Despite the fact that non-aqueous uranium chemistry is over 60 years old, most polarised-covalent uranium-element multiple bonds involve formal uranium oxidation states IV, V, and VI. The paucity of uranium(III) congeners is because, in common with metal-ligand multiple bonding generally, such linkages involve strongly donating, charge-loaded ligands that bind best to electron-poor metals and inherently promote disproportionation of uranium(III). Here, we report the synthesis of hexauranium-methanediide nanometre-scale rings. Combined experimental and computational studies suggest overall the presence of formal uranium(III) and (IV) ions, though electron delocalisation in this Kramers system cannot be definitively ruled out, and the resulting polarised-covalent $\text{U}=\text{C}$ bonds are supported by iodide and $\delta$-bonded arene bridges. The arenes provide reservoirs that accommodate charge, thus avoiding inter-electronic repulsion that would destabilise these low oxidation state metal-ligand multiple bonds. Using arenes as electronic buffers could constitute a general synthetic strategy by which to stabilise otherwise inherently unstable metal-ligand linkages.
In recent years, motivated by a need to develop better extractants to reduce the volume of fission waste products in nuclear fuel cycles\(^1\), there has been sustained interest in probing the chemical bonding in uranium-element linkages\(^2\). Thus, once limited to uranyl(VI) chemistry, polarised-covalent uranium-element multiple bonding has flourished in response to the above need, to now include carbenes, imides and nitrides, phosphinidenes, arsindenes and arsenidos, mono-oxo and heavier chalcogenidene \(^3\)\(^-\)\(^8\). However, although polarised-covalent uranium-element multiple bonds are now relatively common, they mostly encompass the IV, V, and VI oxidation states of uranium\(^9\)\(^-\)\(^11\) even though non-aqueous uranium research is over 60 years old. This situation is perhaps not surprising because polarised-covalent metal-ligand multiple bonds employ charge- and electron-loaded ligands that favour high oxidation state metal ions, and low oxidation state uranium(III) is prone to disproportionation in the presence of strong donor ligands and typically engages in ionic, lanthanide-like bonding that is ill-suited to covalent metal-ligand multiple bonding. This is fundamentally different to amide (\(R\text{C}=\text{NH}\)) and alkoxide (RO\(+\)) complexes, where covalent/dative bonding combinations may occur, or \(\mu\)-heterocyclic/mesoionic carbenes, CO, \(\text{N}_2\), and NO complexes, where the uranium(III)-element bonding is of dative donor-acceptor character\(^13\)\(^-\)\(^21\).

Transition metal carbenes with polarised-covalent M=C double bonds have been known for decades, but it was not until 1981 that the first U=C double bond was isolated in the uranium(IV)–carbene complex \([\text{U}(\eta^6-\text{C}_6\text{H}_6)\{\text{C}(\text{H})\text{PMe}_2\text{Ph}\}]\)\(^22\). After initial advances\(^23\)\(^-\)\(^26\) U=C double bond chemistry fell dormant for nearly 30 years with only occasional matrix isolation and reactive-intermediate contributions to the area\(^27\)\(^-\)\(^35\). The area was rejuvenated from 2009 onwards\(^36\)\(^-\)\(^54\), principally using pincer carbene-like methanediide ligands such as BIPMR \([\text{BIPMR}=\text{C}((\text{PPh}_2\text{NR})_2; \text{R}=\text{SiMe}_3\text{TMS})\])\(^55\), \(2,4,6\)-Me\(_2\)C\(_6\)H\(_4\) (Mes), \(2,6\)-Pr\(_2\)C\(_6\)H\(_3\) (Dipp)\] or alkoxide (RO\+) complexes, where covalent/dative bonding combinations may occur, or \(\mu\)-heterocyclic/mesoionic carbenes, CO, \(\text{N}_2\), and NO complexes, where the uranium(III)-element bonding is of dative donor-acceptor character\(^13\)\(^-\)\(^21\).

During the dormancy of covalent uranium-carbene chemistry, inverted sandwich diuranium(III)-carbon double bond presents an inherent and unmet challenge. During the dormancy of covalent uranium-carbene chemistry, inverted sandwich diuranium–arene complexes emerged. The first examples of such complexes were \([\text{U}[\text{RNC}_{6}\text{H}_{5}\text{H}_{3}-3,5-\text{Me}_{2}]_{2}]\{\text{MC}=\text{N}-\text{Ph}\}^{-\text{Ph}_{2}}\text{C}_{6}\text{H}_{4}\text{Me}_{2}\}\)] (R = \text{Bu} or adamantyl)\(^56\)\(^,\)\(^57\) and then \([\text{U}[\text{C}_{6}\text{H}_{5}]_{2}]_{2}\{\text{MC}=\text{N}-\text{Ph}\}^{-\text{Ph}_{2}}\text{C}_{6}\text{H}_{4}\text{Me}_{2}\]\)\(^58\), and subsequently the area developed with over 40 reported variants of the general form \(\text{L}_n\text{U}(\mu\text{-arene})\text{U}\_n\) (L = anionic ligand, i.e. amide, cyclopentadienyl, halide, BIPMR\(^\text{TMS}^\text{H}\))\(^59\). In a wider context, arene ligands have proven their ability to support low oxidation state metal ions including even formal uranium(II)\(^60\)\(^,\)\(^61\). Two classes of inverted sandwich diuranium complexes have emerged, \(\text{L}_n\text{U}(\mu\text{-arene})\text{U}\_n\) complexes containing \(\text{C}_{6}\text{-arene} \text{dianions and uranium(III) ions, and L}_1\text{U}(\mu\text{-arene})\text{U}_{\text{L}}\) complexes exhibiting \(\text{C}_{6}\text{-arene tetaanions and uranium(V) centres}\)\(^59\)\(^,\)\(^62\)\(^,\)\(^63\). Despite the well-developed nature of the area, it is germane to note that all these complexes are of a ‘one-dimensional’ form \(\text{L}_n\text{U}(\mu\text{-arene})\text{U}\_n\) with a maximum of two uranium ions, where the arenes act as electron reservoirs\(^65\).

Here, we report the synthesis and characterisation of hexauranium nanometre-scale rings that formally contain uranium(III)- and uranium(IV)-methanediides supported by alternating halide and arene bridges. Such a bonding arrangement is facilitated by a reservoir of \(\delta\)-bonding to the arene bridges, thus circumventing the inherent mismatch of strong dianionic donor ligands to low oxidation state uranium(III) that would otherwise disproportionate. Thus, rather than the arene being the functional group focus, here it is overtly performing a role as an ancillary, facilitating ligand to stabilise another metal-ligand functional unit. These ‘two-dimensional’ polyuranium complexes also demonstrate that it is possible to go beyond the previous ‘one-dimensional’ diuranium–arene limit, perhaps paving the way to exploitation in the preparation of novel nanoscale magnetic assemblies\(^66\).

### Results

#### Synthesis and exchange reactions.

Previously, we reported that reducing the uranium(IV) complex \([\text{U}[\text{BIPMTMS}]\{\mu-\text{I}\}]_{2}\) \(^1\) with \(\text{KC}_{6}\) in toluene/THF gave the di(uranium(III)-methanediiodide)arene complex, \([\text{U}[\text{BIPMTMSH}]\{\mu-\eta^6\text{-Ph}_{2}\text{C}_{6}\text{H}_{5}\}]\) \(^2\). The reaction is postulated to generate a uranium(III)-intermediate that deprotonates THF; we therefore envisaged that reducing 1 in the absence of THF might provide a route to uranium(III)-methanediides. Electrochemical interrogation of 1 in THF (see Supplementary Methods and Supplementary Fig. 1), unfortunately the only compatible solvent in which to electrochemically study 1, reveals two irreversible reduction processes \((E_{\text{1/2}}=-0.72 \text{~V} \text{~and} -2.45 \text{~V} \text{vs.} \text{Fc/Fc}^+)\) accompanied by deposition of uranium(0). This indicates that reduction of this complex is realistic with alkali metals, though the putative uranium(III) product is not stable in that scenario and disproportionate to uranium(0) and uranium(IV) and/or attacks the THF solvent. Therefore, 1 was reduced with four equivalents of \(\text{KC}_{6}\) in toluene, and after work up the hexauranium ring complex \([\text{U}[\text{BIPMTMS}]\{\mu-\text{I}\}]_{2}\{\mu-\eta^6\text{-Ph}_{2}\text{C}_{6}\text{H}_{5}\}]\) \(^3\), Fig. 1, was isolated.

As with other diuranium–arene complexes that contain formal uranium(III) ions\(^58\), we find that 3 undergoes toluene–benzene exchange to give \([\text{U}[\text{BIPMTMS}]\{\mu-\text{I}\}]_{2}\{\mu-\eta^6\text{-Ph}_{2}\text{C}_{6}\text{H}_{5}\}]\) \(^4\), Fig. 1 and Supplementary Fig. 2. Complexes 3 and 4 crystallise from arene solutions in poor, but reproducible, yields of 12 and 1%, respectively, when prepared directly in either case. The crystalline products are only sparingly soluble in hydrocarbon and arene solvents; ~6 mg of 3 dissolves in 1 ml of hot \(\text{D}_{6}\)-benzene, with the majority of the sample precipitating within 1 h, and 4 is even less soluble in \(\text{D}_{6}\)-benzene (~1 mg in 1 ml). The addition of coordinating solvents to complexes 3 and 4 (e.g. \(\text{Et}_2\text{O}, \text{THF, MeCN, pyridine})\) causes decomposition.

#### Solid-state structures.

The solid-state structures of 3-6C\(_6\)H\(_4\) and 4-26C\(_6\)H\(_4\) were probed by single crystal X-ray diffraction, Fig. 2a and b and Table 1. These complexes are very similar, so only complex 3 is depicted and discussed (see Supplementary Fig. 3 for the structure of 4-26C\(_6\)H\(_4\)). Complex 3 crystallises as a hexauranium ring with a diameter of ~2.5 nm. The ring topology is constructed from six uranium ions bridged by alternating arene and iodide ligands, with the remaining coordination sphere of each uranium ion completed by a BIPMTMS ligand. The rings adopt extended chair-type conformations, where \(U(1), U(1A), U(3)\), and \(U(3A)\) are essentially co-planar, and \(U(2)\) and \(U(2A)\) each reside 2.108(6) Å above and below the mean plane.
Interestingly, the crystal structure of uranium(IV) centres \([\text{U}^\text{III}]\) and uranium(IV) ions are present; \(\text{U}^\text{III}\) and \(\text{U}^\text{IV}\) correspond to a mixture of uranium(III/IV) ions with the BIPMTMS ligands disordered over two locations \([\text{U}^\text{III/IV}]\). This accounts for three uranium(III) and three uranium(IV) ions required for overall charge neutrality of 3.

The \(\mu^6\eta^6\)-arene rings in 3 are approximately planar and exhibit a wide range of U–C distances [3: range 2.577(9)–2.723 (9) Å], with mean U···U [3: 4.4466(5) Å] and U···arenecentroid [3: 2.224(4) Å] distances that are typical of uranium(III)–arene complexes, and these compare to corresponding values in 2 of 2.553(7)–2.616(7) (U–C), 4.2836(7) (U···U), and 2.142(4) (U···toluenecentroid) Å. The U···toluenecentroid···U angles in 3 deviate

The BIPMTMS ligands in 3 adopt open book\(^{38}\) configurations with short U–C distances [3: range 2.30(3)–2.47(2) Å] that correlate with the trend observed in previously reported uranium–BIPMTMS complexes: uranium(IV)–\([\text{U}^{\text{BIPMTMS}}(\mu-\text{Cl})_2(\text{THF})]\), U = C = 2.322(4) Å;\(^{39}\) uranium(V)–\([\text{U}^{\text{BIPMTMS}}(\text{Cl})_2(\text{I})]\), U = C = 2.268(10) Å;\(^{39}\) uranium(VI)–\([\text{U}^{\text{BIPMTMS}}(\text{Cl})_2(\text{O})]\), U = C = 2.184(3) Å.\(^{43}\) These uranium–carbon distances confirm that the BIPMTMS ligands in 3 and 4 are methanediides, in contrast to the methanides in 2 [U–C methanide = 2.753(9) Å].\(^{43}\) Interestingly, the crystal structure of 3 hints that localised uranium (III) and uranium(IV) ions are present; \(\text{U}^\text{III}\) and \(\text{U}^\text{IV}\) correspond to a mixture of uranium(III/IV) centres [U = C = 2.398(7) Å], U2 and U2A are uranium(III) ions [U = C = 2.413(8) Å], and U1 and U1A correspond to a mixture of uranium(III/IV) ions with the BIPMTMS ligand disordered over two locations [U = C = 2.30(3) and 2.47(2) Å]. This accounts for three uranium(III) and three uranium(IV) ions required for overall charge neutrality of 3.

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**Fig. 1** Synthesis of complexes 2, 3, and 4 along with definitions of computational models used in this study. See ref. \(^{43}\) for the synthesis of complex 2.

**Fig. 2** Molecular structure of 3 at 90 K and displacement ellipsoids set to 40%. a Full structure with hydrogen atoms, lattice solvent, and the disordered Ph\(_3\)PCPPh\(_2\) portion of the BIPMTMS coordinated to U1/U1A are omitted for clarity. b Structure highlighting the U\(_6\)(µ-I)\(_3\)(µ-Cl)\(_2\)(C\(_6\)H\(_8\))\(_3\) core with hydrogen atoms, lattice solvent, silyl-methyls, disordered P-phenyls bar the ipso-carbon, and the disordered Ph\(_3\)PCPPh\(_2\) portion of the BIPMTMS coordinated to U1/U1A are omitted for clarity. Each toluene methyl group is disordered such that they are directed towards the centre of the ring or in the opposite direction outwards and the combinations shown are arbitrary. Key: uranium, green; phosphorus, magenta; silicon, orange; iodide, pink; nitrogen, blue; carbon, grey.
little from linearity [174.6(2)–176.5(18)\textsuperscript{\textdegree}] and there is no mirror symmetry through the arene plane unlike all other uranium arene complexes\textsuperscript{29,30}, thus implicating the presence of U\textsuperscript{III}-(μ-arene)-U\textsuperscript{IV} units in 3 and 4.

The outer perimeter of the \{U\textsubscript{6}I\textsubscript{3}(toluene)\textsubscript{3}\} ring of 3 is completed by the bridging iodides [U–U–U angles range 154.84 (3)–156.77(5)\textdegree]. Three crystallographically distinct, and revealing, U–I distances are observed in 3 [U1–I1, 3.0916(4); U2–I2, 3.1453 (7); U3–I2, 3.1826(7) Å]. The first value is associated with the disordered U\textsuperscript{III}/IV-BIPM fragment and it also has the largest displacement ellipsoid in the structure so is not a reliable measure. However, we note that the shorter U2–I2 distance goes with a long U2–C39 bond length and conversely the long U3–I2 distance is associated with a short U3–C70 distance. The implication is that the methanediide ligand is the strongest donor and thus when it binds more closely the halide recedes.

**NMR and optical spectroscopies.** The \textsuperscript{1}H NMR spectra of 3 and 4 in D\textsubscript{6}-benzene could be obtained. They are fully assignable and only minor protic impurities are observed, despite the low concentrations of 3 and 4 in D\textsubscript{6}-benzene. While the bulk features of the \textsuperscript{1}H NMR spectra of the BIPMTMS ligands in complexes 3 and 4 are similar, they can be distinguished by small variations in their chemical shifts, with diagnostic, differing resonances of the bridging arene ligands (3: δ = 1.35, –0.37, and 0.44; 4: δ = –0.25).

At 298 K no arene exchange of 3 or 4 with D\textsubscript{6}-benzene was observed by \textsuperscript{1}H NMR spectroscopy over 72 h. However, heating 3 in D\textsubscript{6}-benzene at 50 °C for 8 h gave 4-D\textsubscript{6}, almost quantitatively, with formation of a small quantity of intractable by-products (see Supplementary Fig. 2). This reaction was monitored by \textsuperscript{1}H NMR spectroscopy, revealing that the reaction proceeds via at least two intermediates, which we suggest is the sequential replacement of toluenes by benzenes. Kinetic and thermodynamic parameters of this transformation could not be reliably elucidated due to variable precipitation of material during different reactions. Complex 4 was prepared by heating 3 in benzene at 50 °C for 8 h, and also by a competition experiment where 3 was heated in a mixture of D\textsubscript{6}-benzene and benzene (1:1) at 60 °C for 16 h, which gave 4 as the only soluble uranium-containing product. No reaction was observed at 60 °C between 3 and D\textsubscript{8}-toluene, or 4 with either D\textsubscript{6}-benzene or D\textsubscript{8}-toluene, and the use of elevated temperatures led to the formation of intractable products. The low solubilities of 3 and 4 in arene solvents limited the arene exchange experiments to the combinations above.

The electronic absorption spectrum of 3 was obtained (see Supplementary Fig. 4); the solubility of 4 in toluene is too low for a solution spectrum to be collected. In common with 2, 3 dissolves in toluene to give intense brown solutions and its electronic absorption spectrum is dominated by a charge-transfer band trailing in from the ultraviolet region to ~9000 cm\textsuperscript{–1}, which obscures any f→d transitions of uranium(III) that might be in the visible region of the spectrum. This charge-transfer band trails into the NIR region so that only one Laporte forbidden f→f transition was assigned (ν = 11,600 cm\textsuperscript{–1}, ε = 400 M cm\textsuperscript{–1}) based on its similarity to an f→f transition observed for 2 (ν = 11,100 cm\textsuperscript{–1}, ε = 600 M cm\textsuperscript{–1})\textsuperscript{43}. In the 3000–9000 cm\textsuperscript{–1} region, several absorptions characteristic of uranium(III) f→f transitions are observed for 3 (I\textsubscript{11/2}: ν = 4050 cm\textsuperscript{–1}, ε = 700 M cm\textsuperscript{–1}; I\textsubscript{3/2}: ν = 7200 cm\textsuperscript{–1}, ε = 150 M cm\textsuperscript{–1}; I\textsubscript{5/2}: ν = 8700 cm\textsuperscript{–1}, ε = 250 M cm\textsuperscript{–1}), which can be compared to 2 (I\textsubscript{11/2}: ν = 4130 cm\textsuperscript{–1}, ε = 4000 M cm\textsuperscript{–1}; I\textsubscript{3/2}: ν = 7070 cm\textsuperscript{–1}, ε = 900 M cm\textsuperscript{–1}; I\textsubscript{5/2}: ν = 8370 cm\textsuperscript{–1}, ε = 1200 M cm\textsuperscript{–1})\textsuperscript{43}. The absorptions for 3 are approximately an order of magnitude less intense than 2, but 3 contains proportionately half as many uranium(III) ions overall. Not all absorptions in this region could be assigned due to the complexity of the system, but this is a common feature of uranium (III) which can have, not including 5f–6d transitions, 182 crystal field sub-levels\textsuperscript{14}. Notably, the optical spectrum of 3 is very similar to that of 2; the latter by definition does not have inter-valence charge-transfer (IVCT) bands, and there is no evidence of IVCT bands for 3.

**SQUID magnetometry and EPR spectroscopy.** Uranium(III) and uranium(IV) are Kramers (\textsuperscript{5}I\textsubscript{3/2}) and non-Kramers (\textsuperscript{5}I\textsubscript{1/2}) ions, respectively. Because of this, uranium(IV) compounds are usually characterised by a χT product that tends towards zero at low temperature, where χ is the molar magnetic susceptibility, while that for uranium(III) will tend towards a finite value\textsuperscript{13,43,65,66}. At room temperature, complex 3 has a χT of ca. 3.2 cm\textsuperscript{3} K mol\textsuperscript{–1} (which has not reached its high temperature limit), which then decreases on cooling reaching ca. 2.2 cm\textsuperscript{3} K mol\textsuperscript{–1} at 5 K. On further cooling, \chi T increases slightly to ca. 2.4 cm\textsuperscript{3} K mol\textsuperscript{–1} for a 1 kG applied magnetic field; Fig. 3). The general decrease is due to thermal depopulation of the spin–orbit states of the uranium ion. The fact that the data do not tend towards zero suggests that some of the metal ions are uranium (III). This is corroborated by the easy saturation of magnetisation at low temperature, reaching ca. 3.3\textsubscript{μ}B at 3–4 T at 2 K (Fig. 4).

EPR spectra of 3 (observable below ca. 40 K) are unusually complex, with multiple resonances between 0 and 1.8 T at Q-band (34 GHz; Fig. 5). Since EPR is very sensitive to very weak

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**Table 1 Selected bond lengths for 3 (Å)**

| U\textsuperscript{III}/IV-distances | U\textsuperscript{II}/distances | U\textsuperscript{IV}-distances |
|------------------------------------|-----------------------------|-----------------------------|
| U-I                               | 3.0917(4)                   | 3.1453(7)                   |
| U-1/C                             | 2.47(2)                     | 2.438(8)                    |
| U-1/A                             | 2.30(3)                     | 2.398(7)                    |
| U-1/C3                            | 2.717(8)                    | 2.718(8)                    |
| U-1/C4                            | 2.678(9)                    | 2.679(9)                    |
| U-1/C5                            | 2.579(9)                    | 2.647(8)                    |
| U-1/C6                            | 2.608(9)                    | 2.626(9)                    |
| U-1/C7                            | 2.653(9)                    | 2.576(9)                    |
| U-1/C8                            | 2.674(8)                    | 2.664(8)                    |

The oxidation states are formal and provided only as a guide.
interactions, the structure of the spectrum could be due to weak uranium–uranium interactions (peak separations of 0.1–0.2 kG, which corresponds to 0.1–0.2 cm$^{-1}$), which could be consistent with the very low temperature rise in $\chi_T(T)$; a fully isolated uranium(III) ion typically gives a simple EPR spectrum characteristic of the effective $g$-values of the lowest energy Kramers doublet $^6$. Quantitative analysis of the EPR and magnetic data is not possible at this stage given the complexity of the system. The large variations in typical magnetic moments of uranium(III) and uranium(IV) species preclude even a simple additive analysis; this is true even of smaller inverse-sandwich complexes, for example, $^7$ has $\chi_T$ of ca. 1.5 cm$^3$ K mol$^{-1}$ at room temperature$^{43}$, significantly lower than that expected for the sum of two isolated uranium(III) ions (e.g. $[\text{U}^{II}(\text{BIPMTMSH})\text{(THF)}]$ $\chi_T$ of $1.7$ cm$^3$ K mol$^{-1}$ at room temperature$^{43}$). Nevertheless, even acknowledging that formal oxidation states starts to become a diffuse concept with covalently bonded uranium–arene fragments, the observation of EPR spectra at all for 3, together with the magnetic data, are only consistent with a Kramers system.

**X-ray absorption near edge spectroscopy.** To further probe 3 and 4, low-temperature uranium L$_3$-edge X-ray absorption near edge spectroscopy (XANES) spectra were collected. Data were calibrated in energy space using a single oxidation state in-line reference foil. Further experimental details are given in the Supporting Information. The background-subtracted, normalised XANES of 3 and 4 are shown in Fig. 6 alongside data for uranium (III), uranium(IV), and uranium(VI) single oxidation state standards ($[\text{UI}^{III}\text{(THF)}]$, $\text{UO}_2$, and $\text{UO}_2^{2+}$ sorbed onto ferrihydrite, respectively). Samples were collected on two separate beam lines to ensure consistency. The sample spectra have strong white lines.
and are similar in shape to the UO₂ and uranium(III) standards and other uranium(III) and uranium(IV) L₂-edge XANES described in the literature. Complexes 3 and 4 lack a shoulder feature on the high energy side of the white line indicating the absence of uranium(V) or uranium(VI), since a shoulder feature would be indicative of multiple scattering along the trans-dioxo moiety.

We have used the zero-crossing point of the first derivative of the normalised XANES versus energy to define the primary spectral XANES white line energy for our complexes, giving values of 17175.7 and 17175.3 eV for 3 and 4, respectively. These energies are close to those reported for uranium(III)-tacn complexes, and ~1–2 eV lower than those recorded for UO₂ (17176 eV in this study; 17177.2 eV in ref. 65) and a range of uranium(IV)-tacn complexes. It should be noted that the energy separations of edge energies for organometallic species tends to be narrower than in inorganic compounds. Another approach would be to use the point at which the second derivative of the normalised XANES is zero to assign an average uranium oxidation in similar complexes. In that scenario the edge values for complexes 3 and 4, and the [UI₂(THF)₆] and UO₂ standards are now 17169.4, 17169.0, 17168.7, and 17170.7 eV, respectively. Equivalent literature values reported for other uranium(III) complexes range from 17169.0 to 17168.7 eV and 17169.8 to 17170.9 for uranium(IV) complexes and UO₂. Irrespective of whether the first- or second-derivative methods are used, the XANES data collected from 3 and 4 consistently suggest a mixture of uranium(III) and uranium(IV) ions in these complexes.

Quantum chemical calculations. A well-established approach to study organometallic systems is to optimise the geometry with density functional theory (DFT) with subsequent single-point calculations using a high-level multi-reference method to study the electronic structure. While diuranium species such as 2 can be treated in this manner, compounds such as 3 and 4 demand deviations from this ‘standard’ approach due to their size and polymeric nature. Therefore, we first studied 2 at varying levels of theory, including the complete active space self-consistent field (CASSCF) method, followed by second-order perturbation theory (CASPT2), and tested the effect that the truncations in the active space and the ligands have on the computed results; the ligand truncations involved sequential simplification using BIPM₄⁻ = C(PMe₂NSiH₃)₂, BIPM₅⁻ = C(PMe₂NSiH₂)₂, or BIPM₆⁻ = C(PH₂NH)₂, denoted as 2', 2'', and 2, respectively. The results for the largest model (complex with BIPM₆⁻ denoted 3' and 4') with DFT and results with the smallest model (complexes with BIPM₄⁻ denoted 2'' and 4'') with multi-reference methods are presented below while results for other models including computational details, testing of the level of theory, and a discussion of the active space are given in Supplementary Figs. 5–24, Supplementary Tables 1–14, Supplementary Methods, and Supplementary Note 1.

The electronic structure of the ring complexes were explored first with the restricted active space self-consistent field method (RASSCF) for the S = 7/2 to the S = 13/2 states. The active space in the RASSCF calculations is (21e, 2e, 2e; 6o, 11o, 6o) where the notation indicates a RAS space of (n, l; m; i, j, k) where n is the number of electrons in the active space; l is the maximum number of holes in RAS1, and m is the number of electrons allowed in RAS3. Similarly, i, j, and k are the number of orbitals in RAS1, RAS2, and RAS3 respectively. The S = 7/2 state of 4'' is only 0.02 kcal mol⁻¹ higher in energy than the S = 9/2 state (Supplementary Table 4), with the two states differing only in the orientation (spin-up or -down) of the unpaired electrons in the 5f orbitals. The S = 11/2 and 13/2 states are 28.3 and 39.0 kcal mol⁻¹ higher in energy, respectively, than the S = 9/2 state with RASSCF and include excitations out of the 5δ-bonding orbitals. Note that the number of determinants required for spin states lower than S = 7/2 rendered such calculations computationally intractable with this active space; therefore, a smaller active space was employed in which the 5δ-bonding orbitals with the highest occupation numbers (and their corresponding anti-bonding orbitals) were removed from the active space. In that scenario, CASPT2 calculations could be performed with an active space of (9e,17o) for spin states ranging from S = 1/2 to 9/2. Ultimately, these states are separated by at most 0.7 kcal mol⁻¹ at the CASPT2 level of theory, and therefore are within the error of the method (Supplementary Table 10). These states, and other low-lying excited states that we have not explored, likely couple via spin–orbit interactions, but nevertheless the accuracy of CASPT2 is not sufficient to conclusively determine the ordering of the lowest states in such a complex multimetallic array. Since the results for 3 and 4 are expected to be similar, only 4'' was studied with RASSCF and CASPT2. All RASSCF and CASPT2 calculations were performed with Molcas v7.

From the orbital picture that emerges in the RASSCF calculations, a similar bonding scheme is present for each U–arene–U group in 4''. Each of the U–C₆H₆–U groups contains two sets of δ-bonds (Fig. 7) and a set of singly occupied orbitals that are linear combinations of uranium 5f orbitals. The δ-bonds in these systems can be thought of as δ-backboning where the uranium 5f orbitals donate into the π star orbitals on the arene. Each U–C₆H₆–U group contains one δ-bond natural orbital with an occupation number of 1.95–1.97 while the other has a lower occupation number of 1.83–1.88. In Fig. 7, note that the δ-bond in the U–C₆H₆–U group at the top is symmetric, whose structural data suggest that it involves two uranium(IV) ions, while the δ-bonds in the two symmetry equivalent U–C₆H₆–U groups are asymmetric, which again is consistent with the overall presence of U₃(THF)₄–arene–U₄(THF)₄ units.

However, the most important difference between 2 and 4 is the number of unpaired electrons per uranium ion. In 2, four unpaired electrons remain localised on the two uranium(III) centres; note that uranium(III) ions when δ-bonded to arenes exhibit only two clear-cut, localised 5f electrons since the other 5f electron per uranium is involved to some extent in δ-bonding. The U–C₆H₆–U group shown at the top of 4'' in Fig. 7 is symmetrically distinct from the other two U–C₆H₆–U groups and has three unpaired electrons distributed among the two uranium ions. As a result, the formal oxidation state of each uranium in 4'' is higher than in 2, consistent with the top two uranium ions being (IV). The remaining two U–C₆H₆–U groups contain six unpaired electrons distributed among the four uranium centres, reflecting the presence, formally, of three uranium(III) and one uranium(IV) ion in that grouping. Furthermore, the average Mulliken charge on the uranium ions is slightly higher in 4'' (+1.49) than in 2'' (+1.30) reflecting the presence of uranium (III) and (IV) ions in the former but only uranium(III) in the latter.

The RASSCF calculations naturally focus on the role of the arene groups, since those orbitals lie closest to the valence region, and thus contributions from the BIPM ligand were not included in the active space. However, turning to the uranium–BIPM interactions, the orbitals involved in the U–C₆H₆–U interaction for the next set of orbitals below the active space, are energetically well separated lying lower in energy by ~30 kcal mol⁻¹. To interrogate this group of interactions in more detail, we performed DFT (PBE/TZ2P and PBE/def-TZVP) calculations on two larger models, [(U(BIPM₄⁻))₄(µ₁-1)(µ₂-1)μ₂-1]}₉(C₆H₆)₄]
(3′, BIPM\textsuperscript{I} = C(PMe\textsubscript{2}NSiMe\textsubscript{3})\textsubscript{2}) and [(U(BIPM\textsuperscript{I}))\textsubscript{6}(\mu-I)\textsubscript{3}(\mu-\eta\textsubscript{6}: \eta\textsuperscript{5}-C\textsubscript{6}H\textsubscript{5})\textsubscript{3}] (4′, BIPM\textsuperscript{I} = C(PMe\textsubscript{2}NSiMe\textsubscript{3})\textsubscript{2}) to explore the nature of the U–C\textsubscript{BIPM} interaction. At the DFT level, only the high spin \(S = 9/2\) state was computed for 3′ and 4′ since lower spin states are spin-contaminated. The 12 orbitals with contributions primarily from the C\textsubscript{BIPM} 2\(p\) orbitals, but also with contributions from the uranium centres, are shown in Fig. 8.

The bonding between the uranium ions and the bridging arenes imposes an orientation upon the uranium ions, and for this reason the interaction between uranium and C\textsubscript{BIPM} centres does not exhibit idealised \(\pi\)-orbitals; however, there are two doubly-occupied orbitals per uranium indicating double bond interactions. Supporting this notion, Nalewajski–Mrozek bond orders for U \(= \) C\textsubscript{BIPM} give values ranging from 1.15 to 1.16 for 3′ and

![Fig. 7](image.png) Active natural orbitals from a RASSCF calculation on 4″. Electron occupation numbers are given in parentheses. Key: uranium, green; iodide, red; phosphorus, purple; nitrogen, dark blue; carbon, grey; hydrogen, white

![Fig. 8](image.png) Computed DFT molecular orbitals for 4′. Top row: the six uranium–arene \(\delta\)-bonding interactions. Middle and bottoms rows: the 12 U–C \(\pi\)-double bond interactions. Key: uranium, green; iodide, red; phosphorus, purple; nitrogen, dark blue; carbon, grey; hydrogen, white
1.16 to 1.18 for $4'$; $U = C_{\text{BIPM}}$ bond orders tend to be 1.23–1.54 with $U = C_{\text{BIPMH}}$ bond orders being ~0.6 (ref. 30). Additionally, the average charges on the uranium centres are computed with the multiple derived charge analysis (MDC-q) to be +1.19 for $3'$ and +1.18 for $4'$. The molecular orbitals in $4'$ that principally represent the $U = C$ double bond interactions exhibit variable levels of intrusion from other orbital coefficients due to their delocalised nature, but despite this the more localised and thus clear-cut $U = C$ molecular orbital combinations a clear trend emerges; the uranium(III)-, uranium(III/IV)-, and uranium(IV)-$C_{\text{BIPM}}$ bonds show uranium and carbon contributions of 14.57%, 18.40%, and 22.20%, respectively where the total uranium contribution is clearly increasing with increasing oxidation state. Unfortunately, due to the large number of basis functions Natural Bond Orbital analysis was not performed. For similar reasons, although QTAIM data can be computed these metrics should be considered with caution. Nevertheless, $ho$, $V^2\rho$, $H$, and $\varepsilon$ (ellipticity) values of 0.058/0.056, 0.158/0.154, 0.09/0.08, and 0.20/0.19 for uranium(III)/uranium(IV)-$C_{\text{BIPM}}$ bonds show that results in disproportionation, which is indirect evidence for an unstable uranium(III)-methanediide. Further, when THF solutions of the uranium(III)-methanediide $[U(\text{BIPM})_{2}(\text{THF})]$ are reacted with benzyl potassium, the characteristic dark blue-purple colour of uranium(III) is observed for short periods, putatively assigned as the uranium(III)-, uranium(III/IV)-, and uranium(IV)-$C_{\text{BIPM}}$ bonds show uranium and carbon contributions of 14.57%, 18.40%, and 22.20%, respectively, where the total uranium contribution is clearly increasing with increasing oxidation state. Unfortunately, due to the large number of basis functions Natural Bond Orbital analysis was not performed. For similar reasons, although QTAIM data can be computed these metrics should be considered with caution. Nevertheless, $\rho$, $V^2\rho$, $H$, and $\varepsilon$ (ellipticity) values of 0.058/0.056, 0.158/0.154, 0.09/0.08, and 0.20/0.19 for uranium(III)/uranium(IV)-$C_{\text{BIPM}}$ bonds show uranium and carbon contributions of 14.57%, 18.40%, and 22.20%, respectively, where the total uranium contribution is clearly increasing with increasing oxidation state.
mixed-valence system: (i) the U–I distances follow an opposite trend to the U = C bonds, but this can be related to relativistic ligand donor strengths; (ii) magnetic and EPR data confirm the presence of Kramers ions, but this itself does not rule out delocalisation; (iii) XANES data are a composite, as seen in other Class I systems, that shows a mixture of uranium(III) and uranium(IV) but not whether they are localised or delocalised; (iv) DFT presents a more delocalised picture, but this is inherent to DFT. It is certainly the case that not all the uranium ions in 3 and 4 are uranium(IV), and at the very least the U = C bonds involve uranium ions that are lower oxidation state than found previously. So, most of the data suggest the presence of formal uranium(III) ions supported by δ-bonding to the arenes, but at this point we cannot completely rule out the possibility of electron delocalisation in this Kramers system.

Methods

General. Experiments were carried out under a dry, oxygen-free dinitrogen atmosphere using Schlenk-line and glove-box techniques. All solvents and reagents were rigorously dried and deoxygenated before use. Compounds were variously characterised by elemental analyses, electrochemistry, NMR, FTIR, EPR, XANES, and UV/Vis/NIR electronic absorption spectroscopies, single crystal X-ray diffraction studies, Evans methods and SQUID magnetometry, and DFT, QTAIM, CASSCF, CASPT2, and RASSCF computational methods.

Preparation of [(UBIPMTM(η⁶-C₆H₆)₂C₂H₄C₂H₄C₆H₄)₂]₃ (3). Toluene (20 ml) was added to a pre-cooled (~78 °C) mixture of 1 (2.12 g, 0.5 mmol) and KC₈ (0.27 g, 2.2 mmol). The reaction mixture was slowly warmed to allow temperature with stirring over 24 h. The mixture was filtered, reduced in volume to ca. 5 ml, and stored at ambient temperature overnight to afford 3 as dark purple crystals. Yield 0.04 g, 1%.

Preparation of [(UBIPMTM(η⁶-C₆H₆)₂C₂H₄C₂H₄C₆H₄)₂]₄ (4). Benzene (20 ml) was added to a pre-cooled (4 °C) mixture of 1 (3.79 g, 1.66 mmol) and KC₈ (0.90 g, 6.63 mmol). The reaction mixture was slowly warmed to allow temperature with stirring over 24 h. The mixture was filtered, reduced in volume to ca. 3 ml, and stored at 5 °C overnight to afford 4 as dark purple crystals. Yield 0.04 g, 1%. Anal Calcd for C₁₉₀H₁₃₁N₆₂P₆S₆C₆₃₆: C, 43.57; H, 4.61; N, 3.12. Found: C, 43.47; H, 4.87; N, 2.77. ¹H NMR (δ, benzene, 298 K): δ = 1.89 (s, br, 24 H, Ph-CH), 5.14 (s, 24 H, Ph-CH), 4.39 (s, 12 H, Ph-CH), 4.85 (s, 24 H, Ph-CH), 5.43 (s, 24 H, Ph-CH), 5.75 (s, 12 H, Ph-CH), 10.38 (s, 6 H, Ph-CH), 10.83 (s, 12 H, Ph-CH), 14.11 (s, 12 H, Ph-CH), 14.53 (s, br, 54 H, Si(CH₃)₂), 14.96 (s, 12 H, Ph-CH). FTIR ν/cm⁻¹ (Nujol): 1650 (w), 1372 (w), 1243 (m), 1103 (m), 1033 (s), 830 (m), 763 (m), 691 (m), 643 (m), 604 (m), 555 (m), 502 (w).

Preparation of [(UBIPMTM(η⁶-C₆H₆)₂C₂H₄C₂H₄C₆H₄)₂]₅ (5). Toluene (20 ml) was added to a pre-cooled (~78 °C) mixture of 1 (1.22 g, 0.5 mmol) and KC₈ (0.27 g, 2.2 mmol). The reaction mixture was slowly warmed to allow temperature with stirring over 24 h. The mixture was filtered, reduced in volume to ca. 5 ml, and stored at ambient temperature overnight to afford 5 as dark purple crystals. Yield 0.12 g, 12%. Anal Calcd for C₁₉₀H₁₃₃N₆₄P₆S₆C₆₅₆: C, 43.17; H, 4.54; N, 2.78. Found: C, 43.08; H, 4.88; N, 2.95. Found: C, 48.03; H, 4.94; N, 2.66. ¹H NMR (δ, benzene, 298 K): δ = 1.96 (s, br, 12 H, Ph-CH), 1.35 (s, 9 H, toluene Ph-CH), 0.08 (s, br, 54 H, Si(CH₃)₂), 0.37 (s, 6 H, toluene Ph-CH), 0.44 (s, 12 H, toluene CH₃), 4.39 (s, 12 H, Ph-CH), 4.85 (s, 24 H, Ph-CH), 5.39 (s, 24 H, Ph-CH), 5.75 (s, 12 H, Ph-CH), 10.38 (s, 6 H, Ph-CH), 10.83 (s, 12 H, Ph-CH), 14.11 (s, 12 H, Ph-CH), 14.53 (s, br, 54 H, Si(CH₃)₂), 14.96 (s, 12 H, Ph-CH). FTIR ν/cm⁻¹ (Nujol): 1650 (w), 1372 (w), 1243 (m), 1103 (m), 1033 (s), 830 (m), 763 (m), 691 (m), 643 (m), 604 (m), 555 (m), 502 (w).

Data availability. The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 1581465 (3) and 1581466 (4). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request cif. All other data can be obtained from the authors on request.

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Author contributions
AJ.W. and D.P.M. prepared the compounds and recorded and interpreted the characterisation data. B.V. and L.G. conducted the theoretical calculations and interpreted the results. F.T. and E.J.L.M recorded and interpreted the EPR and SQUID data. G.L., A.F., F.K., and M.R. recorded and interpreted the XAS data. W.L. collected, solved, and refined the X-ray crystallographic data. S.T.L. originated the central research idea, analysed all the data, and wrote the manuscript with contributions from all co-authors.

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