mol⁻¹ cm⁻¹).

UI₂(**O-2,6-Me**₂**C**₆**H**₃)₂(**THF**)₃ (6). The synthesis required UI₄(OEt₂)₂ (30.0 mg, 0.034 mmol) and 2,6-dimethylphenol (8.2 mg, 0.067 mmol) in toluene (4 mL). Total yield: 18 mg, 56% yield. Crystals of **6** become pale-green and opaque when dried *in vacuo*. Anal. calcd for UI₂O₅C₂₈H₄₂: C 35.38, H 4.45. Anal. calcd for UI₂O₃C₂₀H₂₆ (*i.e.* UI₂(O-2,6-Me₂C₆H₃)₂(THF)): C 29.79, H 3.25. Anal. calcd for UI₂O₂C₁₆H₁₈ (*i.e.* UI₂(O-2,6-Me₂C₆H₃)₂): C 26.18, H 2.47. Found: C 27.81, H 3.14. ¹H NMR (400 MHz, 25 °C, C₆D₆): δ 42.95 (s, 4H, *meta* CH), 38.77 (s, 12H, CH₃), 30.38 (s, 2H, *para* CH), -18.98 (s, 12H, β-THF), -39.62 (s, 12H, α-THF). UV-vis (Et₂O, 0.22 × 10⁻³ M): 310 nm (sh, ε = 4790 L mol⁻¹ cm⁻¹), 378 nm (ε = 4430 L mol⁻¹ cm⁻¹).

UI₂(OC₆F₅)₂(THF)₃ (7). The synthesis required UI₄(OEt₂)₂ (30.0 mg, 0.034 mmol) and pentafluorophenol (12.4 mg, 0.067 mmol) in toluene (2 mL). Total yield: 21 mg, 58% yield. Crystals of 7 turn opaque and pale-green upon exposure to vacuum. Anal. calcd for UI₂O₅C₂₄F₁₀H₂₄: C 26.83, H 2.25. Anal. calcd for UI₂O₃C₁₆F₁₀H₈ (*i.e.* UI₂(OC₆F₅)₂(THF)): C 20.66, H 0.87. Found: C 20.06, H 0.86. ¹H NMR (400 MHz, 25 °C, C₆D₆): *δ* -20.24 (s, 12H, β-THF), -39.76 (s, 12H, α-THF) ¹⁹F{¹H} NMR (376 MHz, 25 °C, C₆D₆) *δ* -33.84 (s, 4F, *ortho* CF), -71.63 (s, 4F, *meta* CF), -86.54 (s, 2F, *para* CF). UV-vis (Et₂O, 0.24 × 10⁻³ M): 287 nm (sh, ε = 8580 L mol⁻¹ cm⁻¹), 362 nm (ε = 4200 L mol⁻¹ cm⁻¹).

X-Ray Crystallography

The crystal structures of complexes 1, $2 \cdot C_7 H_8$, 3, 5, $6 \cdot 2$ THF and $7 \cdot \frac{1}{2}$ THF, were determined similarly with exceptions noted in the following paragraph. Crystals were mounted on a glass fiber under Paratone-N oil. Data collection was carried out using a Bruker

	1	$2 \cdot C_7 H_8$	3	5	6-2THF	$7 \cdot \frac{1}{2}$ THF
Empirical formula	$C_{12}H_{31}I_5O_3U$	$C_{25}H_{37}I_{3}O_{4}U$	$C_{26}H_{29}I_{3}O_{3}U$	$C_{32}H_{50}I_{2}O_{5}U$	$C_{36}H_{58}I_2O_7U$	$C_{26}H_{28}F_{10}I_2O_{5.5}U$
FW/g mol ⁻¹	1095.90	1020.28	1008.22	1006.55	1094.65	1110.31
Crystal habit, colour	Plate, orange-red	Plate, green	Plate, yellow-green	Plate, green	Block, green	Block, green-blue
Crystal size/mm	$0.20 \times 0.10 \times 0.05$	$0.20 \times 0.20 \times 0.03$	$0.25 \times 0.25 \times 0.06$	$0.24 \times 0.18 \times 0.04$	$0.20 \times 0.10 \times 0.06$	$0.20 \times 0.20 \times 0.15$
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	Pnna	Pbca	C2/c	Pbca	C2/c	$P2_{1}/c$
a/Å	14.141(3)	17.166(3)	19.332(7)	23.0285(16)	13.6892(18)	21.613(3)
b/Å	18.184(4)	12.357(2)	12.547(4)	13.3321(9)	11.8797(15)	10.9881(16)
c/Å	10.585(2)	29.580(5)	24.785(9)	23.6112(17)	24.995(3)	14.154(2)
$\alpha / ^{\circ}$	90	90	90	90	90	90
$\beta/^{\circ}$	90	90	106.953(5)	90	93.130(3)	96.465(3)
$\gamma/^{\circ}$	90	90	90	90	90	90
$V/Å^3$	2721.7(11)	6274.7(19)	5750(3)	7249.1(9)	4058.7(9)	3339.9(8)
Ζ	4	8	8	8	4	4
$D_{ m calcd}/ m Mg~m^{-3}$	2.674	2.160	2.329	1.845	1.791	2.208
μ/mm^{-1}	11.640	8.151	8.890	6.216	5.562	6.799
F_{000}	1936	3760	3680	3840	2112	2064
Total no. reflections	11975	27 765	22 838	57 858	14 998	14985
Unique reflections	2800	5352	5827	7636	4075	4916
$R_{\rm int}$	0.1304	0.1400	0.0795	0.1855	0.1242	0.0550
Final R indices $[I >$	$R_1 = 0.0473,$	$R_1 = 0.0618,$	$R_1 = 0.0548,$	$R_1 = 0.0813,$	$R_1 = 0.0563,$	$R_1 = 0.0432,$
$2\sigma(I)$]	$wR_2 = 0.1047$	$wR_2 = 0.1393$	$wR_2 = 0.1271$	$wR_2 = 0.1324$	$wR_2 = 0.1177$	$wR_2 = 0.0947$
Largest diffraction peak and hole/e $Å^{-3}$	1.92 and -0.88	2.72 and -1.34	5.92 and -1.78	3.57 and –2.14	2.17 and -3.35	2.38 and -0.87
GOF	0.788	1.254	1.079	0.987	0.917	0.970

Table 2X-Ray crystallographic data for complexes 1, $2 \cdot C_7 H_8$, 3, 5, $6 \cdot 2 THF$ and $7 \cdot \frac{1}{2} THF$

3-axis platform diffractometer with a SMART-1000 CCD detector. The instrument was equipped with a graphite monochromatized MoK α X-ray source ($\lambda = 0.71073$ Å). All data were collected at 150(2) K using an Oxford nitrogen gas cryostream system. A hemisphere of data was collected using ω scans and 0.3° frame widths. SMART⁵⁴ was used to determine the cell parameters and data collection. The raw frame data were processed using SAINT.55 The empirical absorption correction was applied based on Psi-scan or SADABS. Subsequent calculations were carried out using SHELXTL.⁵⁶ Structures were solved using Direct methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom of attachment, while the final refinement included anisotropic temperature factors on all non-hydrogen atoms. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.

For 1, 15 second frame exposures were used. In addition, both diethyl ether molecules exhibited large thermal displacements. The C-C and C-O bond distances of these Et₂O molecules were set to 1.50 Å and 1.45 Å, respectively. All atoms of the cationic portion of the molecule were modelled with isotropic temperature factors. For $2 \cdot C_7 H_8$, 20 second frame exposures were used. In addition, a disordered molecule of toluene was found in the asymmetric unit. The aromatic C-C bond lengths were set to 1.40 Å, while the C(ipso)–C(methyl) bond was set to 1.45 Å. The toluene carbon atoms were modelled with isotropic temperature factors, and were restrained to be co-planar. For 3 and 5, 15 second frame exposures were used, while for 6.2THF, 20 second frame exposures were used. In addition, C11 in complex 5 was refined isotropically. For $7 \cdot \frac{1}{2}$ THF, 10 second frame exposures were used. In addition, a disordered molecule of solvent was found in the asymmetric unit which was modelled as THF. The O-C and C-C bond lengths were

set to 1.4 Å, and 1.5 Å, respectively. The C28–C25 bond length was set to 2.3 Å, while O6–C26 and O6–C27 were set to 2.2 Å. The carbon atoms were modelled with isotropic temperature factors. In addition, C24 in complex **7** was refined isotropically. Additional X-ray crystallographic data for complexes **1**, **2**·C₇H₈, **3**, **5**, **6**·2THF, and **7**· $\frac{1}{2}$ THF, can be found in Table 2.

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