**Spontaneous reduction and C–H borylation of arenes mediated by uranium(III) disproportionation\*\***

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**Supplementary information:**

Supporting information is linked to the online paper at <http://www.nature.com/nchem>. It contains full experimental details, details of the kinetic studies and X-ray diffraction experiments as well as additional computational work.

**Keywords:**

uraniu; f-element; arene; benzene reduction; biphenyl; aryloxide; amide; C-H activation; borylation; DFT

**Graphical abstract:**

**

**Abstract**

Transition-metal – arene complexes such as bis(benzene)chromium, Cr(η6-C6H6)2 are historically important to d-orbital bonding theory and have modern importance in organic synthesis, catalysis, and organic spintronics. In investigations of f-block chemistry, however, arenes are invariably used as solvents rather than ligands. Here, we show that simple uranium complexes UX3 (X = aryloxide, amide) spontaneously disproportionate, transferring an electron and X-ligand, allowing the resulting ‘UX2’ to bind and reduce arenes, forming inverse sandwich molecules [X2U(µ-η6:η6-arene)UX2] and a UX4 byproduct. Calculations and kinetic studies suggest a ‘cooperative small-molecule activation’ mechanism involving spontaneous arene reduction as an X-ligand is transferred. These mild reaction conditions allow functionalised arenes such as arylsilanes to be incorporated. The bulky UX3 are also inert to reagents such as boranes that would react with the traditional harsh reaction conditions, allowing a new *in situ* arene C-H bond functionalisation methodology converting C-H to C-B bonds to be developed.

**Main text**

Arenes have a notable history of complex formation with transition metals; both sandwich complexes such as bis(benzene)chromium, Cr(η6-C6H6)2[[1](#_ENREF_1)] and inverse sandwiches such as the triple-decker [{(C5Me5)V}2(μ-η6:η6-C6H6)][[2](#_ENREF_2)]have provided important contributions to d-orbital bonding theory and played a historic role in the growth of d-block organometallic chemistry. The binding of a neutral benzene ligand was not even considered possible in the 1950s, but today transition metal arene complexes, formed by ligand σ- and π-donation, together with metal to ligand π- and δ- back-donation are widespread and have important applications in organic synthesis and catalysis[3](#_ENREF_3). Future potential applications lie in understanding graphite-intercalated battery material behaviour[4](#_ENREF_4) and in organic spintronics[5](#_ENREF_5" \o "Maslyuk, 2006 #102). However, the metal-arene motif remains very rare for the f-block metals.

Following reports that transition metal arene complexes could be made *via* the harsh, reductive Friedel-Crafts procedure that combines an electropositive metal halide, e.g. Ti[[6](#_ENREF_6)], with Al or Mg and AlCl3, the procedure was shown to work for uranium chloride, furnishing the UIII complex [U(C6Me6)(AlCl4)3], in which the arene binds weakly as a neutral donor[7](#_ENREF_7). Similarly, coordinatively-unsaturated UIII complexes [U(ODipp)3]2[[8](#_ENREF_8)], [(C5Me4H)2U][(μ-η6:η1-Ph)(μ-η1:η1-Ph)BPh2], and [(C6Me6)U(BH4)3][[9](#_ENREF_9)], showed η6-interactions with adjacent ligand aryl or arene groups, suggestive of the compatibility of the uranium d/f valence hybrid orbitals for π and δ overlap with arenes[10](#_ENREF_10),[11](#_ENREF_11). Such covalent metal-ligand bonding interactions with soft ligands provide important evidence on the involvement of the f- and other valence orbitals in actinide bonding. Understanding this is key to the handling and separation of the actinides in nuclear waste[12-15](#_ENREF_12). In recent years some unanticipated, but remarkably robust uranium inverse-sandwiches LnU2(μ-η6:η6-C6H5R) (R = H, Me) have been made by potassium metal (or graphite-intercalated potassium) reduction of U complexes in the absence of competing Lewis bases[16-22](#_ENREF_16). Interesting physicochemical properties such as single molecule magnetism have been predicted for these[23](#_ENREF_23),[21](#_ENREF_21), sparking interest in the mechanism of magnetic exchange between the actinide centres[24](#_ENREF_24). Increasingly, uranium(III) complexes are demonstrated to reductively activate traditionally inert molecules including N2, CO, and CO2 through metal- substrate π- and δ- bonding, showing catalytic potential[25](#_ENREF_25) and suggesting more widespread uranium small molecule activation than previously thought. However, the requirement of potassium or AlCl3-type co-reactants precluded the incorporation of functionalised arenes into these (and other electropositive metal) systems. Here, we show how simple UIII complexes can spontaneously bind and reduce an arene by transferring an X ligand to a second sacrificially oxidised UIII, allowing a molecule of UX4 to be eliminated as a byproduct, providing electron and mass balance. Both amido and aryloxo UX3 complexes can successfully activate arenes thermally, even at room temperature. The formal two-electron reduction of the trapped arene enablesarene C-H borylation, proceeding *via* a new C-B bond forming mechanism. This cooperative activation of arenes is facilitated by strong U-arene δ-bonds and provides a new functionalisation methodology unique to uranium-arene compounds.

**Results**

Storage of a brown benzene solution of the common uranium(III) aryloxide [U(ODtbp)3] (Dtbp = 2,6-*t*Bu2C6H3) at 90 ºC in a sealed tube resulted in a darkening of the solution over a few days, and the formation of [{(DtbpO)2U}2(µ-η6,η6-C6H6)] **1** and two equivalents of U(ODtbp)4, Fig. 1; evidenced by 1H NMR spectroscopic analysis. Product formation is quantitative, clean and complete after six days, or up to 40 days at 20 ˚C. Brown crystals of µ-benzene **1** are isolated after drying, washing with diethyl ether to remove the U(ODtbp)4 byproduct, and toluene-recrystallisation, although the similar solubility of the two products resulted in a lower isolated yield of **1** (14 %). The analogous reaction of the common amide [U(N")3] {N" = N(SiMe3)2} proceeded similarly to [{(N")2U}2(µ-η6,η6-C6H6)] **2**, alongside the UIV byproduct [(N")2U(κ2-CH2SiMe2NSiMe3)]and HN(SiMe3)2. It is assumed that the latter two products form from the putative [U(N")4] disproportion product which would be a highly sterically congested UIV compound; a small additional amount of [(N'')2U(κ2-CH2SiMe2NSiMe3)]is also formed from a side reaction of [U(N")3] decomposition. These can be sublimed away, enabling isolation of **2** in 45 % yield, Fig. 1.



***Figure 1.*** Storage of arene solutions of UX3 (X = aryloxide, amide) results in the spontaneous formation of the inverse sandwich arene complex bound to UX2 moieties by two-electron reductive activation of the arene solvent. The reaction is quantitative for [U(ODtbp)3] but [U(N'')3] also shows a side reaction directly to metallacycle which reduces the yield. However, the relative solubilities/volatilities, i.e. ease of separation, of the two products results in far higher isolated yields for the amide sandwich **2** (45 %)than for the aryloxide sandwich **1** (14%). The biphenyl adducts bind exclusively to the same arene ring, unlike lanthanide analogues. The *tri*-tert-butyl phenol analogue **8** is accessible from the preformed inverse arene complex **2**, despite the lack of reactivity of UX3 (X=tri-*tert*-butyl phenol, 2,4,6-O-tBu3C6H2) complex towards arenes.

The trapped arene is formally reduced to a dianion, as deduced from computational studies by us (Supplementary figure S35) and others[16](#_ENREF_16),[17](#_ENREF_17), so the overall redox reaction is a partial oxidation of U, arene reduction, and X ligand transfer, *i.e.* four UIII centres reacting to form two UIII, a benzene dianion and two UIV centres. Both **1** and **2** have been fully characterised, including by X-ray crystallography (Fig. 4), and are very air-sensitive, but highly thermally robust, surviving at temperatures greater than 100 ºC. The benzene hydrogen resonates in the 1H NMR spectrum of **1** at -85.2 ppm, -82.2 ppm in the spectrum of **2**, strongly paramagnetically shifted. The solution magnetic moment is 3.8 µB per molecule for **1** and **2**. The aryloxide **1** is also accessible via a 'traditional' reduction by potassium graphite[16](#_ENREF_16),[26](#_ENREF_26). The tri-*tert*-butyl-substituted U(OTtbp)3 [U(O-2,4,6-*t*Bu3C6H2)3] does not reductively activate benzene, despite marginal steric or electronic differences[26](#_ENREF_26). However, **2** does react with the phenol HOTtbp to form [{(TtbpO)2U}2(µ-C6H6)] **8**, Fig. 1.

The binding of toluene, [{X2U}2(µ-C7H8)] (**1a**, X = ODtbp; **2a**, X = N(SiMe3)2) from UX3 takes longer than benzene, and is lower-yielding with [U(N'')3] (26%) as more uranium(IV) metallacycle forms from the side reaction. This agrees with the relative ease of the reduction of the arenes. UX3 also reacts with molten biphenyl (90 °C, 6 days) to give inverse-sandwiches [{X2U}2(η-C12H10)] X = ODtbp **3** isolated yield:10%, X = N(SiMe3)2 **4** isolated yield:69%, with quantitave formation of µ-biphenyl but lower isolated yield of **3** due to fractional recrystallisation difficulties. Spectroscopy and crystallography (Supplementary figures S24, S25) show coordination through a single phenyl ring, with no dynamic behaviour.

**Functionalised arene chemistry**

These reactions represent the first spontaneous multi-electron reductive activation of arenes in f-block chemistry, and as such an opportunity to incorporate functionalised arenes which would be incompatible with potassium reductants, Friedel-Crafts conditions, or even heat. Phenylsilane, PhSiH3, which is incompatible with group 1 metals, reacts with [U(ODtbp)3] to make [{(DtbpO)2U}2(µ-C6H5SiH3)] **5**, along with two equivalents of [U(ODtbp)4] Fig. 3, but isolation by fractional crystallisation was not possible due to the near-identical product solubilities.

Borylation of the reduced, trapped arene is also now possible, either by adding borane HBR2 to [U(ODtbp)3] in the chosen arene, or to the arene product. This represents a new type of carbon-boron bond forming reaction, and one not possible with potassium reductants. Further, since arene-exchange between the UX2 groups of inverse sandwiches has precedent[18](#_ENREF_18), this has potential to become catalytic.



***Figure 2.*** Reactivity of UX3 complexes with functionalised arenes which are incompatible with standard reductive routes for metal-arene complex formation, and displacement of the boryl-functionalised arenes.

A mixture of [U(ODtbp)3] and the borane HBBN (9-bora-9-bicyclononane) in benzene heated to 90 °C generated the product of µ-arene formation and subsequent C-B bond formation [{(DtbpO)2U}2(µ-C6H5BBN)] **6**, along with two equivalents of the uranium(IV) byproduct [U(ODtbp)4], and dihydrogen, Fig. 2; see also Fig. 4 below for the molecular structure. The same product **6** can also be made from treatment of **1** with HBBN in arene solvent at 90 °C for 16 hours quantitatively yielding the borylated product (45% recrystallised). Toluene and biphenyl are *para-*functionalised at the sandwiched arene, in yields of 34% and 11%, respectively from the one pot reaction, low again only due to fractional crystallisation of the product. Of significant interest is the experiment where [U(ODtbp)3] and HBBN were reacted together in molten naphthalene over 17 hours. Although stable µ-naphthalene compounds could not be isolated (see below), the borylated naphthalene compond was isolated after fractional recrystallisation in low yield presumably because the boryl functional group removes electron density from the ring stabilising the naphthalene inverse sandwich, (SI section 3). The functionalised naphthalene can also be liberated by reaction with benzene over days at 90 °C, which binds in preference, Fig. 2.

**Kinetic study, generalisation to other arenes and weak C-H bonds to probe the mechanism**



***Figure 3.*** Reactions of UX3 with dihydroanthracene to test for X radicals and reactions that demonstrate that fused arenes such as naphthalene can bind and influence the reaction rate, and reactions with transition metal (η-arene) complexes. The results imply that no free X radical is formed, supporting the calculations discussed below of concerted X-ligand and electron transfer between two uranium centres. The fused-arene results also support the importance of a sterically accessible U-X-U bridge forming process.

The computational study, see below, for large X ligands suggests that a key step in the reaction is the formation of a binuclear complex such as **A**, Fig. 3; an arene coordinates and is reduced by one U centre as an X ligand transfers to an adjacent UX3 to form the intermediate (arene)UX2, eliminating UX4. In agreement, a kinetic analysis of the transformation of UX3 to [{X2U}2(µ-C6H6)] and UX4 for X = ODtbp shows that the reaction is *pseudo-*second order in UX3 (arene as the solvent). This explains the long reaction times required for complete conversion and the lack of reaction with one equivalent of arene in alkane solvents.

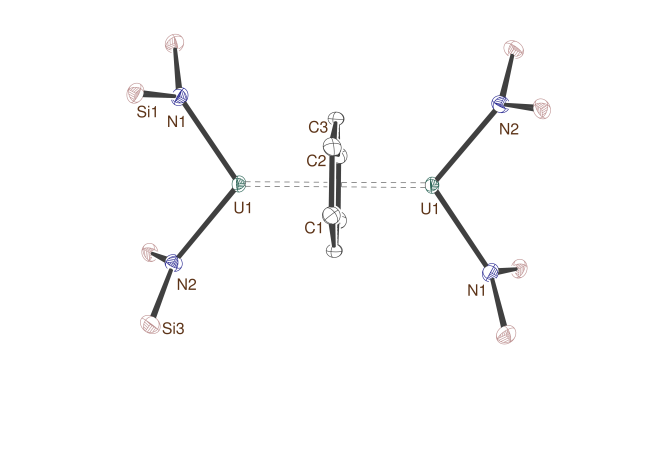
A conceivable alternative mechanism could involve the homolytic cleavage of one U-X bond to make a formally UII UX2 fragment in solution, releasing an X radical which should readily cleave weak C-H bonds, such as the benzylic C-H in 9,9'-dihydroanthracene, DHA. No H-atom abstraction product, indicating no radical involvement, was formed in a reaction to form **2** carried out in the presence of excess DHA, Fig. 3.

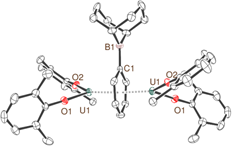
The fused, less aromatic arenes naphthalene and anthracene are significantly easier to reduce than benzene[27](#_ENREF_27),[28](#_ENREF_28) but inverse sandwiches are never isolated if benzene is present, in agreement with the identification of a much stronger U2(μ-arene) interaction. The isolation of the borylated naphthalene compound **10** shows that a diuranium μ-naphthalene sandwich can be formed but this complex is thermally much less stable than **1** or **2**, and can only be isolated if borylated *in situ* to give **10** described above; we have not been able to isolate any anthracene product. However, the addition of a stoichiometric amount of either naphthalene or anthracene to the reaction to form the benzene sandwich complexes appears to reduce the yield of U(ODtbp)3–derivedμ-arene product (Fig. 3, and Suplementary section S3.1, S3.3), but slightly increased yields for [U(N'')3].

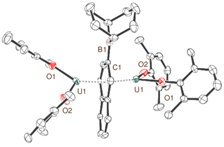
Synthesis of mixed-metal arene compounds were attempted through the reaction of UX3 with [(C6H5OMe)Cr(CO)3] and [Cr(C6H6)2]but the only isolable complex formed was the *iso*-carbonyl [(ODtbp)3U(κ-OC)Cr(CO)2(C6H5OMe)] **7**.

**Structures of the inverse sandwich complexes**

Single crystal X-ray diffraction studies of eleven inverse-arenes were carried out, all having similar U2 arene cores. The molecular structures of **1** and **2** (SI.4 and Fig. 4a) show essentially planar benzene rings (maximum displacement from C6 plane = 0.06 Å in **1**). The UX2 moieties in **1** are mutually twisted out of the O1-U1-U2-O2 plane by 54º on average, and away from a coplanar N1-U1-U2-N2 by 2˚ in **2**. The U-U distances are very similar (4.251 Å in **1**,4.249 Å in **2**,4.308 Å in **10**). The average benzene C-C distance is 1.451 Å in **2**, *c.f.* C-C = 1.438(13) Å in [{U(N[R]Ar)2}2(*µ*-C6D6)][[16](#_ENREF_16)], C-C = 1.40 Å in benzene.

a.

b.

c.

**Figure 4.** Thermal ellipsoid drawings of the molecular structures of [{X2U}2(µ-arene)] complexes: a) [{[(SiMe3)2N]2U}2(µ- C6H6)] **2**, showing the simplicity of the arene-reduced system from a common amide starting material; b) [{X2U}2(µ-C6H5BBN)] **6** X = O-2,6-tBu2C6H4, ODtbp, and c) [{X2U}2(µ-C10H7BBN)] X = O-2,6-tBu2C6H4, ODtbp **10** showing two variations of boron-functionalised arenes: 50 % ellipsoid probabilities. Lattice solvent molecules, CH3 groups and hydrogen atoms omitted for clarity. Selected distances (Å) and angles (º): **2**: U1-U1' 4.249, U1-N1 2.318(3), U1-N2 2.316(3), U-C ave 2.573, C-C ave 1.451 (*c.f.*average C-C distance of 1.452 Å (range 1.442(9) - 1.462(9) Å) in **1** and C-C distance in benzene of 1.40 Å), N2-U1-N1 106.40(9), N1-U1-U1'-N2 1.69. **6**: U1-U1’ 4.256, U1-O1 2.125(3), U1-O2 2.143(3), U-C ave 2.577, C-C ave 1.455, O2-U1-O1 107.86(12), O1-U1-U2-O2 34.7. **10**: U1-U1’ 4.308, U1-O1 2.146(3), U1-O2 2.123(3), U-C ave 2.641, C-Cbound ring ave 1.457, O2-U1-O1 107.13(10), O1-U1-U2-O2 33.15. See section SI.4 for the structures of the benzene product **1**, and the toluene, biphenyl, mixed X-ligand, borylated toluene and biphenyl sandwich products.

**Computational study of the mechanism of formation and C-H borylation**

We have used f-in-core relativistic effective core potentials[29](#_ENREF_29),[30](#_ENREF_30) to build a thermodynamic picture of the mechanism, considering both electron and ligand transfer[31-33](#_ENREF_31), and many steps. The pathway in Fig. 5 was found most favourable for large X ligands (for smaller X see route B, Fig. SI.31). The first step shows concerted benzene binding and X transfer between two UX3 fragments and benzene, forming UX2(benzene) and UX4, **II**. A second concerted coordination/X transfer process then takes place, where one UX3 fragment associates to the benzene unit of UX2(benzene) as a second UX3 accepts a ligand from it, giving the final products, **III**.



**Figure 5**. Four different calculated mechanisms of formation of [{X2U}2(µ-η6,η6-C6H6)] from UX3 and benzene. **a-d,** a, X=OPh; b, X=ODmp **1'**; c, X=N(SiH3)2; d, X=N(SiMe3)2 **2'**), with the differences in energies clearly dependent on the identity of X. The first step is best calculated as a concerted benzene binding and X transfer between two UX3 fragments. The decomposition of UX4 to cyclometallated product and XH is included in computed energies for X = N(SiMe3)2. OPh = OC6H5, ODmp = O-2,6-Me2-C6H3.

The transition states were calculated for case a, (X = OPh), and while not computed directly for larger X due to their complexity, are expected to be closely related to **VI\_VII\_TS** from pathway A (see Figure SI.31) giving an overall barrier of ca. 5 kcal.mol-1, lower than would be expected from the experimental data, probably due to the smaller X used here, and the absence of diffusion considerations. Additionally, in the aryloxide system the transition state geometry contains a stabilising η6 interaction between the uranium centre in UX3 and the C6 ring of a spectator phenoxide ligand of UX3(benzene) (Fig. SI.34); this may help account for the observed differences in reaction rate, and the effects of added fused arenes.

The computed Kohn-Sham orbitals of [{(PhO)2U}2(µ-η6,η6-C6H6)] corroborate previous discussions[16](#_ENREF_16),[21](#_ENREF_21),[29](#_ENREF_29) of a 4-electron U-arene-U interaction involving δ overlap between both uranium centres and the first and second Lowest Unoccupied Molecular Orbitals (LUMOs) of the arene. The same-ring binding of biphenylhighlights the stability of this 4e interaction. Computationally, same-ring **3'** [{(PhO)2U}2(µ-η6,η6-C12H10)] was found to be +17.6 kcal.mol-1 more stable than the staggered-ring binding arrangement, **3″** [{(PhO)2U}2(µ-η6,η6'-C12H10)] which requires two separate 2e U-arene interactions and consequent disruption of the 12-π system of the biphenyl fragment (Fig. SI.35). The stabilities of X2U(arene)UX2 were tested through their displacement with benzene (see SI Section 5), showing a trend in stability C6H6 > C6H5C6H5 > C6H5CH3 >> C10H8, with a 9.6 kcal.mol-1 free energy range.

Borylation of the arene in X2U(arene)UX2 by HBBN (with loss of H2) was computed to be exergonic, with average ΔG = -9.4 kcal.mol-1 (SI Section 5). This is due to increased stability upon borylation, *not* dihydrogen formation.

For the mechanism of borylation of [{(PhO)2U}2(µ-η6,η6-C6H6)], two pathways were considered: an electrophilic aromatic substitution (EAS) pathway, where HBBN adds to a carbon of the arene to form an intermediate before losing dihydrogen; and a 1,2-addition pathway, where the B–H bond of HBBN adds across a C–C bond of the arene (*cf* borane addition to an alkene) to give an intermediate which loses dihydrogen. However, high barriers to intermediate formation and to H2 loss discounted the latter. For the former, a variant of an EAS pathway, two intermediate geometries **A** and **B** were considered with HBCH dihedral angles of 0° and 180° respectively (see Figure 6). **B** was located as an adduct at ΔG = -1.5 kcal.mol-1 but does not allow dihydrogen formation. However, optimisation of **A** gave an unusual and unexpected transition state (ΔG‡ = +34.5 kcal.mol-1) representing a concerted process for the borylation. The transition state geometry exhibits a B–C distance of 1.725 Å (*cf* 1.754 Å in **B**), a long C–H1 distance (1.420 Å) and a short H–H distance (1.071 Å).



**Figure 6**. Two different computed mechanisms of borylation of [{(PhO)2U}2(µ-η6,η6-C6H6)]. A concerted process through **A** (upper) where the H1-C-B-H2 dihedral angle is 0° leads to products, whereas the alternative lower route with a H1-C-B-H2 dihedral angle of 180° gives an adduct, **B**, which does not allow dihydrogen formation. Energies are written in kcal.mol-1, selected distances are in Å.

**Discussion**

We propose that reducing uranium(III) complexes can form adducts with arene molecules with relative ease in arene solution, and where it is possible for one X ligand to bridge and subsequently transfer to another UX3, concomitant with electron transfer from the nascent UX2 fragment, arene reduction becomes possible. This agrees with the lack of reactivity with DHA that suggests a non-radical process. The fused arene inverse sandwich products appear much less thermally stable than the benzene complexes, and are never isolated in the presence of benzene, despite the relative ease of reduction of the fused arene. This allows the displacement of the borylated-naphthalene by benzene. The mono-arene bridge is clearly a robust unit and may be described best formally as a dianion between the two UIII centres[11](#_ENREF_11),[16](#_ENREF_16),[29](#_ENREF_29),[34](#_ENREF_34), with up to four electrons involved in the bonding. The reaction of [U(N'')3] to sandwich **2** shows a small yield enhancement in the presence of a readily reducible fused arene. If an intermediate such as **A** (Fig 3) has a lower energy barrier of formation, but is less thermodynamically stable than the benzene sandwich, then the observations and calculations agree. The addition of fused arene to [U(ODtbp)3] reactions marginally lowers the yield of sandwich **1**, but this appears to be due to the additional formation of byproducts, perhaps from the decomposition of a fused arene sandwich intermediate. These observations also align with the fact that [U(ODtbp)3] readily forms adducts with Lewis bases, unlike [U(N")3][8](#_ENREF_8),[35](#_ENREF_35). Further, some arene pre-complexation prior to X-ligand transfer would explain how the bulkier [{(TtbpO)2U}2(µ-η6,η6-C6H6)] **8** can only be formed through post-synthesis ligand exchange (Fig. 1). We noted previously that the *di*-tert-butyl-substituted [U(ODtbp)3] can bind and reduce dinitrogen but the reaction is readily reversed, whereas [U(OTtbp)3] forms robust [{(TtbpO)3U}2(µ-η2,η2-N2)] with interlocking aryl rings forming a rigid cage around the U2N2 core.[26](#_ENREF_26) Also, [{U(ODipp)3}2][[8](#_ENREF_8)] and [U{N(SiMe2Ph)2}3][[36](#_ENREF_36)], which both feature U…( η -arene) interactions in the solid state, do not activate benzene in our hands. Finally, if the X ligands are small, solvent reduction is computationally allowed but a range of additional unwanted byproducts now also become accessible.

The reducing capabilities of the simplest UIII amides and alkoxides are reported as around -1.2 V (vs ferrocene)[37](#_ENREF_37), significantly weaker than that for potassium metal (lower than -2.3 V); it appears the formation of strong U-arene covalent interactions and stable UIV byproduct help drive the reduction. The resulting absence of X radicals or strong Group 1 metal reductants allows the incorporation of PhSiH3 and the borane HBBN reagents; these are incompatible with group 1 metals and reductants, forming radical anions and decomposition products under conventional conditions[38](#_ENREF_38),[39](#_ENREF_39). Theformation of arene-BBN from an arene is possible either by addition of HBBN to the reaction mixture, or to the pre-formed inverse sandwich, the latter proceeding faster as the arene is already bound and activated.

Arylboron compounds have intriguing properties and are important building blocks for C-C bond formation in chemical synthesis[40](#_ENREF_40), but arenes are well documented to be inert to boranes in the absence of a catalyst. It has been shown that complexes such as [Cp\*Rh(*η*4-C6Me6)] (Cp\* = C5Me5)[41](#_ENREF_41),[42](#_ENREF_42), which can oxidatively add arene C-H bonds, catalyse the high temperature borylation of arenes with HBpin (pin = pinacolate) to form PhBpin. Alternatively, abstraction of the halide from ClBX2 using silylium carborane [Et3Si][[*closo*-1-HCB11H5Br6] can generate a highly electrophilic BX2 cation which is sufficiently reactive to attack arenes via a traditional electrophilic aromatic substitution (EAS) mechanism[43](#_ENREF_43),[44](#_ENREF_44).

This new type of C-B bond forming reaction is so far unique to uranium, involving activation of the arene substrate rather than the normal activation of the electrophile, or oxidative addition of the arene as seen in transition metal systems.[45](#_ENREF_45) Calculations suggest an unusual concerted variant of electrophilic aromatic substitution in which the B–C bond forms as the C–H breaks while the hydrogens are effectively coupled at the boron centre. During this, the hybridisation at carbon, and therefore the strong U-arene-U bonding, remains relatively unchanged, apparently stabilising the concerted mechanism. The less common substitution pattern of borylation of naphthalene at the 2 position is probably influenced by steric factors.

**Conclusions**

The formation of two uranium-arene bonds and tetravalent UX4 byproducts provides sufficient driving force for the first spontaneous and multi-electron reductive activation of an arene in f-block chemistry. A formal disproportionation process is invoked in which two equivalents of UX4 are liberated as one dinuclear molecule of X2U(µ-arene)UX2 is formed, involving a concerted transfer of X ligand and arene binding/reduction. The reaction is bimolecular in UX3, occurs at room-temperature for X = ODtbp, and is accelerated by heat, and the products are remarkably thermally stable, preferring mutual coordination of a single arene in the U(µ-arene)U fragment with covalent δ-symmetry bonding involving up to four electrons, in contrast to transition metal analogues in which π-interactions are more important. The absence of harsh reducing conditions and significant arene reductive activation allows the formation of µ-phenylsilane adducts and *in situ* arene C-H borylation to occur, a new type of homogeneous C-H borylation reaction. Calculations suggest an unusual mechanism in which the strongly reduced arene undergoes a form of electrophilic aromatic substitution in which the C-B and H-H bonds form in the transition state with very little perturbation of the U-bound arene. This differs substantially from previously found mechanisms for both main group and transition metal reagents. Finally, the new co-operative small molecule activation mechanism, in which a metal centre can spontaneously free up its own valence electrons for the reductive activation of a nearby small molecule by interaction with an adjacent metal centre, might have applicability in other areas of chemistry inasmuch as it allows a complex to behave as a stronger reductant than formal redox potentials would suggest.

**Methods summary**

Working under a dry, oxygen-free dinitrogen atmosphere, with reagents dissolved or suspended in non-polar, aprotic solvents, and combined or isolated using cannula and glove box techniques, arene solutions of the trivalent uranium coordination complexes UX3 (X = bulky amide, aryloxide) were heated at 90 ºC for between two and six days, or stored at 20 ºC for up to 40 days, to afford the new, reduced arene inverse sandwich complexes of the UX2 fragment, bimetallic {X2U}2(µ-arene) and the tetravalent byproduct UX4 (two equivalents per arene complex). The complexes could be separated by fractional crystallisation or sublimation of the more volatile by-products. The aryloxide **1** is also accessible via a 'traditional' reduction by potassium graphite, i.e. the reaction of [U(ODtbp)3] with potassium graphite (KC8) in arene, with KODtbp or K[U(ODtbp)4] being formed as a byproduct; the poor solubility of the potassium salts results in easier product isolation so **1** is isolated pure in 28% yield. Repetitions of the reaction with different arenes such as biphenyl confirmed the preference for binding to the same arene ring of polyphenyl hydrocarbons, and the generality of the reaction. Inverse sandwiches of the fused, less aromatic arenes naphthalene and anthracene are never isolated if benzene is present, despite being significantly easier to reduce than benzene. This observation is in agreement with the computational identification of a much stronger U2(μ-arene) interaction for the C6 arene ring. The reduction potential of benzene in DME, *E*red, is -3.93 V[27](#_ENREF_27), for biphenyl is -3.14 V, for naphthalene -3.10 V and for anthracene is -2.47 V (values relative to the ferrocene/ferricenium couple)[28](#_ENREF_28). However, the addition of a stoichiometric amount of either naphthalene or anthracene to the reaction to form the benzene sandwich complexes appears to reduce the yield of [U(ODtbp)3]–derivedμ-arene product (Fig. 3, and SI Section 3.1 and 3.3), but slightly increases yields for UN''3. While this is only a small effect, it agrees with the calculated intermediate **A** in Fig 3, in which anthracene binding is easier.

Attempted syntheses of mixed-metal arene compounds: The reaction of [U(ODtbp)3] with equimolar [(C6H5OMe)Cr(CO)3] gave only the dark red *iso*-carbonyl [(ODtbp)3U(κ-OC)Cr(CO)2(C6H5OMe)] **7**, characterised by X-ray diffraction (Fig. SI.26) and a band at 1741 cm-1 in the FTIR spectrum for the UIII*-iso*-carbonyl stretch. No reaction between [U(N'')3] and [(C6H5OMe)Cr(CO)3], or either UX3 and [Cr(C6H6)2]was observed.

The mild reaction conditions allowed the reaction with phenylsilane, PhSiH3 or alkylboranes R2BH. Phenylsilane reacts with [U(ODtbp)3] to make [{(DtbpO)2U}2(µ-C6H5SiH3)] **5** at 90 ˚C over a few days, and at 20 ˚C over 17 days, along with two equivalents of [U(ODtbp)4] byproduct, but isolation by fractional crystallisation was not possible due to the near-identical product solubilities. In the presence of an alkylborane, the reactions of UX3 generate new C-B functionalised µ-arene inverse sandwiches, and a new type of arene C-H bond functionalisation. All compounds were characterised by a variety of methods, including elemental analysis, magnetic moment measurements, mass spectrometry, NMR spectroscopy, and single crystal X-ray diffraction studies.

Density Functional Theory (DFT) calculations on highly-correlated, open-shell actinide systems have gained increasing credibility through the broken symmetry approach. However, SCF (Self-Consistent Field) convergence problems persist[29](#_ENREF_29). Following recent developments by others[30](#_ENREF_30), we have found the use of f-in-core relativistic effective core potentials efficient and accurate. We have generalised their use in polynuclear, redox active organometallic actinide and lanthanide calculations[31-33](#_ENREF_31), and applied them herein. DFT calculations on the potential modes of reactivity for a range of modelcompounds of UX3 were carried out using the Gaussian 03 program *via* the B3PW91 method. 6-31G\*\* basis sets were used for C, H, N and O and the Stuttgart-Dresden relativistic Effective Core Potential (ECP) and associated basis sets, for Si and U (small core). Basis sets augmented with d-polarisation function in the case of Si (ζ = 0.284). Large core description of U adopted the ECP80MWB quasi-relativistic pseudopotential with associated ECP80MWB-AVTZ basis sets, augmented with a single f-polarisation function from ECP80MWB2f. Geometry optimisations were performed without constraints. Minima and transition states were subjected to analytical frequency calculations and transition states further characterised through IRC (Intrinsic Reaction Coordinate) calculations.

**Competing Interests Statement** The authors declare that they have no competing financial interests.

**Author Contributions** SMM synthesised and characterised the compounds and analysed the data. PLA generated and managed the project, helped analyse the data, and wrote the manuscript. DMcK and LM carried out and interpreted the computational analyses.

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