Actinide Arene-Metalates: Ion Pairing Effects on the Electronic Structure of Unsupported Uranium-Arene Sandwich Complexes

Jesse Murillo, Rina Bhowmick, Katie L. M. Harriman, Alejandra Gomez-Torres, Joshua Wright, Robert W. Meulenberg, Pere Miro Ramirez, Alejandro J. Metta-Magaña, Muralee Murugesu, Bess Vlaisavljevich, Skye Fortier

Submitted date: 20/04/2021 • Posted date: 21/04/2021
Licence: CC BY-NC-ND 4.0
Citation information: Murillo, Jesse; Bhowmick, Rina; Harriman, Katie L. M.; Gomez-Torres, Alejandra; Wright, Joshua; Meulenberg, Robert W.; et al. (2021): Actinide Arene-Metalates: Ion Pairing Effects on the Electronic Structure of Unsupported Uranium-Arene Sandwich Complexes. ChemRxiv. Preprint. https://doi.org/10.26434/chemrxiv.14455983.v1

Chatt reaction methods were employed to synthesize the first well characterized actinide-arene sandwich complexes. Namely, addition of $[\text{UI}_2(\text{THF})_3(\mu-\text{OMe})]_2\cdot\text{THF}$ (2·THF) to THF solutions containing 6 equiv. of $\text{K[C}_{14}\text{H}_{10}]$ generates the dimeric complexes $[\text{K(18-crown-6)(THF)}]_2\cdot\text{U(η}_6\text{-C}_{14}\text{H}_{10})(\eta_4\text{-C}_{14}\text{H}_{10})(\mu-\text{OMe})]_2\cdot4\text{THF}$ (118C6·4THF) and $[[\text{K(THF)}]_3\cdot\text{U(η}_6\text{-C}_{14}\text{H}_{10})(\eta_4\text{-C}_{14}\text{H}_{10})(\mu-\text{OMe})]_2\cdot\text{THF}$ (1THF) upon crystallization of the products in THF in the presence or absence of 18-crown-6, respectively. Both 118C6·4THF and 1THF are thermally stable in the solid-state at room temperature; however, after crystallization, they become insoluble in THF or DME solutions and instead gradually decompose upon standing. X-ray diffraction analysis reveals 118C6·4THF and 1THF to be structurally similar, possessing uranium centers sandwiched between anthracene ligands of mixed tetrahapto and hexahapto ligation modes. Yet, the two complexes are distinguished by the close contact potassium-arene ion pairing that is seen in 1THF but absent in 118C6·4THF, which is observed to have a significant effect on the electronic characteristics of the two complexes. Structural analysis, SQUID magnetometry data, XANES spectral characterization, and computational analyses are generally consistent with U(IV) formal assignments for the metal centers in both 118C6·4THF and 1THF, though noticeable differences are detected between the two species. For instance, the effective magnetic moment of 1THF (3.74 µB) is significantly lower than that of 118C6·4THF (4.40 µB) at 300 K. Furthermore, the XANES data shows the U LIII-edge absorption energy for 1THF to be 0.9 eV higher than that of 118C6·4THF, suggestive of more oxidized metal centers in the former. Of note, CASSCF calculations on the model complex $[[\text{U(η}_6\text{-C}_{14}\text{H}_{10})(\eta_4\text{-C}_{14}\text{H}_{10})(\mu-\text{OMe})]_2]^{2-}$ (1*) shows highly polarized uranium-arene interactions defined by π-type bonds where the metal contributions are primarily comprised by the 6d-orbitals (7.3± 0.6%) with minor participation from the 5f-orbitals (1.5 ± 0.5%). These unique complexes provide new insights into actinide-arene bonding interactions and show the sensitivity of the electronic structures of the uranium atoms to coordination sphere effects.
| File Name                      | Size         | Actions                   |
|-------------------------------|--------------|---------------------------|
| ChemRXIV_SI_U_Arene_Dimer.pdf | 2.80 MiB     | view on ChemRxiv          |
|                              |              | download file             |
| ChemRXIV_U_Arene_Dimer.pdf   | 1.02 MiB     | view on ChemRxiv          |
|                              |              | download file             |
Supporting Information

Actinide Arene-Metalates: Ion Pairing Effects on the Electronic Structure of Unsupported Uranium-Arene Sandwich Complexes

Jesse Murillo,† Rina Bhowmick,‡ Katie L. M. Harriman,† Alejandra Gomez-Torres,† Joshua Wright,¥ Robert W. Meulenberg,± Pere Miró,‡ Alejandro Metta-Magana,† Muralee Murugesu,† Bess Vlaisavljevich,*,‡ and Skye Fortier*,†

†Department of Chemistry and Biochemistry, University of Texas at El Paso, El Paso, Texas 79968, United States
‡Department of Chemistry, University of South Dakota, Vermillion, South Dakota 57069, United States
¶Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada
¥ Department of Physics, Illinois Institute of Technology, Chicago, IL, 60616, United States
± Department of Physics and Astronomy and Frontier Institute for Research in Sensor Technologies, University of Maine, Orono, ME, 04469, United States

*To whom correspondence should be addressed. Email: asfortier@utep.edu, bess.vlaisavljevich@usd.edu
Table of Contents
Materials and Methods ........................................................................................................................................... S5
XANES Experimental Details ................................................................................................................................. S5
Magnetic Measurement Details ............................................................................................................................. S6
X-ray Crystallography Details ............................................................................................................................... S6

Synthesis of 2-THF, [UI₂(THF)₃(μ-OMe)]₂-THF .................................................................................................... S7
Synthesis of 1¹⁸C₆·4THF, [K(18-crown-6)(THF)₂]₂[U(η⁵-C₁₄H₁₀)(η⁴-C₁₄H₁₀)(μ-OMe)]·4THF ......................... S7
Synthesis of 1THF, {[K(THF)₃][U(η⁵-C₁₄H₁₀)(η⁴-C₁₄H₁₀)(μ-OMe)]}_2 ........................................................................ S7

Figure S1. Solid State ORTEP diagram of 2-THF .................................................................................................. S9
Figure S2. Solid State ORTEP diagram of 1¹⁸C₆·4THF ....................................................................................... S10
Figure S3. Bond diagram of coordinated anthracenes of 1¹⁸C₆·4THF ................................................................. S11
Figure S4. Bond diagram of coordinated anthracenes of 1THF ........................................................................... S12
Figure S5. Bending distortions in coordinated anthracene rings of 1¹⁸C₆·4THF and 1THF .............................. S13
Figure S6. Solid State ORTEP diagram of 1THF .................................................................................................. S14

Table S1. X-ray crystallographic data for 1¹⁸C₆·4THF, 1THF, and 2-THF ......................................................... S15
Figure S7. ¹H NMR spectrum of 2 in py-d₅ at 25 °C .......................................................................................... S16
Figure S8. UV-vis spectrum of 2-THF (5.90 mM) in pyridine at 25 °C ................................................................. S17
Figure S9. NIR spectrum of 2-THF (0.31 mM) in pyridine at 25 °C ................................................................. S18
Figure S10. Solid state EPR spectra of 1¹⁸C₆·4THF ............................................................................................ S19

Figure S11. Solid state EPR spectra of 1THF ...................................................................................................... S20
Figure S12. Normalized XANES plot (1st derivative) for 1¹⁸C₆·4THF, 1THF, and uranium standards ....... S21
Figure S13. Normalized XANES plot (1st derivative) showing Y-foil edge alignment ........................................ S22
Figure S14. Normalized XANES plot (1st derivative) showing Y-foil edge alignment ....................................... S22

Table S2. XANES edge energies for 1¹⁸C₆·4THF, 1THF, and uranium standards ........................................ S24
Figure S15. Variable temperature magnetic susceptibility data for 1¹⁸C₆·4THF and 1THF ............................. S25
Figure S16. Temperature dependence of χT under applied dc field for 1¹⁸C₆·4THF ........................................ S26
Figure S17. Temperature dependence of $\chi T$ under applied dc field for $1^{THF}$.......................... S27
Computational Details ............................................................................................................. S28
Additional Computational Details and Discussion............................................................. S30
Additional CASPT2 Calculations to Support Active Space Choice.................................. S31
Table S3. Relative energies for optimized structures of $1^*$ and $1$-$K^*$................................. S32
Figure S18. Spin densities for $1^*$ and $1$-$K^*$ from ground state quintet calculations........... S33
Table S4. Selected U-C bond distances for optimized geometry of compound $1^*$............... S34
Table S5. Selected U-C bond distances for optimized geometry of compound $1$-$K^*$.......... S35
Figure S19. Optimized ground state structures for $1^*$ and $1$-$K^*$...................................... S36
Table S6. Properties at the bond critical points for the $1^*$ and $1$-$K^*$................................. S37
Table S7. Bond order of uranium and coordinated carbon atoms in complex $1^*$ (PBE)........ S38
Table S8. Bond order of uranium and coordinated carbon atoms in complex $1^*$ (TPSS)....... S39
Table S9. Bond order of uranium and coordinated carbon atoms in complex $1$-$K^*$ (PBE)..... S40
Table S10. Bond order of uranium and coordinated carbon atoms in complex $1$-$K^*$ (TPSS).... S41
Table S11. CM5 atomic charges calculated for $1^*$ and $1$-$K^*$........................................... S42
Table S12. CASSCF and CASPT2 relative energies for three active space configurations....... S43
Table S13. RASSCF & RASPT2 energy difference for three spin states.............................. S44
Table S14. LoProp Charges for $1^*$................................................................................. S45
Figure S20. The CASSCF (4e,14o) natural orbitals for quintet state...................................... S46
Figure S21. The CASSCF (4e,14o) natural orbitals for triplet state....................................... S47
Figure S22. The CASSCF (4e,14o) natural orbitals for singlet state..................................... S48
Figure S23. The CASSCF (4e,8o) natural orbitals for the quintet state................................. S49
Figure S24. The CASSCF (4e,8o) natural orbitals for triplet state....................................... S50
Figure S25. The CASSCF (4e,8o) natural orbitals for singlet state..................................... S51
Figure S26. The CASSCF (8e,12o) natural orbitals for quintet state.................................... S52
Figure S27. The CASSCF (8e,12o) orbitals for the septet state of dimer 1*............................... S53

Figure S28. The natural RASSCF orbitals for the quintet state of dimer 1*............................... S54

Figure S29. The natural RASSCF orbitals for the triplet state of dimer 1*............................... S55

Figure S30. The natural RASSCF orbitals for the singlet state of dimer 1*............................... S56

Figure S31. RASSCF spin density for complex 1*................................................................. S57

Table S15. Selected C-C distances and bent angle from PBE-D3 optimized geometries for the triplet, quintet and septet spin states of 1*..........................................................................................................................S58

Table S16. Selected C-C distances and bent angle from PBE-D3 optimized geometries for the triplet, quintet and septet spin states of 1-K*.....................................................................................................................S59

Table S17. Orbital analysis of 1* for the bonding orbitals from the RASSCF (24e', 2h, 2e', 10o,8o,10o) calculation..................................................................................................................................................S60

Table S18. Orbital analysis of 1* for the bonding orbitals from the CASSCF(8e,12o) calculation........ S61

Table S19. Energy decomposition analysis (EDA) for 1*.......................................................... S62

References....................................................................................................................................... S63
General Considerations. All air and moisture-sensitive operations were performed in either an MBraun glovebox under an atmosphere of ultra-high purity nitrogen or in a Vacuum Atmospheres glovebox under an atmosphere of ultra-high purity argon. Diethyl ether, hexanes, and THF were dried using a Pure Process Technology Solvent Purification System and subsequently stored under an inert atmosphere of argon or nitrogen over activated 4 Å molecular sieves. Pyridine-$d_5$ (py-$d_5$) was purchased from Cambridge Isotope Laboratories Inc., degassed by three freeze-pump-thaw cycles, and dried over activated 4 Å molecular sieves for at least 24 h prior to use. Celite and 4 Å molecular sieves were heated, under dynamic vacuum, to 150 °C for at least 24 h and then cooled under vacuum. UI$_3$(dioxane)$_{1.5}$, UCl$_4$, U(O)[N(SiMe$_3$)$_2$)$_3$,$^3$ UO$_2$Cl$_2$(THF)$_3$$^4$ were synthesized following reported procedures. Potassium methoxide (K[OMe]) was synthesized via slow addition of excess dry methanol to metallic potassium suspended in hexanes using air-free Schlenk methods. Anthracene was purchased from Alfa Aesar and used as received. Grade ZG ultra-high purity boron nitride powder with an average particle size of 7.4 μm was purchased from Amazon.com, Inc. and heated under high vacuum at 200 °C for several days and subsequently stored in a glovebox under an inert atmosphere prior to use. All other reagents were purchased from commercial suppliers and used as received. Low temperature EPR measurements were performed on a Bruker EMX Plus X-band spectrometer using a liquid helium cooled cryo-stat. $^1$H NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer. $^1$H NMR spectra are referenced to residual $^1$H solvent peaks as internal standards or the characteristic $^1$H resonances of the solvent. Elemental analyses were performed by Midwest Microlab, LLC. UV-vis/NIR spectra were recorded from pyridine solutions on a Cary 5000 spectrophotometer in airtight match paired UV-vis cuvettes.

X-ray absorption near edge structure (XANES). All X-ray absorption experiments were conducted at sector 10-BM of the Advanced Photon Source at Argonne National Laboratories, currently of the Materials Research Collaborative Access Team (MRCAT).$^5$ Data was collected in the standard transmission geometry mode with an incident beam of 500 × 1000 μm @ $10^{12}$ ph/sec with energies between 17 – 18 keV. All sample energies are referenced to an yttrium foil located between the second and third detectors, and all spectra are aligned to a foil value of 17038.4 eV (Figure S13). Under an inert atmosphere of high purity argon, sample powders were prepared by mixing boron nitride powder with the uranium compounds to concentrations between 20 – 40 wt.
% in the analyte and ground using a mortar and pestle to produce ~0.1 g of a very fine powder. Approximately 0.06 g of the powder was loaded into a pellet press and compressed using a force not exceeding 27 Newton-meters to produce a pellet 7 mm in diameter and 1 – 2 mm in depth. The pellet was then carefully sandwiched between two polypropylene plastic disks for structural support and sealed between two layers of Kapton tape. The pellet assembly was again wrapped in another layer of Kapton, and the package then vacuum sealed inside of a 3 × 3 cm ethylene-vinyl acetate (EVA) pouch. As required by the beamline radiation safety protocols, the seams of the EVA pouch were reinforced with Kapton tape. The integrity of the vacuum seal was monitored over several days and closely reexamined immediately prior to the data collection. The compounds \( \text{UI}_3(\text{dioxane})_{1.5} \), \( \text{UCl}_4 \), \( \text{U(O)[N(SiMe}_3}_2 \})_3 \), and \( \text{UO}_2\text{Cl}_2(\text{THF})_3 \) were used as oxidation state reference standards for U(III), U(IV), U(V), and U(VI), respectively.

Each uranium sample was prepared and measured in duplicate. Presented data was produced as an average of three consecutive scans for each sample. All data was processed and figures generated using Demeter X-ray absorption spectroscopy data analysis software. The edge energies are determined as the inflection point of the first derivative as calculated by the Demeter software program. The white line energies are defined as the peak absorption maxima as identified through the Demeter program.

**Magnetic Measurements.** The magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer MPMS-XL7 operating between 1.8 and 300 K. DC measurements were performed on a polycrystalline sample of 17.0 mg for \( 1^{18\text{C}6}\cdot 4\text{THF} \) and 23.0 mg for \( 1^{\text{THF}} \). The samples were restrained with silicon grease and wrapped in a polyethylene membrane under an inert atmosphere. The samples were subjected to DC fields of -7 to 7 T, and a 3.78 Oe driving field was used for AC measurements. The magnetization data were collected at 100 K to check for ferromagnetic impurities that were absent in both samples. Diamagnetic corrections were applied for the sample holder and the inherent diamagnetism of the samples were estimated with the use of Pascals constants.

**X-ray Crystallography.** Data for \( 2\cdot \text{THF} \), \( 1^{18\text{C}6}\cdot 4\text{THF} \), \( 1^{\text{THF}} \) were collected on a dual source Bruker D8 4-axis diffractometer equipped with a PHOTON II CPAD detector with a \( \text{I}_{\mu}\text{S Mo K}\alpha \) X-ray source (\( \alpha = 0.71073 \) Å) fitted with a HELIOS MX monochromator. The crystals were mounted on a Mitigen Kapton loop coated in NVH oil and maintained at 100(2) K under a flow of
nitrogen gas during data collection. Data collection and cell parameter determination were conducted using the SMART\textsuperscript{7} program. Integration of the data and final cell parameter refinements were performed using SAINT\textsuperscript{8} software with data absorption correction implemented through SADABS.\textsuperscript{9} Structures were solved using intrinsic phasing methods and difference Fourier techniques. All hydrogen atom positions were idealized and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL\textsuperscript{10} or the Olex2\textsuperscript{11} crystallographic package.

In $\text{I}^{18}$C\textsubscript{6}·4THF, the non-coordinated THF molecules in the lattice are highly disordered, due to variable arrangements within the lattice and were not fully modeled. Similarly, $\text{2}·\text{THF}$ displays one disordered THF molecule over two positions in the unit cell, which are not fully resolved in the model. $\text{1THF}$ displays severe positional disorder of one of the three THF molecules coordinated to the potassium atom (K1), which is best represented by modeling as four disordered locations.

Complete crystallographic data has been deposited at the Cambridge Crystallographic Data Center (CCDC Nos. 2071454 ($\text{I}^{18}$C\textsubscript{6}·4THF), 2072886 (I\textsuperscript{THF}), 2071450 (2·THF)).

**Synthesis of [UI\textsubscript{2}(THF)\textsubscript{3}(\mu-\text{OMe})]2·THF (2·THF).** To a 20 mL scintillation vial, UI\textsubscript{3}(dioxane)\textsubscript{1.5} (0.30 g, 0.40 mmol) was suspended in THF (6 mL). To this, while stirring at room temperature, K[OMe] (0.029 g, 0.41 mmol) was added, making a dark blue solution. This reaction stirred at room temperature for 16 h. The ensuing blue suspension was filtered through Celite supported on a medium-porosity glass frit. The dark blue filtrate was concentrated to 3 mL under vacuum, and the dark blue solution was layered with Et\textsubscript{2}O (3 mL). After 48 h of storage at -35 °C, dark blue crystals were isolated. Yield: 0.187 g (0.12 mmol), 60%. $^1$H NMR (25 °C, 400 MHz, py-d\textsubscript{5}): $\delta$ 219.8 (br s, 1H, -OCH\textsubscript{2}H), 112.4 (br s, 2H, -OCH\textsubscript{2}H), 3.62 (s, $\alpha$-THF), 1.58 (s, $\beta$-THF). Note: The $^1$H NMR spectrum of 2·THF is consistent with loss of the co-crystallized THF upon drying. Additionally, the compound is sparingly soluble in THF-d\textsubscript{8}, precluding collection of a satisfactory $^1$H NMR spectrum due to low concentration of the analyte, thus requiring the use of py-d\textsubscript{5} for dissolution. This results in total displacement of the coordinated THF molecules from 2·THF and gives a $^1$H NMR spectrum with two resonances corresponding to the methoxide group, indicative of restricted rotational freedom on the NMR timescale. UV-vis (pyridine, 0.31 mM, 25 °C, nm, L·mol$^{-1}·$cm$^{-1}$): 325 ($\varepsilon = 3868$), 369 ($\varepsilon = 3484$), 400 ($\varepsilon = 2304$), 560 ($\varepsilon = 810$), 683 ($\varepsilon = 675$). NIR (pyridine, 5.90 mM, 25 °C, L·mol−1·cm−1): 911 ($\varepsilon = 259$), 937 ($\varepsilon = 234$), 1023 ($\varepsilon = 148$), 1041 ($\varepsilon$
Yield: 0.084 g (39.1 µmol), 35.5%. Anal. Calcd for 118C6·4THF, C114H158K2O22U2·4THF: C, 56.23; H, 6.55. Anal. Calcd for [K(18-crown-6)(THF)]2[[K(18-crown-6)(THF)][U(η⁶-C14H10)(η⁴-C14H10)(µ-OMe)]2·4THF (114C6·4THF). To a 20 mL scintillation vial, potassium metal (0.026 g, 0.65 mmol) was suspended in THF (5 mL). To this, while stirring at room temperature, anthracene (0.112 mg, 0.63 mmol) was added, resulting in the formation of an intense, dark blue solution. The reaction mixture was stirred at room temperature until all of the potassium metal was consumed, leaving a homogeneous, deep blue solution. The solution was then chilled to -35 °C to which 2·THF (0.170 g, 0.11 mmol) was added. The reaction mixture was left to stir at -35 °C for 16 h. The resulting purple suspension was filtered through Celite supported on a medium-porosity glass frit. The dark blue filtrate was then diluted to a total volume of 15 mL with THF in a 20 mL scintillation vial. To the diluted solution was added 18-crown-6 (0.105 g, 0.40 mmol), and the mixture was stored at -35 °C. After 4 days, dark blue crystals formed. The product mixture was poured over a medium porosity glass frit and the crystalline solid washed with THF (3 × 10 mL) then dried under vacuum. Yield: 0.69 mmol)

Yield: 77.4 mg (43.9 µmol), 36.6%. Anal. Calcd for 11THF, C82H94K2O8U2: C, 55.89; H, 5.38. Anal. Calcd for
\{[\text{K(THF)}][\text{U}(\eta^6-\text{C}_{14}\text{H}_{10})(\eta^4-\text{C}_{14}\text{H}_{10})(\mu-\text{OMe})]2, \text{C}_{66}\text{H}_{62}\text{K}_2\text{O}_4\text{U}_2: \text{C}, 53.79; \text{H}, 4.25. \text{Found: C, 53.26; H, 4.91.}\\

**Figure S1.** ORTEP diagram of 2·THF with 30% probability thermal ellipsoids. Asterisks denote symmetry generated atoms. Hydrogen atoms and the co-crystallized THF molecule are omitted for clarity.
Figure S2. ORTEP diagram of $\text{1}^{18}\text{Ce} \cdot 4\text{THF}$ with 30% probability thermal ellipsoids. Asterisks denote symmetry generated atoms. Hydrogen atoms and the co-crystallized THF molecules are omitted for clarity.
Figure S3. Carbon-carbon bond length diagrams of the coordinated anthracenes of $\text{1}^{\text{18C6}}\text{4THF}$.

a) $\eta^6$-coordinated anthracene and b) $\eta^4$-coordinated anthracene.
**Figure S4.** Carbon-carbon bond length diagrams of the coordinated anthracenes of 1^{THF}. a) $\eta^6$-coordinated anthracene and b) $\eta^4$-coordinated anthracene.
Figure S5. Ring folding angles for the coordinated anthracene rings in a) \(1^{\mathrm{THF}}\) and b) \(1^{18\mathrm{C}6.4\mathrm{THF}}\).
Figure S6. ORTEP diagram of $1^{\text{THF}}$ with 30% probability thermal ellipsoids. Hydrogen atoms and the THF molecules coordinated to the potassium ions are omitted for clarity.
|                  | 2·THF                | 1^{18C6}·4THF | 1^{1THF}  |
|------------------|----------------------|---------------|-----------|
| **Empirical formula** | C_{30}H_{62}I_{4}O_{9}U_{2} | C_{114}H_{158}O_{22}K_{2}U_{2} | C_{82}H_{94}O_{8}K_{2}U_{2} |
| **Cryst. habit, color** | block, blue          | block, dark blue | block, dark purple |
| **Cryst. size (mm)**   | 0.20 × 0.12 × 0.22   | 0.12 × 0.41 × 0.46 | 0.43 × 0.33 × 0.30 |
| **Cryst. system**      | Orthorhombic         | Triclinic      | Monoclinic |
| **Space group**        | Pban                 | P\bar{1}       | P2_1/n    |
| **volume (Å^3)**       | 2327.2(5)            | 3133.91(2)     | 3732.95(2) |
| **a (Å)**              | 14.4373(2)           | 10.3767(3)     | 13.7462(4) |
| **b (Å)**              | 17.215(2)            | 17.8147(5)     | 21.7085(6) |
| **c (Å)**              | 9.3631(1)            | 18.3562(6)     | 13.7497(4) |
| **α (deg)**            | 90                   | 67.675(2)      | 90        |
| **β (deg)**            | 90                   | 89.666(2)      | 114.5220(1) |
| **γ (deg)**            | 90                   | 86.887(2)      | 90        |
| **Z**                  | 2                    | 1              | 2         |
| **Fw (g/mol)**         | 1550.48              | 2434.76        | 1761.86   |
| **Density (calcd) (Mg/m^3)** | 2.218               | 1.280          | 1.546     |
| **Abs coeff (mm^{-1})** | 9.643               | 2.706          | 4.498     |
| **F_{000}**            | 1416.0               | 1222.0         | 1696.0    |
| **Total no. of reflns** | 26741              | 15465          | 30444     |
| **Unique reflns**      | 3438                 | 11505          | 7630      |
| **Final R indices [I > 2σ(I)]** | R1 = 0.0332, wR2 = 0.0782 | R1 = 0.0496, wR2 = 0.1291 | R1 = 0.0911, wR2 = 0.1962 |
| **Largest diff peak and hole (e/Å^3)** | 1.97, -0.76          | 2.25, -1.95   | 3.48, -1.54 |
| **GOF**                | 1.211                | 1.119          | 1.383     |
Figure S7. $^1$H NMR spectrum of 2·THF in py-$d_5$ at 25 °C.
Figure S8. UV-vis spectrum of 2′THF (0.31 mM) in pyridine at 25 °C.
Figure S9. Near-IR spectrum of $\text{2} \cdot \text{THF}$ (5.90 mM) in pyridine at 25 °C. Sharp peaks denoted by * are electronic artifacts and not attributed to absorptions by $\text{2} \cdot \text{THF}$. 
Figure S10. Solid state EPR spectra for $1^{18}C_6\cdot 4THF$ at 4.0 (±1) K.
Figure S11. Solid state EPR spectra for $1^{\text{THF}}$ at 4.0 ($\pm 1$) K.
Figure S12. Normalized XANES plot of the absorption edge energies expressed as the first derivative for $1^{18}$C6·4THF, $1^{\text{THF}}$, and the uranium compounds used as oxidation state reference standards.
Figure S13. Normalized XANES plot of the absorption edge energies expressed as the first derivative for $1^{18C6}$.4THF, $1^{THF}$, and the uranium compounds used as oxidation state reference standards with the yttrium foil reference energy alignment shown by the dotted line.
Figure S14. Normalized XANES plot of the absorption edge energies for $1^{18}$C6-4THF, $1^{\text{THF}}$, and the uranium compounds used as oxidation state reference standards.
Table S2. XANES energies for $^{18}$C6·4THF, $^1$THF, and the uranium standards given as the edge energy at the inflection point (1\textsuperscript{st} derivative) and white line values.

| Compounds             | Inflection Point Energy (eV) | White Line Energy (eV) |
|-----------------------|------------------------------|------------------------|
| UI$_3$(dioxane)$_{1.5}$ | 17158.8                      | 17164.8                |
| UCl$_4$               | 17161.6                      | 17166.4                |
| $^{18}$C6·4THF        | 17161.7                      | 17167.5                |
| $^1$THF               | 17162.6                      | 17168.8                |
| U(O)[N(SiMe$_3$)$_3$]$_3$ | 17163.3                      | 17169.4                |
| UO$_2$Cl$_2$(THF)$_3$ | 17165.1                      | 17168.6                |
Figure S15 Temperature dependence of the $\chi_T$ product at 1000 Oe for $1^{18C6}$·4THF (red) and $1^{\text{THF}}$ (blue).
Figure S16. Temperature dependence of the $\chi T$ product under an applied dc field of 1000 Oe (blue) and 10,000 Oe (red) for $\text{I}^{18}\text{C6}.4\text{THF}$, where $\chi$ is the molar magnetic susceptibility as defined by $M/H$.
Figure S17. Temperature dependence of the $\chi T$ product under an applied dc field of 1000 Oe (blue) and 10,000 Oe (red) for $1^{\text{THF}}$, where $\chi$ is the molar magnetic susceptibility as defined by $M/H$. 
Computational Details. Density functional theory (DFT) calculations were performed to study the model systems \(\{[U(\eta^6-C_{14}H_{10})(\eta^4-C_{14}H_{10})(\mu-OMe)]_2\}^{2-} (1*)\) and \(K_2[U(\eta^6-C_{14}H_{10})(\eta^4-C_{14}H_{10})(\mu-OMe)]_2 (1-K*)\). Geometry optimizations were performed and the structures were confirmed as minima by means of harmonic vibrational analysis as implemented in the Turbomole program package V7.3. In every structure, we observe one to three imaginary frequencies associated with methyl rotations ranging from -14.83 to -113.53 cm\(^{-1}\). The PBE functional and the def2-TZVP basis set were used for all atoms with the exception of uranium, where the def-TZVP basis set and its corresponding ECP were employed. The D3 dispersion correction with Becke–Johnson damping was also used. The resolution of identity (RI) approximation was used for integral evaluation. These results were further analyzed by computing CM5 charges, atomic contributions to the molecular orbitals calculated using the Hirshfeld method, and topological analysis of the electron density with Bader’s Atoms in Molecules (AIM) were performed using the Multiwfn 3.7 software package. To calculate Mayer, Gophinatan-Jug (G-J), and Nalewajski-Mrozek (N-M) bond orders, DFT single point calculations were performed on the optimized ground state structures using the PBE and TPSS functionals as implemented in the Amsterdam Density Functional (ADF) program package. The TZP all electron basis set was used with no frozen core. Scalar relativistic effects were included using the zero-order regular approximation (ZORA). Energy decomposition analysis (EDA) was also performed in ADF with PBE. \(1^*\) was divided into two fragments: one containing a single anthracene ligand and the other containing the remainder of the molecule. The calculation was performed for both the \(\eta^4\) and \(\eta^6\) ligands. A single point calculation was performed on each fragment. The anthracene was taken to be formally -2 and a closed shell singlet, while the remainder of the molecule was neutral and in the high spin quintet state. Several spin states were explored for the uranium-containing fragment and the high spin quintet was the lowest in energy. These fragments were then used as the basis for the calculation on the full molecule (quintet spin, -2 charge).

In addition to the DFT calculations, the electronic structure was studied by the complete active space self-consistent field (CASSCF) method along with second-order energy corrections (CASPT2) only for \(1^*\). Given that the complex has two uranium centers that could have covalent interactions with the arenide ligands, the bonding in the dimer was also studied with restricted active space self-consistent field (RASSCF) method with corrections from second-order perturbation theory (RASPT2), which allows for larger active spaces to be studied than in
CASSCF. Both CASPT2 and RASPT2 calculations were performed using the OpenMolcas 18.094 program package on the geometries obtained from DFT. In the RASSCF and CASSCF(8e,12o) calculations, the ANO-RCC basis set of triple-\( \zeta \) quality was used for uranium and the first coordination sphere of uranium (i.e., the \( \eta^6/\eta^4 \) carbon and oxygen atoms). A minimal basis set was used for peripheral carbon and hydrogen atoms. The specific contractions used were 9s8p6d4f2g1h for U, 4s3p2d1f for O, 4s3p2d1s for coordinating C atoms, 2s1p for peripheral C atoms, and 1s for H. The CASSCF(4e,14o) and CASSCF(4e,8o) calculations and for computing the relative energies at the CASPT2 and RASPT2 levels of theory, an ANO-RCC basis set of triple-\( \zeta \) quality was used for uranium, while a basis set of double-\( \zeta \) quality was used for the first coordination sphere of uranium (i.e., the \( \eta^6/\eta^4 \) carbons and the oxygen atoms). A minimal basis set was used for peripheral carbon and hydrogen atoms. The specific contractions used were 9s8p6d4f2g1h for U, 3s2p1d for O, 3s2p1d for coordinating C atoms, 2s1p for peripheral C atoms, and 1s for H. Scalar relativistic effects are included through the use of the second-order Douglas-Kroll-Hess (DKH) Hamiltonian. The computation of the three-centered integrals was expedited through the use of Cholesky decomposition and local exchange screening. In CASPT2 and RASPT2, an IPEA shift of 0.25 and imaginary shift 0.2 a.u. were used. A discussion of active space choice is included in the results section, and the active orbitals are for all of the calculations are reported (Figures S20 to S30).
**Additional Computational Details and Discussion.**

**Hirshfeld Decomposition.** The four unpaired electrons are in uranium 5f-orbitals that have contributions primarily from uranium, although a small contribution from carbon atoms is present (note that only the contributions from the carbon atoms that coordinate to uranium are included in the percentages reported). SOMO, SOMO-1, SOMO-2 and SOMO-3 are singly occupied. The HOMO-4, HOMO-5, HOMO-6 and HOMO-7 orbitals contain more obvious mixing between the uranium and carbon atomic orbitals (Figure 5). For example, the HOMO-4, HOMO-5, HOMO-6 and HOMO-7 consist of contributions of 27.3%, 27.3%, 26.8% and 26.3% from uranium, respectively. The remaining orbitals and other lower energy orbitals are anthracene based, which is consistent with the observed bond distortions due to ligand reductions. Similar results were observed for 1-K* (Figure 5).

**QTAIM.** In order to further understand the nature of the chemical bonding in 1* and 1-K*, we performed a topological analysis of the electron density using the quantum theory of atoms in molecules (QTAIM) developed by Bader.\(^{24,36}\) In QTAIM, a chemical bond is present if a line of locally maximum electron density joins neighboring atoms. A bond critical point (BCP) is a point along the bond path where the electron density reaches a minimum. At a BCP, the gradient (\(\rho\)) of the electron density is zero and the Laplacian of the electron density, \(\nabla^2(\rho)\), could be positive or negative. A positive Laplacian means a local depletion of charge while a negative value corresponds to a local concentration of charge. In a covalent bond, the Laplacian should be negative since it is a sign of shared interaction of electron density between two linked atoms. A closed-shell interaction is associated with a positive Laplacian and these types of bonds generally are not considered covalent due to depletion of charge at the location of the BCP. The total electronic energy density, \(E(r)\), at the BCP is defined as the sum of the Lagrangian kinetic energy, \(G(r)\), and the potential energy density, \(V(r)\). In clear cases, when \(E(r)\) and the Laplacian electron density are both negative, the bond is covalent. In less clear cases, the Laplacian is positive and the \(E(r)\) is negative then the bond is considered to be dative. On the other hand, if \(E(r)\) is close to zero, then the bond is metallic. Finally, if \(E(r)\) is positive, the bond would be identified as ionic or Van der Waals. Note that in the case of 1-K*, two BCP points also observed for K-anthracene interaction; however, \(E(r)\) and \(\nabla^2(\rho)\) are both positive, which indicates a non-covalent electrostatic interaction.
Additional CASPT2 Calculations to Support Active Space Choice.

In CASSCF, an active space containing the \(5f\) orbitals on each uranium and their corresponding electrons for a total of 4 electrons in 14 orbitals was used. For uranium complexes in the +3 oxidation state or higher, the \(6d\) orbitals do not need to be included in the active space provided that they are not involved in bonding. We also performed CASSCF(4\(e\),8\(o\)) and CASSCF(8\(e\),12\(o\)) to see the \(5f\)-occupation and bonding between uranium and anthracene ligand.

In this complex, the CASSCF calculations do not include the uranium-carbon bonding orbitals in the active space. In order to study this interaction, RASSCF calculations were performed. The eight U-anthracene doubly occupied bonding orbitals are included in RAS1, while the corresponding eight anti-bonding orbitals are included in RAS3 (Figure S29-S32). Two holes are allowed in RAS1 and two electrons are allowed in RAS3. Using the notation of Sauri et al.\(^{37}\), we can describe this space as \((24e,2h,2e; 10o,8o,10o)\). Note that in RAS2, we have truncated the number of \(5f\)-electrons from the CASSCF calculation. If a \(5f\)-orbital had an occupation number larger than 0.01 in CASSCF(4\(e\),14\(o\)) for any of spin states explored, it was included in RAS2. The CASSCF(8\(e\),12\(o\)) calculation was performed starting from the orbitals generated in the RASSCF calculation.
Table S3. Relative energies (kcal/mol) for the RI-PBE-D3/def2-TZVP, def-TZVP on U optimized structures

| Spin     | 1*    | 1-K*  | <S*S> calculated | <S*S> ideal |
|----------|-------|-------|------------------|-------------|
| Triplet  | 7.5   | 6.8   | 3.2              | 2           |
| Quintet  | 0.0   | 0.0   | 6.5              | 6           |
| Septet   | 6.9   | 6.9   | 12.2             | 12          |
Figure S18. RI-PBE-D3/def2-TZVP, def-TZVP on U spin densities for 1* and 1-K* from the ground state quintet calculations.
Table S4. Selected U-C bond distances for PBE-D3 optimized geometry from triplet, quintet and septet spin states of compound 1*. Atom numbers labeled in Figure S19.

| Bond       | Triplet | Quintet | Septet |
|------------|---------|---------|--------|
| 61U-15C    | 2.654   | 2.665   | 2.677  |
| 61U-21C    | 2.635   | 2.638   | 2.64   |
| 61U-27C    | 2.645   | 2.644   | 2.655  |
| 61U-29C    | 2.701   | 2.690   | 2.726  |
| 61U-\(\eta_4\)C avg. | 2.659 | 2.659 | 2.675 |
| 61U-19C    | 2.626   | 2.632   | 2.636  |
| 61U-13C    | 2.77    | 2.780   | 2.788  |
| 61U-18C    | 2.797   | 2.794   | 2.824  |
| 61U-25C    | 2.652   | 2.650   | 2.692  |
| 61U-31C    | 2.826   | 2.811   | 2.837  |
| 61U-26C    | 2.803   | 2.790   | 2.797  |
| 61U-\(\eta_6\)C avg. | 2.746 | 2.743 | 2.762 |
| 62U-30C    | 2.669   | 2.692   | 2.808  |
| 62U-33C    | 2.628   | 2.653   | 2.676  |
| 62U-38C    | 2.619   | 2.641   | 2.665  |
| 62U-46C    | 2.64    | 2.645   | 2.779  |
| 62U-\(\eta_4\)C avg. | 2.639 | 2.658 | 2.732 |
| 62U-40C    | 2.621   | 2.637   | 2.659  |
| 62U-32C    | 2.771   | 2.801   | 2.755  |
| 62U-28C    | 2.781   | 2.818   | 2.787  |
| 62U-35C    | 2.617   | 2.653   | 2.69   |
| 62U-42C    | 2.773   | 2.797   | 2.811  |
| 62U-48C    | 2.776   | 2.784   | 2.789  |
| 62U-\(\eta_6\)C avg | 2.723 | 2.748 | 2.748 |
Table S5. Selected U-C bond distances for PBE-D3 optimized geometry from triplet, quintet and septet spin states of 1-K*. Atom numbers labeled in Figure S19.

| Bond       | Triplet | Quintet | Septet |
|------------|---------|---------|--------|
| 63U-29C    | 2.631   | 2.662   | 2.681  |
| 63U-34C    | 2.610   | 2.636   | 2.635  |
| 63U-24C    | 2.612   | 2.631   | 2.625  |
| 63U-16C    | 2.648   | 2.637   | 2.654  |
| 63U-η⁴ C Avg. | 2.625   | 2.641   | 2.649  |
| 63U-14C    | 2.602   | 2.618   | 2.682  |
| 63U-10C    | 2.783   | 2.779   | 2.817  |
| 63U-12C    | 2.779   | 2.788   | 2.842  |
| 63U-17C    | 2.593   | 2.631   | 2.740  |
| 63U-23C    | 2.765   | 2.804   | 2.854  |
| 63U-19C    | 2.752   | 2.782   | 2.809  |
| 63U-η⁶ C Avg. | 2.712   | 2.734   | 2.790  |
| 64U-32C    | 2.663   | 2.663   | 2.682  |
| 64U-28C    | 2.636   | 2.637   | 2.634  |
| 64U-35C    | 2.631   | 2.631   | 2.624  |
| 64U-43C    | 2.637   | 2.636   | 2.654  |
| 64U-η⁴ C Avg. | 2.642   | 2.642   | 2.649  |
| 64U-41C    | 2.631   | 2.629   | 2.742  |
| 64U-49C    | 2.785   | 2.788   | 2.843  |
| 64C-52C    | 2.765   | 2.779   | 2.815  |
| 64U-47C    | 2.617   | 2.619   | 2.681  |
| 64U-40C    | 2.795   | 2.782   | 2.807  |
| 64U-38C    | 2.810   | 2.802   | 2.854  |
| 64U-η⁶ C Avg. | 2.734   | 2.733   | 2.790  |
**Figure S19.** RI-PBE-D3/def-TZVP/def2-TZVP optimized ground state structures for $1^*$ and $1$-$K^*$ with average U-C($\eta^6/\eta^4$) bond distances.
Table S6: Properties at the bond critical points for 1* and 1-K*. All values are expressed in atomic units. Atom numbers labeled in Figure S19.

| Compounds | Bonds     | $\nabla^2 (\rho)$ | G(r) | V(r)  | E(r)  | $\rho$ |
|-----------|-----------|------------------|------|-------|-------|-------|
| 1*        | 61U-21C   | 0.11434          | 0.03684 | -0.04510 | -0.00826 | 0.05032 |
|           | 61U-15C   | 0.09107          | 0.03209 | -0.04141 | -0.00932 | 0.05048 |
|           | 61U-29C   | 0.09800          | 0.03245 | -0.04040 | -0.00795 | 0.04756 |
|           | 61U-19C   | 0.08272          | 0.03226 | -0.04385 | -0.01159 | 0.05541 |
|           | 61U-25C   | 0.08583          | 0.03171 | -0.04197 | -0.01026 | 0.05222 |
|           | 62U-30C   | 0.09887          | 0.03244 | -0.04017 | -0.00773 | 0.04706 |
|           | 62U-46C   | 0.09054          | 0.03286 | -0.04309 | -0.01023 | 0.05259 |
|           | 62U-38C   | 0.11491          | 0.03671 | -0.04469 | -0.00798 | 0.04958 |
|           | 62U-40C   | 0.08257          | 0.03193 | -0.04321 | -0.01129 | 0.05471 |
|           | 62U-35C   | 0.08472          | 0.03136 | -0.04154 | -0.01018 | 0.05198 |
| 1-K*      | 64U-43C   | 0.09977          | 0.03469 | -0.04443 | -0.00975 | 0.05220 |
|           | 64U-32C   | 0.10465          | 0.03441 | -0.04266 | -0.00825 | 0.04897 |
|           | 64U-35C   | 0.12611          | 0.03908 | -0.04663 | -0.00755 | 0.04931 |
|           | 64U-47C   | 0.07999          | 0.03237 | -0.04475 | -0.01238 | 0.05703 |
|           | 64U-41C   | 0.08281          | 0.03219 | -0.04367 | -0.01148 | 0.05487 |
|           | 63U-24C   | 0.12610          | 0.03906 | -0.04660 | -0.00754 | 0.04929 |
|           | 63U-16C   | 0.09973          | 0.03462 | -0.04431 | -0.00969 | 0.05207 |
|           | 63U-21C   | 0.10466          | 0.03445 | -0.04273 | -0.00828 | 0.04905 |
|           | 63U-17C   | 0.08282          | 0.03210 | -0.04349 | -0.01139 | 0.05466 |
|           | 63U-14C   | 0.08006          | 0.03246 | -0.04491 | -0.01245 | 0.05719 |
|           | 62K-39C   | 0.06872          | 0.01484 | -0.01250 | 0.00234  | 0.01656 |
|           | 62K-43C   | 0.05712          | 0.01217 | -0.01007 | 0.00211  | 0.01411 |
|           | 61K-16C   | 0.05709          | 0.01217 | -0.01006 | 0.00211  | 0.01410 |
|           | 61K-15C   | 0.06874          | 0.01484 | -0.01250 | 0.00234  | 0.01657 |
Table S7. Bond order of uranium and coordinated carbon atoms in 1* (PBE). Atom numbers labeled in Figure S19.

| Bonds     | Distance | Mayer | G-J | N-M(1) | N-M(2) | N-M(3) |
|-----------|----------|-------|-----|--------|--------|--------|
| 61U-15C   | 2.6655   | 0.4812| 0.4265| 0.5355 | 0.7404 | 0.5241 |
| 61U-21C   | 2.6384   | 0.3258| 0.319 | 0.3974 | 0.5302 | 0.3845 |
| 61U-27C   | 2.6441   | 0.3275| 0.3155| 0.3931 | 0.5261 | 0.3804 |
| 61U-29C   | 2.6903   | 0.4597| 0.4064| 0.5101 | 0.714  | 0.4991 |
| U-η⁴C Avg.| 2.660    | 0.40  | 0.37 | 0.46   | 0.63   | 0.45   |
| 61U-19C   | 2.6312   | 0.495 | 0.4395| 0.5532 | 0.736  | 0.5399 |
| 61U-13C   | 2.7789   | 0.2311| 0.1668| 0.2068 | 0.2057 | 0.1961 |
| 61U-18C   | 2.7935   | 0.2354| 0.1848| 0.2293 | 0.2264 | 0.2175 |
| 61U-25C   | 2.6503   | 0.4487| 0.4375| 0.5513 | 0.7527 | 0.5394 |
| 61U-31C   | 2.8105   | 0.2256| 0.1762| 0.2186 | 0.2161 | 0.2073 |
| 61U-26C   | 2.7897   | 0.2237| 0.1611| 0.1999 | 0.1977 | 0.1895 |
| U-η⁶C Avg.| 2.742    | 0.31  | 0.26 | 0.33   | 0.39   | 0.31   |
| 62U-30C   | 2.6922   | 0.4443| 0.3992| 0.5008 | 0.7039 | 0.49   |
| 62U-33C   | 2.6528   | 0.3272| 0.3116| 0.388  | 0.5207 | 0.3755 |
| 62U-38C   | 2.641    | 0.3211| 0.3156| 0.3932 | 0.5242 | 0.3804 |
| 62U-46C   | 2.644    | 0.4832| 0.4351| 0.5462 | 0.7483 | 0.5345 |
| U-η⁴C Avg.| 2.658    | 0.39  | 0.37 | 0.46   | 0.62   | 0.45   |
| 62U-40C   | 2.6368   | 0.4888| 0.4359| 0.5483 | 0.7319 | 0.5352 |
| 62U-32C   | 2.8012   | 0.2165| 0.1537| 0.1906 | 0.1878 | 0.1807 |
| 62U-28C   | 2.8184   | 0.2213| 0.1698| 0.2106 | 0.2085 | 0.1997 |
| 62U-35C   | 2.6534   | 0.4459| 0.4344| 0.547  | 0.7478 | 0.5353 |
| 62U-42C   | 2.7976   | 0.2341| 0.1797| 0.2229 | 0.2198 | 0.2113 |
| 62U-48C   | 2.784    | 0.2315| 0.1649| 0.2044 | 0.2035 | 0.1938 |
| U-η⁶C Avg.| 2.749    | 0.31  | 0.26 | 0.32   | 0.38   | 0.31   |
Table S8. Bond order of uranium and coordinated carbon atoms in 1* (TPSS). Atom numbers labeled in Figure S19.

| Bonds     | Distance | Mayer | G-J  | N-M(1) | N-M(2) | N-M(3) |
|-----------|----------|-------|------|--------|--------|--------|
| 61U-15C   | 2.6655   | 0.5086| 0.4178| 0.5396 | 0.7401 | 0.5267 |
| 61U-21C   | 2.6384   | 0.3376| 0.3044| 0.3903 | 0.5155 | 0.3765 |
| 61U-27C   | 2.6441   | 0.3412| 0.3026| 0.3878 | 0.5139 | 0.3741 |
| 61U-29C   | 2.6903   | 0.4879| 0.3975| 0.5133 | 0.7122 | 0.5008 |
| U-η4C Avg. | 2.660    | 0.42  | 0.36 | 0.46 | 0.62 | 0.44 |
| 61U-19C   | 2.6312   | 0.5163| 0.4319| 0.5599 | 0.7334 | 0.5446 |
| 61U-13C   | 2.7789   | 0.2461| 0.1648| 0.2104 | 0.2087 | 0.1992 |
| 61U-18C   | 2.7935   | 0.2493| 0.1796| 0.2293 | 0.226  | 0.2171 |
| 61U-25C   | 2.6503   | 0.4591| 0.4234| 0.5492 | 0.745  | 0.5358 |
| 61U-31C   | 2.8105   | 0.2425| 0.1732| 0.2211 | 0.2185 | 0.2094 |
| 61U-26C   | 2.7897   | 0.2381| 0.1573| 0.2007 | 0.198  | 0.19   |
| U-η6C Avg. | 2.742    | 0.33  | 0.26 | 0.33 | 0.39 | 0.32 |
| 62U-30C   | 2.6922   | 0.4702| 0.3908| 0.5041 | 0.7029 | 0.4917 |
| 62U-33C   | 2.6528   | 0.3422| 0.299 | 0.3827 | 0.5088 | 0.3692 |
| 62U-38C   | 2.641    | 0.3341| 0.3016| 0.3863 | 0.5099 | 0.3725 |
| 62U-46C   | 2.644    | 0.5098| 0.4267| 0.5507 | 0.7493 | 0.5374 |
| U-η4C Avg. | 2.658    | 0.41  | 0.35 | 0.46 | 0.62 | 0.44 |
| 62U-40C   | 2.6368   | 0.5099| 0.4292| 0.5556 | 0.7308 | 0.5405 |
| 62U-32C   | 2.8012   | 0.231 | 0.1505| 0.1919 | 0.1888 | 0.1816 |
| 62U-28C   | 2.8184   | 0.2384| 0.1676| 0.2137 | 0.2118 | 0.2024 |
| 62U-35C   | 2.6534   | 0.4571| 0.4218| 0.5465 | 0.742  | 0.5331 |
| 62U-42C   | 2.7976   | 0.2476| 0.1751| 0.2234 | 0.22   | 0.2115 |
| 62U-48C   | 2.784    | 0.2461| 0.1634| 0.2083 | 0.2071 | 0.1972 |
| U-η6C Avg. | 2.749    | 0.32  | 0.25 | 0.32 | 0.38 | 0.31 |
Table S9. Bond order of uranium and coordinated carbon atoms in 1-K* (PBE) Atom numbers labeled in Figure S19.

| Bonds      | Distance | Mayer | G-J | N-M(1) | N-M(2) | N-M(3) |
|------------|----------|-------|-----|--------|--------|--------|
| 63U-29C    | 2.6622   | 0.3812| 0.3972| 0.4985 | 0.7298 | 0.4901 |
| 63U-34C    | 2.6367   | 0.2729| 0.3174| 0.3947 | 0.5676 | 0.3844 |
| 63U-24C    | 2.6311   | 0.2703| 0.3214| 0.3998 | 0.572  | 0.3894 |
| 63U-16C    | 2.6371   | 0.4035| 0.4185| 0.5254 | 0.7578 | 0.5168 |
| U-η⁴C Avg. | 2.642    | 0.33  | 0.36 | 0.45   | 0.66   | 0.45   |
| 63U-14C    | 2.6179   | 0.5175| 0.4615| 0.5793 | 0.7523 | 0.5651 |
| 63U-10C    | 2.7791   | 0.2336| 0.1647| 0.2039 | 0.2007 | 0.1934 |
| 63U-12C    | 2.7878   | 0.2386| 0.1808| 0.2238 | 0.2194 | 0.2123 |
| 63U-17C    | 2.6312   | 0.4544| 0.4661| 0.5859 | 0.7797 | 0.5733 |
| 63U-23C    | 2.8042   | 0.2283| 0.1717| 0.2126 | 0.2073 | 0.2016 |
| 63U-19C    | 2.7817   | 0.2274| 0.1629| 0.2017 | 0.1976 | 0.1913 |
| U-η⁶C Avg. | 2.734    | 0.32  | 0.27 | 0.33   | 0.39   | 0.32   |
| 64U-32C    | 2.6629   | 0.3815| 0.397 | 0.4983 | 0.7297 | 0.4899 |
| 64U-28C    | 2.6373   | 0.273 | 0.3172| 0.3946 | 0.5675 | 0.3843 |
| 64U-35C    | 2.6308   | 0.2702| 0.3217| 0.4002 | 0.5724 | 0.3897 |
| 64U-43C    | 2.6358   | 0.405 | 0.4194| 0.5266 | 0.759  | 0.518  |
| U-η⁶C Avg. | 2.642    | 0.33  | 0.36 | 0.45   | 0.66   | 0.45   |
| 64U-41C    | 2.6294   | 0.4556| 0.4674| 0.5876 | 0.7812 | 0.5749 |
| 64U-49C    | 2.7883   | 0.2377| 0.1807| 0.2237 | 0.2192 | 0.2122 |
| 64C-52C    | 2.7797   | 0.2338| 0.1649| 0.2041 | 0.201  | 0.1936 |
| 64U-47C    | 2.6193   | 0.517 | 0.4609| 0.5787 | 0.7517 | 0.5644 |
| 64U-40C    | 2.7823   | 0.2275| 0.1627| 0.2014 | 0.1973 | 0.1911 |
| 64U-38C    | 2.803    | 0.2285| 0.1721| 0.2131 | 0.2079 | 0.2021 |
| U-η⁶C Avg. | 2.734    | 0.32  | 0.27 | 0.33   | 0.39   | 0.32   |
Table S10. Bond order of uranium and coordinated carbon atoms in 1-K* (TPSS). Atom numbers labeled in Figure S19.

| Bonds   | Distance | Mayer | G-J | N-M(1) | N-M(2) | N-M(3) |
|---------|----------|-------|-----|--------|--------|--------|
| 63U-29C | 2.6622   | 0.4187| 0.3861| 0.4972 | 0.7278 | 0.4873 |
| 63U-34C | 2.6367   | 0.2925| 0.3032| 0.3869 | 0.5549 | 0.3755 |
| 63U-24C | 2.6131   | 0.2891| 0.3068| 0.3916 | 0.5583 | 0.38   |
| 63U-16C | 2.6371   | 0.4446| 0.4105| 0.5289 | 0.7604 | 0.5186 |
| U-η^4C Avg. | 2.642 | 0.36 | 0.35 | 0.45 | 0.65 | 0.44 |
| 63U-14C | 2.6179   | 0.5465| 0.4538| 0.5854 | 0.7514 | 0.5689 |
| 63U-10C | 2.7791   | 0.2509| 0.1635| 0.2076 | 0.2047 | 0.1966 |
| 63U-12C | 2.7878   | 0.2545| 0.1776| 0.2257 | 0.2208 | 0.2136 |
| 63U-17C | 2.6312   | 0.4756| 0.4539| 0.586  | 0.7762 | 0.5714 |
| 63U-23C | 2.8042   | 0.2461| 0.1699| 0.2159 | 0.2106 | 0.2044 |
| 63U-19C | 2.7817   | 0.243 | 0.159 | 0.2019 | 0.1979 | 0.1912 |
| U-η^8C Avg. | 2.734 | 0.34 | 0.26 | 0.34 | 0.39 | 0.32 |
| 64U-32C | 2.6629   | 0.4192| 0.3859| 0.497  | 0.7276 | 0.4871 |
| 64U-28C | 2.6373   | 0.2927| 0.303 | 0.3866 | 0.5548 | 0.3753 |
| 64U-35C | 2.6308   | 0.2889| 0.307 | 0.3919 | 0.5586 | 0.3803 |
| 64U-43C | 2.6358   | 0.4465| 0.4114| 0.5301 | 0.7615 | 0.5198 |
| U-η^8C Avg. | 2.642 | 0.36 | 0.35 | 0.45 | 0.65 | 0.44 |
| 64U-41C | 2.6294   | 0.477 | 0.4552| 0.5877 | 0.7777 | 0.5731 |
| 64U-49C | 2.7883   | 0.2536| 0.1775| 0.2255 | 0.2206 | 0.2135 |
| 64U-52C | 2.7797   | 0.2512| 0.1636| 0.2078 | 0.205  | 0.1967 |
| 64U-47C | 2.6193   | 0.5461| 0.4533| 0.5847 | 0.7507 | 0.5683 |
| 64U-40C | 2.7823   | 0.2431| 0.1588| 0.2017 | 0.1977 | 0.1909 |
| 64U-38C | 2.803    | 0.2464| 0.1703| 0.2164 | 0.2111 | 0.2048 |
| U-η^8C Avg. | 2.734 | 0.34 | 0.26 | 0.34 | 0.39 | 0.32 |
Table S11. CM5 atomic charges calculated with PBE-D3 for ground state. Atom numbers labeled in Figure S19.

|       | I*      |       | 1-K*     |
|-------|---------|-------|----------|
| η⁶-anth | charge | η⁴-anth | charge | η⁶-anth | charge | η⁴-anth | charge |
| 3C    | -0.135712 | 1C    | -0.146814 | 3C    | -0.116917 | 1C    | -0.11734 |
| 4C    | -0.131343 | 2C    | -0.129511 | 4C    | -0.113379 | 2C    | -0.111855 |
| 5C    | -0.105196 | 6C    | -0.145033 | 5C    | -0.094434 | 6C    | -0.115609 |
| 9C    | -0.114061 | 8C    | -0.0245   | 8C    | -0.104466 | 7C    | -0.022022 |
| 13C   | -0.053981 | 10C   | -0.130339 | 10C   | -0.048973 | 11C   | -0.112761 |
| 18C   | -0.053587 | 11C   | -0.023901 | 12C   | -0.050151 | 13C   | -0.021182 |
| 19C   | -0.199262 | 7C    | -0.129518 | 14C   | -0.19386  | 9C    | -0.127132 |
| 25C   | -0.206817 | 22C   | -0.133598 | 17C   | -0.205062 | 20C   | -0.13428 |
| 26C   | -0.052764 | 12C   | -0.018362 | 19C   | -0.04865  | 15C   | -0.090193 |
| 31C   | -0.051481 | 23C   | -0.018494 | 23C   | -0.047233 | 16C   | -0.238805 |
| 34C   | -0.106295 | 15C   | -0.2038   | 22C   | -0.094341 | 21C   | -0.09148 |
| 39C   | -0.1142   | 21C   | -0.179069 | 27C   | -0.104671 | 24C   | -0.227181 |
| 41C   | -0.136128 | 27C   | -0.177437 | 25C   | -0.11706  | 29C   | -0.235047 |
| 45C   | -0.13105  | 29C   | -0.199834 | 31C   | -0.112809 | 34C   | -0.225073 |
| 65H   | 0.073471  | 63H   | 0.067846  | 91H   | 0.08837   | 75H   | 0.0937   |
| 66H   | 0.074386  | 64H   | 0.074341  | 92H   | 0.088557  | 76H   | 0.101463 |
| 67H   | 0.088855  | 68H   | 0.068215  | 93H   | 0.088744  | 77H   | 0.102208 |
| 70H   | 0.084013  | 71H   | 0.0741    | 94H   | 0.09468   | 78H   | 0.091724 |
| 78H   | 0.092993  | 69H   | 0.07738   | 85H   | 0.08804   | 79H   | 0.089654 |
| 83H   | 0.089141  | 81H   | 0.076353  | 86H   | 0.088599  | 80H   | 0.088001 |
| 88H   | 0.088394  | 73H   | 0.081749  | 87H   | 0.088671  | 81H   | 0.088741 |
| 92H   | 0.084498  | 85H   | 0.08092   | 88H   | 0.09476   | 82H   | 0.089906 |
| 94H   | 0.073142  | 80H   | 0.094978  | 89H   | 0.096589  | 83H   | 0.09021 |
| 96H   | 0.074424  | 84H   | 0.09531   | 90H   | 0.089737  | 84H   | 0.08844 |
| SUM   | -0.77     | SUM   | -0.87     | SUM   | -0.55     | SUM   | -0.95    |
| U     | 1.01      | O     | -0.52     | U     | 1.03      | O     | -0.52    |
Table S12. CASSCF and CASPT2 relative energies in kcal/mol for three different active space configurations.

| Spin   | CASSCF (4e,14o) | CASPT2 (4e,14o) | CASSCF (4e,8o) | CASPT2 (4e,8o) | CASSCF (8e,12o) | CASPT2 (8e,12o) |
|--------|----------------|-----------------|----------------|----------------|----------------|----------------|
| Singlet| 0.0            | 0.0             | 0.0            | 0.0            | 0.0            | 0.0            |
| Triplet| -0.001         | 0.3             | -0.001         | 0.3            | 0.0            | 0.3            |
| Quintet| -0.002         | 0.3             | -0.002         | 0.3            | -0.002         | 0.2            |
| Septet | -              | -               | -              | -              | 25.3           | 13.0           |
**Table S13.** RASSCF and RASPT2 energy differences in kcal/mol for three spin states.

| Spin     | RASSCF | RASPT2 |
|----------|--------|--------|
| Singlet  | 0.0004 | 0.00   |
| Triplet  | 0.00   | 0.25   |
| Quintet  | 0.0002 | 0.18   |
Table S14. LoProp Charges for coordinated carbon atoms, oxygen and uranium from RASSCF calculation of \( \text{I}^* \). Atom numbers labeled in Figure S19.

| \( \eta^8 \)-anth | charge | \( \eta^4 \)-anth | charge |
|-------------------|--------|-------------------|--------|
| 3C                | -0.1389| 1C                | -0.1468|
| 4C                | -0.1313| 2C                | -0.1325|
| 5C                | -0.1130| 6C                | -0.1448|
| 9C                | -0.1300| 8C                | -0.0063|
| 13C               | -0.0602| 10C               | -0.1341|
| 18C               | -0.0517| 11C               | -0.0035|
| 19C               | -0.5147| 7C                | -0.1952|
| 25C               | -0.5235| 22C               | -0.1998|
| 26C               | -0.0567| 12C               | 0.0486 |
| 31C               | -0.0485| 23C               | 0.0526 |
| 34C               | -0.1138| 15C               | -0.4839|
| 39C               | -0.1292| 21C               | -0.2361|
| 41C               | -0.1385| 27C               | -0.2314|
| 45C               | -0.1314| 29C               | -0.4743|
| 65H               | 0.0726 | 63H               | 0.0761 |
| 66H               | 0.0724 | 64H               | 0.0808 |
| 67H               | 0.0914 | 68H               | 0.0762 |
| 70H               | 0.0728 | 71H               | 0.0806 |
| 78H               | 0.0972 | 69H               | 0.0743 |
| 83H               | 0.0751 | 81H               | 0.0638 |
| 88H               | 0.0890 | 73H               | 0.076 |
| 92H               | 0.0733 | 85H               | 0.0765 |
| 94H               | 0.0725 | 80H               | 0.0974 |
| 96H               | 0.0724 | 84H               | 0.0963 |
| **SUM**           | -1.49  | **SUM**           | -1.49  |
| U                 | 2.78   | O                 | -1.03  |
Figure S20. The CASSCF \((4e,14\sigma)\) natural orbitals are shown for the quintet state for \(1^*\). Occupation numbers are in parentheses. An iso-value of 0.04 a.u. was used.
Figure S21. The CASSCF (4e,14o) natural orbitals are shown here for triplet state for 1*.
Occupation numbers are in parentheses. An isovalue of 0.04 a.u. was used.
Figure S22. The CASSCF \((4e,14\sigma)\) natural orbitals are shown here for singlet state for \(1^*\). Occupation numbers are in parentheses. An isovalue of 0.04 a.u. was used.
Figure S23. The CASSCF (4e,8o) natural orbitals are shown for the quintet state for 1∗. Occupation numbers are in parentheses. An isovalue of 0.04 was used.
Figure S24. The CASSCF \((4e,8o)\) natural orbitals are shown here for triplet state for \(1^*\). Occupation numbers are in parentheses. An isovalue of 0.04 was used.
Figure S25. The CASSCF(4e,8o) natural orbitals are shown here for singlet state for 1*. Occupation numbers are in parentheses. An isovalue of 0.04 was used.
Figure S26. The CASSCF(8e,12o) natural orbitals are shown here for quintet state for 1*. The orbitals from singlet and triplet state are qualitatively same. The occupations are also same for these three states; therefore, they are not plotted separately. Occupation numbers are in parentheses. An isovalue of 0.04 was used.
**Figure S27.** The CASSCF(8e,12o) natural orbitals are shown for septet state for 1*. Occupation numbers are in parentheses. An isovalue of 0.04 was used.
Figure S28. The RASSCF natural orbitals are shown for the quintet state of 1*. The occupation numbers are in parentheses. The percentage contribution from uranium and the coordinated carbon atoms are shown only for bonding orbitals. An isovalue of 0.04 a.u. was used.
**Figure S29.** The RASSCF natural orbitals are shown for the triplet state of $1^*$. The occupation numbers are in parentheses. An 0.04 isovalue was used.
Figure S30. The RASSCF natural orbitals are shown for the singlet state of dimer 1*. The occupation numbers are in parentheses. An iso-value of 0.04 a.u. was used.
Figure S31. RASSCF spin density for $1^*$. a) quintet state, b) triplet state.
Table S15: Selected C-C distances and bent angle from PBE-D3 optimized geometries for the triplet, quintet and septet spin states of 1*. Average values are also reported. Distances are in angstrom (Å). Coordinated C-C bonds are bolded. Bent angle for quintet state is shown in the bottom row in degrees.

| Bonds \(\eta^6\)-anth | Triplet | Quintet | Septet | Bonds \(\eta^4\)-anth | Triplet | Quintet | Septet |
|-------------------------|---------|---------|--------|-------------------------|---------|---------|--------|
| 25C-18C                 | 1.43663 | 1.43716 | 1.43436| C29-C27                | 1.43324 | 1.43364 | 1.42851|
| 18C-13C                 | 1.44461 | 1.44505 | 1.44345| C27-C21                | 1.39486 | 1.39543 | 1.39883|
| 13C-19C                 | 1.43771 | 1.43625 | 1.43696| C21-C15                | 1.43376 | 1.43392 | 1.42903|
| 19C-26C                 | 1.43525 | 1.43584 | 1.43449| C15-C12                | 1.45107 | 1.44865 | 1.44624|
| 26C-31C                 | 1.44394 | 1.44431 | 1.44437| C12-C23                | 1.45758 | 1.45809 | 1.45902|
| 31C-25C                 | 1.43848 | 1.4379  | 1.43551 | C23-C29              | 1.44638 | 1.44546 | 1.44163|
| 31C-39C                 | 1.41641 | 1.41756 | 1.41635 | C23-C22              | 1.39664 | 1.39641 | 1.39965|
| 39C-45C                 | 1.39429 | 1.39372 | 1.39585 | C22-C11              | 1.41766 | 1.4175  | 1.41603|
| 45C-41C                 | 1.40372 | 1.40378 | 1.40225 | C11-C8               | 1.44421 | 1.44427 | 1.44592|
| 41C-34C                 | 1.39369 | 1.39404 | 1.396  | C8-C7                | 1.42008 | 1.41923 | 1.41744|
| 34C-26C                 | 1.41693 | 1.41671 | 1.41725 | C7-C12              | 1.39409 | 1.39509 | 1.39572|
| 18C-9C                  | 1.4173  | 1.4169  | 1.41804 | C23-C22              | 1.41511 | 1.41596 | 1.41598|
| 9C-4C                   | 1.39313 | 1.3922  | 1.39323 | C22-C11              | 1.39306 | 1.39235 | 1.39195|
| 4C-3C                   | 1.40374 | 1.40496 | 1.40301 | C11-C8              | 1.40707 | 1.40761 | 1.40846|
| 3C-5C                   | 1.3946  | 1.39428 | 1.39643 | C8-C7                | 1.39062 | 1.39182 | 1.39125|
| 5C-13C                  | 1.41701 | 1.41662 | 1.41493 | C7-C12              | 1.41795 | 1.41744 | 1.41809|
| Average                 | 1.418  | 1.418  | 1.418  | Average             | 1.420  | 1.420  | 1.419  |
| Bent Angle              | 19.0    |         |        | 16.2                  |         |         |        |

S58
Table S16. Selected C-C distances and bent angle from PBE-D3 optimized geometries for the triplet, quintet and septet spin states of 1-K*. Average values are also reported. Distances are in angstrom (Å). Coordinated C-C bonds are bolded. Bent angle for quintet state is shown in the bottom row in degrees.

| Bonds  | Triplet | Quintet | Septet | Bonds  | Triplet | Quintet | Septet |
|--------|---------|---------|--------|--------|---------|---------|--------|
| η⁶-anth |         |         |        | η⁴-anth |         |         |        |
| 41C-38C | 1.44084 | 1.43929 | 1.4292 | 32C-28C | 1.44009 | 1.4398  | 1.43768 |
| 38C-40C | 1.44013 | 1.44108 | 1.44396| 28C-35C | 1.40617 | 1.40587 | 1.40748 |
| 40C-47C | 1.43711 | 1.43651 | 1.43011| 35C-43C | 1.44031 | 1.44073 | 1.44029 |
| 47C-52C | 1.43866 | 1.4373  | 1.43201| 43C-45C | 1.45668 | 1.4559  | 1.4535  |
| 52C-49C | 1.44213 | 1.4413  | 1.44393| 45C-39C | 1.46569 | 1.46545 | 1.46633 |
| 49C-41C | 1.43829 | 1.43904 | 1.42935| 39C-32C | 1.45247 | 1.45328 | 1.4511  |
| 49C-53C | 1.41736 | 1.41724 | 1.41961| 39C-37C | 1.39778 | 1.3964  | 1.39825 |
| 53C-57C | 1.39048 | 1.39053 | 1.38882| 37C-46C | 1.42455 | 1.42501 | 1.42365 |
| 57C-58C | 1.40475 | 1.40484 | 1.40686| 46C-51C | 1.43948 | 1.43962 | 1.44042 |
| 58C-56C | 1.39146 | 1.3906  | 1.38985| 51C-50C | 1.42534 | 1.42478 | 1.42409 |
| 56C-52C | 1.41649 | 1.41796 | 1.41756| 50C-45C | 1.39395 | 1.3951  | 1.39593 |
| 40C-36C | 1.41689 | 1.41691 | 1.41822| 46C-44C | 1.41408 | 1.41405 | 1.41452 |
| 36C-30C | 1.39056 | 1.39111 | 1.39088| 44C-48C | 1.38886 | 1.38869 | 1.38839 |
| 30C-26C | 1.4048  | 1.40473 | 1.40502| 48C-54C | 1.40705 | 1.40715 | 1.4072  |
| 26C-33C | 1.39092 | 1.3912  | 1.3905 | 54C-55C | 1.38921 | 1.38902 | 1.38927 |
| 33C-38C | 1.4153  | 1.41627 | 1.41887| 55C-51C | 1.41326 | 1.41319 | 1.41331 |
| Average | 1.417   | 1.417   | 1.416  | Average | 1.422   | 1.422   | 1.422   |
| Bent Angle | 22.2 |         |        |         | 17.5    |         |        |
Table S17. Orbital analysis of $1^*$ for the bonding orbitals from the RASSCF($24e^-, 2h, 2e^-; 10o, 8a, 10o$) calculation. The percent contributions are averaged from the singlet, triplet and quintet state orbitals.

| Orbital index | Total U | U 7s | U 6p | U 6d | U 5f | Total C | $\eta_1^6C$ | $\eta_1^4C$ | $\eta_2^6C$ | $\eta_2^4C$ |
|---------------|---------|------|------|------|------|---------|--------------|--------------|--------------|--------------|
| 287           | 11.73   | 0.28 | 2.25 | 7.44 | 1.30 | 86.78   | 54.14        | 1.17         | 23.65        | 0.58         |
| 288           | 12.45   | 0.56 | 2.59 | 6.73 | 1.14 | 87.02   | 0.44         | 5.56         | 5.81         | 68.14        |
| 289           | 12.03   | 0.47 | 2.37 | 6.68 | 1.01 | 87.10   | 4.90         | 55.91        | 1.13         | 17.93        |
| 290           | 12.68   | 0.13 | 2.51 | 7.86 | 1.31 | 85.57   | 23.72        | 0.48         | 53.53        | 0.98         |
| 291           | 17.62   | 2.43 | 2.62 | 7.97 | 2.11 | 80.77   | 2.54         | 63.77        | 0.21         | 8.41         |
| 292           | 14.95   | 0.88 | 2.44 | 7.57 | 2.14 | 84.57   | 0.78         | 8.52         | 3.07         | 65.75        |
| 293           | 15.28   | 1.58 | 1.67 | 8.38 | 1.90 | 82.97   | 32.23        | 3.97         | 32.46        | 3.75         |
| 294           | 17.69   | 5.04 | 2.12 | 7.43 | 1.90 | 81.23   | 30.42        | 4.96         | 31.26        | 4.28         |
| 295           | 14.79   | 1.81 | 3.35 | 6.43 | 1.15 | 84.41   | 3.74         | 19.82        | 6.56         | 45.91        |
| 296           | 13.42   | 0.71 | 2.68 | 6.86 | 1.05 | 86.14   | 6.24         | 61.43        | 1.28         | 9.50         |
Table S18. Orbital analysis of $1^*$ for the bonding orbitals from the CASSCF(8e,12o) calculation. The percent contributions are average from the singlet, triplet and quintet state orbitals.

| Orbital index | Total U | U 7s | U 6p | U 6d | U 5f | Total C | $\eta_1^4$C | $\eta_1^4$C | $\eta_2^6$C | $\eta_2^4$C |
|---------------|---------|------|------|------|------|---------|------------|------------|------------|------------|
| 295           | 16.43   | 3.29 | 1.98 | 7.20 | 1.46 | 82.20   | 0.33       | 5.99       | 3.24       | 62.52      |
| 296           | 15.47   | 1.65 | 1.53 | 7.92 | 1.44 | 83.93   | 3.14       | 64.65      | 0.36       | 5.86       |
Table S19. Energy decomposition analysis (EDA) for 1* using the PBE functional. Energies reported in kcal/mol.

|                  | 1* η^4  | 1* η^6  |
|------------------|---------|---------|
| Total Orbital Interaction | -166.71 | -170.37 |
| Electrostatic Interaction   | -170.53 | -165.48 |
| Pauli Repulsion          | 186.87  | 180.99  |
| Steric                  | 16.34   | 15.51   |
| Total Bonding Energy    | -150.37 | -154.86 |
| Total Repulsive (pauli)  | 186.87  | 180.99  |
| Total Attractive (elec and orb) | -337.24 | -335.85 |
| Ionic Contribution      | 50.57   | 49.27   |
| Orbital Contribution    | 49.43   | 50.73   |
References

1. Monreal, M. J.; Thomson, R. K.; Cantat, T.; Travia, N. E.; Scott, B. L.; Kiplinger, J. L., U₁₄(1,4-
dioxane)$_₂$, [UCl₆(1,4-dioxane)]$_₂$, and UΙ₃(1,4-dioxane)$_{1.5}$: Stable and Versatile Starting Materials for Low-
and High-Valent Uranium Chemistry. *Organometallics* **2011**, *30*, 2031-2038.

2. Kiplinger, J. L.; Morris, D. E.; Scott, B. L.; Burns, C. J., Convenient Synthesis, Structure, and
Reactivity of (C₅Me₅)₃U(CH₂C₆H₅)$_₃$: A Simple Strategy for the Preparation of Monopentamethylcyclopentadienyl Uranium(IV) Complexes. *Organometallics* **2002**, *21*, 5978-5982.

3. Fortier, S.; Brown, J. L.; Kaltsoyannis, N.; Wu, G.; Hayton, T. W., Synthesis, Molecular and
Electronic Structure of UV(O)[N(SiMe₃)$_3$. *Inorg. Chem.** 2012, *51*, 1625-1633.

4. Wilkerson, M. P.; Burns, C. J.; Paine, R. T.; Scott, B. L., Synthesis and Crystal Structure of
UO₂Cl₂(THF)$_₃$: A Simple Preparation of an Anhydrous Uranyl Reagent. *Inorg. Chem.* **1999**, *38*, 4156-4158.

5. C.U. Segre, N.E. Leyarovska, L.D. Chapman, W.M. Lav-ender, P.W. Plag, A.S. King, A.J. Kropf, B.A.
Bunker, K.M. Kemner, P. Dutta, R.S. Duran and J. Kaduk, CP521, Synchrotron Radiation Instrumentation:
Eleventh U.S. National Conference, ed. P. Pianetta, et al., p419-422, (American Institute of Physics, New
York, 2000).

6. Ravel, B.; Newville, M., ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption
spectroscopy using IFEFFIT. *J. Synchrotron Rad.* **2005**, *12*, 537-541.

7. SMART Apex II,Version 2.1; Bruker AXS Inc.: Madison, WI.

8. SAINT Software User's Guide,Version 7.34a; Bruker AXS Inc.: Madison, WI.

9. Blessing, R.Acta Crystallogr. A1995, A51.

10. Sheldrick, G. M. SHELXTL6.12; Bruker Analytical X-Ray Systems, Inc.: Madison, WI.

11. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. J. Appl.
Cryst.2009, 42, 339.

12. TURBMOLE V7.3 2018, a development of the University of Karlsruhe and Forschungszentrum
Karlsruhe GmbH, 1989-2007, TURBMOLE GmbH, since 2007; available from http://www.turbomole.com

13. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Phys.
Rev. Lett.* **1996**, *77*, 3865-3868.

14. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., A consistent and accurate ab initio parametrization of
density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*,
154104.

15. Grimme, S.; Ehrlich, S.; Goerigk, L., Effect of the damping function in dispersion corrected density
functional theory. *J. Comput. Chem.* **2011**, *32*, 1456-1465.

16. Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R., RI-MP2: optimized auxiliary basis sets and
demonstration of efficiency. *Chem. Phys. Lett.* **1998**, *294*, 143-152.

17. Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R., Auxiliary basis sets for main row atoms and
transition metals and their use to approximate Coulomb potentials. *Theor. Chem. Acc.* **1997**, *97*, 119-124.

18. Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H., Energy - adjusted pseudopotentials for the actinides.
Parameter sets and test calculations for thorium and thorium monoxide. *J. Chem. Phys.* **1994**, *100*, 7535-
7542.

19. Cao, X.; Dolg, M.; Stoll, H., Valence basis sets for relativistic energy-consistent small-core actinide
pseudopotentials. *J. Chem. Phys.* **2003**, *118*, 487-496.

20. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., A consistent and accurate ab initio parametrization of
density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*,
154104.

21. Grimme, S.; Ehrlich, S.; Goerigk, L., Effect of the damping function in dispersion corrected density
functional theory. *J. Comput. Chem.* **2011**, *32*, 1456-1465.
22. Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R., Auxiliary basis sets to approximate Coulomb potentials. *Chem. Phys. Lett.* **1995**, *240*, 283-290.
23. Lu, T.; Chen, F., Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, *33* (5), 580-592.
24. Roos, B. O.; Lindh, R.; Malmqvist, P.-Å.; Widmark, P.-O., Main Group Atoms and Dimers Studied with a New Relativistic ANO Basis Set. *J. Phys. Chem. A* **2004**, *108*, 2851-2858.
25. Roos, B. O.; Lindh, R.; Malmqvist, P.-Å.; Veryazov, V.; Widmark, P.-O., New relativistic ANO basis sets for transition metal atoms. *J. Phys. Chem. A* **2005**, *109*, 6575-9.
26. Douglas, M.; Kroll, N. M., Quantum electrodynamical corrections to the fine structure of helium. *Annals of Physics* **1974**, *82*, 89-155.
27. Aquilante, F.; Gagliardi, L.; Pedersen, T. B.; Lindh, R., Atomic Cholesky decompositions: A route to unbiased auxiliary basis sets for density fitting approximation with tunable accuracy and efficiency. *J. Phys. Chem. A* **2009**, *130*, 154107.
28. Aquilante, F.; Lindh, R.; Pedersen, T. B., Analytic derivatives for the Cholesky representation of the two-electron integrals. *J. Chem. Phys.* **2008**, *129*, 034106.
29. Aquilante, F.; Malmqvist, P.; Pedersen, T. B.; Ghosh, A.; Roos, B. O., Cholesky Decomposition-Based Multiconfiguration Second-Order Perturbation Theory (CD-CASPT2): Application to the Spin-State Energetics of Co(III)(diiminato)(NPh). *J. Chem. Theory Comput.* **2008**, *4*, 694-702.
30. Aquilante, F.; Pedersen, T. B.; Lindh, R., Low-cost evaluation of the exchange Fock matrix from Cholesky and density fitting representations of the electron repulsion integrals. *J. Chem. Phys.* **2007**, *126*, 194106.
31. Bader, R. F. W., A Bond Path: A Universal Indicator of Bonded Interactions. *J. Phys. Chem. A* **1998**, *102*, 7314-7323.
ABSTRACT: Chatt reaction methods were employed to synthesize the first well characterized actinide-arene sandwich complexes. Namely, addition of [UI$_2$(THF)$_3$(μ-OMe)]$_2$·THF (2·THF) to THF solutions containing 6 equiv. of K[C$_{14}$H$_{10}$] generates the dimeric complexes [K(18-crown-6)(THF)$_2$][U(η$_6$-C$_{14}$H$_{10}$)(η$_4$-C$_{14}$H$_{10}$)(μ-OMe)]$_2$·4THF (I$^{18C_6}$·4THF) and {[K(THF)$_3$][U(η$_6$-C$_{14}$H$_{10}$)(η$_4$-C$_{14}$H$_{10}$)(μ-OMe)]}$_2$ (I$^{THF}$) upon crystallization of the products in THF in the presence or absence of 18-crown-6, respectively. Both I$^{18C_6}$·4THF and I$^{THF}$ are thermally stable in the solid-state at room temperature; however, after crystallization, they become insoluble in THF or DME solutions and instead gradually decompose upon standing. X-ray diffraction analysis reveals I$^{18C_6}$·4THF and I$^{THF}$ to be structurally similar, possessing uranium centers sandwiched between anthracene ligands of mixed tetrahapto and hexahapto ligation modes. Yet, the two complexes are distinguished by the close contact potassium-arene ion pairing that is seen in I$^{THF}$ but absent in I$^{18C_6}$·4THF, which is observed to have a significant effect on the electronic characteristics of the two complexes. Structural analysis, SQUID magnetometry data, XANES spectral characterization, and computational analyses are generally consistent with U(IV) formal assignments for the metal centers in both I$^{18C_6}$·4THF and I$^{THF}$, though noticeable differences are detected between the two species. For instance, the effective magnetic moment of I$^{THF}$ (3.74 μ$_B$) is significantly lower than that of I$^{18C_6}$·4THF (4.40 μ$_B$) at 300 K. Furthermore, the XANES data shows the U L$_{III}$-edge absorption energy for I$^{18C_6}$·4THF to be 0.9 eV higher than that of I$^{THF}$, suggestive of more oxidized metal centers in the former. Of note, CASSCF calculations on the model complex {[U(η$_6$-C$_{14}$H$_{10}$)(η$_4$-C$_{14}$H$_{10}$)(μ-OMe)]}$_2$ (I$^*$) shows highly polarized uranium-arene interactions defined by π-type bonds where the metal contributions are primarily comprised by the 6$d$-orbitals (7.3 ± 0.6%) with minor participation from the 5$f$-orbitals (1.5 ± 0.5%). These unique complexes provide new insights into actinide-arene bonding interactions and show the sensitivity of the electronic structures of the uranium atoms to coordination sphere effects.
**Introduction**

The structural elucidation of bis(benzene)chromium, \( \text{Cr(\eta^6-C_6H_6)_2} \), by E. O. Fischer was a landmark discovery as it established a new chemical bonding paradigm for both transition metal and carbon molecules alike,\(^1\) expanding upon the seminal structural characterization of ferrocene a few years earlier.\(^2\) In \( \text{Cr(\eta^6-C_6H_6)_2} \), the molecule features a formally chromium(0) atom sandwiched between two neutral benzene rings wherein stabilization is bidirectional: donation of the benzene \( \pi \)-electrons into empty metal orbitals accompanied by backbonding of occupied metal orbitals into the empty benzene \( \pi^* \)-orbitals.\(^3\) This contrasts the bonding scheme in \( \text{Cp}_2\text{Fe} \) (\( \text{Cp} = \eta^5\text{-C}_5\text{H}_5 \)), which is considered to contain an iron(II) center sandwiched between two \( \pi \)-donating, anionic, aromatic \( \text{Cp}^– \)ligands with negligible backbonding character.\(^4\) Indeed, subsequent analysis of the bonding in \( \text{Cr(\eta^6-C_6H_6)_2} \) suggests that chromium \( \delta \)-backdonation is the largest contributor to the bonding interactions.\(^5\)

Not surprisingly, \( \text{Cr(\eta^6-C_6H_6)_2} \) has been the focus of several structural studies, providing valuable insights into metal bonding and chemistry.\(^7\) Notably, \( \text{Cr(\eta^6-C_6H_6)_2} \) is more than a simple curiosity as chromium mono- and bis(arene) complexes have become important reagents for organic synthesis and catalysis.\(^8\)

Consequently, \( \text{Cr(\eta^6-C_6H_6)_2} \) has spawned a rich and diverse field of metal-arene chemistry spanning the \( d \)-block and growing to encompass the main group element series.\(^9\) On the other hand, glaringly lacking are metal-arene\(^1\) sandwich complexes belonging to the \( 4f \)-and \( 5f \)-metals. Using electron-beam vaporization techniques, Cloke and co-workers accomplished the remarkable synthesis of a few, thermally stable homoleptic lanthanide-arene sandwich compounds of the type \( \text{Ln(\eta^6-\text{Bu}_3\text{C}_6\text{H}_3)_2} \) (\( \text{Ln} = \text{Nd}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{and Lu} \)) and the thermally unstable species \( \text{Ln(\eta^6-\text{Bu}_3\text{C}_6\text{H}_3)_2} \) (\( \text{Ln} = \text{La}, \text{Pr}, \text{Sm} \)).\(^12\)-\(^14\) Electronic structure calculations show substantial lanthanide \( d \)-orbital \( \rightarrow \pi^* \)-arene backbonding.\(^15\)-\(^17\) This is illuminating and surprising in many regards as the bonding of the lanthanide metals is typically considered to be predominantly ionic in nature, yet it is still possible for these metals to participate in covalent backbonding interactions through \( 5d \)-orbital contributions. Furthermore, the study validates the core-like nature of the \( 4f \)-orbitals and their unavailability for bonding. Though, in 2017, Mazzanti and co-workers reported the synthesis of the triple decker complex \([\text{K}(2.2.2\text{-crypt})]_2[\{(\text{KL}_3\text{Ce})(\mu-\eta^6-\text{\text{\eta}C}_6\text{H}_3)_2}\]_2\text{Ce} \) (\( \text{L} = \text{O} \text{Si(O}^\text{Bu})_3 \)) from the reduction of \([\text{KCeL}_4]\).\(^18\) This trinuclear compound features a cerium arene-sandwich \([\text{Ce(\eta^6-\text{C}_7\text{H}_7)_2}]^2 \) core, and DFT calculations show that each of the cerium atoms engages the toluene moieties through \( \delta \)-bonding involving the \( 4f \)-orbitals.

Homoleptic actinide-arene sandwich complexes would be particularly noteworthy and important for studying actinide bonding behavior as the \( 5f \)-orbitals extend beyond the core. Compounds such as these may give way to interesting molecules possessing exotic \( \sigma \)-type bonds.\(^19\)-\(^20\) Understanding these types of molecules and their bonding character are important for addressing one of the more poorly understood areas of actinide science, namely the role and participation of the \( 5f \)- and \( 6d/7s/7p \)-valence orbital combinations to chemical bonding.\(^21\)

Yet, with respect to the actinides, all efforts to use similar vaporization techniques to produce the analogous \( \text{An(\text{\eta}^6-\text{\text{\eta}C}_6\text{H}_6)_2} \) compounds have failed,\(^16\) though gas-phase reactions have successfully detected the formation of \([\text{U(\eta^6-\text{\text{\eta}Bu}_3\text{C}_6\text{H}_3)_2}]^2 \)\(^22\) suggesting an achievability for such molecules. In fact, quantum calculations predict \( \text{U(\eta^6-\text{\text{\eta}Bu}_3\text{C}_6\text{H}_3)_2} \) to have a metal-arene bond disruption enthalpy of 88 kcal/mol, exceeding that of the analogous \( \text{Ln(\eta^6-\text{\text{\eta}Bu}_3\text{C}_6\text{H}_3)_2} \) (\( \text{Ln} = \text{Ce} – \text{Yb} \)) (28 – 72 kcal/mol) and \( \text{M(\eta^6-\text{\text{\eta}Bu}_3\text{C}_6\text{H}_3)_2} \) (\( \text{M} = \text{Group 4, Group 5; 49 – 79 kcal/mol} \)) complexes;\(^17\) though, the reliability of the calculated enthalpy value for uranium has been called into question due to the complicated electronic structure of the actinides.\(^15\)

In 1970, Cesari et al. demonstrated that unsupported actinide-monoarene adducts could be accessed by applying Fischer’s reductive Friedel-Crafts conditions used in the synthesis of \( \text{Cr(\eta^6\text{-C}_6\text{H}_6)_2} \). Specifically, the treatment of \( \text{UCl}_4 \) with an excess of \( \text{AlCl}_3 \) and \( \text{A}^0 \) in benzene gives the \( \text{U(III)} \) complex \([\text{U(\eta^6\text{-C}_6\text{H}_6)}\text{U(AlCl}_3)]_3 \).\(^23\) Following a similar strategy, Cotton, Schwotzer, and others subsequently reported the synthesis and structural characterization of a handful of uranium-monoarene adducts including the first \( \text{U(IV)} \) arene complex \([\{(\eta^6\text{-C}_6\text{Me})\text{UCl}_2]_2(\mu-\text{Cl})_3\}]\text{AlCl}_4 \).\(^24\)-\(^27\) Later, Ephritikhine et al. showed that thermal decomposition of \( \text{U(BH}_3) \) in mesitylene affords \( \text{U(\eta^6-C}_6\text{Me}_3\text{U(BH}_3) \), which undergoes facile ligand displacement with hexamethylbenzene to give \( \text{U(\eta^6-C}_6\text{Me}_3)\text{U(BH}_3) \).\(^28\) The U-arene bonding in these complexes is likely to be electrostatic in nature with the neutral arene coordinating through the \( \pi \)-electron cloud as a Lewis base to the highly electron deficient uranium.
centers. Consequently, inspection of the C\textsubscript{ ary}–C\textsubscript{ ary} distances reveals no bond length distortions,\textsuperscript{27} indicating a lack of metal backbonding, with the arene readily displaced by coordinating solvents such as THF.\textsuperscript{24} More recently, Braunschweig \textit{et al.} reported the first actinide π-complexes with neutral 1,4-diborabenzenes to give (dbb)AnCl\textsubscript{L} (dbb = 1,4-bis(cAAC)\textsubscript{2})–1,4-diborabenzenes; An = Th, U; L = THF, MeCN). In this case, the dbb An bond was found to be very strong, though, also primarily electrostatic in character.\textsuperscript{29} In specific regards to thorium, Gambartotta and co-workers have reported the synthesis of the thorium naphthalene complexes [Li(DME)\textsubscript{3}][{[K(DME)][(Et\textsubscript{S}-calix[4]tetrapyrrole)Th(\eta\textsuperscript{2}–C\textsubscript{10}H\textsubscript{8})]}], \textsubscript{30} and [O–2,4′–Bu\textsubscript{2}–C\textsubscript{6}H\textsubscript{2}(CH\textsubscript{2})\textsubscript{2}Th(\eta\textsuperscript{4}–C\textsubscript{10}H\textsubscript{8})\textsubscript{2}][K(18-crown-6)].\textsuperscript{31} The latter is the only reported actinide-arene sandwich complex; however, low yields and persistent impurities prevented characterization beyond the determination of its solid-state molecular structure.

Compounds containing actinide-arene interactions have become increasingly important moieties in 5f-element chemistry. So-called inverted sandwich complexes featuring An-arene-An cores have become nearly commonplace in uranium organometallic chemistry in recent years.\textsuperscript{32} These complexes have provided valuable electronic insight into actinide bonding, particularly with respect to δ-interactions, while enabling rich redox chemistry and other novel reactivity patterns such as the C–H borylation of arenes.\textsuperscript{32,44} For example, U(O–2,6′–Bu\textsubscript{2}–C\textsubscript{6}H\textsubscript{3})\textsubscript{3} reacts with benzene in the presence of HBBN (HBBN = 9-bora-9-bicyclononane) to give the inverted sandwich product [U(O–2,6′–Bu\textsubscript{2}–C\textsubscript{6}H\textsubscript{3})\textsubscript{2}][\mu–\eta\textsuperscript{6}–\eta\textsuperscript{6}–C\textsubscript{6}H\textsubscript{6}(BBN)].\textsuperscript{43} Moreover, uranium-arene interactions play key roles in the stabilization of the rare U(II) oxidation state in [K(2.2.2-cryptand)][{(\eta\textsuperscript{4}–Mes)\textsubscript{2}ArO)\textsubscript{2}U\textsuperscript{2+}][{(\eta\textsuperscript{4}–Mes)\textsubscript{2}ArO)\textsubscript{2}Mes = \kappa\textsuperscript{3}–\eta\textsuperscript{6}–C\textsubscript{6}Me\textsubscript{3}(CH\textsubscript{2})(O–C\textsubscript{6}H\textsubscript{2}MeAd)}].\textsuperscript{45} and U(\kappa\textsuperscript{3}–\eta\textsuperscript{6}–NHA\textsubscript{ArPh}\textsuperscript{46} = (2,4,6′–Pr\textsubscript{3}–C\textsubscript{6}H\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3}).\textsuperscript{46} where the uranium-arene bonds are enforced through intramolecular ligand tethering. Interestingly, it has been predicted by means of density functional theory (DFT) that uranium-arene complexes may also provide access to the unknown U(I) oxidation state.\textsuperscript{47} 

On this note, the use of tethered ligand manifolds to encourage supported actinide-arene interactions has become a popular approach within recent years.\textsuperscript{45–46,48–57} Bart, Meyer, and coworkers first demonstrated that uranium-arene δ-bonding was a key feature of their U(III) complex [(\textsuperscript{Bu,\textsubscript{Bu}}ArO)\textsubscript{3}Mes]U,\textsuperscript{48} while Arnold and coworkers showed that redox isomerization of the trans-calix[2]benzene[2]pyrllide (bz\textsubscript{2}pyr\textsuperscript{2–}) uranium complex gives rise to the supported sandwich compound (κ\textsuperscript{2}–\eta\textsuperscript{6}–\eta\textsuperscript{6}–bz\textsubscript{2}pyr\textsuperscript{2–})U\textsuperscript{III}X (X = I, BH\textsubscript{4}, O–2,6′–Bu\textsubscript{2}–C\textsubscript{6}H\textsubscript{3}, N(SiMe\textsubscript{3})\textsubscript{2}).\textsuperscript{52–53} In our own work, we have utilized an N,N′-tethered uranium-arene platform, viz. [(κ\textsuperscript{2}–\eta\textsuperscript{6}–L\textsuperscript{Ar})U\textsuperscript{III}]+ (L\textsuperscript{Ar})\textsuperscript{2–} = 2,2′-bis(2,6′–Pr\textsubscript{2}–C\textsubscript{6}H\textsubscript{3}N)–p-terphenyl, to stabilize an unusual U–Fe bond and separately generate a highly reactive uranium-

![Scheme 1](image_url)

\textit{Scheme 1.} Synthesis of complexes 1\textsuperscript{18Cs} and 1\textsuperscript{THF} from 2.
Regardless, the ancillary ligand coordination in these systems provides additional bonding contributions and potential ligand strain effects that can compete with or affect the actinide-arene bonding.

Considering the soft nature of neutral aromatic hydrocarbons and the hard Lewis acidic character of the actinide ions, we hypothesized that the formation of unsupported 5f-sandwich arene complexes would be best accessed through the use of Chatt reaction conditions as popularized by Ellis and others.10 This method specifically refers to the reaction of a metal salt with a reduced arene anion to give metal-arene products through salt metathesis. The compounds produced in these reactions are often found to form “-ate” complexes, which have been referred to as “arene-metalates.”

Through these means, we herein report the synthesis and characterization of the first unsupported uranium arene-metalate sandwich complexes, namely [K(18-crown-6)(THF)2][U(η6-C14H10)(η4-C14H10)(μ-OMe)]2·4THF (118C6·4THF) and ion contact paired {[K(THF)3][U(η6-C14H10)(η4-C14H10)(μ-OMe)]}2(1THF), formed from the reaction of excess K[C14H10] with the methoxy-iodide dimer [UI2(THF)3(μ-OMe)]2(2). Compounds 118C6·4THF and 1THF are isolated in modest yields, and their structural and electronic properties have been thoroughly characterized through X-ray diffraction analysis, EPR spectroscopy, SQUID magnetometry, XANES spectroscopy, DFT, and multireference wavefunction-based computational methods. The magnetic and XANES data show a clear difference in the electronic properties of 118C6·4THF from 1THF, revealing a key sensitivity of the electronic structure to coordination sphere ion pairing effects.

Results and Discussion

Synthesis. In one instance, addition of UI3(dioxane)1.5 to a stirring solution of 6 equiv. of K[C14H10] (prepared in-situ) in DME at -35 °C produced an intensely dark blue solution. Filtration of the reaction mixture at room temperature afforded a dark blue solid that solubilized in THF to which excess 18-crown-6 was added, resulting in the formation of a few single crystals after 12 h at -35 °C. Single crystal X-ray diffraction analysis revealed the formation of the uranium bis(anthracene) sandwich dimer 118C6·4THF (Figures 1 and S2), with the units conjoined through two bridging methoxide ligands. The formation of the methoxide groups in 118C6 was unexpected but is presumably formed from the reductive cleavage of the DME solvent, a phenomenon that is preceded in f-element

![Figure 1. ORTEP diagram of 118C6·4THF with 30% thermal probability ellipsoids. Hydrogen atoms, co-crystallized THF, and the non-coordinated cations ([K(18-crown-6)(THF)2]+) are omitted for clarity. * denote symmetry generated atom positions.](image-url)
Multiple attempts to reproduce this synthesis failed, giving \([\text{K}(18\text{-crown-6})(\text{THF})_2][\text{C}_{14}\text{H}_{10}]\) as the only isolable product.

We postulate that the uncontrolled reductive cleavage of the reaction solvent to form the methoxy ligands of \(\text{I}^{18}\text{C}_6\) is primarily responsible for the irreproducibility of the reaction and therefore set out to pre-install the methoxy groups on uranium prior to \(\text{K}[\text{C}_{14}\text{H}_{10}]\) addition. Adding one equiv. of \(\text{K}[\text{OMe}]\) to \(\text{UI}_3(\text{dioxane})_{1.5}\) in THF gives \(2\cdot\text{THF}\) as a blue crystalline solid upon workup in 60\% yield (Equation 1) (Figure S1).

This uranium(III) methoxy-bridged precursor, 2, proved ideal as conversion to \(\text{I}^{18}\text{C}_6\) can be accomplished directly through salt metathesis, thus avoiding the necessity for adventitious DME cleavage. Addition of \(2\cdot\text{THF}\) to a cold, stirring solution of 6 equiv. of \(\text{K}[\text{C}_{14}\text{H}_{10}]\) in THF followed by filtration and addition of 2 equiv. of 18-crown-6 reproducibly generates \(\text{I}^{18}\text{C}_6\cdot4\text{THF}\) in modest yields of 35\% as a highly crystalline, midnight-blue colored product (Scheme 1). Forgoing the use of 18-crown-6 produces the THF-solvated complex \(\text{I}^{\text{THF}}\) in comparable yields (Scheme 1) (Figure S6). In these reactions, 2 equiv. of anthracene are also produced that can co-deposit in the product mixture. Yet, after crystallization, both \(\text{I}^{18}\text{C}_6\cdot4\text{THF}\) and \(\text{I}^{\text{THF}}\) exhibit insolubility in DME and THF with the residual anthracene readily removed by thorough washing of the crystalline material with THF to give analytically pure products as shown by combustion analyses.

These compounds are also insoluble in non-polar solvents and aromatics such as toluene.

Compounds \(\text{I}^{18}\text{C}_6\cdot4\text{THF}\) and \(\text{I}^{\text{THF}}\) are exceedingly air-sensitive, instantaneously bleaching in color upon exposure. On the other hand, they are thermally stable as solids and can be stored indefinitely under dinitrogen or argon atmospheres. Suspensions of isolated samples of \(\text{I}^{18}\text{C}_6\cdot4\text{THF}\) and \(\text{I}^{\text{THF}}\) in THF are unstable, and despite their insolubility, will gradually decompose (under N\(_2\) or Ar) to give black insoluble material and dark blue solutions with \(\text{K}[\text{C}_{14}\text{H}_{10}]\) as the only product detectable by electronic absorption spectroscopy (UV-vis/NIR). This solution-phase instability suggests that \(\text{I}^{18}\text{C}_6\cdot4\text{THF}\) and \(\text{I}^{\text{THF}}\) are likely the kinetic products of the reaction.

The solid-state molecular structures of \(\text{I}^{18}\text{C}_6\cdot4\text{THF}\) (Figures 1 and S2) and \(\text{I}^{\text{THF}}\) (Figure S6) are nearly isostructural with the differences arising from the potassium ion pairing, yielding a charge-separated, non-interacting pair in the former and a close contact pair in the latter, possessing K-C\text{arene} interactions. Otherwise, both complexes feature a [[\(\text{U}(\eta^4\cdot\text{C}_{14}\text{H}_{10})(\eta^4\cdot\text{C}_{14}\text{H}_{10}(\mu\cdot\text{OMe}))_2\)__2] dimeric core. By far, the most salient feature of \(\text{I}^{18}\text{C}_6\cdot4\text{THF}\) and \(\text{I}^{\text{THF}}\) is the sandwiching of each uranium center between two anthracene units that are observed to adopt distinct \(\eta^4\) and \(\eta^6\)-coordination. The mixed binding modes of the anthracenes is an uncommon feature for electronically unsaturated bis(arene)-metalatides and, to the best of our knowledge, has been documented in only a few cases. (62-64)

\[
\text{UI}_3(\text{dioxane})_{1.5} + \text{KOMe} \xrightarrow{\text{THF, RT, -Kl}} 0.5 \left[\text{UI}_2(\text{THF})_3(\mu\cdot\text{OMe})\right]_2 \quad (1)
\]
The solid-state molecular structure of 1\textsuperscript{THF} is afflicted with severe positional disorder of its potassium-coordinated THF molecules, consequently affecting the data quality, leading to slightly reduced precision of the bond metrics. Therefore, only the structural features of 1\textsuperscript{BEC-4THF} are discussed here in detail.

Complex 1\textsuperscript{BEC-4THF} crystallizes in the triclinic space group $P\overline{1}$ with one half of the molecule in the asymmetric unit, generating the full complex through crystallographic inversion symmetry, rendering the metrics within the monomeric units identical. The U1-($\eta^4$-C\texttext{-}arene) distances narrowly range from 2.638(5) to 2.676(6) Å. Tetrahapto coordination of aromatic or carbocyclic ligands to the actinides is rare, but a handful of cyclobutadiene complexes are known. The U1-($\eta^5$-C\texttext{-}arene) distances in 1\textsuperscript{BEC-4THF} are significantly longer than the uranium-cyclobutadiene distances found in [Na(12-crown-4)]\textsuperscript{[}[[\eta^4-C_4(SiMe_3)_3]U(BH_4)]\textsuperscript{]} (U-C\textsubscript{Cb} = 2.522(5) – 2.556(4) Å) and [U[$\eta^4$-C_4(SiMe_3)_3]($\mu$-BH$_2$)(K(THF))$_2$] (U-C\textsubscript{Cb} = 2.46(2) – 2.56(2) Å) but fall within the upper range of those in [U[$\eta^4$-C_4(SiMe_3)_3]($\eta^5$-C_5H(SiMe_3)_5-CH$_2$SiMe$_2$(BH$_4$))] (U-C\textsubscript{Cb} = 2.550(5) – 2.650(6) Å). Closer comparison can be made to the thorium compound {[O-2,4-Bu$_2$-C$_6$H$_7$(CH$_2$)$_2$Th($\eta^4$-C$_{10}$H$_8$)$_2$]}[K(18-crown-6)]\textsuperscript{2} which features Th-C\texttext{-}arene bonds that range from 2.671(8) to 2.784(8) Å,\textsuperscript{31} where the elongation of the thorium-arene distances as compared to 1\textsuperscript{BEC-4THF} possibly result from the slight size difference in the ionic radii between thorium and uranium (e.g., Th(IV), C.N. = 6, r = 0.94 Å vs. U(IV), C.N. = 6, r = 0.89 Å).\textsuperscript{66}

Inspection of the U1-($\eta^6$-C\texttext{-}arene) distances reveals two sets of bond lengths, two shorter (U1-C\textsubscript{arene} = 2.557(5) – 2.571(6) Å) and four longer (U1-C\textsubscript{arene} = 2.766(5) – 2.797(5) Å), that differ by approximately 0.2 Å, a consequence of the observed ring puckering of the anthracene ligand (vide infra). The range of the U1-C\textsubscript{arene} distances along with the nominal uranium-centroid distance U1-($\eta^6$-C\textsubscript{cent}) = 2.31 Å of 1\textsuperscript{BEC-4THF} are significantly shorter than those found in the monoarene Friedel-Crafts type complexes [($\eta^6$-C$_6$H$_6$)U(AlCl$_4$)$_3$] (U-C\textsubscript{cent} = 2.56 Å, avg. U-C\textsubscript{arene} = 2.91 Å) and [([($\eta^6$-C$_6$Me$_6$)UCl$_2$]($\mu$-Cl)$_3$)[AlCl$_4$] (avg. U-C\textsubscript{cent} = 2.55 Å, avg. U-C\textsubscript{arene} = 2.92 Å),\textsuperscript{23-24} Comparison to inverted sandwich complexes,\textsuperscript{32} namely the organometallic inverted benzene sandwich (Cp*$_2$U)($\mu$-$\eta^5$-$\eta^4$-C$_6$H$_6$) (Cp* = $\eta^5$-C$_5$Me$_5$),\textsuperscript{42} possessing a puckered benzene ring, shows an avg. U-C\textsubscript{arene} = 2.20 Å that is sizably shorter than 1\textsuperscript{BEC-4THF} but with a comparable U-C\textsubscript{arene} = 2.51(1) – 2.73(1) Å bond range. The shorter U-C\textsubscript{arene} distances in 1\textsuperscript{BEC-4THF}, as compared to [($\eta^6$-C$_6$H$_6$)U(AlCl$_4$)$_3$] and [([($\eta^6$-C$_6$Me$_6$)UCl$_2$]($\mu$-Cl)$_3$)[AlCl$_4$] with their neutral arene ligands, suggests a strong bonding interaction that may be due to increased charge accumulation within the anthracene moieties. As such, the U-C\textsubscript{arene} bond metrics in 1\textsuperscript{BEC-4THF} better match the parameters of (Cp*$_2$U)($\mu$-$\eta^6$-$\eta^4$-C$_6$H$_6$), where the bridging benzene moiety is assigned a dianionic charge.

In line with this, both the $\eta^6$-C$_{14}$H$_{10}$ and $\eta^4$-C$_{14}$H$_{10}$ rings of 1\textsuperscript{BEC-4THF} show distortions from planarity (Figure 2a), which is typically considered an indication of localized anionic charge character in monometallic arene-metallate systems.\textsuperscript{67} In fact, for magnesium anthracenes featuring (C$_{14}$R$_{10}$)$_2$, the central ring fold angles are 28.6° in [Mg($\eta^2$-C$_{14}$H$_{10}$)(THF)$_3$] and 41.0° in [Mg($\eta^2$-1,4-Me$_2$C$_{14}$H$_{10}$)(THF)$_3$].\textsuperscript{58-60} Along these lines, a few examples of mononuclear 4f-element anthracene complexes are known, and they too show similar folding (cf. CpLu($\eta^2$-C$_{14}$H$_{10}$),\textsuperscript{70} 35.8°; ($\eta^2$-C$_{14}$H$_{10}$)TmI(DME)$_2$,\textsuperscript{71} 37.8°). In comparison, the $\eta^6$-C$_{14}$H$_{10}$ ligand in 1\textsuperscript{BEC-4THF} shows a shallow bend angle of 18.8° across the central, bridgehead C15/C22 bond vector (Figures 2a and S2). The more acute folding of the anthracene ring in 1\textsuperscript{BEC-4THF} suggests carbon atom hybridization at C15 and C22 that is closer to sp$^2$-character. In support of this idea, the fold angle in dibenzo-7-dimethylgermanobornadiene (Me$_2$GeA; A = C$_{14}$H$_{10}$) is 56.8°, wherein the germanium atom is bound to sp$^3$-hybridized bridgehead carbons.\textsuperscript{72} In addition, the $\eta^7$-C$_{14}$H$_{10}$ ligand of 1\textsuperscript{BEC-4THF} exhibits a bend angle of 26.8° from planarity at its terminal, coordinating ring. Similar $\eta^9$-C$_{14}$H$_{10}$ bending has been observed in a number of complexes,\textsuperscript{10} and the deviation from planarity is comparable to that found in the bis(anthracene) niobium compound {[K(18-crown-6)(THF)]($\eta^4$-C$_{14}$H$_{10}$)$_2$}N$\text{b}[P(OMe)$_3$)] (28.4°).\textsuperscript{73}

The structural distortion of these arene rings can be accounted through localized population of C-C $\pi^*$-orbitals. Consequently, it would be expected that formal reduction of the anthracene ring should also manifest in elongated C-C bonds; though, in uranium inverted sandwich complexes, it is not unusual to find planar, bridging arenides with little to no obvious C-C bond lengthening.\textsuperscript{32}

Inspection of the C-C bond lengths within the $\eta^6$-C$_{14}$H$_{10}$ and $\eta^4$-C$_{14}$H$_{10}$ rings of 1\textsuperscript{BEC-4THF} shows obvious bond distance perturbations as compared to neutral, aromatic anthracene,\textsuperscript{74} and the C-C ring distances of 1\textsuperscript{BEC-4THF} are

6
shown in Figure 2b. In the case of \( \eta^6-C_{14}H_{10} \), the C-C bond distances of the central, coordinated ring narrowly range from 1.429(9) to 1.456(8) Å with an average distance of 1.44 Å, which is slightly longer than the average C-C distances within the peripheral rings, both 1.40 Å, the latter falling nicely within the expected C-C bond length of 1.41 Å for aromatic hydrocarbon bonds. The slight elongations are consistent with formal reduction of the \( \eta^6-C_{14}H_{10} \) ligand and, as such, compares favorably with the corresponding C-C distances of \([\text{Mg}(\text{C}_{14}H_{10})(\text{THF})_2]\) (C-C = 1.42(2) – 1.49(2) Å, avg. 1.45 Å) and \( \text{CpLu}(\eta^2-C_{14}H_{10}) \) (C-C = 1.43(1) – 1.47(2) Å, avg. 1.45 Å). Turning to the \( \eta^4-C_{14}H_{10} \) ring, the bond distances of the coordinated carbon atoms are C1-C2 = 1.441(8) Å; C2-C3 = 1.371(8) Å; and C3-C4 = 1.438(8) Å with the three adjoining, non-coordinating bonds ranging from 1.452(9) – 1.466(7) Å, while the remaining C-C distances of the \( \eta^4-C_{14}H_{10} \) ring conform to standard aromatic bond lengths (avg. 1.39 Å). (Note that the pattern in the bond distances is present in the DFT geometries (Table S15), vide infra.) This long-short bond pattern of the C2 to C4 moiety is consistent with a localized ‘-ene’ dianion form having the charge centers at C1 and C4. Yet, while the structural parameters clearly indicate negative charge accumulation on the coordinated \( \eta^6-C_{14}H_{10} \) and \( \eta^5-C_{14}H_{10} \) rings, the ability of anthracene to access and sustain both monoanionic and dianionic forms complicates the charge picture.

**EPR.** In an effort to better define the charge states and assess the electronic structure of the uranium bis(anthracene) compounds, X-band EPR measurements were performed on powdered samples of \(^{18}\text{C}_6\cdot4\text{THF} \) and \(^1\text{THF} \) at 4 (±1) K. In these samples, a strong and clear isotropic signal centered at \( g = 2.000 \) for \(^1\text{THF} \) and \( g = 2.017 \) for \(^{18}\text{C}_6\cdot4\text{THF} \) is observed (Figures S10 and S11), consistent with isolated S = \( \frac{1}{2} \) spins. These peaks persist at room-temperature, retaining its relative signal intensity, and point to the presence of an anthracene-based radical in both complexes with the slightly larger \( g \)-value of \(^{18}\text{C}_6\cdot4\text{THF} \) indicating modest metal-orbital contribution. Similar EPR spectra have been observed in arene-metalates such as \([\text{K}(18\text{-crown}-6)][\text{Cr}_2(\text{C}_{10}H_{18})_2] \) (\( g = 1.987 \)) where the radical is largely localized on the arene ligand. Resonances corresponding to uranium-based signals were not observed.

The appearance of the EPR signals for \(^{18}\text{C}_6\cdot4\text{THF} \) and \(^1\text{THF} \) definitively establishes negative charge states within the anthracene ligands but provides only a general picture. For instance, the observed EPR resonances are at odds with a closed-shell \( \text{C}_{14}H_{10} \) ligand form, suggesting \( \text{C}_{14}H_{10}^- \) radical monoanion character in at least one of the coordinated anthracenes; however, this must be taken with caution as it has been shown that anthracene dianions do have accessible triplet excited states where the population energies are heavily dependent on the character of the cation, solvent, and temperature.

**Magnetic Susceptibility.** To provide further insight into the paramagnetic character of these complexes, magnetic susceptibility studies were performed on crushed polycrystalline samples of \(^{18}\text{C}_6\cdot4\text{THF} \) and \(^1\text{THF} \) using SQUID magnetometry in the temperature range of 1.8 – 300 K at 0.1 T. A plot of the effective magnetic moment (\( \mu_{\text{eff}} \)) versus temperature is shown in Figure 3. The data for \(^{18}\text{C}_6\cdot4\text{THF} \) and \(^1\text{THF} \) follow a similar trend as the \( \mu_{\text{eff}} \) gradually decreases as a function of temperature, curving downwards to 0.80 and 0.43 \( \mu_B \) at 1.8 K, respectively. Curiously, despite their structural similarity at uranium, the overall \( \mu_{\text{eff}} \) values for \(^1\text{THF} \) are lower than that of \(^{18}\text{C}_6\cdot4\text{THF} \). For instance, at 300 K, \(^{18}\text{C}_6\cdot4\text{THF} \) and \(^1\text{THF} \) exhibit \( \mu_{\text{eff}} \) values of 4.40 \( \mu_B \) and 3.74 \( \mu_B \), respectively, with a sizable \( \Delta(\mu_{\text{eff}}) = 0.66 \mu_B \) at room temperature that reduces to \( \Delta(\mu_{\text{eff}}) = 0.37 \mu_B \) at lower temperatures. This indicates that the contact pairing of the potassium cations plays a critical role in the modulation of the electronic structure of the \([\text{U}(\eta^6-\text{C}_{14}H_{10})(\eta^4-\text{C}_{14}H_{10})(\mu-\text{OMe})_2]_3 \) cores in \(^{18}\text{C}_6\cdot4\text{THF} \) and \(^1\text{THF} \). We postulate that the Lewis acidity of the contact-paired potassium cations in \(^1\text{THF} \) polarizes and concentrates electron density onto the coordinated portion of the \( \eta^4 \)-anthracene ligands, thus giving rise to point charge accumulation that leads to a stronger crystal field splitting effect, and consequently lower \( \mu_{\text{eff}} \) for \(^1\text{THF} \). This enhanced charge buildup is supported by analyzing DFT atomic charges as discussed below (see Electronic Structure Analysis).

Qualitatively, the curvatures of both magnetization plots in Figure 3 are characteristic of U(IV) complexes that approach singlet ground states upon cooling to low temperatures due to thermal depopulation of the metal excited
However, the $\mu_{\text{eff}}$ of $^{18}$RC6·4THF (4.40 $\mu_B$) and $^{1}$THF (3.74 $\mu_B$) at 300 K, possible ligand radical contributions aside, are much lower than the expected $\mu_{\text{eff}} = 5.06$ $\mu_B$ for a U(IV) dimer (3.58 $\mu_B$ per $5f^2$, $^3H_4$ ion) with magnetically isolated metal centers.\textsuperscript{77-78} In relation to inverted sandwich complexes, the $\mu_{\text{eff}}$ of $^{18}$RC6·4THF and $^{1}$THF are higher than those found for (Cp*$_2$U$^{\text{III}}$)$_2$(μ-η$_6$:η$_6$-C$_6$H$_6$) ($\mu_{\text{eff}} = 2.1$ $\mu_B$),\textsuperscript{42} [K$_2${(U(V)O(Si(OPr$_3$)$_2$)$_2$})]$_2$(μ-η$_6$:η$_6$-C$_6$H$_6$) ($\mu_{\text{eff}} = 2.23$ $\mu_B$),\textsuperscript{40} and [{[HC(SiMe$_2$N(4-MeC$_6$H$_5$)$_3$)]U(V)}]$_2$(μ-η$_6$:η$_6$-C$_6$H$_6$) ($\mu_{\text{eff}} = 3.32$ $\mu_B$)\textsuperscript{39} at room temperature. Moreover, factoring in potential ligand radical contributions, while maintaining U(IV) assignments, gives near room temperature calculated values that range from $\mu_{\text{eff}} = 5.35$ $\mu_B$ (one ligand radical) to $\mu_{\text{eff}} = 6.14$ $\mu_B$ (four, non-interacting ligand radicals) and higher. The analysis is further confounded by the fact that $\mu_{\text{eff}}$ values for uranium are highly variable,\textsuperscript{77} and this does not factor in possible uranium superexchange and other magnetic coupling interactions between spin carriers. In comparison to the U(IV) dimer [{[(Mes)PDI]$^6$}U$^{\text{III}}$]$_2$ ([MesPDI]$^6$ = [2,6-(MesN=CMe)NC$_6$H$_3$]$^+$) possessing ligand-centered PDI-radicals, its $\mu_{\text{eff}}$ displays a much narrower range from $\mu_{\text{eff}} = 1.03 - 2.66$ $\mu_B$ (2 - 300 K), where the low temperature $\mu_{\text{eff}}$ is said to derive from the unquenched spins of the ligand radicals.

**XANES.** Given the difficulty of definitively assigning charge states to the ligands and uranium centers for $^{18}$RC6·4THF and $^{1}$THF based upon the intermediacy of the structural parameters and magnetism data, transmission mode U L$\text{III}$-edge X-ray absorption near edge spectroscopy (XANES) measurements were performed at room temperature. The samples consisted of pulverized, compressed pellets of $^{18}$RC6·4THF and $^{1}$THF diluted in X-ray transparent boron nitride matrices vacuum sealed under an argon atmosphere in polyethylene envelopes (see Supporting Information for further detail).

XANES spectroscopy has become an effective tool for the delineation of metal oxidation states in actinide compounds.\textsuperscript{37-38, 79-82} With regards to uranium, the U L$\text{III}$-edge energy corresponds to an electric-dipole allowed ($2p^63d^{10})5f^66d^2 \rightarrow (2p^63d^{10})5f^66d^1$) photoexcited core electron transition,\textsuperscript{79,81} where the excitation energy is dependent upon the shielding environment of the 2p-electrons and their relative binding energies, providing insights into the effective nuclear charge of the uranium. Consequently, the X-ray absorption energy correlates to the charge character of the absorbing uranium ion, allowing for formal oxidation state assignments. This can be quantified through the absorption threshold of the edge energy, defined as the inflection point in the first derivative of the XANES spectrum, as well as the peak “white line” energy.

The background-subtracted and intensity normalized XANES spectra for $^{18}$RC6·4THF and $^{1}$THF is presented in Figure 4a and is plotted alongside spectra collected for the respective U(III)-U(VI) standards UI$_3$(dioxane)$_3$, UCl$_4$, UO$_2$, U(O)[N(SiMe$_2$)$_2$)$_3$, and UO$_2$Cl$_2$(THF)$_3$. The inflection point energies for $^{18}$RC6·4THF and $^{1}$THF are much higher than that of UI$_3$(dioxane)$_3$ by 2.9 and 3.8 eV, respectively, but closer in range to that found for UCl$_4$ (Δ(eV) = +0.1 eV ($^{18}$RC6·4THF); +1.0 eV ($^{1}$THF)). However, $^{1}$THF is only 0.7 eV lower than that found for pentavalent U(O)[N(SiMe$_3$)$_2$]$_3$. Turning to the white line energies for further comparison, the peaks of $^{18}$RC6·4THF and $^{1}$THF exceed that of UCl$_4$ by 1.1 and 2.4 eV, respectively, with the latter compound falling 0.6 eV below the white line value of U(O)[N(SiMe$_3$)$_2$]$_3$. 

![Figure 3](image-url)
Altogether, the data is generally consistent with a tetravalent oxidation state assignment for the uranium centers in $^{18}$C$_6$·4THF. The data also clearly indicates a more oxidized uranium species in the case of $^{1}$THF, pinning the formal charge of its uranium atoms between U(IV)-U(V). To illustrate this, a plot of the inflection energies versus the oxidation states of the standards are provided in Figure 4b containing a linear regression for the series. This analysis has been previously applied for the corroboration of oxidation state assignments in uranium coordination compounds. When plotting $^{1}$THF and $^{1}$THF, the respective calculated values for their metal oxidation states are found to be U$^{+4.31}$ and U$^{+4.76}$. The difference in the calculated charges is significant and provides a possible explanation for the observed disparity in their $\mu_{\text{eff}}$ plots (Figure 3). Namely, the more oxidized, ion-paired $^{1}$THF shows a lower overall $\mu_{\text{eff}}$ as compared to more electron rich $^{1}$THF. Additionally, the $g$-value for $^{1}$THF also exhibits less metal contribution. As such, the contact pairing of the potassium cations in $^{1}$THF play a sizable effect on the relative charge state of the uranium metal centers, despite the ion-pairing taking place beyond the immediate coordination sphere of uranium. A somewhat related phenomenon has been observed in the inverted sandwich complex $\{\text{U}^{IV}\text{[OSi(OBu)$_3$]}_3\} (\mu_6^\text{-}6\text{-C}_7\text{H}_8)$ where addition of KOTf results in the cation-mediated disproportionation to U(IV)/U(IV) and U(IV)/U(V) complexes, a feat that does not occur upon treatment with non-coordinating cations such as [NBu$_4$]$^+$. These observations signal that the electronic structure of uranium is highly sensitive to subtle perturbations within its ligand environment, especially when adding other interacting Lewis acid cations.

Furthermore, assuming formal U(IV) assignments for the uranium centers in $^{1}$THF and $^{1}$THF yields a charge formulation of (C$_{14}$H$_{10}$)$^2$ for each of the anthracene ligands. Nevertheless, each anthracene still adopts a distinctive coordination mode to uranium. In order to gain further insights into the electronic structure and the bonding interactions between uranium and the anthracenes, electronic structure analyses were performed.

**Electronic Structure Analysis.** Density functional theory (DFT) calculations (RI-PBE-D3/def2-TZVP, 83-86 def-TZVP for U$^{57-89}$) were performed in the Turbomole program package to study the model systems $\{[\text{U}(\eta^2\text{-}C_{14}H_{10})(\eta^1\text{-}C_{14}H_{10})(\mu_{\text{-}OMe})]_2\}^2$ ($1^*$) and $\{[\text{K}[\text{U}(\eta^2\text{-}C_{14}H_{10})(\eta^1\text{-}C_{14}H_{10})(\mu_{\text{-}OMe})]]_2 (1-K^*$ (see SI for full computational details). Both $1^*$ and $1-K^*$ were optimized in the triplet, quintet, and septet spin states and confirmed as minima by harmonic vibrational analysis. The optimized structures for all three spin states were compared to those obtained from the X-ray determined structures by comparing U-C bond distances as summarized in Table 1 and detailed in Tables S4 and S5. The root-mean-square deviation (RMSD) for each DFT optimized structure was also calculated. The geometry from the ground state quintet is in closest agreement with both experimental structures (Figures S2 and S6); however, comparing the RMSD values for all three spin states suggests that all of the calculated geometries are in satisfactory agreement with the experimental data. For $1^*$, the RMSD for the triplet, quintet, and septet states are 0.311, 0.326, and 0.331 Å, respectively. Similarly, the RMSD values for the same states are
with respect to the relative calculated energies, the quintet ground state is favored for both 1* and 1-K* (Table S3, Figure S18) as both the triplet and septet states lie approximately 7 kcal/mol higher in comparison. The electronic structures of 1* and 1-K* in the quintet state are comparable; though, the calculated average U-C bond distances of 1-K* are found to be slightly shorter than for 1* (Table 1). In the quintet state, each uranium is in a $5d^2$ electronic configuration, supporting the U(IV) assignments determined from the XANES data (Figure 4) and the curvature of the temperature dependent $\mu_{\text{eff}}$ plots (Figure 3).

To provide insight into the nature of the U-C bonds, bond order analyses for both 1* and 1-K* were calculated using the Amsterdam Density Functional program package (ADF)\(^{91}\) at the PBE/TZVP level of theory. Generally, a Mayer bond order of 1, 2, or 3 corresponds to a single, double, or triple bond between two atoms, respectively, although deviations from integer values are expected for highly polarized bonds.\(^{92}\) The average Mayer bond order of the U-C(\(\eta^4\)) bonds in 1* and 1-K* are 0.40 and 0.33, respectively (Table S7 and S9). This indicates slightly greater orbital overlap between the $\eta^1$-C\(_{10}\)H\(_{10}\) ligands and the uranium atoms in 1* versus that of 1-K*. Though, no significant differences are observed when determining the total bond orders through Gopinathan-Jug or Nalewajski-Mrozek methods (Table S7 and S9). In comparison, the Mayer bond orders for the U-C(\(\eta^6\)) interactions are unaffected by the presence of the potassium ion and found to range from 0.22 to 0.50 (avg. 0.31) for 1* (Table S7) and 0.23 to 0.52 (avg. 0.32) for 1-K* (Table S9). The nature of the U-C(\(\eta^6\)) and U-C(\(\eta^4\)) interactions was also studied by dividing the molecule into two fragments along the U-anthracene bonds of each ligand type in order to perform energy decomposition analysis (EDA) (Table S19). The bond energy for 1* is -150.37 and -154.86 kcal/mol for the $\eta^4$- and $\eta^6$-anthracene ligands, respectively. Furthermore, orbital interactions contribute 49.4% and 50.7% to the attractive energy. Both values indicate a slightly stronger interaction with the $\eta^6$-anthracene ligand.

Quantum theory of atoms in molecules (QTAIM) analyses for 1* and 1-K* identified two bond critical points (BCPs) between the uranium centers and the $\eta^2$-rings and three bond critical points for the $\eta^1$-anthracene ligands. At all BCPs, the total electronic energy density, $E(r)$, is negative (1*: -0.0077 – -0.0116; 1-K*: -0.0075 – -0.0125), and the Laplacian of the density, $\nabla^2 \rho$, is positive (1*: 0.0825 – 0.1149; 1-K*: 0.0800 – 0.1261) (Table S6). In addition, the electron density values, $\rho$, are small (1*: 0.0471 – 0.0554; 1-K*: 0.0490 – 0.0572), altogether indicating U-C dative bonding where the interactions can be described as primarily ionic or exhibiting strongly polarized bonding character.\(^{93}\)

The DFT frontier molecular orbitals of 1* and 1-K* are illustrated in Figure 5 and show that the U-C(\(\eta^6\)) interactions for both 1* and 1-K*, as defined by the crystallographically determined uranium-carbon bond lengths for 1\(^{1BC6-4THF}\) and 1\(^{THF}\) (vide supra), are nominally hexahapto. The electronic structure shows the coordination mode of this anthracene to be better described as bidentate with the strongest interactions occurring through $\pi$-bonding at the bridgehead carbon atoms with negligible contributions from the remaining carbons of the central ring, consistent

| Compounds | Spin   | U1-C(\(\eta^6\)) | U1-C(\(\eta^4\)) | U2-C(\(\eta^6\)) | U2-C(\(\eta^4\)) | U-O   |
|-----------|--------|------------------|------------------|------------------|------------------|-------|
| 1*        | triplet| 2.746            | 2.659            | 2.723            | 2.639            | 2.331 |
|           | quintet| 2.743            | 2.659            | 2.748            | 2.658            | 2.333 |
|           | septet | 2.762            | 2.675            | 2.748            | 2.732            | 2.323 |
| Exp.      |        | 2.713            | 2.658            | 2.713            | 2.658            | 2.328 |
| 1-K*      | triplet| 2.712            | 2.625            | 2.734            | 2.642            | 2.323 |
|           | quintet| 2.734            | 2.641            | 2.733            | 2.642            | 2.326 |
|           | septet | 2.790            | 2.649            | 2.790            | 2.649            | 2.313 |
| Exp.      |        | 2.700            | 2.674            | 2.700            | 2.674            | 2.336 |
with the findings of the QTAIM BCPs. With respect to the U-C(η^4) fragments of 1* and 1-K*, orbital overlap is observed with all four carbon atoms, albeit more so at the C1/C4 fold atoms.

The DFT-calculated frontier molecular orbitals of 1* and 1-K* in Figure 5 are displayed with the total percent electronic contribution of the uranium centers and sum of the carbon orbitals involved in the bonds. In both cases, the singly occupied molecular orbitals (SOMOs), SOMO to SOMO-3, are predominately 5f in character with HOMO-4 through HOMO-7 defining the U-C interactions. In 1*, HOMO-6 and HOMO-7 are also primarily defined by the orbitals of the U-C(η^6) interactions. Yet, in 1-K*, the corresponding frontier orbitals are comprised by the U-C(η^4) bonding compositions. In either case, the bonds appear highly polarized with the contributions from the uranium atoms approaching 25% and those from the carbon atoms nearing 40%.

The Charge Model 5 (CM5) atomic charges were found for each system (Table S11). The average charge of each uranium ion is +1.0 for both 1* and 1-K*. On the other hand, the ion pairing has a significant effect on the relative charges of the arenide anions. The combined partial charges for the carbon atoms for each of the η^4-C_{14}H_{10} and η^6-C_{14}H_{10} ligands in 1* are -0.87 and -0.77, respectively. This decreases in 1-K* to -0.55 for the η^6-C_{14}H_{10} ligands but increases to -0.95 for the η^4-C_{14}H_{10} anthracenides, where the presence of the coordinated potassium cations allows for greater charge accumulation in the latter. Note that in both cases, the relative charge on the η^4-C_{14}H_{10} ligands exceed those of the η^6-C_{14}H_{10} arenides.

Since uranium complexes often exhibit multiconfigurational electronic structures not adequately treated with DFT, the electronic structure was studied by the complete active space self-consistent field (CASSCF) method.
along with second-order energy corrections (CASPT2\textsuperscript{94-95} for \textit{I}*. In CASPT2, including only the 5f-orbitals and their corresponding electrons in the active space (4\textit{e},14\textit{o}), the singlet, triplet, and quintet states are effectively degenerate lying within 0.3 kcal/mol of one another. As such, we cannot assign a single spin state as the ground state. We expect that the true ground state is a spin-orbit coupled state with contributions from the singlet, triplet, and quintet spin-free states.

Since the DFT shows covalent interactions between the uranium centers and the arenide ligands, the bonding in dimer \textit{I}*- was also studied with the restricted active space self-consistent field (RASSCF) method with corrections from second-order perturbation theory (RASPT2),\textsuperscript{96-97} allowing for larger active spaces to be studied than in CASSCF. All CASPT2 and RASPT2 calculations were performed in Open Molcas.\textsuperscript{98}

The active space would ideally include all of the molecular orbitals that are linear combinations of uranium 5f-orbitals and orbitals that include bonding or antibonding interactions between uranium and the arenide ligands. While there are total of 14 5f-orbitals in \textit{I}*, they are not all occupied due to crystal field effects. Therefore, after the aforementioned (4\textit{e},14\textit{o}) active space was used, it was determined that only 8 of these orbitals need be included, (4\textit{e},8\textit{o}) (Figures S20 to S25). By inspection of the (4\textit{e},8\textit{o}) orbitals, 10 pairs of \pi-bonding and anti-bonding orbitals were also identified. This surpasses the number of orbitals one can include in CASSCF; therefore, the RASSCF method was used to restrict excitations in a subset of the active space.

Specifically, RASSCF/RASPT2 calculations were performed including the 10 \pi-orbitals in the so-called RAS1 space, eight 5f-orbitals in the RAS2 space, and 10 \pi*-orbitals in the RAS3 space. All excitations are allowed within RAS2 but only configurations with up to two holes are allowed in RAS1 and up to two electrons in RAS3, denoted (24\textit{e},2\textit{h},2\textit{e};10\textit{a},8\textit{a},10\textit{o}) using the notation of Sauri \textit{et al.}\textsuperscript{97} The calculations yield occupation numbers for the \pi-orbitals in RAS1 that are 1.96 or higher, consistent with a doubly occupied orbital. Likewise, those in RAS3 have occupation numbers of 0.04 or less, signaling empty orbitals. Based on the RASSCF results, the active space can be further reduced to (8\textit{e},12\textit{o}), the results of which remain similar to RASSCF (Table S12-S13).

### Tables

| \pi\textsubscript{1}(1.99) | \pi\textsubscript{2}(1.99) | \pi\textsubscript{6}(1.98) | \pi\textsubscript{5}(1.98) | \pi\textsubscript{10}(1.98) |
|-------------------------|------------------------|------------------------|------------------------|------------------------|
| U=11.73% C=79.54%      | U=12.68% C=78.72%      | U=13.41% C=78.46%      | U=14.78% C=76.05%      | U=12.03% C=79.87%      |

| \pi\textsubscript{3}(1.98) | \pi\textsubscript{4}(1.98) | \pi\textsubscript{6}(1.97) | \pi\textsubscript{6}(1.96) | \pi\textsubscript{6}(1.98) |
|-------------------------|------------------------|------------------------|------------------------|------------------------|
| U=15.27% C=72.42%      | U=17.69% C=70.92%      | U=14.97% C=78.11%      | U=17.62% C=74.93%      | U=12.46% C=79.93%      |

### Figure

**Figure 6.** RASSCF natural orbitals and occupation numbers are shown for the quintet state of \textit{I}*. The \pi-orbitals are in RAS1 and the 5f-orbitals are in RAS2. RAS3 is not plotted (see Figure S28). Percent contributions of uranium to the RAS1 orbitals are included. An isovalue of 0.04 a.u. was used. U in blue, C in grey, O in red, and H in white.
RASPT2 predicts that the singlet, triplet, and quintet states are within 0.3 kcal/mol of one another. Note that DFT cannot describe the multiconfigurational singlet and triplet states in which the 5f-electrons are weakly coupled with one another; however, both CASPT2 and RASPT2 suggest interpreting the DFT high-spin quintet state to understand the uranium-carbon interactions is reasonable.

The RASSCF orbitals for the quintet state are included in Figure 6, although the singlet and triplet orbitals are qualitatively the same (Figures S29-S30). In the RAS1 space, the total uranium orbital contribution to the U-C π-interactions across the U-C(η4) and U-C(η3) bonds range from 11.7% to 17.7% in 1*. The average uranium contribution between the U-C(η4) (avg. 14.3%) and U-C(η3) bonds (avg. 14.2%) are comparable. Of particular note, in contrast to the DFT orbital picture, the 5f-orbitals play a minimal to negligible role in the U-C bonding of 1* (Figure 6). The average contributions of the uranium orbitals to the bonding scheme in the quintet state is 7.3 ± 0.6% (6d), 2.5 ± 0.4% (6p), 1.5 ± 0.4% (5f), and 1.4 ± 1.4% (7s). Accordingly, the uranium 6d-orbitals are the dominant contributors accompanied by some semi-core 6p-orbital participation.

Noticeably absent are metal-arene bonding interactions that can be described as δ-bonds, which is a significant departure from the bonding schemes determined for actinide inverted sandwich complexes.32 For example, CASSCF analyses on (µ-η6:η4-C7H8)U2[2(N(Bu)(3.5-C6H3Me2))4]37 and [U(BIPM)]6(µ-η4:η6-C6H6)3 (BIPM = (C(PH2NH2)2)3)38 both show significant δ-bond overlap between the π*-orbitals of the arenes and filled 5f-orbitals. The sandwiched rings in these compounds are formally tetravalent and bound by two metals, which together limits structural distortions and favors the δ-bonding. In our case, formal two-electron reduction of each of the anthracene ligands leads to ring folding that greatly diminishes the possibility for uranium-anthracene δ-bonding.

Lastly, while the EPR spectral results are not consistent with a purely closed shell anthracene ligand in the cases of 118C6·4THF and 11THF, DFT, CASSCF, and RASSCF calculations predict that all of the unpaired spin density in the gas phase 1* and 1-K* structures is metal centered. This follows the SQUID magnetometry and XANES spectral analysis for 118C6·4THF and 11THF that generally support a formal oxidation state of U(IV) for both complexes. Our electronic structure analysis does not include thermal contributions, and we have not systematically explored low-lying electronic states or the effect of crystal packing that could be contributing to the observed EPR spectra.

Summary

Metal-arene sandwich complexes are an important class of molecules that have been instrumental in understanding the electronic properties and orbital characteristics of the d-block series while providing access to important arene-functionalization chemistry. Extension of these systems to the f-elements has been limited to only a handful of lanthanide-arene sandwich complexes, mainly synthesized by electron beam vaporization techniques,12-14 and the poorly characterized, heteroleptic thorium species [O-[2.4′-Bu2-C6H4(CH2)3]2;Th(η4-C6H6)]2 (K(18-crown-6))2.31 Utilizing Chatt reaction protocols popularized by Ellis,10 we have shown that the reaction of [UI2(THF)]3(µ-OMe)]2 (2) with 6 equiv. of K[C10H10] produces the unprecedented, unsupported uranium arene-metalate sandwich complexes [K(18-crown-6)(THF)]2[U(η4-C6H10)(µ-OMe)2]2 (118C6) and [[K(THF)]3[U(η5-C14H10)(η4-C14H10)(µ-OMe)]2(11THF)] in the presence and absence of 18-crown-6, respectively.

As shown through X-ray diffraction, the arene ligands in both complexes display notable ring fold angles, indicative of formal reduction and partial de aromatization of the anthracene moieties. While the cores of both 118C6 and 11THF comprise of a dimeric [{[U(η4-C14H10)(η4-C14H10)(µ-OMe)]2}2- unit, the two systems are distinguished by close-contact arene-pairing of the potassium cation that occurs in 11THF but is missing in 118C6·4THF, due to polyether sequestration of the potassium cations in the latter. Despite their structural similarity, XANES analysis and magnetic characterization of 118C6·4THF and 11THF show appreciable differences in their electronic and magnetic properties. For instance, the effective magnetic moment of 118C6·4THF (µeff = 4.40 µB) is significantly higher than 11THF (µeff = 3.74 µB) at 300 K, though both complexes show a temperature dependent µeff response in line with U(IV) centers (Figure 3). The XANES spectra shows an obvious difference in the level of oxidation between the uranium atoms of 118C6·4THF and 11THF (Figure 4a), with the linear regression fitting of the edge energies yielding formal charges of U+4.31 for 118C6·4THF and U+4.76 for 11THF (Figure 4b). Together, the data clearly signals that the
close-contact ion pairing of the potassium cations has a direct effect on the electronic structure of the actinide centers and the oxidation states of the metal centers. We attribute this to enhanced bond polarization effects enabled by the coordinated, Lewis acidic potassium cations, which leads to greater localized charge character at the $\eta^4$-anthracene ligands.

Electronic structure analysis of the isolated diuranium complexes $1^*$ and $1-K^*$ by DFT calculations and $1^*$ by RASPT2 methods indicates that the uranium-carbon bonding is highly polarized with modest orbital contributions from the uranium atoms. DFT analysis of $1-K^*$ also substantiates increased charge polarization at the potassium-bound anthracenes. In stark contrast to thorium and uranium inverted sandwich complexes, $\delta$-bonding between uranium and the arene moieties is not observed in $1^*$ or $1-K^*$, which we ascribe to the bent nature of the anthracene ligands that prevents metal-arene $\delta$-symmetry orbital overlap. Instead, the metal-ligand bonding is best described as comprising of $\pi$-type bonds. Interestingly, RASSCF calculations reveal little participation of the $5f$-orbitals to the uranium-carbon interactions, with the $6d$-orbitals providing the greatest contributions.

Efforts are currently underway to modify the reaction conditions and choice of arene ligands in order to obtain homoleptic uranium-arene sandwich complexes to further probe the electronic and chemical properties of this unique class of molecules.

ACKNOWLEDGMENTS

We are grateful to the Welch Foundation (AH-1922-20200401; S.F.) and the NSF (DMR-1827745; CHE-1827875) for financial support of this work. S.F. is an Alfred P. Sloan Foundation research fellow and is thankful for their support. MRCAT operations are supported by the Department of Energy and the MRCAT member institutions. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. Computations supporting this project were performed on High Performance Computing systems at the University of South Dakota, funded by NSF Award OAC-1626516. B.V. would like to thank the University of South Dakota for start-up funds. B.V., P.M., and R.B. acknowledge that the land their research was performed on is the original homelands of the Dakota, Lakota, and Nakota tribal nations. K.L.M.H. and M.M. are grateful for the support and funds from the University of Ottawa, the Natural Sciences and Engineering Research Council of Canada, and the Canadian Foundation for Innovation

REFERENCES

1. Seyferth, D., Bis(benzene)chromium. 2. Its Discovery by E. O. Fischer and W. Hafner and Subsequent Work by the Research Groups of E. O. Fischer, H. H. Zeiss, F. Hein, C. Elschenbroich, and Others. Organometallics 2002, 21, 2800-2820.

2. Astruc, D., Why is Ferrocene so Exceptional? Eur. J. Inorg. Chem. 2017, 6-29.

3. Werner, H., At Least 60 Years of Ferrocene: The Discovery and Rediscovery of the Sandwich Complexes. Angew. Chem. Int. Ed. 2012, 51, 6052-6058.

4. Osborne, J. H.; Trogler, W. C.; Morand, P. D.; Francis, C. G., Electronic-Structures of Bis(Benzene)Chromium and the $C_{3v}$ and $C_{2v}$ Isomers of Bis(Naphthalene)Chromium. Organometallics 1987, 6, 94-100.

5. Weber, J.; Kundig, E. P.; Goursot, A.; Penigault, E., The Electronic-Structures of Bis($\eta^5$-Benzene)- and Bis($\eta^5$-Naphthalene)Chromium(0). Can. J. Chem. 1985, 63, 1734-1740.

6. Rayón, V. M.; Frenking, G., Bis(benzene)chromium is a $\delta$-Bonded Molecule and Ferrocene is a $\pi$-Bonded Molecule. Organometallics 2003, 22, 3304-3308.
1. Sahnoun, R.; Mijoule, C., Density Functional Study of Metal–Arene Compounds: Mono(benzene)chromium, Bis(benzene)chromium and Their Cations. *J. Phys. Chem. A* 2001, 105, 6176-6181.

2. Rosillo, M.; Domínguez, G.; Pérez-Castells, J., Chromium arene complexes in organic synthesis. *Chem. Soc. Rev.* 2007, 36, 1589-1604.

3. Pampaloni, G., Aromatic hydrocarbons as ligands. Recent advances in the synthesis, the reactivity and the applications of bis(η⁶-arene) complexes. *Coord. Chem. Rev.* 2010, 254, 402-419.

4. Ellis, J. E., The Chatt reaction: conventional routes to homoleptic arenemetalates of d-block elements. *Dalton Trans.* 2019, 48, 9538-9563.

5. The term “arene” is here defined as any neutral monocyclic or polycyclic hydrocarbon that possesses aromatic character prior to metal ligation and is distinguished from other carbocyclic ligands, such as Cp, which only achieve aromaticity upon chemical transformation or reduction of their parent hydrocarbon.

6. Brennan, J. G.; Cloke, F. G. N.; Sameh, A. A.; Zalkin, A., Synthesis of bis(η⁶-1,3,5-tri-t-butylbenzene) sandwich complexes of yttrium(0) and gadolinium(0): the X-ray crystal structure of the first authentic lanthanide(0) complex, [Gd(η⁶-Bu₃C₆H₃)₂]. *J. Chem. Soc., Chem. Comm.* 1987, 1668-1669.

7. Anderson, D. M.; Cloke, F. G. N.; Cox, P. A.; Edelstein, N.; Green, J. C.; Pang, T.; Sameh, A. A.; Shalimoff, G., On the Stability and Bonding in Bis(η-Arene)Lanthane Complexes. *J. Chem. Soc. Chem. Comm.* 1989, 53-55.

8. Cloke, F. G. N., Zero Oxidation-State Compounds of Scandium, Yttrium, and the Lanthanides. *Chem. Soc. Rev.* 1993, 22, 17-24.

9. Hong, G. Y.; Schautz, F.; Dolg, M., Ab initio study of metal-ring bonding in the bis(η⁶-benzene)lanthanide and -actinide complexes M(C₆H₆)₂ (M = La, Ce, Nd, Gd, Tb, Lu, Th, U). *J. Am. Chem. Soc.* 1999, 121, 1502-1512.

10. Dolg, M., Combined Pseudopotential and Density Functional Study of Bis- η⁶-benzene d and f Element Complexes. *J. Chem. Inf. Model.* 2001, 41, 18-21.

11. King, W. A.; DiBella, S.; Lanza, G.; Khan, K.; Duncalf, D. J.; Cloke, F. G. N.; Fragala, I. L.; Marks, T. J., Metal-ligand bonding and bonding energetics in zerovalent lanthanide, group 3, group 4, and group 6 bis(arene) sandwich complexes. A combined solution thermochemical and ab initio quantum chemical investigation. *J. Am. Chem. Soc.* 1996, 118, 627-635.

12. Kelly, R. P.; Maron, L.; Scoppelliti, R.; Mazzanti, M., Reduction of a Cerium(III) Siloxide Complex to Afford a Quadruple-Decker Arene-Bridged Cerium(II) Sandwich. *Angew. Chem. Int. Ed.* 2017, 56, 15663-15666.

13. Minasian, S. G.; Keith, J. M.; Batista, E. R.; Boland, K. S.; Clark, D. L.; Kozimor, S. A.; Martin, R. L.; Shuh, D. K.; Tytlyszczak, T., New evidence for 5f covalency in actinocenes determined from carbon K-edge XAS and electronic structure theory. *Chem. Sci.* 2014, 5, 351-359.

14. Kelley, M. P.; Popov, I. A.; Jung, J.; Batista, E. R.; Yang, P., delta and phi back-donation in An(IV) metallacycles. *Nat. Commun.* 2020, 11.

15. Neidig, M. L.; Clark, D. L.; Martin, R. L., Covalency in f-element complexes. *Coord. Chem. Rev.* 2013, 257, 394-406.
22. Yin, W. W.; Marshall, A. G.; Marcalo, J.; Dematos, A. P., Gas-Phase Synthesis and Ft/Icr Mass-Spectrometric Characterization of Sandwich Complexes of Sc+, Y+, and Lanthanide Ions with 1,3,5-Tri-Tert-Butylbenzene. *J. Am. Chem. Soc.* 1994, 116, 8666-8672.

23. Cesari, M.; Pedretti, U.; Zazzetta, Z.; Lugli, g.; Marconi, W., Synthesis and structure of a π-arene complex of uranium(III) - aluminum chloride. *Inorg. Chim. Acta* 1971, 5, 439-444.

24. Cotton, F. A.; Schwotzer, W., Preparation and structure of [U(η^6-C6M6)2Cl]⁺, the first uranium(IV) complex with a neutral arene in η^6-coordination. *Organometallics* 1985, 4, 942-943.

25. Campbell, G. C.; Cotton, F. A.; Haw, J. F.; Schwotzer, W., Syntheses, Structures, and Solid-State C-13 NMR of two η^6-Arene Uranium(IV) Complexes, [U(C6M6)Cl2(μ-Cl)]3Cl and U(C6M6)Cl2(μ-Cl),μCl2(μ-Cl),μCl3(C6M6). *Organometallics* 1986, 5, 274-279.

26. Cotton, F. A.; Schwotzer, W.; Simpson, C. Q., [U(μ3-Cl)(μ3-Cl)(μ-η^2-AlCl4)(μ-η^6-C6M6)3][AlCl4] - a Trinuclear Arene Complex of U(III). *Angew. Chem. Int. Edit.* 1986, 25, 637-639.

27. Cotton, F. A.; Schwotzer, W., Syntheses and Structural Comparison of the η-6-Arene Complexes Sm(C6M6)(AlCl3) and U(C6M6)(AlCl4). *Organometallics* 1987, 6, 1275-1280.

28. Baudry, D.; Bulot, E.; Charpin, P.; Ephritikhine, M.; Lance, M.; Nierlich, M.; Vigner, J., Arene Uranium Borohydrides - Synthesis and Crystal-Structure of (η^6-C6M6)U(BH4)3. *J. Organomet. Chem.* 1989, 371, 155-162.

29. Paprocki, V.; Hrobárik, P.; Harriman, K. L. M.; Luff, M. S.; Kupfer, T.; Kaupp, M.; Murugesu, M.; Braunschweig, H., Stable Actinide π Complexes of a Neutral 1,4-Diborabenzen. *Angew. Chem. Int. Ed.* 2020, 59, 13109-13115.

30. Korobkov, I.; Gambarotta, S.; Yap, G. P. A., The first thorium arene complex: A divalent synthon. *Angew. Chem. Int. Ed.* 2003, 42, 814-818.

31. Korobkov, I.; Gambarotta, S.; Yap, G. P. A., Amide from dinitrogen by in situ cleavage and partial hydrogenation promoted by a transient zero-valent thorium synthon. *Angew. Chem. Int. Ed.* 2003, 42, 4958-4961.

32. Liddle, S. T., Inverted sandwich arene complexes of uranium. *Coord. Chem. Rev.* 2015, 293-294, 211-227.

33. Murillo, J.; Fortier, S., Actinides: Pentavalent Organometallics. Evans, W. J. and Hanusa, T. P., Eds.; John Wiley & Sons, Ltd. *Encyclopedia of Inorganic and Bioinorganic Chemistry* 2018.

34. Hayton, T. W.; Kaltsoyannis, N., Organometallic Actinide Complexes with Novel Oxidation States and Ligand Types. Gibson, J. K. and de Jong, W. A., Eds. John Wiley & Sons, Ltd. *Experimental and Theoretical Approaches to Actinide Chemistry* 2018, 181-236.

35. Diaconescu, P. L.; Arnold, P. L.; Baker, T. A.; Mindiola, D. J.; Cummins, C. C., Arene-Bridged Diuranium Complexes: Inverted Sandwiches Supported by δ Backbonding. *J. Am. Chem. Soc.* 2000, 122, 6108-6109.

36. Diaconescu, P. L.; Cummins, C. C., Diuranium Inverted Sandwiches Involving Naphthalene and Cyclooctetetraene. *J. Am. Chem. Soc.* 2002, 124, 7660-7661.

37. Vlaisayljevich, B.; Diaconescu, P. L.; Lukens, W. L.; Gagliardi, L.; Cummins, C. C., Investigations of the Electronic Structure of Arene-Bridged Diuranium Complexes. *Organometallics* 2013, 32, 1341-1352.
38. Wooles, A. J.; Mills, D. P.; Tuna, F.; McInnes, E. J. L.; Law, G. T. W.; Fuller, A. J.; Kremer, F.; Ridgway, M.; Lewis, W.; Gagliardi, L.; Vlaissavljevich, B.; Liddle, S. T., Uranium(III)-carbon multiple bonding supported by arene delta-bonding in mixed-valence hexauranium nanometre-scale rings. *Nat. Commun.* 2018, 9, 2097.

39. Patel, D.; Tuna, F.; McInnes, E. J. L.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T., A triamidouranium(V) inverse-sandwich 10 π-toluene tetraanion arene complex. *Dalton Trans.* 2013, 42, 5224-5227.

40. Camp, C.; Mougel, V.; Pécaut, J.; Maron, L.; Mazzanti, M., Cation-Mediated Conversion of the State of Charge in Uranium Arene Inverted-Sandwich Complexes. *Chem. Eur. J.* 2013, 19, 17528-17540.

41. Yu, C.; Liang, J. F.; Deng, C.; Lefevre, G.; Cantat, T.; Diaconescu, P. L.; Huang, W. L., Arene-Bridged Dithorium Complexes: Inverse Sandwiches Supported by a δ Bonding Interaction. *J. Am. Chem. Soc.* 2020, 142, 21292-21297.

42. Evans, W. J.; Kozimor, S. A.; Ziller, J. W.; Kaltsoyannis, N., Structure, reactivity, and density functional theory analysis of the six-electron reductant, [(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆H₆), synthesized via a new mode of (C₅Me₅)₃M reactivity. *J. Am. Chem. Soc.* 2004, 126, 14533-14547.

43. Arnold, P. L.; Mansell, S. M.; Maron, L.; McKay, D., Spontaneous reduction and C-H borylation of arenes mediated by uranium(III) disproportionation. *Nat. Chem.* 2012, 4, 668-674.

44. Arnold, P. L.; Halliday, C. J. V.; Puig-Urrea, L.; Nichol, G. S., Instantaneous and Phosphine-Catalyzed Arene Binding and Reduction by U(III) Complexes. *Inorg. Chem.* 2021, 60, 4162-4170.

45. La Pierre, H. S.; Scheurer, A.; Heinemann, F. W.; Hieringer, W.; Meyer, K., Synthesis and Characterization of a Uranium(II) Monoarene Complex Supported by δ Backbonding. *Angew. Chem. Int. Ed.* 2014, 53, 7158-7162.

46. Billow, B. S.; Livesay, B. N.; Mokhtarzadeh, C. C.; McCracken, J.; Shores, M. P.; Boncella, J. M.; Odom, A. L., Synthesis and Characterization of a Neutral U(II) Arene Sandwich Complex. *J. Am. Chem. Soc.* 2018, 140, 17369-17373.

47. Tian, J. N.; Zheng, M.; Li, L.; Schreckenbach, G.; Guo, Y. R.; Pan, Q. J., Theoretical investigation of U(I) arene complexes: is the elusive monovalent oxidation state accessible? *New J. Chem.* 2019, 43, 1469-1477.

48. Bart, S. C.; Heinemann, F. W.; Anthon, C.; Hauser, C.; Meyer, K., A New Tripodal Ligand System with Steric and Electronic Modularity for Uranium Coordination Chemistry. *Inorg. Chem.* 2009, 48, 9419-9426.

49. Halter, D. P.; La Pierre, H. S.; Heinemann, F. W.; Meyer, K., Uranium(IV) Halide (F-, Cl-, Br-, and I-) Monoarene Complexes. *Inorg. Chem.* 2014, 53, 8418-8424.

50. La Pierre, H. S.; Kameo, H.; Halter, D. P.; Heinemann, F. W.; Meyer, K., Coordination and Redox Isomerization in the Reduction of a Uranium(III) Monoarene Complex. *Angew. Chem. Int. Edit.* 2014, 53, 7154-7157.

51. Franke, S. M.; Tran, B. L.; Heinemann, F. W.; Hieringer, W.; Mindiola, D. J.; Meyer, K., Uranium(III) Complexes with Bulky Aryloxide Ligands Featuring Metal-Arene Interactions and Their Reactivity Toward Nitrous Oxide. *Inorg. Chem.* 2013, 52, 10552-10558.

52. Arnold, P. L.; Farnaby, J. H.; White, R. C.; Kaltsoyannis, N.; Gardiner, M. G.; Love, J. B., Switchable pi-coordination and C-H metallation in small-cavity macrocyclic uranium and thorium complexes. *Chem. Sci.* 2014, 5, 756-765.
53. Arnold, P. L.; Farnaby, J. H.; Gardiner, M. G.; Love, J. B., Uranium(III) Coordination Chemistry and Oxidation in a Flexible Small-Cavity Macrocyle. *Organometallics* **2015**, *34*, 2114-2117.

54. Suova, M.; O’Brien, K. T. P.; Farnaby, J. H.; Love, J. B.; Kaltsoyannis, N.; Arnold, P. L., Thorium(IV) and Uranium(IV) trans-Calix[2]benzene[2]pyrrolide Alkyl and Alkynyl Complexes: Synthesis, Reactivity, and Electronic Structure. *Organometallics* **2017**, *36*, 4669-4681.

55. Fortier, S.; Aguilar-Calderon, J. R.; Vlaisavljevich, B.; Metta-Magana, A. J.; Goos, A. G.; Botez, C. E., An N-Tethered Uranium(III) Arene Complex and the Synthesis of an Unsupported U-Fe Bond. *Organometallics* **2017**, *36*, 4591-4599.

56. Yadav, M.; Metta-Magana, A. J.; Fortier, S., Intra- and intermolecular interception of a photochemically generated terminal uranium nitride. *Chem. Sci.* **2020**, *11*, 2381-2387.

57. Inman, C. J.; Frey, A. S. P.; Kilpatrick, A. F. R.; Cloke, F. G. N.; Roe, S. M., Carbon Dioxide Activation by a Uranium(III) Complex Derived from a Chelating Bis(aryloxide) Ligand. *Organometallics* **2017**, *36*, 4539-4545.

58. Arunachalampillai, A.; Crewdson, P.; Korobkov, I.; Gambarotta, S., Ring Opening and C–O and C–N Bond Cleavage by Transient Reduced Thorium Species. *Organometallics* **2006**, *25*, 3856-3866.

59. Korobkov, I.; Gorelsky, S.; Gambarotta, S., Reduced Uranium Complexes: Synthetic and DFT Study of the Role of pi Ligation in the Stabilization of Uranium Species in a Formal Low-Valent State. *J. Am. Chem. Soc.* **2009**, *131*, 10406-10420.

60. Gunko, Y. K.; Hitchcock, P. B.; Lappert, M. F., Activation of a C-O Bond by Reaction of a Tris(Cyclopentadienyl)Lanthanide Complex with an Alkali-Metal in Dimethoxyethane (DME) - Crystal-Structures of [Nd(η⁵-C₅H₅(SiMe₃)₂-1,3)₂(μ-OMe)₂Li(DME)] and [(Ce(η⁵-C₅H₅Bu₂-1,3)₂(μ-OMe))₂]. *J. Organomet. Chem.* **1995**, *499*, 213-219.

61. Castillo, M.; Metta-Magaña, A. J.; Fortier, S., Isolation of gravimetrically quantifiable alkali metal arenides using 18-crown-6. *New J. Chem.* **2016**, *40*, 1923-1926.

62. Seaburg, J. K.; Fischer, P. J.; Young, J., Victor G.; Ellis, J. E., First Isolation and Structural Characterization of Bis(Anthracene)Metal Complexes: [Ti(η⁴-C₅H₄H₁₀)(η⁴-C₅H₁₀)(η⁴-dmpe)] and [Ti(η⁴-C₅H₄H₁₀)(η⁴-C₅H₁₀)(η⁴-C₅Me₃)]−. *Angew. Chem. Int. Ed.* **1998**, *37*, 155-158.

63. Bochkarev, M. N.; Fedushkin, I. L.; Fagin, A. A.; Schumann, H.; Demtschuk, J., Triple-decker naphthalene complex of thulium(III); synthesis and molecular structure of [(Tm(DME))₂(μ₂-η⁴-C₁₀H₈)₂(μ₂-η⁴-C₁₀H₈)]. *Chem. Commun.* **1997**, 1783-1784.

64. Labrum, N. S.; Losovyj, Y.; Caulton, K. G., A new access route to dimetal sandwich complexes, including a radical anion. *Chem. Commun.* **2018**, *54*, 12397-12399.

65. Tsoureas, N.; Mansikkamaki, A.; Layfield, R. A., Uranium(IV) cyclobutadienyl sandwich compounds: synthesis, structure and chemical bonding. *Chem. Commun.* **2020**, *56*, 944-947.

66. Shannon, R. D., Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Crystallogr. A* **1976**, *32*, 751-767.

67. Falceto, A.; Casanova, D.; Alemany, P.; Alvarez, S., Distortions of π-Coordinated Arenes with Anionic Character. *Chem. Eur. J.* **2014**, *20*, 14674-14689.
68. Engelhardt, L. M.; Harvey, S.; Raston, C. L.; White, A. H., Organo-Magnesium Reagents - the Crystal-Structures of [Mg(Anthracene)(THF)] and [Mg(Triphenylmethyl)Br(OEt₂)₂]. *J. Organomet. Chem.* 1988, 341, 39-51.

69. Bogdanovic, B., Magnesium anthracene systems and their application in synthesis and catalysis. *Acc. Chem. Res.* 1988, 21, 261-267.

70. Roitershtein, D. M.; Eltern, A. M.; Antipin, M. Y.; Rybakova, L. F.; Struchkov, Y. T.; Petrov, E. S., The First Structurally Characterized Organolanthanoid Compound with an Anthracene Dianion Ligand. Synthesis and Structure (at 143 K) of η⁵-(C₅H₅)Lu(C₁₄H₁₀₂⁻)·2THF (THF = tetrahydrofuran). *Mendeleev Commun.* 1992, 2, 118-120.

71. Fedushkin, I. L.; Bochkarev, M. N.; Dechert, S.; Schumann, H., A chemical definition of the effective reducing power of thulium(II) diiodide by its reactions with cyclic unsaturated hydrocarbons. *Chem. Eur. J.* 2001, 7, 3558-3563.

72. Velian, A.; Transue, W. J.; Cummins, C. C., Synthesis, Characterization, and Thermolysis of Dibenzo-7-dimethylgermanorbornadiene. *Organometallics* 2015, 34, 4644-4646.

73. Brennessel, W. W.; Ellis, J. E.; Roush, S. N.; Strandberg, B. R.; Woisetschlager, O. E.; Young, V. G., Tris(1-4-η⁴-anthracene)niobate(1-), the first polyaromatic hydrocarbon complex of niobium. *Chem. Commun.* 2002, 2356-2357.

74. Lusi, M.; Vitorica-Yrezabal, I. J.; Zaworotko, M. J., Expanding the Scope of Molecular Mixed Crystals Enabled by Three Component Solid Solutions. *Cryst. Growth Des.* 2015, 15, 4098-4103.

75. Fortenberry, R. C.; Novak, C. M.; Lee, T. J.; Bera, P. P.; Rice, J. E., Identifying Molecular Structural Aromaticity for Hydrocarbon Classification. *ACS Omega* 2018, 3, 16035-16039.

76. Minsky, A.; Meyer, A. Y.; Poupko, R.; Rabinovitz, M., Paramagnetism and Antiaromaticity - Singlet Triplet Equilibrium in Doubly Charged Benzenoid Polycyclic Systems. *J. Am. Chem. Soc.* 1983, 105, 2164-2172.

77. Kindra, D. R.; Evans, W. J., Magnetic Susceptibility of Uranium Complexes. *Chem. Rev.* 2014, 114, 8865-8882.

78. Fortier, S.; Melot, B. C.; Wu, G.; Hayton, T. W., Homoleptic Uranium(IV) Alkyl Complexes: Synthesis and Characterization. *J. Am. Chem. Soc.* 2009, 131, 15512-15521.

79. Bes, R.; Rivenet, M.; Solari, P. L.; Kvashnina, K. O.; Scheinost, A. C.; Martin, P. M., Use of HERFD-XANES at the U L-3- and M-4-Edges To Determine the Uranium Valence State on [Ni(H₂O)₄][U(OH₂(O)UO₂)₆O₁₂(OH)₃]. *Inorg. Chem.* 2016, 55, 4260-4270.

80. Kosog, B.; La Pierre, H. S.; Denecke, M. A.; Heinemann, F. W.; Meyer, K., Oxidation State Delineation via U L₃-Edge XANES in a Series of Isostructural Uranium Coordination Complexes. *Inorg. Chem.* 2012, 51, 7940-7944.

81. Anderson, N. H.; Odoh, S. O.; Williams, U. J.; Lewis, A. J.; Wagner, G. L.; Pacheco, J. L.; Kozimor, S. A.; Gagliardi, L.; Schelter, E. J.; Bart, S. C., Investigation of the Electronic Ground States for a Reduced Pyridine(diimine) Uranium Series: Evidence for a Ligand Tetraanion Stabilized by a Uranium Dimer. *J. Am. Chem. Soc.* 2015, 137, 4690-4700.
82. Kraft, S. J.; Williams, U. J.; Daly, S. R.; Schelter, E. J.; Kozimor, S. A.; Boland, K. S.; Kikkawa, J. M.; Forrest, W. P.; Christensen, C. N.; Schwarz, D. E.; Fanwick, P. E.; Clark, D. L.; Conradsion, S. D.; Bart, S. C., Synthesis, Characterization, and Multielectron Reduction Chemistry of Uranium Supported by Redox-Active alpha-Diimine Ligands. Inorg. Chem. 2011, 50, 9838-9848.

83. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized gradient approximation made simple. Phys. Rev. Lett. 1996, 77, 3865-3868.

84. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J. Chem. Phys. 2010, 132, 154104.

85. Grimme, S.; Ehrlich, S.; Goerigk, L., Effect of the damping function in dispersion corrected density functional theory. J. Comput. Chem. 2011, 32, 1456-1465.

86. Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R., RI-MP2: optimized auxiliary basis sets and demonstration of efficiency. Chem. Phys. Lett. 1998, 294, 143-152.

87. Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R., Auxiliary basis sets for main row atoms and transition metals and their use to approximate Coulomb potentials. Theor. Chem. Acc. 1997, 97, 119-124.

88. Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H., Energy-adjusted pseudopotentials for the actinides. Parameter sets and test calculations for thorium and thorium monoxide. J. Chem. Phys. 1994, 100, 7535-7542.

89. Cao, X.; Dolg, M.; Stoll, H., Valence basis sets for relativistic energy-consistent small-core actinide pseudopotentials. J. Chem. Phys. 2003, 118, 487-496.

90. TURBMOLE V7.3 2018, a development of the University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBMOLE GmbH, since 2007; available from http://www.turbomole.com

91. G. te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Guerra, C. F.; Van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T., Chemistry with ADF. J. Comput. Chem. 2001, 22, 931-967.

92. Mayer, I., Bond orders and valences from ab initio wave functions. Int. J. Quantum Chem. 1986, 29, 477-483.

93. Huang, Q.-R.; Kingham, J. R.; Kaltsoyannis, N., The strength of actinide–element bonds from the quantum theory of atoms-in-molecules. Dalton Trans. 2015, 44, 2554-2566.

94. Andersson, K.; Malmqvist, P. A.; Roos, B. O., 2nd-Order Perturbation-Theory with a Complete Active Space Self-Consistent Field Reference Function. J. Chem. Phys. 1992, 96, 1218-1226.

95. Andersson, K.; Malmqvist, P. A.; Roos, B. O.; Sadlej, A. J.; Wolinski, K., 2nd-Order Perturbation-Theory with a CASSCF Reference Function. J. Phys. Chem. 1990, 94, 5483-5488.

96. Malmqvist, P. A.; Pierloot, K.; Shahi, A. R. M.; Cramer, C. J.; Gagliardi, L., The restricted active space followed by second-order perturbation theory method: Theory and application to the study of CuO2 and Cu2O2 systems. J. Chem. Phys. 2008, 128.

97. Sauri, V.; Serrano-Andres, L.; Shahi, A. R. M.; Gagliardi, L.; Vanoille, S.; Pierloot, K., Multiconfigurational Second-Order Perturbation Theory Restricted Active Space (RASPT2) Method for Electronic Excited States: A Benchmark Study. J. Chem. Theory Comput. 2011, 7, 153-168.
98. Aquilante, F.; Autschbach, J.; Carlson, R. K.; Chibotaru, L. F.; Delcey, M. G.; De Vico, L.; Galvan, I. F.; Ferre, N.; Frutos, L. M.; Gagliardi, L.; Garavelli, M.; Giussani, A.; Hoyer, C. E.; Li Manni, G.; Lischka, H.; Ma, D. X.; Malmqvist, P. A.; Muller, T.; Nenov, A.; Olivucci, M.; Pedersen, T. B.; Peng, D. L.; Plasser, F.; Pritchard, B.; Reiher, M.; Rivalta, I.; Schapiro, I.; Segarra-Martí, J.; Stenrup, M.; Truhlar, D. G.; Ungur, L.; Valentini, A.; Vancoillie, S.; Veryazov, V.; Vysotskiy, V. P.; Weingart, O.; Zapata, F.; Lindh, R., Molcas 8: New capabilities for multiconfigurational quantum chemical calculations across the periodic table. J. Comput. Chem. 2016, 37, 506-541.
