"This is the peer reviewed version of the following article: [*J. Am. Chem. Soc.* 2023, 145, 29, 16271– 16283] which has been published in final form at [Link to final article using the DOI: <u>https://doi.org/10.1021/jacs.3c05626</u>]. This article may be used for non-commercial purposes in accordance with the American Chemical Society Terms and Conditions for Self-Archiving."

Multielectron redox chemistry of uranium by accessing the +II oxidation state and enabling reduction to a U(I) synthon

Megan Keener,[‡]^a R. A. Keerthi Shivaraam,[‡]^a Thayalan Rajeshkumar,^c Maxime Tricoire,^a Rosario Scopelliti,^d Ivica Zivkovic,^b Anne-Sophie Chauvin,^a Laurent Maron, ^{*}^c and Marinella Mazzanti.^{*}^a

^aGroup of Coordination Chemistry, Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.

^bLaboratory for Quantum Magnetism, Institute of Physics, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.

^cLaboratoire de Physique et Chimie des Nano-objets, Institut National des Sciences Appliquées, 31077 Toulouse, France. ^dX-Ray Diffraction and Surface Analytics Platform, Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.

ABSTRACT: The synthesis of molecular uranium complexes in oxidation states lower than +3 remains a challenge despite the interest for their multielectron transfer reactivity and electronic structures. Herein, we report the one- and two-electron reduction of a U(III) complex supported by an arene-tethered, tris(siloxide) tripodal ligand leading to the mono-reduced complexes, [K(THF)U((OSi(O'Bu)₂Ar)₃-arene)(THF)] (**2**) and [K(2.2.2-cryptand)][U((OSi(O'Bu)₂Ar)₃-arene)(THF)] (**2-crypt**), and to the di-reduced U(I) synthons, [K₂(THF)₃U((OSi(O'Bu)₂Ar)₃-arene)]_∞ (**3**) and [(K(2.2.2-cryptand))]₂[U((OSi(O'Bu)₂Ar)₃-arene)] (**3-crypt**). EPR and UV/Vis/NIR spectroscopies, magnetic, cyclic voltammetry, and computational studies provide strong evidence that complex **2-crypt** is best described as U(II), where the U(II) is stabilized by δ -bonding interactions between the arene anchor and the uranium frontier orbitals, whereas complexes **3** and **3-crypt**, are best described as having a U(III) ion supported by the di-reduced arene anchor. Three quasi-reversible redox waves at E_{1/2} = -3.27, -2.45, and -1.71 V were identified by cyclic voltammetry studies, and were assigned to the U(IV)/U(III), U(III)/U(III) and U(II)/U(III)-(arene)²⁻ redox couples. The ability of complexes **2** and **3** in transferring two-and three-electrons, respectively, to oxidizing substrates was confirmed by the reaction of **2** with azobenzene (PhNNPh) leading to the U(IV) complex, [K(Et₂O)U((OSi(O'Bu)₂Ar)₃-arene)(PhNNPh)(THF)] (**4**), and of complex **3** with cycloheptatriene (CHT), yield-ing the U(IV) complex, [(K(Et₂O))₂U((OSi(O'Bu)₂Ar)₃-arene)(η^7 -Cr₄T₇]_∞ (**6**). These results demonstrate that the arene-tethered tris(siloxide) tripodal ligand provides an excellent platform for accessing low-valent uranium chemistry, while implementing multielectron transfer pathways as shown by the reactivity of complex **3**, which provides the third example of a U(I) synthon.

INTRODUCTION

Recent advances in molecular *f* element chemistry have significantly extended the number of oxidation states accessible in molecular complexes of the 4*f* and 5*f* elements.¹⁻¹⁵ Notably, molecular complexes of uranium were only known in oxidation states ranging from +3 to +6 before identification in 2013 by Evans and coworkers of the first formal U(II) ion in a crystalline molecular complex based on cyclopentadienyl ligands,¹⁶ while

the first complex of uranium in the formal +1 oxidation state was very recently identified in 2022 by Layfield and coworkers.¹² In the last ten years, several other cyclopentadienide complexes of U(II) were synthesized.¹⁷⁻²⁰ However, isolation of uranium complexes in the +2 oxidation state still remains very challenging, even when the +2 oxidation state is electrochemically and chemically accessible,²¹⁻²² where the presence of U(II) could be confirmed by spectroscopic and computational studies.^{17, 22, 23} Notably, transient U(II) species were obtained by reduction of the heteroleptic U(III) complexes, $[(C_5Me_5)_2U^{III}(N(SiMe_3)_2)]$ and $[(C_5Me_5)U^{III}(N(SiMe_3)_2]$, which rapidly formed U(III) C–H bond activation products.²⁴

To date, only four additional ligand systems led to the isolation of U(II) complexes, ^{19,25-27} and generally, the reactivity studies of U(II) complexes remain extremely rare. Notably, the possibility of further reduction of an isolated U(II) complex was so far only demonstrated in a single case, which led very recently to the identification of the first formal U(I) molecular compound, [K(2.2.2-cryptand)][U(η^5 -C₅ⁱPr⁵)₂].^{20, 12} All other reported U(II) complexes were produced by reduction of the analogous U(III) complex with excess alkali reducing agent, suggesting that lower redox states were not accessible. In a recent report from J. Arnold and coworkers, the reduction of the amidate-supported U(III) mono(arene) complex, [U{N-(2,6-diisopropylphenyl)-pivalamido}₃], with excess reducing agent, was found to result in a two-electron reduction, accompanied by loss of one ligand.²⁷

Scheme 1. Reactivity of complexes 1, 2, 3, and 2-crypt with reducing agents and/or 2.2.2-cryptand.



resulting anionic bis(arene) complex, [K(2.2.2-The cryptand)][U{N-(2,6-di-isopropylphenyl)-pivalamido}_2], was described as a U(II) ion supported by a ligand framework with a mono-reduced arene, but reacted as a U(I) synthon behaving as a three-electron transfer reagent. In contrast, three-electron processes were not available for the only example of an isolated U(I) complex, most likely due to the high stability of the U(II) analogue.¹² It should be noted that arene ligands have been utilized to bind and stabilize uranium in low oxidation states.²⁸⁻³³ A distinct class of arene-bound uranium complexes, inversesandwich complexes, in which two uranium ions are bridged by an arene,³⁴⁻⁴⁰ have been isolated in different oxidation states, including the seminal reports of uranium complexes in a +2 formal oxidation state, $[\{(C_5Me_5)_2U\}_2(\mu-\eta^6:\eta^6-C_6H_6)]^{34}$ and $(\mu-\eta^6:\eta^6-C_6H_6)^{34}$ $C_7H_8)[U(N[R]Ar)_2]_2$.³⁵ Although these complexes are better described as U(III)-(arene)²-U(III) species, they were found to act as U(II) synthons, effecting multielectron transfer reactions. In contrast, the use of an arene anchor for tethering aryloxide ligands resulted in the controlled synthesis of U(III) complexes with unusual stoichiometric and catalytic reactivity, 41-42 and led to the identification of the first U(II) stabilized by δ -back bonding interactions, which was obtained in the presence of excess reducing agent.²⁵ Cyclic voltammetry studies indicated that access to lower oxidation states was unlikely in this ligand system, which was in part due to the observed ligand-based reactivity in the utilized conditions.43-44

Very recently, we reported the two- and three-electron reduction of a oxo-bridged diuranium(IV) complex supported by monodentate triphenylsiloxide ($-OSiPh_3$) ligands, [{(Ph₃SiO)₃(DME)U}₂(μ -O)]. The two- and three-electron reductions of the U(IV)/U(IV) complex resulted in ligand migration, yielding formal "U(II)/U(IV)", and "U(I)/U(IV)" complexes, respectively, where the U(II) and U(I) synthons are stabilized by uranium-arene δ -bonding interactions. Two-electron redox reactivity was reported for the reduced complexes, but the involved ligand rearrangement which limited the system versatility.⁴⁵

Considering the ability of siloxide ligands to stabilize uranium in low oxidation states,^{38, 46, 45} their high stability both in reducing⁴⁷ and oxidizing conditions,^{46, 7, 10} and their ability to support original reactivity with small molecules,^{38, 48, 49} we reasoned that a tris(siloxide) arene-anchored tripodal ligand may allow access to lower oxidation states, while promoting unprecedented redox-reactivity. Indeed, we very recently showed that the tris(tert-butoxy)siloxide arene can stabilize cerium complexes in four states of charge.⁵⁰ Herein, we report the synthesis of the neutral tris(tert-butoxy)siloxide arene U(III) complex, [U((OSi(O'Bu)₂Ar)₃-arene)(THF)] (1), and demonstrate that this complex undergoes two quasi-reversible redox processes. Chemical reduction by one-electron afforded a new U(II) complex, supported by δ -bonding interactions with the arene anchor, which can be further reduced to yield a complex that is best described as a U(III)-(arene)²⁻ species, but acts as a U(I) synthon by transferring three-electrons to cycloheptatriene (CHT).

RESULTS AND DISCUSSION

Synthesis of uranium tripodal siloxide complexes

At first, we investigated the synthesis of the neutral tris(tertbutoxy)siloxide arene U(III) complex, $[U((OSi(O'Bu)_2Ar)_3$ arene)(THF)] (1), by protonolysis (Scheme 1). Addition of 1.0 equiv. of $[U(N(SiMe_3)_2)_3]$ to 1.0 equiv. of the $(HOSi(O'Bu)_2Ar)_3$ arene⁵⁰ ligand in THF at room temperature, resulted in a color change from purple to dark brown-red. Analysis of the reaction mixture by ¹H NMR spectroscopy indicated the disappearance of the precursor $[U(N(SiMe_3)_2)_3]$ and concomitant formation of HN(SiMe_3)_2. Brown-red needles of complex **1** were obtained from a concentrated THF solution at -40 °C in 84% yield. The room temperature ¹H NMR spectrum of isolated complex **1** displays resonances at δ 2.56, 3.02, 3.72, 4.90, 9.49, and 10.68 ppm corresponding to the aryl/arene and $-OSi(O'Bu)_2$ moieties. The solid-state molecular structure of complex **1** was determined by X-ray diffraction studies, and shows the presence of a neutral [U((OSi(O'Bu)_2Ar)_3-arene)(THF)] complex (Figure S34). The U(III) ion is centrally located in the core of the tris(tert-butoxy)siloxide ligand with U1–O_{siloxide} bond distances of 2.182(3)-2.214(3) Å and O–U1–O bond angles of 113.08(11)-122.04(12)°.



Figure 1. Molecular structures of (a) $[K(THF)U((OSi(O'Bu)_2Ar)_3-arene)(THF)]$, 2, (b) the anion $[U((OSi(O'Bu)_2Ar)_3-arene)(THF)]^-$ in 2crypt, (c) $[K_2(Et_2O)U((OSi(O'Bu)_2Ar)_3-arene)]_3$, 3b, (d) the anion $[U((OSi(O'Bu)_2Ar)_3-arene)]^2$ - in 3-crypt, with thermal ellipsoids at drawn at the 50% probability level. Hydrogen atoms and methyl groups on the $-OSi(O'Bu)_2$ ligands have been omitted for clarity. The monomeric unit of complex 3b has been depicted for clarity.

The U(III) ion interacts with the planar arene anchor in a η^{6} -fashion with C-Carene bonds (1.403(5)-1.417(5) Å) and a U1-Ccentroid bond distance of 2.485(2) Å (Table 1). The observed bonding mode is analogous to what was observed in the previously reported U(III) tripodal tris(aryloxide) arene complex, [U((^{R,R}'ArO)₃mes)],^{51, 25} but with a slightly elongated U1-Ccentroid distance of 2.487(4) Å in 1 vs. 2.33 Å in [U((tBuArO)3mes)], which can be related to the longer U1-Osiloxide bond lengths (2.201(3); 2.209(3); 2.210(3)) in 1 compared to [U((1^{Bu}ArO)₃mes)] (2.168(2) Å). Therefore, the longer U1-C_{centroid} distance indicates a weaker δ-backbonding interaction between the U(III) center and the arene backbone in 1, which is most likely associated to the weaker donating ability of the siloxides compared to the aryloxides of [U(((BuArO)3mes)]. This is supported by DFT calculations, which shows that the δ -bonding interaction in 1 in not occupied and is in fact the LUMO of the system (Figure S62). With the U(III) complex 1 in hand, we next explored the reduction chemistry in the absence and presence of 2.2.2cryptand to prepare new low-valent uranium species and to compare potential changes in electronic and bonding interactions.

Addition of 1.0 equiv. of KC₈ to a solution of 1 in d_8 -THF at -40 °C, led to the consumption of 1 and the appearance of new resonances as seen by ¹H NMR spectroscopy (Figure S23a). Dark purple crystals of complex, [K(THF)U((OSi(O'Bu)₂Ar)₃-arene)(THF)] (2), were obtained from a mixture of THF and *n*-hexanes at -40 °C in 83% yield (Scheme 1). The solid-state molecular structure of complex 2 was determined by X-Ray diffraction studies (Figure 1a), and shows the presence of a neutral complex where the K⁺ cation is bound by the siloxide arms of the [U((OSi(O'Bu)₂Ar)₃-arene)(THF)] moiety, and contains two molecules of 2 per asymmetric unit.

Compared to complex 1, the O–U1–O bond angles of 2 vary significantly (92.45(17); 118.47(19); 120.78(18)°), where the smallest bond angle corresponds to the binding of the K⁺ cation to four oxygens of the two –OSi(O'Bu)₂ arms, decreasing the O–U1–O bite angle. The U1–O_{siloxide} bond lengths increase (2.236(5)-2.250(5) Å) compared to those found in 1 (2.183(3)-2.213(3) Å). The U1 ion interacts with the arene anchor in a η^6 -fashion, similar to 1, but with a significant contraction of the

U1– $C_{centroid}$ bond distance (2.255(9) Å versus 2.487(4) Å in 1). These bond metrics are suggestive of an increased δ -bonding interaction between the uranium center and the arene.²⁵⁻²⁷ The planarity of the arene ring is significantly distorted in complex 2, adopting a boat conformation with varying C– C_{arene} bonds,

where two bonds are significantly shorter (C18-C19: 1.404(9); C15-C20: 1.405(10) Å) than the remaining bonds (1.422(9)-1.455(10) Å), and have significant torsion angles with values of 22.0(11); 16.4(11); 17.4(11); 20.8(11); 1.1(11); and 3.1(12)°.

Table 1. Selected bond lengths (Å) and angles (°) for complexes 1, 2, 2-crypt, 3b, 3-crypt.

Complex	1	2	2-crypt	3b	3-crypt
ЦО	2.201(3); 2.209(3);	2.236(5); 2.241(5);	5); 2.2181(18); 2.234(3); 2.241(3) 2.2182(18); 2.218	2.234(3); 2.241(3);	2.207(8); 2.285(8);
U-O _{siloxide}	2.210(3)	2.250(5)	2.2183(18); 2.2197(18)	2.250(3)	2.307(7)
	2.841(4); 2.846(4);	2.546(7); 2.556(8);	2.632(2); 2.644(3);	2.527(5); 2.542(5);	2.519(13); 2.540(10);
U-Carene	2.851(4); 2.863(4);	2.692(7); 2.720(8);	2.665(2); 2.686(3);	2.550(5); 2.555(5);	2.551(13); 2.557(11);
	2.868(3); 2.884(4)	2.730(7); 2.742(8)	2.670(3); 2.707(2)	2.563(5); 2.584(5)	2.565(13); 2.583(13)
	1.403(5); 1.406(5);	1.404(9); 1.405(10);	1.409(4); 1.411(4);	1.429(6); 1.437(7);	1.378(17); 1.417(17);
C-Carene	1.410(5); 1.410(5);	1.422(9); 1.429(10);	1.426(3); 1.428(4);	1.439(7); 1.442(7);	1.420(18); 1.435(18);
	1.412(5); 1.417(5)	1.455(10); 1.455(10)	1.435(4); 1.440(4)	1.445(7); 1.449(7)	1.438(19); 1.44(2)
U-C _{centroid}	2.485(2)	2.255(9)	2.256(1)	2.109(5)	2.121(13)
	112 09(11)	92.45(17);		91.65(12);	
U-O-U	113.08(11)- 122.04(12)°	118.47(19);	107.28(7)-113.26(7)°	113.21(12;	103.2(3)-110.6(3)°
		120.78(18)°		108.65(13)°	
Torsion angles	0 4(6) 2 2(6)	1 1(11) 22 0(11)	2 0(2) 8 7(2) 9	0.0(7) 5.0(7)	1.0(10) 5.6(19)9
arene	0.4(0)-2.5(0)	1.1(11)-22.0(11)	3.0(3)-8.7(3)	0.9(7)-3.9(7)	1.0(19)-3.0(18)

This distortion is also reflected in the U1–C_{arene} bond distances, where C16 and C19 lie above the plane and display the shortest distances of 2.546(7) and 2.556(8) Å, respectively, whereas the remaining carbons are farther from U1 (2.692(7)-2.742(8) Å) (Table 1). To investigate if the distortion of the arene backbone could arise from coordination of the K⁺ cation to the – OSi(O'Bu)₃ arms of the ligand, we pursued the removal of the inner sphere K⁺ cation.

We found that addition of 1.0 equiv. of 2.2.2-cryptand to a solution of **2** in d_8 -THF at -40 °C, resulted in the appearance of a new ¹H NMR resonance consistent with the K-sequestered moiety, [K(2.2.2-cryptand)]⁺ (Figure S25b). Similarly, we found that addition of 1.0 equiv. KC₈ and 1.0 equiv. 2.2.2-cryptand to a solution of 1 in THF at -40 °C also led to the formation of an analogous reaction mixture (Figure S24a). Dark purple crystals suitable for XRD analysis of the 2.2.2-cryptand derivative of 2, [K(2.2.2-cryptand)][U((OSi(O'Bu)₂Ar)₃-arene)(THF)] (2 **crypt**), could be obtained from a concentrated toluene mixture at -40 °C (Figure 1b), whereas bulk isolation was obtained from a mixture of THF and *n*-hexanes in 89% yield (Scheme 1). The identical ligand resonances of complexes 2 and 2-crypt at -40 °C, without and with 2.2.2-cryptand, respectively, suggests structural similarities when in THF solution.

The solid-state molecular structure of **2-crypt** was determined by XRD studies and shows the presence of an ion pair consisting of one outer sphere $[K(2.2.2\text{-cryptand})]^+$ cation and the $[U((OSi(O'Bu)_2Ar)_3\text{-arene})(THF)]^-$ anion. Compared to complex **2**, the U1 ion is centrally located in the tris(tert-butoxy)siloxide arms with O–U1–O bond angles (107.28(7)-113.26(7)°), similar to the previously reported U(II) complex, [K(2.2.2 $crypt)][U((^{Ad,Me}ArO)_3mes)] (O–U–O: 111.49(8)°).^{25}$

The U1–O_{siloxide} bond distances (2.2181(18)-2.2197(18) Å) have slightly increased in comparison to complex **1** (2.183(3)-2.213(3) Å) and are slightly shorter than those of complex **2** (2.236(5)-2.250(5) Å). The U1 ion interacts with the arene anchor in a consistent η^6 -fashion, where the U1–C_{centroid} bond distance (2.249(3) Å) is consistent with **2** (2.256(1) Å). The removal of potassium from the inner coordination sphere shows that, alternative to **2**, the arene backbone is not disturbed by the reduction, indicating that the distortion observed in **2** was due to potassium binding.

Notably, the arene anchor in 2-crypt adopts a planar geometry, with U1–Carene (2.632(2)-2.707(3) Å) and C–Carene bond lengths, in which two of the bonds (C2-C3: 1.411(4); and C5-C6: 1.409(4) Å) are slightly shorter than the remaining five bonds (1.426(4)-1.440(4)) Å, where the torsion angles are minimal (3.0(3)-8.7(3)°) compared to complex 2 (1.1(11)-22.0(11)°; Table 1), and are consistent with C-Carene bond lengths and torsion angles in previously reported U(II) complexes with neutral arenes (U(NHAr^{iPr6})₂: 1.388-1.442 Å, 1.44-12.19° (note: these metrics were manually measured via the deposited crystal structure on the CCDC); and [K(2.2.2-cryptand)][U(TDA)₂]: 1.389(7)-1.440(6) Å; 0.9(4)-4.6(4)°.26-27 Therefore, these bond metrics are suggestive of a metal-centered reduction resulting in an increased δ -bonding interaction between the uranium and the arene backbone compared to the U(III) analogue, complex 1.

Since a second redox process was observed in the cyclic voltammogram of 1 (vide infra), we next explored if chemical access to a lower-valent species by the addition of excess reducing agent was possible. We found that addition of 2.0 equiv. of KC8 to a solution of 1 in d_8 -THF at -40 °C led to a color change from brown-red to purple-blue with the consumption of 1, the appearance of complex 2, and new resonances evidenced by ¹H NMR spectroscopy (Figure S23b). Alternatively, when the reduction of 1 is carried out in the presence of 3.0 equiv. KC_8 in d_8 -THF at -40 °C, a dark blue solution is obtained. Analysis of the reaction mixture by ¹H NMR spectroscopy indicated the full consumption of complexes 1 and 2, with the formation of the new resonances (Figure S23c) also seen in the 2.0 equiv. reaction. The same species was also obtained by reduction of the isolated complex 2 and 2.0 equiv. of KC₈ in THF (Figure S27b). We found that depending on the crystallization conditions utilized, two crystallographically similar solid-state molecular structures

could be identified by XRD analysis, namely, the polymeric and trimeric complexes, [K₂(THF)₃U((OSi(O'Bu)₂Ar)₃-arene)]_∞ (3) (Scheme 1) and [K₂(Et₂O)U((OSi(O'Bu)₂Ar)₃-arene)]₃ (**3b**), respectively. Few crystals of complex 3b could be obtained from a mixture of THF/n-hexanes/Et₂O, whereas complex 3 was obtained in bulk isolation from a mixture of THF and *n*-hexanes at -40 °C in 84% yield. Attempts to isolate larger batches of 3b were unsuccessful due to instability in Et₂O over the crystallization timeframe, as well as the concomitant isolation of **3** from the reaction mixture over multiple trials. It is important to note that **3** and **3b** display similar structural parameters and bonding interactions (Figure S38), but mostly vary by their trimeric and polymeric forms due to coordinated THF versus Et₂O. The solid-state molecular structure of complex 3b displays a trimeric structure where three $[K_2(Et_2O)U((OSi(O'Bu)_2Ar)_3$ arene)]₃ moieties are bridged by the K2 cation, which binds η^6 to the arene backbone, while creating a bridge to another molecule, binding one –O'Bu moiety and a η^3 -phenyl of the tripodal ligand framework (Figure 1c). The O-U-O bond angles vary significantly (91.65(12); 113.21(12); 108.65(13)°), where the smallest bond angle corresponds to the binding of the K2 cation to three oxygens of the two -OSi(O'Bu)2 arms, decreasing the O-U-O bite angle. The U-O_{siloxide} bond lengths are elongated (2.234(3)-2.250(3) Å) compared to those of the complexes 1 (2.182(3)-2.214(3) Å) and 2 (2.2181(18)-2.2197(18) Å), and a significant contraction of the U-C_{centroid} bond distance (2.109(5) Å), compared to complexes 2 and 2-crypt (2.255(9) and 2.256(1) Å, respectively) is observed. The U1 ion interacts with the arene anchor in a η^6 -fashion, in which K1 is trans to the U1 ion. The arene anchor in 3b adopts a planar geometry, with U-Carene (2.527(5)-2.584(5) Å) and C-Carene bond lengths of 1.429(6)-1.449(7) Å, with minimal torsion angles (0.9(7)-5.9(7)°) (Table 1).

To assess the effect of the bound K⁺ cations in the electronic and geometric structures of complex **3**, we next explored sequestering the K⁺ cations. Addition of 3.0 equiv. of KC₈ and 3.0 equiv. of 2.2.2-cryptand to a solution of **1** in d_8 -THF at -40 °C, led to the full consumption of **1**, and the formation of a NMR silent species (Figure S24c). Crystals suitable for XRD analysis of the K-sequestrated derivative of complex **3**, [(K(2.2.2-cryptand))]₂[U((OSi(O'Bu)₂Ar)₃-arene)] (**3-crypt**), were obtained from a concentrated 2-methyltetrahydrofuran (2-Me-THF) solution (Figure 1d), whereas bulk isolation (71% yield) was obtained by layering a THF solution of **3-crypt** with *n*-hexanes at -40 °C (Scheme 1).

Although the ¹H NMR spectrum of **3-crypt** at -40 °C is silent, when the spectrum is collected at room temperature, resonances are observed and differ to those found in complex **3** (Figure S16). The solid-state molecular structure of **3-crypt** was determined by XRD studies and shows the presence of an ion pair consisting of two outer sphere [K(2.2.2-cryptand)]⁺ cations and the [U((OSi(O'Bu)₂Ar)₃-arene)]⁻ anion, in which there are four molecules of **3-crypt** per asymmetric unit. Compared to complexes **3/3b**, **3-crypt** shows a range of similar U1–O_{siloxide} bond distances and shows a η^6 -planar geometry of the arene anchor (Table 1), suggesting that for the di-reduced species, K-binding versus K-sequestration does not significantly affect the geometrical parameters.

Electrochemical studies

In this study, we first investigated the redox reactivity of the uranium tris(tert-butoxy)siloxide arene complexes 1 to **3-crypt** by cyclic voltammetry studies.

The cyclic voltammogram for complex **1** in THF (Conditions: [NBu₄][BPh₄] electrolyte; decamethylferrocene (Fc^{*}) as the internal reference) revealed three quasi reversible redox events (I, II, and III) at values of $E_{1/2}$ = -3.27, -2.45, and -1.70 V vs. Fc^{+/0}, respectively (Figure 2). Waves II and I display reduction events with E_{red} values of -2.52 V and -3.34 V vs. Fc^{+/0}, consistent with the chemical reduction to complexes **2/2-crypt** and **3/3-crypt**, respectively.

The E_{red} value measured for wave II is similar to the reduction potential measured for the U(III) tris(aryloxide) arene complex, [U((^{Ad,Me}ArO)₃mes)] (-2.495 V vs. Fc^{+/0}), and is in the range of values measured for the reduction of cyclopentadienide complexes (-3.11 to -2.26 V vs. Fc^{+/0}), including [U(η^5 -C₅⁻Pr₅)₂I] (-2.33 V vs. Fc^{+/0}), which were assigned to the U(III)/U(II) couple. Thus, the redox event associated with wave II can be reasonably assigned to the metal centered reduction U(III)/U(II).



Figure 2. Cyclic voltammograms for complexes, **1** (red); **2** (orange); **2-crypt** (green); **3** (blue), and **3-crypt** (purple); 0.1 M [NBu₄][BPh₄] electrolyte in THF, where arrows indicate the scan direction (Pt disk working electrode, 100 mVs⁻¹ scan rate, referenced to the Fc/Fc⁺ couple).

Notably, further reduction of a U(II) derivative was only reported for the U(III) complex, $[U(\eta^5-C_5!Pr_5)_2I]$, and was assigned to the U(II)/U(I) couple at -3.28 V vs. Fc^{+/0}, leading eventually to the isolation of the first example of a U(I) complex by chemical reduction of $[U(\eta^5-C_5!Pr_5)_2]$.¹² Here, the E_{red} value measured for wave I (-3.34 V vs Fc^{+/0}) of complex 1 is similar to the reduction potential found for the U(II)/U(I) couple at - 3.28 V vs. Fc^{+/0} for the U(II) complex, $[U(\eta^5-C_5!Pr_5)_2]$. Thus, the redox event associated to wave I could be assigned tentatively to either a U(II)/U(I) couple, or to reduction of the arene anchor, however, no similar redox event was unambiguously determined for the U(II) tris(aryloxide) arene complex,

 $[K(2.2.2-cryptand)][U((^{Ad,Me}ArO)_3mes)],$ in THF with $[NBu_4][PF_6]$ as the supporting electrolyte.²⁵

Wave III reveals an oxidative event with an E_{ox} value of -1.56 V, most likely corresponding to the U(IV)/U(III) redox couple. The cyclic voltammograms for complexes **2**, **2-crypt**, **3**, and **3-**

crypt further confirmed these assignments, and revealed similar wave potentials for I, II, and III. However, for complexes **2** and **3**, wave I (two-electron reduction) deviates from the trend and reveals an irreversible redox feature, which can be rationalized by the presence of an inner sphere K^+ cation in comparison to complexes **1**, **2-crypt**, and **3-crypt**.





Analysis of the ¹H NMR data for the two-electron reduced species, **3/3-crypt**, confirmed that in THF solutions, the K⁺ cations remain bound for **3** in comparison to **3-crypt**. Alternatively, wave II (assigned to the U(III)/U(II) couple) is the same for complexes **1**, **2**, and **2-crypt**, and is in agreement with the ¹H NMR studies, which shows identical spectra for **2/2-crypt**, indicating that the K⁺ cation is not bound in solution, suggesting that these are similar U(II) species.

It should be noted that the cyclic voltammogram of complex **1** is very different from that previously reported for the analogous Ce(III) complex, [Ce((OSi(O'Bu)_2Ar)_3-arene)(THF)], which displayed only one chemically reversible reduction wave at $E_{1/2} = -2.90 \text{ V}^{.50}$ Since no reduction events were observed within the window permitted by THF in the voltammogram of the ligand salt, ((OSi(O'Bu)_2Ar)_3-arene)K_3, the redox event was tentatively assigned to a metal-centered reduction (Ce(III)/Ce(II)). The important differences observed in the voltammograms of the Ce(III) and U(III) complexes, in which the ions are of similar charge and ionic radii, confirms the assignment of wave II as a U(III)/U(II) couple, with formulations of **2** and **2-crypt** in solution as U(II) complexes (Table S5).

Redox reactivity of low-valent complexes

Based on the cyclic voltammetry studies of complexes 2/2crypt and 3/3-crypt, we reasoned that these complexes can potentially transfer two- and three-electrons, respectively. Therefore, representative complexes 2 and 3 were investigated for their ability to effect multielectron transformations of small molecules such as azobenzene (PhNNPh) and cycloheptatriene (CHT), as these can accept two- and three-electrons, respectively.

First, we probed the addition of 1.0 equiv. of PhNNPh to a solution of **2** in d_8 -THF at -40 °C, which revealed the consumption of **2** and the formation of new broad resonances as indicated by ¹H NMR spectroscopy (Figure S29). Single crystals suitable for X-ray diffraction studies were obtained from a mixture of Et₂O

and *n*-hexanes at -40 °C, and identified as complex, $[K(Et_2O)U((OSi(O'Bu)_2Ar)_3-arene)(PhNNPh)(THF)]_2$ (4) in 96% yield (Scheme 2). The solid-state molecular structure of complex 4 displays the presence of a dimeric bimetallic struc- $[K(Et_2O)U((OSi(O'Bu)_2Ar)_3$ ture where two arene)(PhNNPh)(THF)] moieties are bridged by two K⁺ atoms, which bind four phenyl rings (η^6 and η^1) of the two [PhNNPh]²⁻ ligands, from two different complexes (Figure 3a, Figure S39). Similar to the starting complex 2, the O–U1–O bond angles vary (92.28(9)); 102.16(9); 126.21(9)°), where the smallest bond angle most likely corresponds to the binding of the K⁺ cation to two oxygens of one $-OSi(O'Bu)_2$ arm, and the η^6 interaction to one phenyl ring of the [PhNNPh]²⁻ moiety. The U1-Osiloxide bond distances (2.178(2)-2.203(2) Å) are significantly shorter compared to complex 2 (2.236(5)-2.250(5) and are in agreement with previously reported U(IV) siloxide complexes,⁵² indicating complex 2 has transferred two-electrons to yield a dianionic [PhNNPh]²⁻, U(IV) complex. The U1 ion no longer interacts with the planar arene anchor (1.390(5)-1.404(5) Å), and the U1– $C_{centroid}$ distance (3.813(2) Å; Table 2) is significantly longer than the U1-Ccentroid distances found in the previously reported U(IV) terminal [K(2.2.2oxo, cryptand)][((^{Ad,Me}ArO)₃mes)U(O)] (2.810(6) Å), and U(IV) halide, $[((^{Ad,Me}ArO)_3mes)U(X)(THF)]]$ (where X = F; 2.666, Cl; 2.657, Br; 2.645, and I; 2.664 Å), tris(aryloxide) mestitylene complexes.^{53,42} The N1-N2 (1.458(4) Å) and U1-N_{PhNNPh} bond distances (2.283(3) and 2.310(3) Å) of the dianionic [PhNNPh]²⁻ moiety are consistent with the bond metrics found in the only other dianionic U(IV)-PhNNPh example, [K(2.2.2cryptand)][U(PhNNPh)(N(SiMe₃)₂)₃]⁵⁴ The N1-N2 bond length (1.458(4) Å) is similar to that reported for the salt, [K(18C6)]₂[PhNNPh] (1.40(3) Å),⁴⁵ and is elongated compared to PhNNPh (1.25 Å) and to the singly reduced derivative, [K(2.2.2-cryptand)][PhNNPh] (1.34(3) Å) obtained from the reaction of the only isolated U(I) complex with azobenzene.¹².

It is important to note that the reaction with **2-crypt** and 1.0 equiv. of PhNNPh at -40 °C led to an analogous color change with the formation of broad resonances in the ¹H NMR spectrum, similar to those observed for complex **4** (Figures S30 and S31). Attempts to identify the product by XRD analysis proved unsuccessful due to the poor crystalline quality. However, the

addition of 1.0 equiv. of 2.2.2-cryptand to a solution of complex 4 in d_8 -THF at -40 °C, led to identical ¹H NMR resonances as observed after addition of PhNNPh to **2-crypt**, confirming the presence of the same solution species.



Figure 3. Molecular structures of (a) $[K(Et_2O)U((OSi(O'Bu)_2Ar)_3-arene)(PhNNPh)(THF)]_2$, **4**, (b) $[K(Et_2O)U((OSi(O'Bu)_2Ar)_3-arene)(\eta^5-C_7H_8)]$, **5**, (c) $[(K(Et_2O))_2)U((OSi(O'Bu)_2Ar)_3-arene)(\eta^7-C_7H_7)]_{\infty}$, **6**, with thermal ellipsoids at drawn at the 50% probability level. Hydrogen atoms, except the CHT moiety of complex **5**, and methyl groups on the $-OSi(O'Bu)_2$ ligands have been omitted for clarity. The monomeric units of complexes **4** and **6** have been depicted for clarity.

Table 2. Selected bond lengths (A) and angles (°) for complexes 4, 5, and 6.						
Complex	4	5	6			
U–O _{siloxide}	2.178(2)-2.203(2)	2.193(3)-2.264(3)	2.245(3)-2.331(3) Å			
U–C _{arene}						
C–C _{arene}	1.390(5)-1.404(5)	1.391(6)-1.407(5)	1.380(7)-1.402(7)			
U-C _{centroid}	3.813(2)	4.144(2)	4.324(2)			
U–O–U	92.28(9)); 102.16(9); 126.21(9)	90.67(11)); 102.3(11); 102.82(11)	86.10(13)); 97.75(13); 98.78(13)°			
N–N _{PhNNPh}	1.458(4)					
		CH–CH ₂ ; C55-C56: 1.507(10);				
C–C _{CHT}		C56-C57: 1.533(10); 1.365(11)-	1.389(11)-1.422(10)			
		1.427(11)				

Following the isolation of complex **4**, we next sought to further investigate the reactivity of complex **2**, and probe other multielectron transformations, such as a three-electron transfer pathway to yield a possible U(V) analogue. Accordingly, we utilized the [7]-annulene, cycloheptatriene (CHT; C_7H_8), as this carbocycle achieves aromaticity when the ligand is reduced by three-electrons and undergoes H₂ elimination, forming the planar $C_7H_7^{3-}$ anion.^{55, 27} Although there are a large number of transition metal CHT complexes reported,⁵⁵ where the CHT is typically found as the tropylium cation ($C_7H_7^{+}$), the uranium analogues, which all contain CHT in its trianionic form (η^7 - $C_7H_7^{3-}$), still remain rare. ^{56-59, 27}

Addition of 1.1 equiv. CHT to a solution of **2** in d_8 -toluene resulted in the full consumption of **2** and the formation of new resonances indicated by ¹H NMR spectroscopy (Figure S32). Single crystals suitable for X-ray diffraction studies were obtained from a mixture of Et₂O and *n*-hexanes at -40 °C and identified as the CHT complex, [K(Et₂O)U((OSi(O'Bu)₂Ar)₃-arene)(η^6 -C₇H₈)] (**5**), in 87% yield (Scheme 2).The solid-state molecular structure for complex **5** displays a neutral complex with an inner sphere siloxide-bound K⁺ cation (Figure 3b). Similar to the U(II) precursor **2**, the O–U–O bond angles vary (90.67(11)); 102.3(11); 102.82(11)°), where the smallest bond

angle corresponds to the binding of the K⁺ cation to four oxygens of two -OSi(O'Bu)2 arms. The U-Osiloxide bond distances (2.193(3)-2.264(3) Å) are similar to those of complex 2 (2.236(5)-2.250(5) Å). The U1 ion no longer interacts with the planar arene anchor (1.387(6)-1.407(5) Å), and the U1–C_{centroid} distance (4.144(2) Å) is significantly elongated compared to the U(IV) complex 4 (3.813(2) Å). The uranium atom binds six of the 7 carbons (η^6) in the CHT moiety, where two of the C-C_{CHT} bond lengths are elongated (CH-CH₂: C55-C56: 1.507(10); and C56-C57: 1.533(10) Å) in comparison to the remaining five bonds (1.365(11)-1.427(11) Å; Table 2). These bond lengths are slightly elongated compared to free CHT (where C=C: 1.356; C-C; 1.446; CH-CH₂: 1.505 Å)⁶⁰ and neutral CHT bound to early transition metals (1.364(4)-1.498(5) Å),⁶¹ and is in agreement with the partial reduction of the CHT moiety as indicated by computational studies (vide infra). Although CHT $(\eta^6-C_7H_8)$ complexes are known for transition metals,⁵⁵ this is the first example with uranium. These results demonstrated that although complex 2 can transfer two electrons to PhNNPh, it is not capable of transferring three-electrons to CHT to yield the cycloheptatrienyl derivative. Therefore, we next investigated if complex 3 could instead act as U(I) synthon by transferring three-electrons to CHT. It should be noted that the recently isolated U(I) complex, $[U(\eta^5-C_5^iPr_5)_2]^2$, could only transfer oneelectron to oxidizing substrates due the high stability of the U(II) analogue,¹² however, the U(I) synthon, U(II)-(arene)¹⁻, reported by J. Arnold, could transfer three-electrons to the CHT ligand.²⁷ Addition of 1.1 equiv. of CHT to a solution of **3** in d_{δ} -

toluene at -40 °C led to the formation of new resonances with the concomitant formation of H_2 as evidenced by ¹H NMR spectroscopy.



Figure 4. (left) X-band EPR spectra of complexes 1, 2, 2-crypt, 3, and 3-crypt in the solid-state at 6 K. For all reduced species, the small signal observed at g = 2.00 is due to a radical impurity.^{64, 25} (right) Temperature dependence (2-300 K) of the $\mu_{eff}(\mu_B)$ in a field of 1 T for complexes 1, 2, 2-crypt, 3, 3-crypt, and 6.

Single crystals suitable for XRD studies were obtained from a mixture of Et₂O and *n*-hexanes at -40 °C and identified as the complex, $[(K(Et_2O))_2)U((OSi(O'Bu)_2Ar)_3-arene)(\eta^7-C_7H_7)]_{\infty}$ (6), in 65% yield (Scheme 2). The solid-state molecular structure of complex 6 displays a 1D infinite coordination polymer with two inner sphere K⁺ cations and the [U((OSi(O'Bu)₂Ar)₃arene)(η^7 -C₇H₇)] moiety (Figure 3c, Figure S40). The polymeric structure in **6** arises from K1 binding to the η^7 -C₇H₇ moiety, creating a bridge, in which another [KU((OSi(O'Bu)₂Ar)₃arene) $(n^7-C_7H_7)$ moiety binds through interaction with the tripodal ligand. Similar to complex 5, the O-U1-O bond angles vary (86.10(13)); 97.75(13); 98.78(13)°), where the smallest bond angle corresponds to the binding of the K⁺ cation to four oxygens of two -OSi(O'Bu)2 arms. The U1-Osiloxide bond distances (2.245(3)-2.331(3) Å) are slightly shorter compared to the precursor **3** (2.234(3)-2.250(3) Å) and slightly longer than in the U(IV) complex 5 (2.193(3)-2.264(3) Å), but altogether is in agreement with the presence of U(IV), consistent with the magnetism studies (vide infra). The U1 ion no longer interacts with the planar arene anchor (1.380(7)-1.402(7) Å), where the U1-C_{centroid} distance (4.324(2) Å) is significantly elongated compared to complex 5 (4.144(2) Å). The planar CHT moiety binds in an η^{7} -fashion, where all C–C_{CHT} (1.389(11)-1.422(10) Å) and U1–C_{CHT} bond lengths (Table 2) are consistent with the only other three reports of trianionic CHT (η^7 -C₇H₇³⁻) complexes of uranium. 57-58, 27

EPR, magnetism, and UV/Vis/NIR studies

X-band EPR and magnetic measurements were carried out on complexes 1, 2/2-crypt, and 3/3-crypt, as well as magnetic data for complex 6, to further investigate the electronic structure of these compounds. The X-band EPR spectrum of the U(III)

complex 1, obtained at 6 K in the solid-state (left, Figure 4), reveals a rhombic signal with simulated *g* values of [1.850, 1.450, 1.225], indicative of a f^{3} ⁴I_{9/2} U(III) ion, and is consistent with the previously reported U(III) tris(aryloxide) arene complex, [U((^{Ad,Me}ArO)₃mes)] (g = [1.58, 1.46, 1.20]).²⁵

Upon the one-electron reduction to complexes **2** and **2-crypt**, the EPR spectra becomes silent, which is expected for a non-Kramer's U(II) f^4 (⁵I₄) ion. Upon the two-electron reduction of **1** to yield complexes **3** and **3-crypt**, the solid-state spectra at 6 K reveals a rhombic set of values for complex **3** with simulated *g* values at [2.820, 2.360, 1.105], whereas **3-crypt** displays a nearly axial signal with *g* values = [2.721, 2.680, 1.078], both indicative of U(III) ions. In comparison to the U(III) complex **1**, the U(III)-(arene)²⁻ complexes, **3** and **3-crypt**, display significantly lower *g* values, with changes to the signal features and intensity. This is most likely accredited to the increased uranium-arene interaction upon the two-electron reduction of the arene backbone, and are well within the reported *g* values for other U(III) complexes.^{62, 25, 63} For all reduced species, the small signal observed at *g* = 2.00 is due to a radical impurity.^{64, 25}

The magnetic susceptibility (μ_{eff}) data for complexes 1 to 3crypt, and complex 6, were measured by performing a temperature sweep in the 2-300 K range under an applied magnetic field of 1 T (right, Figure 4). The magnetic moments (μ_{eff}) for the (2) and (2-crypt) complexes, were determined to be 2.36 and 2.34 μ_B at 300 K, respectively, with both decreasing monotonically until ~40 K, where the decrease becomes more dramatic until 2 K is reached (where $\mu_{eff} = 0.36$ and 0.28 μ_B , respectively). The magnetic susceptibility (χ_M T) approaches zero at low-temperature, suggesting a weak temperature-dependent paramagnetism, which is consistent with a non-magnetic or integer spin ground state,²⁶ which are in agreement with the absence of an EPR signal for complexes **2** and **2-crypt**.



Figure 5. (a) UV/Vis and (b) NIR optical spectra for complexes 1 (red), 2 (orange), 2-crypt (teal), 3 (blue), 3-crypt (purple), and 4 (light blue) in THF, and complex 5 (green) in toluene. UV/Vis data were collected in concentration ranges of 0.625 to 5.0 mM (see supporting information), and NIR data were collected at high concentration (10 mM). Relative y-axis scaling of the spectra for both (a) and (b) are shown for clarity (see supporting information for baselined plots).

Although the room-temperature μ_{eff} value of the complexes 2 and 2-crypt is similar to that of the U(III) complex 1, the temperature-dependence of the μ_{eff} shows a curvature reminiscent of previously reported U(II) complexes, where the values are within the reported ranges (μ_{eff} ranges: 0-1.95 μ_B at 2 K; 2.20-2.8 μ_B at 300 K).^{25, 17, 26, 20, 27} Moreover, the similar low temperature values of the magnetic moment for the complexes, 2 and 2-crypt suggests that the two complexes could have a similar electron configuration in the range of temperatures 2-300 K.

For complexes **3** and **3-crypt**, the magnetic moments (μ_{eff}) at 300 K (μ_{eff} = 2.36 and 2.46 μ_{B} , respectively) were found to be similar to complexes 2/2-crypt described above. However, the temperature-dependence of the μ_{eff} shows a different curvature, in which there is little variation in the magnetic moment until at \sim 8 K, then there is a more abrupt decrease before arriving at 2 K ($\mu_{eff} = 1.66$ and 1.53 μ_B). This trend is most consistent with a U(III) ion, however, 3 and 3-crypt have significantly greater μ_{eff} and $\chi_M T$ values at low-temperature compared to the U(III) complex 1. This observation is most likely accredited to the two-electron reduction of the arene backbone and the strong U(III)-(arene)²⁻ interaction, which is in line with the EPR and computational studies. In 3-crypt, the low-temperature upturn observed in the $\chi_M T$ vs. T plot, which is reproducible in triplicate samples, remains undetermined, but could arise from magnetic ordering (Figure S48d). Finally, the magnetic moment of the U(IV) complex 6 was determined to be 2.47 μ_B at 300 K and 0.43 μ_B at 2 K, with a monotonous decrease in the magnetic moment toward zero. These values are in excellent agreement

with the values found for complexes of the U(IV) f^2 (³H₄) ion, which often exhibits temperature-independent paramagnetism at low-temperatures, resulting in μ_{eff} values of ~0.5 μ B.⁶⁵⁻⁶⁸

Lastly, the UV/Vis/NIR (ultraviolet/visible/near-infrared) electronic absorption spectra were collected for complexes **1** to **5** in the spectral range of 250-2200 nm (Figure 5). The U(III) complex **1** displays broad and ill-defined, low-intensity absorption bands over the entire spectral range ($\epsilon \approx 100$ to 2000 M⁻¹cm⁻¹), consistent with Laporte-forbidden f \rightarrow f transitions, typical of a 5f⁸ U(III) ion.^{34, 51, 36, 16, 26}

Upon the one-electron reduction to the U(II) complexes, **2** and **2-crypt**, the low-intensity and ill-defined features between 250-1200 nm of **1** are lost, and a strong well-defined absorbance at $\lambda_{max} = 516$ nm ($\varepsilon = 8756$ and 7088 M⁻¹cm⁻¹, for **2** and **2-crypt** respectively) is observed for both complexes.

Due to the high intensity, these absorbances could arise from Laporte-allowed d \rightarrow f transitions,^{16,17} and/or from charge transfer from the uranium δ -bonding orbital to the arene backbone π^* orbital²⁵ (see computational section). Additionally, there are very weak absorptions between $\lambda = 1200-2200$ nm, which are most consistent with the previously reported U(II) 5*f*⁴ complex, [K(2.2.2-cryptand)][U((^{Ad,Me}ArO)₃mes)]²⁵, which also showed a single mid-intensity absorption in the visible region ($\lambda_{max} = 600$ nm, $\varepsilon \approx 750$ M⁻¹cm⁻¹). Also, the identical features for **2** and **2-crypt** support that in THF solutions, the electronic structure properties are similar, which is consistent with the ¹H NMR spectroscopy and electrochemical studies.



Figure 6. Frontier Molecular Orbital (FMO) diagrams for **2-crypt** and **3-crypt** in the quintet (s=2) and quartet (s=3/2) spin states, respectively. The DFT molecular orbital diagrams for the HOMO-2/HOMO-3 (**2-crypt**) and AMO-HOMO-2/AMO-HOMO-3 (**3-crypt**) are not shown for clarity (see supporting information; AMO: alpha molecular orbital and BMO; beta molecular orbital).

The absorption spectra for the two-electron reduced U(III)(arene)²⁻ species, **3** and **3-crypt**, features stronger absorbances, compared to the U(III) complex **1**, at $\lambda_{max} = 582$ ($\epsilon = 8520$ M⁻¹cm⁻¹) and 680 nm ($\epsilon = 9430$ M⁻¹cm⁻¹), respectively, giving rise to the observed dark blue color, with mid-intensity and broad f \rightarrow f transitions between $\lambda = 1600-2200$ nm. The observed features suggest a stronger interaction between the U(III) and di-reduced arene-backbone of **3/3-crypt** compared to complex **1**.

Computational studies

To gain insight into the electronic structures of 1, and the subsequent one- (2 and 2-crypt) and two-electron (3-crypt) reduction species, as well as complex 5, density functional theory (DFT) calculations (B3PW91 functional), including dispersion corrections, were performed. Calculations for 3 were also attempted but due to the polymeric nature, the system was too large and calculations were not tractable.

To further validate the computational approach (DFT, see supporting information for details), geometry optimization was carried out without symmetry constraints for two different spin states for complex 1. The quartet (s=3/2) was found to be more stable than the doublet by 10.0 kcal mol⁻¹. The optimized geometries are in excellent agreement with the experimental values,

with the main distances (Table S7) reproduced within a precision of 0.02 Å. Bonding analysis using the Natural Bonding Orbital (NBO) approach does not evidence strong U-arene interactions. In fact, only small donations are found at the second order donor-acceptor level. This is further corroborated by the analysis of both the frontier orbitals and the unpaired spin density plots (Figure S62). For the quartet spin states, the three SO-MOs are pure 5*f* atomic orbitals, and the unpaired spin density is fully located at the uranium center. Therefore, this suggests that the uranium center is in the +3-oxidation state, coupled with a neutral arene ring. Notably, the LUMO of the system exhibits contribution from both the uranium center and the arene π^* .

The one-electron reduced species, namely complexes 2 and 2crypt, were computed analogously to determine whether there is an influence of the coordinated K⁺ cation in the first coordination sphere. Three different spin states were computed for these two complexes, namely a quintet, a triplet, and a singlet. Interestingly, for the two complexes, the triplet (s=1) and the quintet (s=2) were found to be almost degenerate (1.2 kcal mol⁻¹), whereas the singlet (s=0) is much higher in energy (14.6 kcal mol⁻¹). Moreover, the energy differences are identical for both 2 and 2-crypt. The main distances in the optimized geometries for both the quintet and the triplet compare well within the experimental values for complex **2**, whereas the quintet geometry compares better for **2-crypt**. It is important to note that for complex **2**, the quintet and triplet geometries display vast differences in planarity of the arene backbone. For example, the triplet state in complex **2** displays heavy distortion, indicating reduction of the arene backbone, whereas the quintet displays a planar, neutral arene. When comparing the computed geometries to the heavy arene distortion found in the solid-state structure of complex **2**, one would be tempted to suggest a triplet state (s=1) of the uranium ion (U(IV)-(arene)²⁻). The distorted, di-reduced arene backbone was found to occur due to a first order Jahn-Teller effect, arising from pairing two-electrons in the π^* orbital (s=0), in which an arene-radical signal would not be expected in the EPR spectrum.

Alternatively for complex **2-crypt**, the planar geometry of the arene backbone in the solid-state molecular structure is in line with the computed quintet (s=2) ground state, which is best described as a formal U(II) system (Figure 6). In both 2 and 2crypt, the U-C_{centroid} distance is well reproduced and decreases upon reduction (by up to 0.2 Å). This decrease leads to a stronger U-arene interaction as reflected by the different U-C Wiberg bond indexes (WBI). The U-C WBI are an average of 0.3 in complexes 2 and 2-crypt, whereas they are roughly 0.2 for the U(III) complex 1. However, these U-C WBI are lower than those found for the U-O bonds (0.6-0.7), indicating a weakly covalent U-arene interaction. This is reflected in the frontier orbitals, where for the triplet or the quintet, the SOMOs are either on a f orbital or weak U–arene δ -bonds, respectively. The latter is corroborated by the unpaired spin density plot, which clearly in both systems, displays full localization at the uranium atom.

Therefore, for complex 2, the computed triplet and quintet electronic configurations $(U(IV)-(arene)^{2-} \text{ or } U(II)-arene^{0})$ have the same energy, whereas 2-crypt can be described as a U(II) system. These assignments are in line with the EPR analysis, as well as with the bonding analysis found in the U(II) system of Meyer and coworkers.²⁵ Although the distortion of the arene ring from planarity observed in the solid-state structure of 2 is better reproduced by a triplet state, the similar variable temperature magnetic data measured in the range 2-300 K for the two complexes suggests that they are both best described as U(II) species. This is further supported by the computation of the UV/Vis spectrum of 2-crypt. Indeed, the experimental UV/Vis absorption spectrum is most consistent with the quintet (s=2), and involves an excitation from either the δ -bond to π^* of the ligand, or from a uranium-based orbital to the ligand (Figure S68).

However, it is clear from computation that small variations in the supporting ligand such as the modification of the electron-donating character of the ligand by $K^{\scriptscriptstyle +}$ binding can lead to electronic redistributions.

A similar computational analysis was carried out only on the direduced complex **3-crypt**. Three different spin states were also considered for the geometry optimization, namely a sextet (s=5/2), a quartet (s=3/2), and a doublet (s=1/2). The quartet and doublet are almost degenerate (0.8 kcal mol⁻¹) while the sextet is 15.0 kcal mol⁻¹ higher in energy. Once again, the optimized geometry obtained for the quartet and doublet compares very well with the experimental values (Table S23). The U–centroid distance is well reproduced with another 0.1 Å decrease upon the second reduction. This decrease leads to a stronger U–C interaction as highlighted by the U–C WBI, which are now higher

than 0.4. This stronger interaction is evidenced by the donation from the arene to the uranium center at the second order NBO level. The frontier orbitals found for either the quartet or the doublet clearly shows two singly occupied U-arene δ -bonds, with an unpaired spin density fully localized at the uranium center (Figures 6 and S69). Since the two δ -bonds are singly occupied, this prevents the first order Jahn-Teller effect found in complex 2 (the two degenerate π^* are occupied in the same way) so that no distortion of the arene is observed, although the arene backbone is formally reduced by two-electrons. Therefore, complex **3-crypt** is best described as a U(III)-(arene)²⁻ and is in line with the observed EPR spectra, where only a signal attributed to the U(III) ions is observed. However, since twoelectrons are located on the U-arene δ interactions, one may also consider 3-crypt as a U(I) synthon. Additionally, TDDFT calculations of 3-crypt show that the experimental UV/Vis spectrum is most consistent with the quartet (s=3/2) spin state. Once again, these maxima most likely correspond to a transition from the δ -bond to the ligand, consistent with a U(III) oxidation state (Figure S71).

Lastly, calculations were also carried out on complex 6 to determine whether the system is a formal U(II), or if the electrons have been transferred to the CHT substrate, yielding a two-electron reduction of the CHT moiety. Like complexes 2 and 2crypt, three spin states were also considered, namely a quintet (s=2), a triplet (s=1), and a singlet (s=0). Here, the triplet is found to be the ground state by more than 25 kcal mol⁻¹. The optimized geometry is in excellent agreement with the experimental values with a maximum deviation of 0.04 Å. The U-Ccentroid of the arene backbone has become significantly elongated (4.20 Å vs. 4.144 Å by XRD analysis), while the U-Ccentroid distance of the CHT moiety is consistent with a strong bonding interaction (2.12 vs. 2.17 by XRD analysis), in which both distances are well produced. The strong U-CHT interaction is also reflected by the U-C WBI and the frontier orbitals. Indeed, the U-C WBI are around 0.4 in average and the frontier orbitals exhibit the presence of a doubly-occupied U–CHT δ -bond. The unpaired spin density is fully localized at the uranium center and is best described as a U(IV)-(CHT)²⁻.

CONCLUSIONS

In summary, we have reported the synthesis, structure, and redox reactivity of the new arene-anchored tris(siloxide) U(III) complex, [U((OSi(O'Bu)₂Ar)₃-arene)(THF)] (1), which undergoes two quasi-reversible redox processes ($E_{1/2} = -3.27$ and -2.45 V vs. $Fc^{+/0}$) that are comparable to those previously assigned to U(II)/U(I) and U(III)/U(II) couples, respectively. The products of the one- and two-electron reduction of the U(III) complex could be cleanly generated by addition of an alkali reducing agent. Remarkably, the one-electron reduced species, 2 and 2-crypt, which contain an inner- and outer-sphere K⁺ cation respectively, showed either a distorted (2) or planar arene anchor (2-crvpt), that could be interpreted in terms of a different degree of reduction of the arene ring. Computational studies confirmed that the triplet (U(IV)-(arene)²⁻) and quintet (U(II)arene⁰) spin states are very close in energy for the mono-reduced species, but result in a ring distortion or no distortion, for complexes 2 and 2-crypt, respectively. EPR and UV/Vis/NIR spectroscopies, magnetic, cyclic voltammetry, and computational studies provide strong evidence that complex 2-crypt is best described as U(II). The UV/Vis/NIR, ¹H NMR spectroscopy, and cyclic voltammetry data measured for 2 and 2-crypt are very similar, indicating that both complexes are best described as U(II)-arene⁰ in solution. The solid state EPR and magnetic data measured for 2 and 2-crypt are also very similar, suggesting that, despite the different solid-state structures, 2 can also be described as U(II)-arene⁰. The two-electron reduction products could also be isolated with either sequestered (3-crypt) or bound K⁺ cations (3/3b). Computational studies, EPR, and magnetic susceptibility data suggests that 3/3-crypt are best described as U(III)-(arene)²⁻ complexes. From a reactivity standpoint, the mono- and di- reduced complexes 2 and 3, respectively, behave as U(II) and U(I) synthons. These complexes can transfer two- and three-electrons to oxidizing substrates such as azobenzene (PhNNPh) or cycloheptatriene (CHT), leading to the isolation of the U(IV) complexes 4 and 6, respectively. These results demonstrate that the robust arene-tethered tris(siloxide) tripodal ligand provides an excellent platform for lowvalent uranium chemistry, while implementing multielectron transfer pathways as shown by the reactivity of complex 3, which provides the third example of a U(I) synthon.

ASSOCIATED CONTENT

Supporting Information

X-ray data for, complexes **1-6** (CIF), and additional crystallographic details, experimental procedures, ¹H NMR spectra, EPR, cyclovoltammetry, and computational details (PDF).

The Supporting Information is available free of charge on the ACS Publications website. Accession Codes CCDC ACS Publications website. Accession Codes: 2247818 (complex 1); 2236461 (complex 2); 2247817 (complex 2-crypt); 2247819 (complex 3); 2225989 (complex 3b); 2239743 (complex 3-crypt); 2247822 (complex 4); 2247823 (complex 5); and 2247824 (complex 6), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

The data that support the findings of this study are openly available in the Zenodo repository at 10.5281/zenodo.8071482.

AUTHOR INFORMATION

Corresponding Author

*Marinella Mazzanti. Email: marinella.mazzanti@epfl.ch.

Author Contributions

^{*}M. K. and R. A. K. S. contributed equally to this work.

Funding Sources

We acknowledge support from the Swiss National Science Foundation grant number 200020_212723 and the Ecole Polytechnique Fédérale de Lausanne (EPFL).

ACKNOWLEDGMENT

We thank F. Fadaei-Tirani for important contributions to the Xray single crystal structure analyses (collection and resolution of structures of **2**, **3b**, and **3-crypt**), Dr. Andrzej Sienkiewicz for support with EPR data collection, and Romain Aeschlimann for the support in synthesizing the ligand precursor.

REFERENCES

1. Langeslay, R. R.; Fieser, M. E.; Ziller, J. W.; Furche, F.; Evans, W. J., Synthesis, structure, and reactivity of crystalline molecular complexes of the { C5H3(SiMe3)(2) (3)Th}(1-) anion containing thorium in the formal+2 oxidation state. *Chem. Sci.* **2015**, *6*, 517-521.

2. Langeslay, R. R.; Fieser, M. E.; Ziller, J. W.; Furche, F.; Evans, W. J., Expanding Thorium Hydride Chemistry Through Th2+, Including the Synthesis of a Mixed-Valent Th4+/Th3+ Hydride Complex. *J. Am. Chem. Soc.* **2016**, *138*, 4036-4045.

3. Woen, D. H.; Evans, W. J., *Handbook on the Physics and Chemistry of Rare Earths*. Elsevier: 2016; Vol. 50, p 337-394.

4. Windorff, C. J.; Chen, G. P.; Cross, J. N.; Evans, W. J.; Furche, F.; Gaunt, A. J.; Janicke, M. T.; Kozimor, S. A.; Scott, B. L., Identification of the Formal+2 Oxidation State of Plutonium: Synthesis and Characterization of {Pu-II $C_5H_3(SiMe_3)(2)$ (3)}(-). J. Am. Chem. Soc. **2017**, 139, 3970-3973.

5. Su, J.; Windorff, C. J.; Batista, E. R.; Evans, W. J.; Gaunt, A. J.; Janicke, M. T.; Kozimor, S. A.; Scott, B. L.; Woen, D. H.; Yang, P., Identification of the Formal+2 Oxidation State of Neptunium: Synthesis and Structural Characterization of {Np-II C5H3(SiMe3)(2) (3)}(1-). *J. Am. Chem. Soc.* **2018**, *140*, 7425-7428.

6. Huh, D. N.; Roy, S.; Ziller, J. W.; Furche, F.; Evans, W. J., Isolation of a Square-Planar Th(III) Complex: Synthesis and Structure of Th((OC6H2Bu2)-Bu-t-2,6-Me-4)(4) (1-). *J. Am. Chem. Soc.* **2019**, *141*, 12458-12463.

7. Palumbo, C. T.; Zivkovic, I.; Scopelliti, R.; Mazzanti, M., Molecular Complex of Tb in the+4 Oxidation State. *J. Am. Chem. Soc.* **2019**, *141*, 9827-9831.

8. Rice, N. T.; Popov, I. A.; Russo, D. R.; Bacsa, J.; Batista, E. R.; Yang, P.; Telser, J.; La Pierre, H. S., Design, Isolation, and Spectroscopic Analysis of a Tetravalent Terbium Complex. *J. Am. Chem. Soc.* **2019**, *141*, 13222-13233.

9. Rice, N. T.; Popov, I. A.; Russo, D. R.; Gompa, T. P.; Ramanathan, A.; Bacsa, J.; Batista, E. R.; Yang, P.; La Pierre, H. S., Comparison of tetravalent cerium and terbium ions in a conserved, homoleptic imidophosphorane ligand field. *Chem. Sci.* **2020**, *11*, 6149-6159.

10. Willauer, A. R.; Palumbo, C. T.; Fadaei-Tirani, F.; Zivkovic, I.; Douair, I.; Maron, L.; Mazzanti, M., Accessing the +IV Oxidation State in Molecular Complexes of Praseodymium. *J. Am. Chem. Soc.* **2020**, *142*, 5538-5542.

11. Wedal, J. C.; Evans, W. J., A Rare-Earth Metal Retrospective to Stimulate All Fields. J. Am. Chem. Soc. 2021, 143, 18354-18367.

12. Barluzzi, L.; Giblin, S. R.; Mansikkamaki, A.; Layfield, R. A., Identification of Oxidation State+1 in a Molecular Uranium Complex. *J. Am. Chem. Soc.* **2022**, *144*, 18229-18233.

13. Rice, N. T.; Popov, I. A.; Carlson, R. K.; Greer, S. M.; Boggiano, A. C.; Stein, B. W.; Bacsa, J.; Batista, E. R.; Yang, P.; La Pierre, H. S., Spectroscopic and electrochemical characterization of a Pr^{4+} imidophosphorane complex and the redox chemistry of Nd³⁺ and Dy³⁺ complexes. *Dalton Trans.* **2022**, *51*, 6696-6706.

14. Wedal, J. C.; Cajiao, N.; Neidig, M. L.; Evans, W. J., Anion-induced disproportionation of Th(III) complexes to form Th(II) and Th(IV) products. *Chem. Commun.* **2022**, *58*, 5289-5291.

15. Willauer, A. R.; Douair, I.; Chauvin, A. S.; Fadaei-Tirani, F.; Bünzli, J. C.; Maron, L.; Mazzanti, M., Structure, reactivity and luminescence studies of triphenylsiloxide complexes of tetravalent lanthanides. *Chem. Sci.* **2022**, *13*, 681– 691.

16. MacDonald, M. R.; Fieser, M. E.; Bates, J. E.; Ziller, J. W.; Furche, F.; Evans, W. J., Identification of the+2 Oxidation State for Uranium in a Crystalline Molecular Complex, K(2.2.2-Cryptand) (C5H4SiMe3)(3)U. J. Am. Chem. Soc. **2013**, *135*, 13310-13313.

17. Windorff, C. J.; MacDonald, M. R.; Meihaus, K. R.; Ziller, J. W.; Long, J. R.; Evans, W. J., Expanding the Chemistry of Molecular U2+ Complexes: Synthesis, Characterization, and Reactivity of the { C5H3(SiMe3)(2) (3)U}(-) Anion. *Chem. Eur. J.* **2016**, *22*, 772-782.

18. Huh, D. N.; Ziller, J. W.; Evans, W. J., Chelate-Free Synthesis of the U(II) Complex, (C5H3(SiMe3)(2))(3)U (1-), Using Li and Cs Reductants and Comparative Studies of La(II) and Ce(II) Analogs. *Inorg. Chem.* **2018**, *57*, 11809-11814.

19. Ryan, A. J.; Angadol, M. A.; Ziller, J. W.; Evans, W. J., Isolation of U(ii) compounds using strong donor ligands, C5Me4H and N(SiMe3)(2), including a three-coordinate U(ii) complex. *Chem. Commun.* **2019**, *55*, 2325-2327.

20. Guo, F. S.; Tsoureas, N.; Huang, G. Z.; Tong, M. L.; Mansikkamaki, A.; Layfield, R. A., Isolation of a Perfectly Linear Uranium(II) Metallocene. *Angew. Chem. Int. Ed. Engl.* **2020**, *59*, 2299-2303.

21. Wedal, J. C.; Barlow, J. M.; Ziller, J. W.; Yang, J. Y.; Evans, W. J., Electrochemical studies of tris(cyclopentadienyl)thorium and uranium complexes in the+2,+3, and+4 oxidation states. *Chem. Sci.* **2021**, *12*, 8501-8511.

22. Wedal, J. C.; Ziller, J. W.; Furche, F.; Evans, W. J., Synthesis and Reduction of Heteroleptic Bis(cyclopentadienyl) Uranium(III) Complexes. *Inorg. Chem.* **2022**, *61*, 7365-7376.

23. Wedal, J. C.; Furche, F.; Evans, W. J., Density Functional Theory Analysis of the Importance of Coordination Geometry for 5f(3)6d(1) versus 5f(4) Electron Configurations in U(II) Complexes. *Inorg. Chem.* **2021**, *60*, 16316-16325.

24. Wedal, J. C.; Bekoe, S.; Ziller, J. W.; Furche, F.; Evans, W. J., C-H Bond Activation via U(II) in the Reduction of Heteroleptic Bis(trimethylsilyl)amide U(III) Complexes. *Organometallics* **2020**, *39*, 3425-3432.

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

26. 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.

27. Straub, M. D.; Ouellette, E. T.; Boreen, M. A.; Britt, R. D.; Chakarawet, K.; Douair, I.; Gould, C. A.; Maron, L.; Del Rosal, I.; Villarreal, D.; Minasian, S. G.; Arnold, J., A Uranium(II) Arene Complex That Acts as a Uranium(I) Synthon. *J. Am. Chem. Soc.* **2021**, *143*, 19748-19760.

28. Cotton, F. A.; Schwotzer, W., syntheses and structural comparison of the eta-6-arene complexes Sm(C6Me6)(AlCl4)3 AND U(C6Me6)(AlCl4)3. *Organometallics* **1987**, *6*, 1275-1280.

29. Vandersluys, W. G.; Burns, C. J.; Huffman, J. C.; Sattelberger, A. P., Uranium Alkoxide Chemistry .1. Synthesis and the Novel Dimeric Structure of the 1st Homoleptic Uranium(Iii) Aryloxide Complex. *J. Am. Chem. Soc.* **1988**, *110*, 5924-5925.

30. Marcalo, J.; Leal, J. P.; deMatos, A. P.; Marshall, A. G., Gas-phase actinide ion chemistry: FT-ICR/MS study of the reactions of thorium and uranium metal and oxide ions with arenes. *Organometallics* **1997**, *16*, 4581-4588.

31. Hong, G. Y.; Schautz, F.; Dolg, M., Ab initio study of metal-ring bonding in the bis(eta(6)-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.

32. Li, J.; Bursten, B. E., Bis(arene) actinide sandwich complexes, (eta(6)-C6H3R3)(2)An: Linear or bent? J. Am. Chem. Soc. **1999**, *121*, 10243-10244.

33. Infante, I.; Raab, J.; Lyon, J. T.; Liang, B.; Andrews, L.; Gagliardi, L., Experimental and theoretical evidence for U(C6H6) and Th(C6H6) complexes. *J. Phys. Chem. A* **2007**, *111*, 11996-12000.

34. Evans, W. J.; Kozimor, S. A.; Ziller, J. W.; Kaltsoyannis, N., Structure, reactivity, and density functional theory analysis of the six-electron reductant, $(C_3Me5)(2)U$ (2)(mu-eta(6):eta(6)-C₆H₆), synthesized via a new mode of $(C_5Me_5)(3)M$ reactivity. *J. Am. Chem. Soc.* **2004**, *126*, 14533-14547.

35. Diaconescu, P. L.; Arnold, P. L.; Baker, T. A.; Mindiola, D. J.; Cummins, C. C., Arene-bridged diuranium complexes: Inverted sandwiches supported by delta backbonding. *J. Am. Chem. Soc.* **2000**, *122*, 6108-6109.

36. Mills, D. P.; Moro, F.; McMaster, J.; van Slageren, J.; Lewis, W.; Blake, A. J.; Liddle, S. T., A delocalized arenebridged diuranium single-molecule magnet. *Nat. Chem.* **2011**, *3*, 454-460.

37. Diaconescu, P. L.; Cummins, C. C., mu-eta(6),eta(6)-Arene-Bridged Diuranium Hexakisketimide Complexes Isolable in Two States of Charge. *Inorg. Chem.* **2012**, *51*, 2902-2916.

38. Mougel, V.; Camp, C.; Pecaut, J.; Coperet, C.; Maron, L.; Kefalidis, C. E.; Mazzanti, M., Siloxides as Supporting Ligands in Uranium(III)-Mediated Small-Molecule Activation. *Angew. Chem. Int. Ed. Engl.* **2012**, *51*, 12280-12284.

39. Camp, C.; Mougel, V.; Pecaut, 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.

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

41. Halter, D. P.; Heinemann, F. W.; Bachmann, J.; Meyer, K., Uranium-mediated electrocatalytic dihydrogen production from water. *Nature* **2016**, *530*, 317-321.

42. Halter, D. P.; Heinemann, F. W.; Maron, L.; Meyer, K., The role of uranium-arene bonding in H_2O reduction catalysis. *Nat. Chem.* **2018**, *10*, 259-267.

43. 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. Ed. Engl.* **2014**, *53*, 7154-7157.

44. Palumbo, C. T.; Halter, D. P.; Voora, V. K.; Chen, G. P.; Chan, A. K.; Fieser, M. E.; Ziller, J. W.; Hieringer, W.; Furche, F.; Meyer, K.; Evans, W. J., Metal versus Ligand Reduction in Ln(3+) Complexes of a Mesitylene-Anchored Tris(Aryloxide) Ligand. *Inorg. Chem.* **2018**, *57*, 2823-2833.

45. Shivaraam, R. A. K.; Keener, M.; Modder, D.; Rajeshkumar, T.; Živković, I.; Scopelliti, R.; Maron, L.; Mazzanti, M., A Route to Stabilize Uranium(II) and Uranium(I) Synthons in Multimetallic Complexes. *Angew. Chem. Int. Ed.* **2023**, *62*, e202304051.

46. Chatelain, L.; Scopelliti, R.; Mazzanti, M., Synthesis and Structure of Nitride-Bridged Uranium(III) Complexes. *J. Am. Chem. Soc.* **2016**, *138*, 1784-1787.

47. Andrez, J.; Pecaut, J.; Bayle, P.-A.; Mazzanti, M., Tuning Lanthanide Reactivity Towards Small Molecules with Electron-Rich Siloxide Ligands. *Angew. Chem. Int. Ed. Engl.* **2014**, *53*, 10448-10452.

48. Falcone, M.; Chatelain, L.; Scopelliti, R.; Zivkovic, I.; Mazzanti, M., Nitrogen reduction and functionalization by a multimetallic uranium nitride complex. *Nature* **2017**, *547*, 332-+.

49. Jori, N.; Barluzzi, L.; Douair, I.; Maron, L.; Fadaei-Tirani, F.; Zivkovic, I.; Mazzanti, M., Stepwise Reduction of Dinitrogen by a Uranium-Potassium Complex Yielding a U(VI)/U(IV) Tetranitride Cluster. *J. Am. Chem. Soc.* **2021**, *143*, 11225-11234.

50. Hsueh, F. C.; Rajeshkumar, T.; Maron, L.; Scopelliti, R.; Sienkiewicz, A.; Mazzanti, M., Isolation and Redox Reactivity of Cerium Complexes in Four Redox States. *Chem. Sci.* **2023**, 14, 6011-6021.

51. 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.

52. Camp, C.; Pecaut, J.; Mazzanti, M., Tuning Uranium-Nitrogen Multiple Bond Formation with Ancillary Siloxide Ligands. J. Am. Chem. Soc. **2013**, *135*, 12101-12111.

53. 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.

54. Modder, D. K.; Palumbo, C. T.; Douair, I.; Scopelliti, R.; Maron, L.; Mazzanti, M., Single metal four-electron reduction by U(II) and masked "U(II)" compounds. *Chem. Sci.* **2021**, *12*, 6153-6158.

55. Green, M. L. H.; Ng, D. K. P., Cycloheptatriene and cycloheptatrienyl complexes of the early transition-metals. *Chem. Rev.* **1995**, *95*, 439-473.

56. Arliguie, T.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M., Inverse cycloheptatrienyl sandwich complexes - crystal-structure of $U(BH_4)_2(OC_4H_8)_5$ (BH₄)₃U(μ - η -7, η -7-C₇H₇)U(BH₄)₃. *J. Chem. Soc. Chem. Commun.* **1994**, 847-848.

57. Arliguie, T.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M., synthesis and crystal-structure of $K(C_{12}H_{24}O_6)U(\eta$ -C₇H₇)(2), the first cycloheptatrienyl sandwich compound. *J. Chem. Soc. Chem. Commun.* **1995**, 183-184.

58. Arliguie, T.; Lance, M.; Nierlich, M.; Ephritikhine, M., Inverse cycloheptatrienyl sandwich complexes of uranium and neodymium. *J. Chem. Soc.Dalton Trans.* **1997**, 2501-2504.

59. Li, J.; Bursten, B. E., Electronic structure of cycloheptatrienyl sandwich compounds of actinides: $An(\eta-(7)-C_7H_7)(2)$ (An = Th, Pa, U, Np, Pu, Am). J. Am. Chem. Soc. **1997**, *119*, 9021-9032.

60. Traetteberg, M., Molecular structure of 1,3,5cycloheptatriene in vapor phase as determined by sector electron diffraction method. *J. Am. Chem. Soc.* **1964**, *86*, 4265-4270.

61. Hadley, F. J.; Gilbert, T. M.; Rogers, R. D., Crystalstructures of $(\eta^6-C_7H_8)M(CO)_3$ (M = Cr, W) - comparisons among a homologous series of cycloheptatriene complexes and experimental-evidence for a boat conformation of the coordinated ring. *J. Organomet. Chem.* **1993**, 455, 107-113.

62. Nakai, H.; Hu, X. L.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K., Synthesis and characterization of N-heterocyclic carbene complexes of uranium(III). *Inorg. Chem.* **2004**, *43*, 855-857.

63. Jung, J.; Loffler, S. T.; Langmann, J.; Heinemann, F. W.; Bill, E.; Bistoni, G.; Scherer, W.; Atanasov, M.; Meyer, K.; Neese, F., Dispersion Forces Drive the Formation of Uranium-Alkane Adducts. *J. Am. Chem. Soc.* **2020**, *142*, 1864-1870.

64. Ichimura, A. S.; Wagner, M. J.; Dye, J. L., Anisotropic charge transport and spin-spin interactions in K^+ (cryptand 2.2.2) electride. *J. Phys. Chem. B* **2002**, *106*, 11196-11202.

65. Franke, S. M.; Heinemann, F. W.; Meyer, K., Reactivity of uranium(IV) bridged chalcogenido complexes U-IV-E-U-IV (E = S. Se) with elemental sulfur and selenium: synthesis of polychalcogenido-bridged uranium complexes. *Chem. Sci.* **2014**, *5*, 942-950.

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

67. Liddle, S. T., The Renaissance of Non-Aqueous Uranium Chemistry. *Angew. Chem. Int. Ed. Engl.* 2015, 54, 8604-8641.

68. Seed, J. A.; Birnoschi, L.; Lu, E. L.; Tuna, F.; Wooles, A. J.; Chilton, N. F.; Liddle, S. T., Anomalous magnetism of uranium(IV)-oxo and -imido complexes reveals unusual doubly degenerate electronic ground states. *Chem* **2021**, *7*, 1666-1680.

