

Instantaneous and phosphine-catalyzed arene binding and reduction by U(III) complexes

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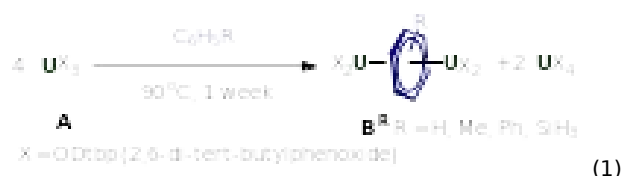
Abstract: Neutral arenes such as benzene have never been considered suitable ligands for electropositive actinide cations, yet we find that even simple U^{III} UX₃ aryloxide complexes such as U(ODipp)₃ bind and reduce arenes spontaneously at room temperature, forming inverse arene sandwich (IAS) complexes X_nU(μ-C₆D₆)UX_m (n,m = 2,3), ODipp = OC₆H₃ⁱPr₂-2,6). In some cases, further arene reduction can occur as a result of X ligand redistribution. These unexpected spontaneous reactions explain the anomalous spectra and reported lack of further reactivity of strongly reducing U^{III} centers. Further, phosphines that are not considered suitable ligands for actinides can catalyze the formation of the IAS complexes, and out-compete THF, traditionally considered a strong donor ligand for f-block ions. This enables otherwise inaccessible asymmetric and less congested IAS complexes to be isolated and the bonding in this series compared.

Introduction

There is a sustained interest in the use of soft, i.e. polarizable, small molecules and their anions as ligands for the hard, electropositive f-block metal cations because these can highlight the differences in orbital participation and bonding covalency between different f-block cations.¹⁻⁶ An increased understanding of these differences is a necessary contribution to the efforts that are needed to reduce the environmental damage caused by separating the technology-critical rare earth elements, and for the safe handling of civil nuclear waste.⁷⁻¹⁰ Weakly ligating groups, such as neutral phosphines, are almost without exception incorporated into polydentate, anionic ligands, which makes it difficult to tease apart their contributions to covalency.^{11, 12}

The burgeoning area of small molecule activation by actinides has relied on the strongly reducing U^{III} → U^{IV} reduction couple to activate molecules typically considered kinetically and thermodynamically inert e.g. N₂.^{1, 13} We showed that simple U^{III} aryloxide complexes UX₃

such as (U(ODtbp)₃; **A** (ODtbp = O-2,6-^tBu₂C₆H₃) originally made by Sattelberger et al. in 1988, are adept at the reductive activation of CO, CO₂ and N₂.^{14, 15} and that storage of arene solutions of at 90 °C for 6-7 days provide the unusual inverse arene sandwich (IAS) complexes {(ODtbp)₂U}₂(μ-η⁶:η⁶-C₆H₅R) **B** (R = H) and functionalized adducts **B^R** (R = Me, Ph or SiH₃), along with an oxidized by-product [U(ODtbp)₄], equation 1.¹⁶



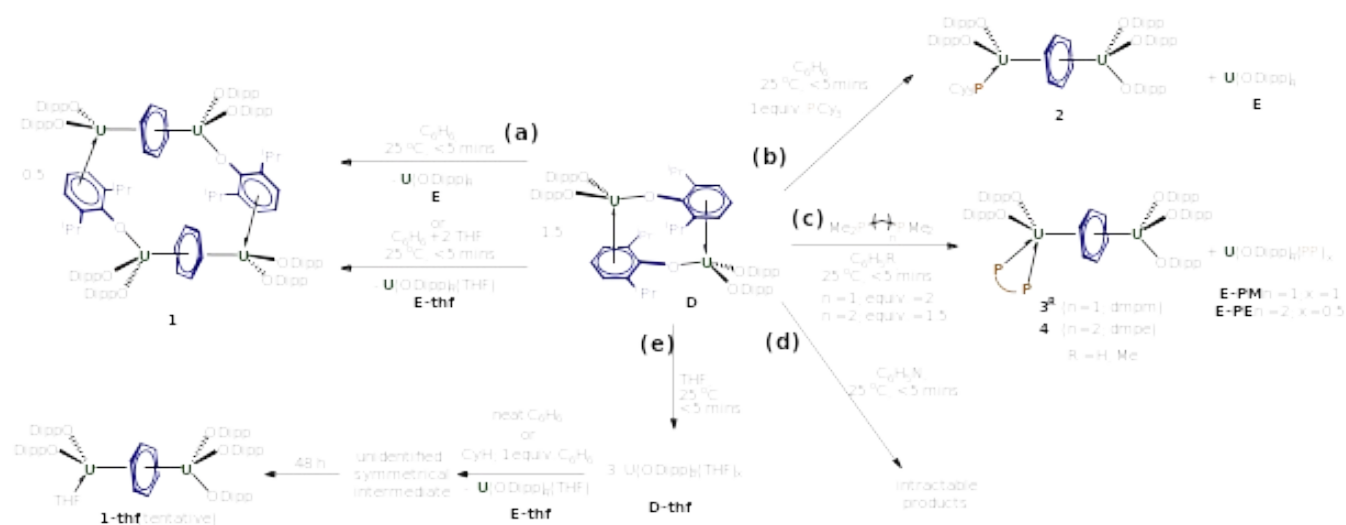
This surprising result showed that simple U^{III} complexes that have formal reduction potentials of around -1.2 V vs Fc⁺⁰ can reduce arenes, which have reduction potentials closer to -3.4 V.¹⁷ This latter value is more negative than potassium, which had previously been considered necessary to provide the reducing electrons in the formation of diuranium IAS complexes. The favorable π and δ overlap of the uranium (d and f) orbitals with arene LUMOs provide the additional stabilization energy that favors product formation, although the precise definition of these bonding interactions is still difficult to quantify or predict *a priori*. The mild, potassium-free conditions allow functionalized arenes and other reagents to be incorporated in one-pot transformations, enabling, for example, the selective conversion of C-H to C-B bonds in the reduced arenes.¹⁶ The storage of electrons in the bridging arene also allows the molecule to react as a U(II) synthon by expulsion of the neutral arene,¹⁸⁻²¹ an otherwise difficult fragment to access.²²⁻²⁵

Unexpected interactions between actinide cations and neutral hydrocarbons are increasingly challenging the presumptions of the bonding and reactivity of the

actinides,^{26, 27} and recently helped us stabilize metallacyclic actinide(IV) catalysts that could reduce N₂ to ammonia or secondary silylamines.⁴

The favorable U-arene π - and δ -symmetry orbital overlap is also confirmed in the very rare monometallic uranium complexes that have weaker interactions with an arene; the piano-stool complexes (C₆Me₆)U(BH₄)₃, in which the

arene is clearly close to charge-neutral, being the prime example.²⁹ Beyond synthetic organometallic applications, metal-arene complexes have been put forward as interesting candidates for organic spintronic components for quantum computing and high-density information storage.³⁰⁻³⁶



Scheme 1. (a) The spontaneous disproportionation of **E** to yield **1** and **F**. (b) The arene-induced disproportionation of **1** in the presence of phosphine donors. (c) The observed reactivity in the presence of THF. (d) The observed decomposition in the presence of pyridine. (e) The observed reactivity of **E** with THF. The precise identity of the adduct **1-thf** remains unknown.

The arene can be an excellent mediator for ferromagnetic coupling between metal ions, and the high symmetry of the metal-arene ligand field can afford high spin-reversal barriers to single ion (/molecule) magnets (SIMs or SMMs) based on the anisotropic f-block ions,³⁷ of potential use as molecular qubits.³⁸ Arenes can also be used to compatibilize or deliver molecules to graphene surfaces and single walled carbon nanotubes to build up larger spin-systems.³⁹

Attempts to classify the formal oxidation states of the uranium centers and formal level of reduction in the bridging arene of IAS complexes bearing two X ligands per uranium (as in **B**) and three X ligands per uranium (such as in the complex $\{((\text{O}^t\text{Bu})_3\text{SiO})_3\text{U}\}_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_7\text{H}_8)$, **C**) have been made. A range of techniques including X-ray diffraction measured distances, solution spectroscopies, and an array of computational studies, as well as simple X-ligand counting have been employed. These methods have generated controversy since the interpretation of spectroscopic data for dinuclear U complexes is not yet

straightforward while computational simulations are non-trivial.^{40, 41} Inverse arene sandwich complexes clearly exhibit highly covalent interactions, which would encourage a less reduced arene, and accordingly low metal oxidation state (U^{III} or U^{IV}) from the Pauling electroneutrality principle. For example, we characterized the complex $\{[(\text{N}(\text{SiMe}_3)_2)\text{U}]\}_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_6\text{H}_6)$ as containing U^{III} and a bridging dianion using a variety of solution and solid state methods.¹⁶ We then used variable pressure crystallography to study the compressibility of the structure, recognizing that the covalent bonds in diamond are extremely incompressible whilst ionic sodium chloride is highly compressible; even at gigapascals pressure the solid state structure showed only a minimal shortening of the metal-arene distance, indicative of a less compressible covalent interaction.⁴² At the other extreme, arguments based on a combination of principally ionic bonding and simple Hückel aromaticity theory would suggest complexes containing a 4⁻ (10 π -electron) charge on the

bridging arene and higher metal oxidation state (U^{IV}), i.e. $X_3U^{IV}(\eta^6\text{-arene})U^{IV}X_3$ and a tetraanionic bridging C_6 ring.

Combined synthetic/computational chemical approaches have provided important information on the involvement of the f- and other valence orbitals.^{43, 44} However, computational analyses of weaker, π , and δ -bonded (and higher nodality) interactions with these relativistic, strongly paramagnetic molecules are notoriously difficult to run and interpret.^{16, 45, 46, 47} Reports on quantum chemistry calculations of charge distribution in actinide ions have noted the difficulties associated with functional choice and the chances to produce different results.⁴⁸

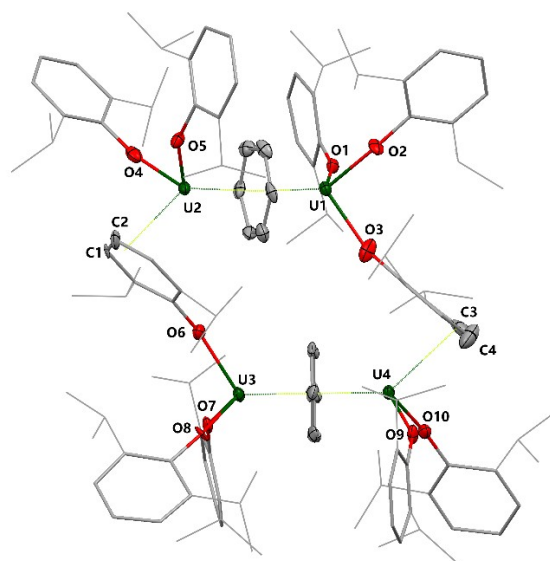
The lowest level of arene reduction was assigned for the piano stool monoarene-U interaction in the other homoleptic U^{III} aryloxy complex reported by Sattelberger *et al.* in 1988, $U(\text{ODipp})_3$ (**D**). Complex **D** contains the smaller (with respect to ODtbp employed in the synthesis of **A**) aryloxy ODipp (2,6-di-*iso*-propylphenoxide, O-2,6-*i*-Pr₂C₆H₃).¹⁵ Both **A** and **D** are readily prepared in good yield via protonolysis from $U\{N(\text{SiMe}_3)\}_3$. The authors focused on the unusual solid-state structure of **D** which forms a dimer through U - η^6 -arene rather than U - O bonds to the other metal's aryloxy ligand. However, NMR spectroscopy of benzene-*d*₆ solutions shows just one ligand environment which was attributed to cleavage of the dimer and "...consistent with either mononuclear $U(\text{O}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)_3$ or $(C_6D_6)U(\text{O}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)_3$." The possible existence of two types of U-arene interaction highlighted this compound as an ideal candidate for further investigation. Here we show previously unanticipated arenes and neutral phosphines, atypical donors for actinides, can play a crucial role in stabilizing molecular uranium fragments for arene reduction and binding.

Results

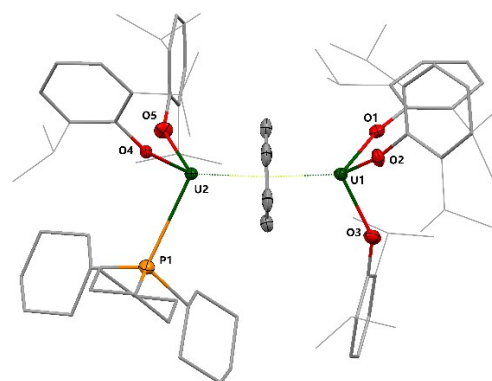
Dissolution of dark purple **D** in arene solvents results in an immediate color change to brown/black, as noted in the original study.¹⁵ Integration of the single observable set of ligand resonances in ¹H NMR spectra of C₆H₆ solutions in the presence of an internal standard (Si(SiMe₃)₄) support the fact that an immediate reaction has taken place and only 30% of the material is visible in solution. Removal of volatiles yields a black powder which, when dissolved in n-pentane and stored over night at -40 °C furnishes black crystals of the new IAS complex $\{(\text{DippO})_3U(\mu\text{-C}_6\text{H}_6)U(\text{ODipp})_2\}_2$ **1** (Scheme 1a), as determined by single

crystal X-ray diffraction (Figure 1), in 75 % yield. The supernatant contains the U^{IV} by-product $U(\text{ODipp})_4$ **E**, and whose chemical shifts were originally, and understandably, assigned to **D**. The lower solubility and large number of different ligand environments in **1** generates many small and broadened resonances that are difficult to observe and assign.

a)



b)



c)

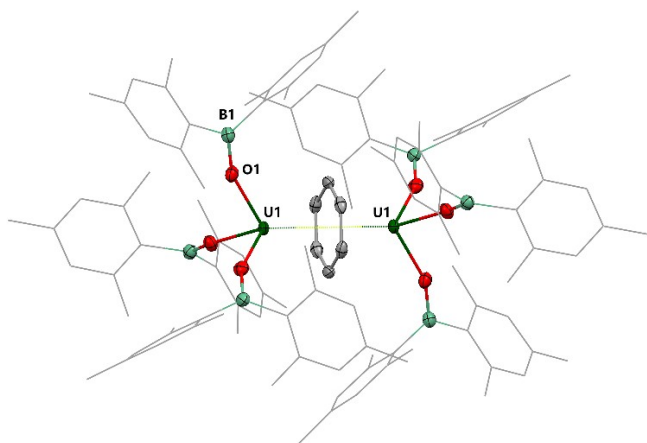


Figure 1. The solid-state structure of **1** (a), **2**(b), and **6** (c). ODipp and OBMe₂ ligands are depicted as capped sticks and wireframe for clarity. Hydrogen atoms are omitted; thermal ellipsoids at 30% probability. Selected distances (Å) and angles (deg): **1** U1-U2 4.132(8), U1-O1 2.088(8), U1-O2 2.091(8), U1-O3 2.203(7), U2-O4 2.115(8), U2-O5 2.131(8), U1-C_{arene} ave. 2.611(12), U2-C_{arene} ave. 2.645(12), bridging C-C ave. 1.427(19); **2**, U1-U2 4.3867(7), U1-O1 2.105(7), U1-O2 2.109(7), U1-O3 2.139(6), U2-O4 2.125(6), U2-O5 2.123(7), U1-C_{bridging} ave. 2.588(17), U2-C_{bridging} ave. 2.620(17), U2-P1 3.099(3), bridging C-C ave. 1.401(18) U1-centroid-U2 175.2(3); **6**, U1-U1' 4.4323(7), U1-O1 2.256(6), U-C_{bridging} ave. 2.636(9), arene C-C ave. 1.434(15) U1-centroid-U1' 180.

Complex **1** is the first example of a neutral IAS complex in which each uranium bears a different number of X ligands formed spontaneously from a U^{III} species (notably however, a similar mixed valence IAS compound was recently reported via KC₈ reduction of a U^{IV} precursor⁴⁹). Interestingly, **1** is formed immediately at room temperature in high yields (96%) and is unchanged by extended heating (i.e. does not form X₂U^{III}(η⁶-arene)U^{III}X₂, the direct analogue of **B^R**).¹⁶

Conventional wisdom dictates that uranium forms principally ionic interaction with hard donor atoms. Thus the facile binding of a neutral arenes inspired us to screen other neutral, σ-donor and π-acceptor L ligands that are considered atypical ligands for uranium, Scheme 1 b, c, d. If **1** is dissolved in an aromatic solvent containing one equiv. of PCy₃, dmpm, or dmpe (Cy = C₆H₁₁; *cyclo*-hexyl, dmpm = bis(dimethylphosphino)methane dmpe = bis(dimethylphosphino)ethane) a new IAS complex, (DippO)₃U(μ-C₆D₆)U(ODipp)₂(PCy₃) (**2**), (DippO)₃U(μ-C₆H₅R)U(ODipp)₂(dmpm) (R = H (**3^H**) or Me (**3^{Me}**)) and (DippO)₃U(μ-C₆H₆)U(ODipp)₂(dmpe) (**4**) (Scheme 1) are formed; a rare series of phosphine adducts of a low valent

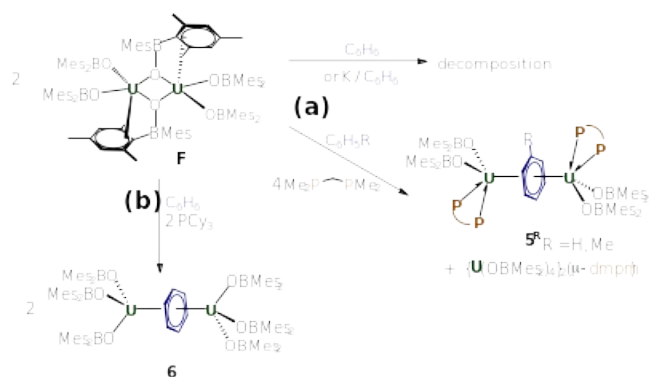
uranium center. The U^{IV} by-products (Scheme 1b/c) are U^{IV}: **E**, U(ODipp)₄(dmpm) (**E-PM**), and {U(ODipp)₄}₂(μ-dmpe) (**E-PE**)⁵⁰ respectively. Complexes **2** - **4** show sharp, paramagnetically-shifted NMR spectral resonances suggestive of conformational stability at room temperature. Neither very large phosphines (e.g. biaryl phosphine XPhos) nor poorly donating phosphines (e.g. PPh₃) break up dimeric **1**. To date, only a few simple phosphine adducts of U^{III} and U^{IV} have been amenable to study; Cp*₂UCl(PMe₃)_x loses phosphine too readily to be characterized,⁵¹ UCl₄(PMe₃)₃ has to be crystallized from neat PMe₃⁵² but (C₅H₄Me)₃UCl(PMe₃)⁵³ and the borohydride PEt₃ adducts⁵⁴ have been isolated. A handful of U^{IV} and Th^{IV} dmpe adducts have been isolated and dmpe was useful in one instance to stabilize a monomeric U^{III} hydride.¹¹ Their study has provided important bonding comparisons with their 4f congeners.⁵⁵

Dissolution of **D** in C₆H₆ containing two equiv. THF affords the base-free IAS **1** and the THF-solvated U^{IV} by-product U(ODipp)₄(THF). The conversion to **1** still occurs even in the presence of 10 equivalents of THF, in contrast to **A** which reacts with stoichiometric THF in C₆H₆ forms red **A-thf** that shows no further reactivity. The THF adduct of **D**, **D-thf** does react with C₆H₆ in cyclohexane or neat C₆H₆ over 48h. First a resonance in the ¹H NMR spectrum at -127 ppm is observed, suggesting an intermediate that is tentatively assigned as an arene adduct. This resonance is lost and replaced by a new low frequency resonance at -114 ppm which is consistent with the chemical shifts observed for the isolated phosphine adducts, so could be assigned as belonging to the bridging arene of (DippO)₃U(μ-C₆D₆)U(ODipp)₂(THF), **1-thf** Scheme 1e, and U(ODipp)₄(THF) (**E-thf**) is formed at the same time, in support of this. However, unequivocal assignments of either based on paramagnetically shifted NMR spectral data alone is not possible at this time.

We recently reported that the complex {U(OBMe₂)₃}₂, **F**, (Mes = 2,4,6-Me₃-C₆H₂) which has more flexible O-donor ligands is fragile and decomposes when stored in common aprotic solvents, while reactions with KC₈ in toluene or benzene yield only the decomposition product K₂[{(OBMe₂)₃U}₂(μ-O)₂].⁵⁶ However, inspired by **2** - **4**, addition of dmpm to an arene solution of **F** yields the IAS [{(dmpm)(OBMe₂)₂U}₂(μ-η⁶:η⁶-C₆H₅R)] **5^R** (R = H (**5^H**) or R

= Me (5^{Me}) and the U^{IV} by-product $\{\text{U}(\text{OBMe}_2)_4\}_2(\mu\text{-dmpm})$ (Scheme 2a).

Complexes **5^R** and **6** (Scheme 2, figures S25, S26) are, to our knowledge, the only examples of uranium IAS complexes in which both neutral U_2X_4 and U_2X_6 structures are accessible with the same X ligand. We note that PCy_3 provides a route to the IAS complex $[\{(\text{OBMe}_2)_3\text{U}\}_2(\mu\text{-}\eta^6,\eta^6\text{-C}_6\text{H}_6)]$ (**6**) (Scheme 2b) but does not remain coordinated to the product, i.e. functioning as a catalyst.



Scheme 2. (a) The disproportionation of **F** in aromatic solvents in the presence of dmpm or dmpe to yield phosphine-stabilized U_2X_4 type uranium IAS complexes. (b) The formation of the U_2X_6 IAS complex **6** in the presence of PCy_3 .

Discussion

To understand the level of arene reduction and metal oxidation state in **1** – **4** their structural parameters were compared to similar IAS complexes that have previously been assigned different formal redox states, Fig. 2. Tables 1 and 2 contain the two parameters agreed to be the best measures of the degree of electron transfer; the arene C-C and $\text{U-C}_{\text{arene}}$ distances. The first provides a measure of the arene π^* LUMO occupation that will arise from U back-bonding.[‡] The second assumes that a greater formal electron transfer to the arene results in a more tightly bound arene. We find the number of X ligands, and the U-O distances are not good indicators of formal oxidation state or arene reduction level and the latter vary significantly within closely related molecules. As mentioned above, different computational analyses on near-identical systems provide a wide variation of possible

answers, as such we have elected to focus on experimental data to provide a cohesive picture across the full range of nuclearities observed for uranium IAS complexes.

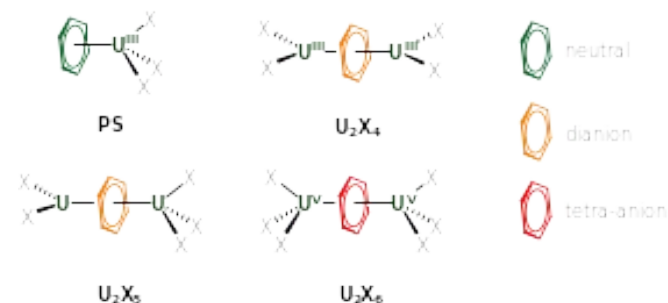


Figure 2. The four uranium arene complex types with their literature-proposed formal uranium oxidation states.

The piano stool (PS) (Figure 2) complexes like **D** are considered neutral arene adducts of U^{III} or U^{IV} with minimal arene reduction. The sample of PS complexes (Table S1 entries 1-4) display an average arene C-C distances of 1.397 Å (cf. free benzene: 1.40 Å) and an average U-C distance of 2.928 Å (range 2.919(13) Å – 2.934(17) Å); the longest U-C distance of the systems studied in agreement with the proposal of little to no formal electron transfer from metal to arene (Table 1).

Complexes **B^R** and **B^R-BBN** (Table S1 entries 5 – 10) (**B^R** = $[\{(\text{ODtbp})_2\text{U}\}_2(\mu\text{-}\eta^6,\eta^6\text{-C}_6\text{H}_5\text{R})]$; **B^R-BBN** = $[\{(\text{ODtbp})_2\text{U}\}_2(\mu\text{-}\eta^6,\eta^6\text{-C}_6\text{H}_4(\text{BBN})\text{R})]$; $\text{R} = \text{H, Me, Ph}$ or SiH_3) of the form $(\text{X}_2\text{U})_2(\mu\text{-arene})$ (U_2X_4) represent a rare IAS series that vary only in the bridging aromatic. They are formulated as two U^{III} centers and a dianionic C_6 ring $(\text{X}_2\text{U}^{\text{III}})_2(\mu\text{-arene})^{2-}$, from a combination of X-ray diffraction structures and DFT calculations which corroborate the observations of prior studies on structurally related complexes.¹⁶ Long C-C_{arene} bonds (1.452 Å avg.) and short U-C bonds (2.580 Å avg.) support this assignment.

We anticipated this trend to continue for the $(\text{X}_3\text{U})_2(\mu\text{-arene})$ type (U_2X_6) complexes, formally assigned as containing two U^{IV} centers and a bridging tetraanion. Unexpectedly we found that the bound arene C-C distances for the known complexes of this type (Table S1 entries 19-21) fall in the range of 1.423(3) Å – 1.440(6) Å with an average value of 1.432 Å. It is instructive to

compare these to the arene tetraanion complexes of the lanthanides published by Diaconescu in which the C-C distances fall in the range 1.420(3) Å - 1.496(7) Å with an overall average of 1.465 Å⁵⁷ and to those of thorium recently described by the same research group in which the average C-C distances fall in the range 1.442(14) Å - 1.462(4) Å with an overall average of 1.453 Å.⁵⁸ The formulation of these bridging arenes as tetraanions is also still worth further discussion given that the ligand scaffold

employed contains a potentially redox active ferrocenyl group. The U-C distances fall in the range 2.636(9) Å - 2.696(3) Å with an overall average of 2.668 Å. These values suggest a comparable level of arene reduction to the **U₂X₄** class; a slight increase in U-C distance is attributed to the presence of an extra electron donating X ligand per uranium which lowers the level of donation from the arene to uranium.

Table 1. Comparison of averaged structural parameters of uranium arene complexes. Distances given in Å.

Type	Entries Table S1	Originally proposed uranium oxidation state	Bound Arene. C-C	UX ₃ U-C	UX ₂ U-C	U-C _{ave.}	Suggested uranium oxidation state
PS	1-4	3+	1.398			2.929	3+
U₂X₄	5-11	3+/3+	1.452		2.583	2.580	3+/3+
U₂X₅	12-17	-	1.412	2.597	2.622	2.615	3+/4+
U₂X₆	18-20	5+/5+	1.432	2.668		2.668	4+/4+

Table 2. Comparison of averaged structural parameters of C, C-K and C-K₂. Distances given in Å. (UOS = Uranium Oxidation State)

Compound	Avg. Bound Arene. C-C	U-C _{ave.}	Originally proposed uranium oxidation state	Suggested uranium oxidation state
[{U(OSi(O ^t Bu) ₃) ₂ (μ-C ₆ H ₅ Me)}, C	1.423(3)	2.692(3)	5+/5+	4+/4+
K[{{U(OSi(O ^t Bu) ₃) ₂ (μ-C ₆ H ₅ Me)}, C-K	1.440(18)	2.642(11)	5+/4+	3+/4+
K ₂ [{{U(OSi(O ^t Bu) ₃) ₂ (μ-C ₆ H ₅ Me)}, C-K₂	1.452(6)	2.605(4)	4+/4+	3+/3+

Complexes **1** - **4**, **U₂X₅** IAS complexes (Table S1 entries 12-16) are assigned as X₃U^(IV)(μ-η⁶:η⁶-arene)²⁻U^(III)X₂. We observe average C-C_{bridging} of 1.407 Å (range 1.391(16) Å - 1.427(19) Å), and average U-C distances of 2.609 Å (range 2.595(10) Å - 2.628(12) Å). The U-C distances fall midway between those in **U₂X₄** and **U₂X₆** and the X₃U-C distance is shorter than X₂U-C distance. The average C-C distances are longer, and more like those of the less-reduced arenes in the **PS** complexes, a factor we attribute to competition for π-backdonation with the phosphines; π back-bonding to either phosphine or arenes is preferential to binding the σ-donor THF, in agreement with the low assigned oxidation states. These data are augmented by the mixed valent system recently reported by Liddle *et al.* which is formulated as containing U^{III} and U^{IV} centers and a dianionic arene (Table S1 entries 17 and 18).⁴⁹

Analyzing the crystallographic data now available for **U₂X₄**, **U₂X₅** and **U₂X₆** compounds, and noting the lack of measurable contraction in U-C distance on moving from **U₂X₄** to **U₂X₆** IAS complexes, there appears no need to assign a U(V) and bridging tetraanion state to any **U₂X₆** complexes. We suggest that in all the U IAS complexes reported to date, the similarity in U valence and arene LUMO energy levels allows them all to be classified as containing the arene dianion: **U₂X₄**, X₂U^(III)(μ-η⁶:η⁶-arene)²⁻U^(III)X₂; **U₂X₅**, X₃U^(IV)(μ-η⁶:η⁶-arene)²⁻U^(III)X₂; **U₂X₆**, X₃U^(IV)(μ-η⁶:η⁶-arene)²⁻U^(IV)X₃.

To conclude, as originally postulated by Sattelberger, the dissolution of {U(ODipp)₃}₂ (**D**) in aromatic solvents does disrupt the dimeric structure,¹⁵ but an instant solvent reduction yields {(DippO)₃U(μ-C₆D₆)U(ODipp)₂}₂ (**1**), the first neutral, mixed valent IAS X₃U^(IV)(μ-η⁶:η⁶-arene)²⁻U^(III)X₂ complex formed from spontaneous arene reduction. In

systems with small X ligands, phosphines can catalyze the reductive activation of benzene by stabilizing intermediates, alternatively they can stabilize the reduction products. These new methods contribute a new range of $(\text{DippO})_3\text{U}(\mu\text{-C}_6\text{H}_6)\text{U}(\text{ODipp})_2(\mathbf{L})$ and otherwise inaccessible boroxide complexes **5^R** and **6** to the IAS class. Comparisons of the structural parameters of previously known IAS complexes and those newly reported here has enabled better comparisons of the metal-arene interaction over a range of structure types, leading us to suggest that all of the U IAS complexes reported to date can be classified as simply containing a doubly reduced arene. Prior to this investigation $\{\text{U}(\text{ODipp})_3\}_2$ was thought to lack reactivity with small molecules; the reinvestigation of these reactions in innocent solvents will be reported in due course.

Experimental Section

General Procedures and Techniques

Standard high vacuum Schlenk-line techniques and MBraun and Vac glove boxes were used to store and manipulate air- and moisture-sensitive compounds under an atmosphere of air free and dried argon (Schlenk-line) or dinitrogen (glove box). Reactions and manipulations were carried out under an inert atmosphere unless stated otherwise. All gases were supplied by BOC gases UK. All glassware was dried in an oven at 160 °C, cooled under vacuum and purged with argon or dinitrogen prior to use. All Fisherbrand® 1.2 µm retention glass microfiber filters and cannula were dried in an oven at 160 °C before use.

Toluene, THF and DME were dried with a Vac Atmospheres solvent tower drying system, where they had been passed over a column of molecular sieves for a minimum of 12 hours prior to collection, degassed by dinitrogen purge, and, stored in ampoules containing activated 4 Å molecular sieves. Benzene was refluxed over potassium for 3 days, distilled and collected in an ampoule containing activated 4 Å molecular sieves. *n*-pentane was purchased anhydrous from Sigma-Aldrich, transferred to an ampoule containing activated 4 Å molecular sieves and stored for at least three days prior to use. All solvents were degassed prior to use. C_6D_6 was heated under reflux over potassium for 24 hours, degassed and distilled by trap-to-trap distillation and stored under an atmosphere of dinitrogen or argon. All solvents were purchased from Sigma Aldrich or Fisher Scientific.

All NMR spectroscopic analyses were recorded at 298 K using Bruker Avance III 400 or 500 MHz spectrometers with ^1H NMR spectra run at 400.13 MHz or 500.12 MHz respectively. ^{11}B NMR spectra were recorded at 160.46 MHz using a Bruker Avance III 500 MHz spectrometer. The ^1H spectra are referenced internally to the residual solvent H resonance in deuterated solvents. A number of spectra were recorded in proteo solvents, in these cases the referencing given in NMR spectra figure captions. ^{11}B NMR is referenced to an external standard of $\text{Et}_2\text{O}\cdot\text{BF}_3$.

Elemental analyses were performed by Mr. Stephen Boyer at the London Metropolitan University or Pascher Labor, Germany. Mass spectrometric measurements were carried out on a 12T SolariX FT-ICR-MS with an Infinity cell (Bruker Daltonics) fitted with an APPI II ion source (Bruker Daltonics) equipped with krypton lamp. 10 µM solution samples were prepared, transported and injected under a dinitrogen atmosphere.

All commercially available solid reagents were dried under vacuum and liquids were either dried by storage over potassium or activated molecular sieves, and vacuum transferred and stored under a dinitrogen atmosphere. $\{\text{U}(\text{ODipp})_3\}_2$ (**D**)¹⁵ and $\{\text{U}(\text{OBMes}_2)_3\}_2$ (**F**)⁶⁰ were synthesized according to literature procedures.

Syntheses

General Synthesis of IAS Diphosphine Adducts

To $\{\text{U}(\text{ODipp})_3\}_2$ (1.5 equiv., 0.032 mmol, 50 mg) and a teflon-coated stirrer bar in a 7 mL vial was added a pre-prepared 13 µmol cm^{-3} standard solution of phosphine in the substrate arene. For dmpe ($n = 2$, 1.5 equiv., 0.032 mmol, 2.46 mL); for dmpm ($n = 1$, 2 equiv., 0.043 mmol, 3.28 mL). Upon addition of the phosphine solution, a colour change from dark purple to dark red/brown is observed immediately. The reaction is stirred for 5 minutes to ensure dissolution of all solids. All volatiles are subsequently removed under vacuum and the solid residue dissolved in the minimum volume of *n*-pentane. Storage of this *n*-pentane solution in a -30 °C freezer for 24 h furnishes black crystals of the corresponding uranium IAS (% yield: [PP = dmpm; R = H] = 87 %; [PP = dmpm; R = Me] = 96 %; [PP = dmpe; R = H] = 75 %). Separation of the pale green supernatant from the IAS crystals followed by further storage in a -30 °C freezer (3 - 5 days) subsequently furnishes pale yellow-green crystals of the phosphine adducts of the U^{IV} disproportionation by-products (% yield: [PP = dmpm; R = H] = 86 %; [PP = dmpm; R = Me] = 96 %; [PP = dmpe; R = H] = 80 %). The crystalline material isolated from these reactions is suitable for single crystal x-ray diffraction experiments.

$\{(DippO)_3U(\mu-C_6H_6)U(ODipp)_2\}_2 - \mathbf{1}$

To $\{U(ODipp)_3\}_2$ (1.5 equiv., 0.505 mmol, 778 mg) and a teflon-coated stirrer bar in a Schlenk tube was added C_6H_6 (10 mL). This resulted in an immediate colour change from dark purple solid to a dark brown/black solution. The reaction is stirred overnight to ensure the reaction reaches completion (N.B. NMR scale reactions indicate completion in <30 minutes). Removal of volatiles under reduced pressure afforded black solid residues which were suspended in n-pentane (20 mL) and sonicated for 20 minutes. Storage of this n-pentane solution in a -30 °C freezer for 24 h furnishes a dark brown/black powder. The solid is isolated by filtration and dried under vacuum before being further washed and sonicated in n-pentane (3 x 5 mL). $\{(DippO)_3U(\mu-C_6H_6)U(ODipp)_2\}_2$ is isolated as a brown/black powder in 95% purity (75 % yield) (5% $U(ODipp)_4$ impurity as determined by 1H NMR spectroscopy). (N.B. The 1H NMR resonances of $\{(DippO)_3U(\mu-C_6H_6)U(ODipp)_2\}_2$ are broadened at room temperature.) The yield of pure isolated material can be determined by addition of an internal integration standard ($Si(SiMe_3)_4$) and a suitable bidentate phosphine (L) which generates the adduct $(DippO)_3U(\mu-C_6H_6)U(ODipp)_2(L)$ with sharper resonances. Crystals suitable for a single crystal x-ray diffraction experiment may be grown from a concentrated n-pentane solution stored at -30 °C for 24 h.

1H -NMR (500 MHz, C_6D_6) δ 13.20, 10.49, 6.55, 3.93, 2.86, -6.56, -29.22, -51.40. Resonances for **1** are mostly broadened to baseline and not observable. In the 1H NMR spectra of the crude reaction mixture which contains both **1** and $U(ODipp)_4$, only those of the latter are clearly observed. EA: for $C_{132}H_{182}O_{10}U_2$: calc. C 55.03; H 6.37; N 0 %. Found C ave 46.59 from six determinations (range 45.16 – 49.00); H 5.56 (5.30 – 5.91); N 0 %. Given that the synthesis of $\{(DippO)_3U(\mu-C_6H_6)U(ODipp)_2\}_2$ is separated from precursor salts by two synthetic steps and repeated extractions, the presence of inorganic impurities is unlikely, and the low and variable carbon determination is attributed to carbide formation or the high sensitivity of the compound.

$(DippO)_3U(\mu-C_6H_6)U(ODipp)_2(PCy_3) - \mathbf{2}$

To $\{U(ODipp)_3\}_2$ (1.5 equiv., 0.032 mmol, 50 mg) and a teflon-coated stirrer bar in a 7 mL vial was added a pre-prepared $13 \mu mol cm^{-3}$ standard solution of PCy_3 in C_6H_6 (1 equiv., 0.021 mmol, 1.64 mL of standard solution). On addition of the phosphine solution a colour change from dark purple to dark red/brown is observed immediately. The reaction is stirred for 5 minutes to ensure dissolution of all solids. All volatiles are

subsequently removed under vacuum and the solid residue dissolved in minimum n-pentane. Storage of this n-pentane solution in a -30 °C freezer for 24 h furnishes black crystals of $(DippO)_3U(\mu-C_6H_6)U(ODipp)_2(PCy_3)$ (59 % yield). N.B. If excess (2 equivalents) of phosphine are used the same result is achieved however free phosphine will also crystallize from the n-pentane solution rather than the U^{IV} phosphine adduct. Separation of the pale-yellow supernatant from the IAS crystals followed by 1H NMR spectroscopic analysis shows formation of $U(ODipp)_4$ (spectroscopically-determined yield: 84 %). The crystalline material isolated is suitable for a single crystal x-ray diffraction experiment.

1H -NMR (400 MHz, C_6H_6) δ 12.76 (br d, J = 7.40 Hz, 4H, **B**), 9.92 (br t, J = 7.40 Hz, 2H, **A**), 9.00 (br d, J = 7.44 Hz, 6H, **F**), 7.89 (br t, J = 7.44 Hz, 3H, **E**), 4.50 (s, 6H, **G**), 3.93 (br s, 4H, **D**), 2.15 (s, 36H, **H**), -0.61 (s, 6H, **K/L/M**), -1.07 (s, 12H, **K/L**), -2.59 (s, 6H, **K/L/M**), -11.56 (s, 6H, **K/L/M**), -13.39 (s, 6H, **K/L/M**), -14.12 (s, 3H, **J**), -88.95 (s, 6H, **I**). As with the bisphosphine adducts **3^H**, **3^{Me}**, **4** methyl resonance **C** is not observed. EA: for $C_{84}H_{124}O_5P_1U_2$: calc. C 58.63; H 7.26; N 0 %. Found C 41.42; H 4.92; N 0 %. We cannot attribute the low values to anything other than the high air-sensitivity of the compound.

$(DippO)_3U(\mu-C_6H_6)U(ODipp)_2(dmpm) - \mathbf{3^H}$

1H -NMR (400 MHz, C_6H_6) δ 12.94 (br d, J = 7.22 Hz, 4H, **B**), 10.24 (br t, J = 7.22 Hz, 2H, **A**), 8.87 (br d, J = 6.87 Hz, 6H, **F**), 7.55 (br t, J = 6.87 Hz, 3H, **E**), 4.46 (s, 6H, **G**), 3.36 (s, 4H, **D**), 1.54 (s, 24H, **C**), 1.33 (s, 36H, **H**), -117.15 (s, 6H, **I**). Resonances corresponding to the phosphine are not observed in either 1H or ^{31}P NMR spectra.

EA: for $C_{71}H_{105}O_5P_2U_2$: calc. C 54.09; H 6.71; N 0 %. Found C 51.40; H 6.66; N 0 %. The low carbon analysis is attributed to carbide formation during sample combustion.

$(DippO)_3U(\mu-C_6H_5Me)U(ODipp)_2(dmpm) - \mathbf{3^{Me}}$

1H -NMR (400 MHz, C_7H_8) δ 12.48 (d, J = 7.78 Hz, 4H, **B**), 9.87 (t, J = 7.78 Hz, 2H, **A**), 8.83 (d, J = 7.53 Hz, 6H, **F**), 7.56 (t, J = 7.53 Hz, 3H, **E**), 4.83 (s, 6H, **G**), 1.29 (s, 36H, **H**), -104.99 (s, 1H, **L**), -116.78 (s, 2H, **J/K**), -118.07 (s, 2H, **J/K**). Resonances corresponding to the $U(ODipp)_2(dmpm)$ portion of the molecule are not observed with the exception of the *meta*- and *para*- protons of the aryloxide ligands. The methyl group of the bridging toluene molecule is also not observed; these resonances are likely obscured by the toluene solvent resonances. EA: for $C_{72}H_{107}O_5P_2U_2$: calc. C 54.37; H 6.78; N 0 %. Found C 54.18; H 6.58; N 0 %.

(DippO)₃U(μ-C₆H₆)U(ODipp)₂(dmpe) - **4**

¹H-NMR (400 MHz, C₆H₆) δ 12.76 (d, J = 7.58 Hz, 4H, **B**), 10.26 (t, J = 7.58 Hz, 2H, **A**), 8.85 (d, J = 7.48 Hz, 6H, **F**), 7.58 (t, J = 7.48 Hz, 3H, **E**), 3.96 (s, 6H, **G**), 1.08 (s, 36H, **H**), -121.26 (s, 6H, **I**). Resonances corresponding to the U(ODipp)₂(dmpe) portion of the molecule are largely unobserved with the exception of the arene backbone. EA: for C₇₂H₁₀₇O₅P₂U₂: calc. C 54.37; H 6.78; N 0 %. Found C 54.14; H 6.55; N 0 %.

General Synthesis of [{(dmpm)(OBMes₂)₂U}₂(μ-η⁶:η⁶-C₆H₅R)] - **5^a**

dmpm (10 μL, 0.064 mmol, 2 equiv.) was added to a magnetically stirred arene (toluene or benzene) solution (1 mL) of {U(OBMes₂)₃}₂ (66 mg, 0.032 mmol, 1 equiv.) in a 7 mL vial and the solution was allowed to stir for 15 min providing a black solution which contained the title product, and an off-white precipitate which contains the by-products. Crystals of **5^{Me}** suitable for single crystal X-ray diffraction studies were grown by slow diffusion of hexanes into the reaction mixture.

[{(dmpm)(OBMes₂)₂U}₂(μ-η⁶:η⁶-C₆H₆)] - **5^H**

¹H NMR (500 MHz, C₆D₆): δH 7.76 (**B**, 16H); 4.75 (**C**, 48H); 2.58 (**A**, 24H); -14.42 (**F**, 24H); -41.54 (**G**, 4H); -75.08 (**E**, 6H). ¹¹B NMR (160 MHz, C₆D₆): δB -16.77 (OBMes).

[{(dmpm)(OBMes₂)₂U}₂(μ-η⁶:η⁶-C₆H₅Me)] - **5^{Me}**

¹H NMR (500 MHz, C₆D₆): δH 7.62 (**B**, 16H); 6.69 (**C**, 48H); 2.05 (**A**, 24H); -5.55 (**H**, 24H); -26.09 (**I**, 4H); -77.01 (**D**, 6H, C₆H₆). ¹¹B NMR (160 MHz, C₆D₆): δB -16.67 (OBMes). MS (APPI): C₄₁H₅₈B₂O₂P₂U⁺ ([M+H]⁺): calculated 905.4684, found 905.4692 (0.8 ppm).

[{(OBMes₂)₃U}₂(μ-η⁶:η⁶-C₆H₆)] with PCy₃ - **6**

PCy₃ (28 mg, 0.1 mmol, 2 equiv.) was added to a stirred benzene solution (1 mL) of {U(OBMes₂)₃}₂ (103 mg, 0.05 mmol, 1 equiv.) in a 7 mL vial and the solution allowed to stir for 18 hours. Crystalline [(OBMes₂)₃U]₂(μ-η⁶:η⁶-C₆H₆) was obtained from slow diffusion of hexane into the reaction mixture over 3 days. Yield: 20 mg, 19%. ¹H NMR (500 MHz, C₆D₆): δH 6.40 (**B**, 24H); 2.12 (**A**, 36H); -0.63 (**C**, 72H); -81.89 (**D**, 6H). ¹¹B NMR (160 MHz, C₆D₆): δB -16.40 (OBMes).

Supplementary Information Available

Data for by-products, and full characterizing data and crystallographic experimental details are available online. CIF crystallographic data are available from the CCDC, structure codes 2042764-2042772.

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Associated content

Supporting Information available: full experimental and characterizing data for the complexes. CIF files available for the structurally characterized complexes from <https://www.ccdc.cam.ac.uk/codes/2042764-2042772>.

References and footnotes

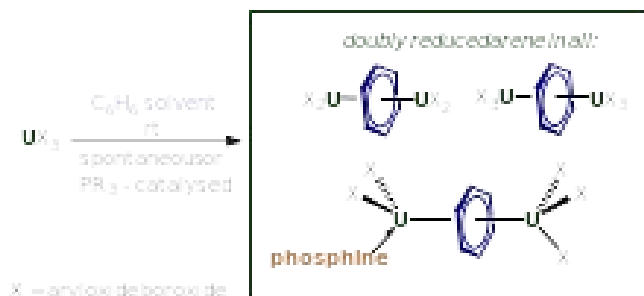
‡ Benzene adducts typically show higher standard uncertainties for M-C and CC bonds than those of substituted aromatics such as toluene due to rotational disorder.

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TOC Graphic and text



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A range of simple U^{III} UX_3 complexes bind and reduce arenes spontaneously at room temperature, forming inverse arene sandwich (IAS) complexes $X_nU(\mu-C_6D_6)U_xm$ ($n, m = 2, 3$), ODipp = $OC_6H_3^iPr_2-2,6$). Phosphines can catalyse the reactions where smaller X ligands would otherwise be unstable. Analysis of this family, and comparisons with literature examples suggests that all those reported to date can be classified as simply containing a doubly reduced arene.