## Supporting Information

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

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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<sub>3</sub>(dioxane)<sub>1.5</sub>,<sup>1</sup> UCl<sub>4</sub>,<sup>2</sup> U(O)[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>,<sup>3</sup> UO<sub>2</sub>Cl<sub>2</sub>(THF)<sub>3</sub><sup>4</sup> 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. <sup>1</sup>H NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer. <sup>1</sup>H NMR spectra are referenced to residual <sup>1</sup>H solvent peaks as internal standards or the characteristic <sup>1</sup>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).<sup>5</sup> Data was collected in the standard transmission geometry mode with an incident beam of  $500 \times 1000 \,\mu\text{m} \oplus 10^{12} \,\text{ph/sec}$  with energies between  $17 - 18 \,\text{keV}$ . 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 S16). In a glovebox 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  $3 \times 3$  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 re-examined immediately prior to the data collection. The compounds UI<sub>3</sub>(dioxane)<sub>1.5</sub>, UCl<sub>4</sub>, U(O)[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>, and UO<sub>2</sub>Cl<sub>2</sub>(THF)<sub>3</sub> 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.<sup>6</sup> 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<sup>18C6.4</sup>THF and 23.0 mg for 1<sup>THF</sup>. 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. THF,  $1^{18C6.4}$ THF,  $1^{THF}$  were collected on a dual source Bruker D8 4-axis diffractometer equipped with a PHOTON II CPAD detector with a IµS 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<sup>7</sup> program. Integration of the data and final cell parameter refinements were performed using SAINT<sup>8</sup> software with data absorption correction implemented through SADABS.<sup>9</sup> 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<sup>10</sup> or the Olex2<sup>11</sup> crystallographic package.

In  $1^{18C6.4THF}$ , the non-coordinated THF molecules in the lattice are highly disordered, due to variable arrangements within the lattice and were not fully modelled. Similarly, 2. THF displays one disordered THF molecule over two positions in the unit cell, which are not fully resolved in the model.  $1^{THF}$  displays severe positional disorder of one of the three THF molecules coordinated to the potassium atom (K1), which is best represented by modelling as four disordered locations.

Complete crystallographic data has been deposited at the Cambridge Crystallographic Data Center (CCDC Nos. 2071454 (1<sup>18C6</sup>·4THF), 2072886 (1<sup>THF</sup>), 2071450 (2·THF)).

Synthesis of [UI2(THF)3(µ-OMe)]2·THF (2 THF). To a 20 mL scintillation vial, UI3(dioxane)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<sub>2</sub>O (3 mL). After 48 h of storage at -35 °C, dark blue crystals were isolated. Yield: 0.187 g (0.12 mmol), 60%. <sup>1</sup>H NMR (25 °C, 400 MHz, py- $d_5$ ):  $\delta$ 219.8 (br s, 1H, -OCH<sub>2</sub>H), 112.4 (br s, 2H, -OCH<sub>2</sub>H), 3.62 (s, α-THF), 1.58 (s, β-THF). Note: The <sup>1</sup>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- $d_8$ , precluding collection of a satisfactory <sup>1</sup>H NMR spectrum due to low concentration of the analyte, thus requiring the use of  $py-d_5$  for dissolution. This results in total displacement of the coordinated THF molecules from 2. THF and gives a <sup>1</sup>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<sup>-1</sup>·cm<sup>-1</sup>): 325 ( $\epsilon$  = 3868), 369 ( $\epsilon$  = 3484), 400 ( $\epsilon$  = 2304), 560 ( $\epsilon$  = 810), 683 ( $\epsilon$  = 675). NIR (pyridine, 5.90 mM, 25 °C, L·mol-1·cm-1): 911 (ε = 259), 937 (ε =234), 1023 (ε = 148), 1041 (ε = 162), 1100 ( $\varepsilon$  = 253), 1146 ( $\varepsilon$  = 344), 1265 ( $\varepsilon$  = 100), 1443 ( $\varepsilon$  = 89). Combustion analysis of **2**·THF yielded unsatisfactory results as the carbon content was unreasonably low. We attribute this to poor combustion properties of 2·THF.

of  $[K(18-crown-6)(THF)_2]_2[U(\eta^6-C_{14}H_{10})(\eta^4-C_{14}H_{10})(\mu-OMe)]_2 \cdot 4THF$ **Synthesis** (1<sup>18C6.</sup>4THF). To a 20 mL scintillation vial, potassium metal (0.028 g, 0.72 mmol) was suspended in THF (5 mL). To this, while stirring at room temperature, anthracene (0.123 mg, 0.69 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 d, dark blue crystals formed. The product mixture was poured over a medium porosity glass frit and the crystalline solid washed with THF ( $3 \times 10$  mL) then dried under vacuum. Yield: 0.084 g (39.1 µmol), 36%. Anal. Calcd for 1<sup>18C6.</sup>4THF, C<sub>114</sub>H<sub>158</sub>K<sub>2</sub>O<sub>22</sub>U<sub>2</sub>·4THF: C, 56.23; H, 6.55. Anal. Calcd for  $[K(18-crown-6)(THF)_2][K(18-crown-6)(THF)][U(\eta^6-C_{14}H_{10})(\eta^4-C_{14}H_$ C<sub>14</sub>H<sub>10</sub>)(µ-OMe)]<sub>2</sub>, C<sub>94</sub>H<sub>118</sub>K<sub>2</sub>O<sub>17</sub>U<sub>2</sub>: C, 54.42; H, 5.74. Found: C, 53.95; H, 5.37.

Synthesis of {[K(THF)3][U( $\eta^6$ -C14H10)( $\eta^4$ -C14H10)( $\mu$ -OMe)]}2 (1<sup>THF</sup>). 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 blue solution was chilled to -35 °C, to which **2**·THF (0.168 g, 0.11 mmol) was added. The reaction mixture was left to stir at -35 °C for 16 h. The resulting purple suspension was subsequently filtered through Celite supported on a medium-porosity glass frit. The dark purple filtrate was transferred to a 20 mL scintillation vial and layered with hexanes (6 mL). Crystals were grown from storage of the layered solution at -35 °C for 48 h. 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: 77.4 mg (43.9 µmol), 37%. Anal. Calcd for **1<sup>THF</sup>**, C82H94K2O8U2: C, 55.89; H, 5.38. Anal. Calcd for

{[K(THF)][ $U(\eta^6-C_{14}H_{10})(\eta^4-C_{14}H_{10})(\mu-OMe)$ ]}<sub>2</sub>, C<sub>66</sub>H<sub>62</sub>K<sub>2</sub>O<sub>4</sub>U<sub>2</sub>: C, 53.79; H, 4.25. Found: C, 53.26; H, 4.91.

**EPR Measurements**. X-band EPR measurements were performed on powdered samples of  $1^{18C6.4}$ THF and  $1^{THF}$  at 4(±1) K. All EPR measurements were performed on a Bruker EMX Plus X-band spectrometers. Low temperature measurements were taken using a liquid helium cooled cryo-stat. Samples were prepared from pulverized single crystals and loaded into quartz EPR tubes. Continuous wave experiments at low temperature were performed at a microwave frequency of 9.64760 GHz. Experiments at room temperature were conducted at a microwave frequency of 9.40145 GHz.

In these samples, a clear signal centred at g = 2.000 for  $1^{THF}$  and g = 2.017 for  $1^{18C6.4}$ THF is observed (Figures S10 and S11), consistent with isolated S =  $\frac{1}{2}$  spins. These peaks persist at room-temperature (Figures S13 and S14). Resonances corresponding to uranium-based signals were not observed.

While similar EPR spectra have been observed in arene-metalates such as  $[K(18\text{-crown-}6)][Cr_2(C_{10}H_8)_2]$  (g = 1.987) where the radical is largely localized on the arene ligand,<sup>12</sup>the appearance of the EPR signals for  $1^{18C6}$ .4THF and  $1^{THF}$  might suggest radical monoanionic character in at least one of the coordinated anthracenes in the dimeric compounds. 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 counterion, solvent, and temperature.<sup>13</sup>

Critically, the presence of the radical ligand character is inconsistent with the electronic structures determined through magnetism, XANES analysis, and computational methods. The EPR signals remain present across independently prepared samples. However, in comparison with the EPR spectra of pure  $[K(18-crown-6)(THF)_2][C_{14}H_{10}]$  (Figure S12), we find that the observed signal is most likely explained by the presence of trace co-crystallized  $[K(18-crown-6)(THF)_2][C_{14}H_{10}]$  in the crystal lattices of  $1^{18C6} \cdot 4THF$  and  $1^{THF}$ , or potentially, crystal packing effects.



**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  $1^{18C6.4}$ 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  $1^{18C6.}$ 4THF. a)  $\eta^6$ -coordinated anthracene and b)  $\eta^4$ -coordinated anthracene.



**Figure S4.** Carbon-carbon bond length diagrams of the coordinated anthracenes of  $1^{\text{THF}}$ . a)  $\eta^6$ -coordinated anthracene and b)  $\eta^4$ -coordinated anthracene.



Figure S5. Ring folding angles for the coordinated anthracene rings in a)  $1^{\text{THF}}$  and b)  $1^{18C6.4}$  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 <sup>18C6</sup> .4THF	1 <sup>THF</sup>
Empirical formula	$C_{30}H_{62}I_4O_9U_2$	$C_{114}H_{158}O_{22}K_2U_2$	$C_{82}H_{94}O_8K_2U_2$
Cryst. habit, colour	block, blue	block, dark blue	block, dark purple
Cryst. size (mm)	$0.20 \times 0.12 \times 0.22$	$0.12 \times 0.41 \times 0.46$	$0.43 \times 0.33 \times 0.30$
Cryst. system	Orthorhombic	Triclinic	Monoclinic
Space group	Pban	$P\overline{1}$	<i>P</i> 2 <sub>1</sub> /n
volume (Å <sup>3</sup> )	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)
a (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 <sup>3</sup> )	2.218	1.280	1.546
Abs coeff (mm <sup>-1</sup> )	9.643	2.706	4.498
F <sub>000</sub>	1416.0	1222.0	1696.0
Total no. of reflns	26741	15465	30444
Unique reflns	3438	11505	7630
Final R indices $[I > 2\sigma(I)]$	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

 Table S1. X-ray Crystallographic Data for 1<sup>18C6.4</sup>THF, 1<sup>THF</sup>, 2. THF



**Figure S7.** <sup>1</sup>H NMR spectrum of  $2 \cdot$  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 **2**·THF (5.90 mM) in pyridine at 25 °C. Sharp peaks denoted by \* are electronic artifacts and not attributed to absorptions by **2**·THF.



Figure S10. Solid state EPR spectra for  $1^{18C6}$  4THF at 4.0 (±1) K.



**Figure S11.** Solid state EPR spectra for  $\mathbf{1}^{\text{THF}}$  at 4.0 (±1) K.



**Figure S12.** Overlay of the solid-state EPR spectra for  $1^{\text{THF}}$ ,  $1^{18C6.4}$ THF, and [K(18-crown-6)(THF)<sub>2</sub>][C<sub>14</sub>H<sub>10</sub>] at 4.0 (±1) K.



Figure S13. Scaled stacked plot of the solid-state EPR spectra for  $1^{18C6.4}$ THF at room temperature and at 4.0 (±1) K.



**Figure S14.** Scaled stacked plot of the solid-state EPR spectra for  $1^{\text{THF}}$  at room temperature and at 4.0 (±1) K.



Figure S15. Normalized XANES plot of the absorption edge energies expressed as the first derivative for  $1^{18C6.4}$ THF,  $1^{THF}$ , and the uranium compounds used as oxidation state reference standards.



Figure S16. 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 S17. Normalized XANES plot of the absorption edge energies for  $1^{18C6.4}$ THF,  $1^{THF}$ , and the uranium compounds used as oxidation state reference standards.

Compounds	Inflection Point Energy (eV)	White Line Energy (eV)
UI <sub>3</sub> (dioxane) <sub>1.5</sub>	17158.8	17164.8
UCl <sub>4</sub>	17161.6	17166.4
1 <sup>18C6.</sup> 4THF	17161.7	17167.5
1 <sup>THF</sup>	17162.6	17168.8
$U(O)[N(SiMe_3)_3]_3$	17163.3	17169.4
UO <sub>2</sub> Cl <sub>2</sub> (THF) <sub>3</sub>	17165.1	17168.6

**Table S2.** XANES energies for  $1^{18C6.4}$ THF,  $1^{THF}$ , and the uranium standards given as the edge energy at the inflection point ( $1^{st}$  derivative) and white line values.



**Figure S18.** Temperature dependence of the  $\chi T$  product at 1000 Oe for  $1^{18C6.}$  4THF (red) and  $1^{THF}$  (blue).



**Figure S19.** Temperature dependence of the  $\chi T$  product under an applied dc field of 1000 Oe (blue) and 10,000 Oe (red) for 1<sup>18C6.</sup>4THF, where  $\chi$  is the molar magnetic susceptibility as defined by *M/H*.



**Figure S20.** Temperature dependence of the  $\chi T$  product under an applied dc field of 1000 Oe (blue) and 10,000 Oe (red) for  $\mathbf{1}^{\text{THF}}$ , 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  $K_2[U(\eta^6-C_{14}H_{10})(\eta^4-C_{14$  $C_{14}H_{10}$  ( $\mu$ -OMe)]<sub>2</sub> (**1-K**<sup>\*</sup>). 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.<sup>14</sup> In every structure, we observe one to three imaginary frequencies associated with methyl rotations ranging from -14.83 to -113.53 cm<sup>-1</sup>. The PBE<sup>15-18</sup> 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.<sup>19-21</sup> The D3 dispersion correction with Becke–Johnson damping was also used.<sup>22-23</sup> The resolution of identity (RI) approximation was used for integral evaluation.<sup>24</sup> These results were further analysed by computing CM5 charges, atomic contributions to the molecular orbitals calculated using the Hirshfeld method,<sup>25</sup> and topological analysis of the electron density with Bader's Atoms in Molecules (AIM) were performed using the Multiwfn 3.7 software package.<sup>26</sup> 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<sup>27</sup> functionals as implemented in the Amsterdam Density Functional (ADF) program package.<sup>28</sup> 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 centres 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<sup>29</sup> 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).<sup>30-31</sup> 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.<sup>32-33</sup> The computation of the three-centered integrals was expedited through the use of Cholesky decomposition and local exchange screening.<sup>34-37</sup> 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 S23 to S34).

#### Additional Computational Details and Discussion.

**Hirshfeld Decomposition.** The four unpaired electrons are in uranium 5*f*-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.<sup>26, 38</sup> In QTAIM, a chemical bond is present if a line of locally maximum electron density joins neighbouring 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 in 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 5*f* 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 6*d* orbitals do not need to be included in the active space provided that they are not involved in bonding. We also performed CASSCF(4e,8o) and CASSCF(8e,12o) to see the 5*f*-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 (Figures S32-S35). Two holes are allowed in RAS1 and two electrons are allowed in RAS3. Using the notation of Sauri *et al.*<sup>39</sup>, we can describe this space as (24e,2h,2e; 10o,8o,10o). Note that in RAS2, we have truncated the number of 5*f*-electrons from the CASSCF calculation. If a 5*f*-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>	<s*s> ideal</s*s>
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 S21**. RI-PBE-D3/def2-TZVP, def-TZVP on U spin densities for **1**\* and **1-K**\* from the ground state quintet calculations.

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- <b></b> <i>η</i> 4C 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-η6C 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-η4C 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-η6C avg	2.723	2.748	2.748

**Table S4.** Selected U-C bond distances for PBE-D3 optimized geometry from triplet, quintet andseptet spin states of compound 1\*. Atom numbers labelled in Figure S22.

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- $\eta^4$ 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-η <sup>6</sup> 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-η <sup>4</sup> 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-η <sup>6</sup> C Avg.	2.734	2.733	2.790

**Table S5.** Selected U-C bond distances for PBE-D3 optimized geometry from triplet, quintet and septetspin states of 1-K\*. Atom numbers labelled in Figure S22.



**Figure S22.** 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.

Compounds	Bonds	<b>∇</b> <sup>2</sup> (ρ)	G(r)	V(r)	E(r)	ρ
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 S6**: Properties at the bond critical points for **1**\* and **1-K**\*. All values are expressed in atomic units. Atom numbers labelled in Figure S22.

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- $\eta^4$ C 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-η <sup>6</sup> C 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- $\eta^4$ C 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-η <sup>6</sup> C Avg.	2.749	0.31	0.26	0.32	0.38	0.31

**Table S7**. Bond order of uranium and coordinated carbon atoms in 1\* (PBE). Atom numbers labelled in Figure S22.

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-η <sup>6</sup> C 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-η <sup>4</sup> C 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-η <sup>6</sup> C Avg.	2.749	0.32	0.25	0.32	0.38	0.31

**Table S8.** Bond order of uranium and coordinated carbon atoms in 1\* (TPSS). Atomnumbers labelled in Figure S22.

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-η <sup>4</sup> C 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-η <sup>6</sup> C 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-η <sup>4</sup> C 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-η <sup>6</sup> C Avg.	2.734	0.32	0.27	0.33	0.39	0.32

**Table S9.** Bond order of uranium and coordinated carbon atoms in 1-K\* (PBE) Atom numbers labelled in Figure S22.

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	2.6311	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 <sup>4</sup> CAvg.	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- <i>η</i> <sup>6</sup> CAvg.	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 <sup>4</sup> C 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
64C-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 <sup>6</sup> C Avg.	2.734	0.34	0.26	0.34	0.39	0.32

**Table S10**. Bond order of uranium and coordinated carbon atoms in **1-K**\* (TPSS). Atom numbers labelled in Figure S22.

r	1	*		1-K*				
η <sup>6</sup> -anth	charge	$\eta^4$ -anth	charge	$\eta^6$ -anth	charge	$\eta^4$ -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	0.07434	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	Ο	-0.52	U	1.03	Ο	-0.52	

Table S11. CM5 atomic charges calculated with PBE-D3 for ground state. Atom numbers labelled in Figure S22.

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 S12**. CASSCF and CASPT2 relative energies in kcal/mol for three different active space configurations.

Spin	RASSCF	RASPT2
Singlet	0.0004	0.00
Triplet	0.00	0.25
Quintet	0.0002	0.18

 Table S13. RASSCF and RASPT2 energy differences in kcal/mol for three spin states.

η <sup>6</sup> -anth	charge	η <sup>4</sup> -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	0	-1.03

**Table S14.** LoProp Charges for coordinated carbon atoms, oxygen and uranium from RASSCFcalculation of 1\*. Atom numbers labelled in Figure S22.



Figure S23. The CASSCF (4e, 14o) 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 S24**. 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 S25**. The CASSCF (4e, 14o) 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 S26**. The CASSCF (4e,8o) natural orbitals are shown for the quintet state for **1**<sup>\*</sup>. Occupation numbers are in parentheses. An isovalue of 0.04 was used.



**Figure S27**. 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 S28**. 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 S29. 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 S30**. The CASSCF(8*e*,12*o*) natural orbitals are shown for septet state for **1**\*. Occupation numbers are in parentheses. An isovalue of 0.04 was used.



**Figure S31**. 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 S32**. 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 S33**. The RASSCF natural orbitals are shown for the singlet state of dimer 1\*. The occupation numbers are in parentheses. An isovalue of 0.04 a.u. was used.



**Figure S34**. RASSCF natural orbitals and occupation numbers are shown for the quintet state of 1\*. The  $\pi$ -orbitals are in RAS1 and the 5*f*-orbitals are in RAS2. RAS3 is not plotted (see Figure S31). 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.



**Figure S35**. RASSCF spin density for **1**\*. a) quintet state, b) triplet state.

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	1.44435	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	

**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 η <sup>6</sup> -anth	Triplet	Quintet	Septet	Bonds $\eta^4$ -anth	Triplet	Quintet	Septet
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 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.

Orbital index	Total U	U 7s	U 6p	U 6d	U 5f	Total C	η1 <sup>6</sup> C	η1 <sup>4</sup> C	η2 <sup>6</sup> C	$\eta_2^4 C$
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 S17.** Orbital analysis of **1**\* for the bonding orbitals from the RASSCF( $24e^{-}$ , 2h,  $2e^{-}$ ; 10o, 8o, 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	η1 <sup>6</sup> C	η1 <sup>4</sup> C	η2 <sup>6</sup> 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 S18.** Orbital analysis of **1**\* for the bonding orbitals from the CASSCF(8*e*,12*o*) calculation. The percent contributions are average from the singlet, triplet and quintet state orbitals.

	$1^* \eta^4$	$1^* \eta^6$
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

Table S19. Energy decomposition analysis (EDA) for 1\* using the PBE functional. Energies reported in kcal/mol.

Compounds	Spin	U1-C(η <sup>6</sup> )	U1-C(η <sup>4</sup> )	U2-C(η <sup>6</sup> )	U2-C(η <sup>4</sup> )	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

**Table S20.** Selected metal-ligand distances from RI-PBE-D3/def2-TZVP optimized geometries for the triplet, quintet, and septet spin states of **1**\* and **1-K**\*. Values are averaged. Distances are in angstroms (Å).

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