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A Route to Stabilize Uranium(II) and Uranium(I) Synthons in Multimetallic Complexes

R. A. Keerthi Shivararam,^[a] Megan Keener,^[a] Dieuwertje K. Modder,^[a] Thayalan Rajeshkumar,^[c] Ivica Živčović,^[b] Rosario Scopelliti,^[a] Laurent Maron,^[c] and Marinella Mazzanti*^[a]

[a] R. A. K. Shivararam, Dr. M. Keener, D. K. Modder, Prof. M. Mazzanti

Group of Coordination Chemistry
Institut des Sciences et Ingénierie Chimiques
Ecole Polytechnique Fédérale de Lausanne (EPFL)
1015 Lausanne (Switzerland)
E-mail: marinella.mazzanti@epfl.ch

[b] Dr. Ivica Živčović

Laboratory for Quantum Magnetism, Institute of Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015, Lausanne, Switzerland

[c] T. Rajeshkumar, Prof. L. Maron

Laboratoire de Physique et Chimie des Nano-objets
Institut National des Sciences Appliquées
31077 Toulouse, Cedex 4 (France)

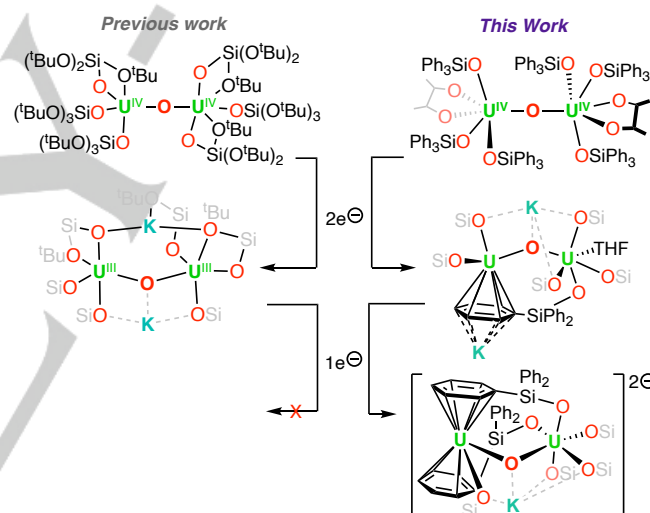
Abstract: Herein, we report the redox reactivity of a multimetallic uranium complex supported by triphenylsiloxide ($-\text{OSiPh}_3$) ligands, where we show that low valent synthons can be stabilized via an unprecedented mechanism involving intramolecular ligand migration. The two- and three-electron reduction of the oxo-bridged diuranium(IV) complex $[(\text{Ph}_3\text{SiO})_3(\text{DME})\text{U}]_2(\mu\text{-O})$, **4**, yields the formal “U(II)/U(IV)”, **5**, and “U(I)/U(IV)”, **6**, complexes via ligand migration and formation of uranium-arene δ -bond interactions. Remarkably, complex **5** effects the two-electron reductive coupling of pyridine affording complex **7**, which demonstrates that the electron-transfer is accompanied by ligand migration, restoring the original ligand arrangement found in **4**. This work provides a new method for controlling the redox reactivity in molecular complexes of unstable, low-valent metal centers, and can lead to the further development of f -elements redox reactivity.

Introduction

Multimetallic complexes of uranium have recently proven very effective in the activation and transformation of unreactive small molecules and of dinitrogen, in particular, due to the cooperative binding of substrate and the large number of available electrons.^{[1]-[2]} Multimetallic intermediates are also most likely involved in the reduction of small molecules effected by low valent mononuclear uranium complexes.^[3]

However, so far only few examples of multimetallic complexes containing more than one uranium in the +3 oxidation state have been reported^[4, 1f, 5] and multimetallic complexes containing uranium in oxidation states lower than +3 remain unknown. Notably, only few mononuclear U(II) complexes have been reported so far,^[6] and very recently the very first complex of U(I)^[7] has been discovered. The reactivity studies of these complexes are very limited^[6c, 8, 6h] due to the difficulty of accessing these species,^[9] but putative U(II) intermediates, although not unambiguously identified, are likely to be involved in the reactivity of reduced U(III) species towards C-H activation^[10] and small molecule activation.^[3c] It has also been shown that complexes associating low valent uranium (U(III) or U(IV)) and redox-active ligands capable of accepting electrons behave as easy to handle

U(II) synthons that can store electrons in the ligand and render them available for the reduction of substrates.^[11]



Scheme 1. (left) Previous and (right) current reactivity of diuranium bridging oxo complexes toward reducing agents.

Inverse-sandwich complexes represent a particular class of low valent multimetallic complexes of uranium where arene ligands act as bridging ligands between uranium centers.^[12a-d, 2b, 12e-h] In these multimetallic systems, the electrons localized on the bridging arene can become available for the reduction of various substrates, but result in disruption of the multimetallic complex. Very recently, Arnold and coworkers reported the first example of a mononuclear complex acting as a U(I) synthon by storing electrons via the intramolecular reduction of a pendant aromatic group on the ligand.^[6h] Inspired by this work, we reasoned that a similar approach could be used to access U(II) and U(I) synthons in multimetallic complexes.

We recently showed that a bridging oxide moiety can be used as linker for building polymetallic complexes of uranium in the +4 and +3 oxidation states, that showed original redox reactivity.^[1f, 5b] The $-\text{OSi}(\text{O}^t\text{Bu})_3$ diuranium(III) complex was obtained by reduction of the diuranium(IV) analogue (Scheme 1) but further reduction of the uranium could not be effected.

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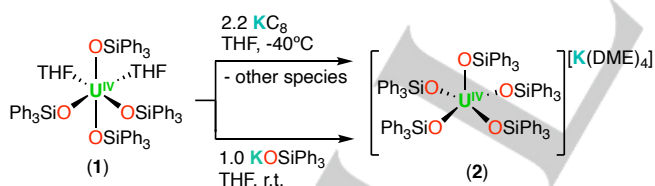
We anticipated that the phenyl group in the trisphenylsiloxide ($-\text{OSiPh}_3$) ligand should act as an electron reservoir, therefore storing a large number of electrons in multimetallic complexes. The $-\text{OSiPh}_3$ ligand failed to stabilize U(II) or U(I) synthons in mononuclear complexes. However, we demonstrate that the two-electron and three-electron reduction of the diuranium(IV) complex $[\{(\text{Ph}_3\text{SiO})_3(\text{DME})\text{U}\}_2(\mu\text{-O})]$, **4**, leads to stabilization of the U(II) and U(I) synthons in multimetallic complexes by ligand migration and storing electrons in bridging phenyl groups. The process is accompanied by an unprecedented inner-sphere ligand migration which results in the formation of uranium mono- and bis-arene complexes.

The reduced dinuclear complexes can overall transfer up to three electrons to oxidizing substrates restoring the original ligand distribution.

Results and Discussion

At first, we explored the possibility of using the $-\text{OSiPh}_3$ ligand to prepare mononuclear complexes of uranium in low oxidation states. Two independent routes were explored, first the reduction of a U(IV) complex and then the direct synthesis of a U(III) complex by protonolysis of $[\text{U}\{\text{N}(\text{SiMe}_3)_2\}_3]$ were studied.

First, we synthesized the precursor, $[\text{U}(\text{OSiPh}_3)_4(\text{THF})_2]$, **1**, by reacting $\text{U}_4(\text{dioxane})_{3.5}$ with 4.0 equiv. of KOSiPh_3 in tetrahydrofuran (THF) at room temperature. Lilac crystals of **1** were obtained in 84% yield by slow diffusion of hexane into a THF solution of **1**. In the solid-state molecular structure of complex **1**,^[13] the uranium center is coordinated by four $-\text{OSiPh}_3$ ligands and two THF molecules, with the THF molecules binding to the metal centre in a *cis* fashion (Figure S48). The U–O_{siloxide} bond lengths (2.1457(16), 2.1687(16) Å) are similar to those reported for the $[\text{U}\{\text{OSi}(\text{O}^t\text{Bu})_3\}_4(\text{pyr})_2]$ complex (U1–O_{avg} 2.177(12) Å).^[14] The ¹H NMR spectrum of **1** features four broad signals at room temperature in both $[\text{D}_8]\text{THF}$ (Figure S2) and $[\text{D}_8]\text{Toluene}$ (Figure S4), but sharpen upon decrease in temperature (Figure S3), indicating a decrease in fluxionality of the ligands. Complex **1** is stable in THF for at least a week at room temperature (Figure S5).



Scheme 2. Reduction of **1** and synthesis of **2** via two alternative pathways.

Addition of 2.2 equiv. of KC_8 to a solution of **1** at -40°C in THF was required to ensure complete consumption of **1** (Figure S6). Crystallization by slow diffusion of hexane into a DME solution of the brown reaction mixture led to the isolation of crystals of the U(IV) complex, $[\text{K}(\text{DME})_4][\text{U}(\text{OSiPh}_3)_3]$, **2**, as confirmed by X-ray crystallography^[13] (Figure S49). The ¹H NMR spectrum (Figure S6) of the reaction mixture at -40°C shows resonances corresponding to **2**. Light pink crystals of **2** were also isolated in 70% yield by an independent route, involving the addition of 1.0 equiv. of KOSiPh_3 to **1** (Scheme 2). Complex **2** is stable in THF for at least a week at room temperature (Figure S12). These

results suggest that the reduction of **1** leads to unstable species which decompose/disproportionate to yield **2** and unidentified products as indicated by ¹H NMR spectroscopy. The disproportionation to U(IV) and unidentified U⁰ or U(II) species of U(III) intermediates not sufficiently stabilized by the supporting ligands, have been reported, although the low valent species were never identified.^[2a, 15]

To isolate a U(III) complex of the $-\text{OSiPh}_3$ ligand, we pursued an alternative synthetic route.

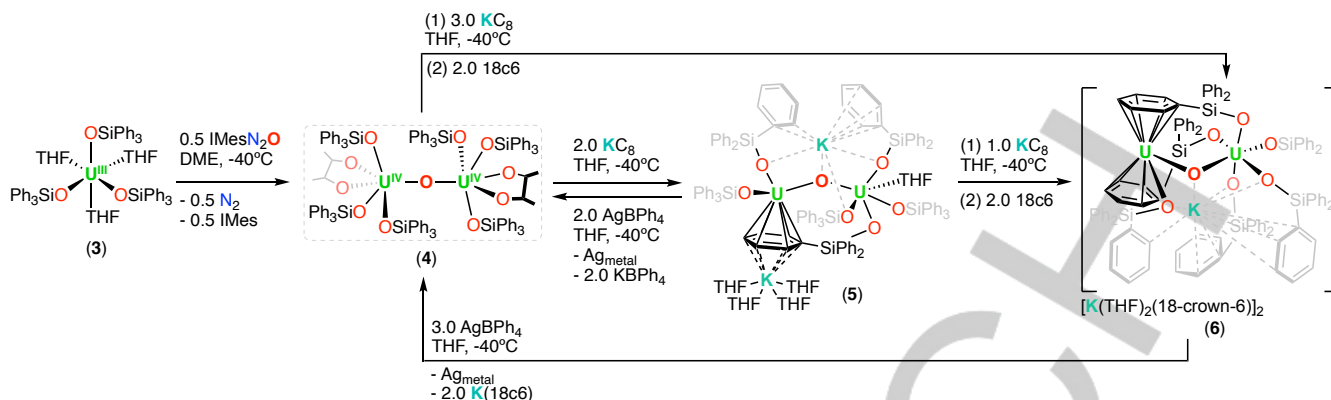
Complex $[\text{U}(\text{OSiPh}_3)_3(\text{THF})_3]$, **3**, was obtained by protonolysis of $[\text{U}\{\text{N}(\text{SiMe}_3)_2\}_3]$ with 3.0 equiv. of Ph_3SiOH at -40°C in THF (Figure S50). The reaction is immediate and storing the reaction mixture at -40°C afforded dark brown crystals of **3** in 64% yield. The solid-state molecular structure of complex **3**^[13] shows the presence of a mononuclear U(III) ion six-coordinated by three $-\text{OSiPh}_3$ and three THF ligands with an octahedral geometry, making it isomorphous to the previously reported tris- $-\text{OSiPh}_3$ complexes of lanthanides(III).^{[16] [17]} The U–O_{siloxide} bond lengths (2.202(5) - 2.229(5) Å) in **3** are comparable to those of the terminal siloxides in the U(III) dimeric complex $[\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_2(\mu\text{-OSi}(\text{O}^t\text{Bu})_3)_2]$ (U–O_{avg} = 2.193(4)) previously reported by our group.^[2b] The ¹H NMR spectrum of **3** in $[\text{D}_8]\text{THF}$ at -40°C features two peaks at 7.37 ppm and 9.94 ppm in the ratio 3:2, corresponding to aromatic protons of the ligand in the C_3 -symmetric complex **3** (Figure S15). Complex **3** is highly reactive in both the solid and solution state and must be always stored at -40°C . In THF solution at room temperature, full decomposition can be observed after three days (Figure S19), and in the solid state roughly only 50% of the complex remains after one day at room temperature. The compound is stable for at least a week at -40°C in THF (Figure S16) and decomposes immediately upon dissolution in toluene.

Reduction of **3** with 1.0 equiv. KC_8 led to complex **2** as the only identified disproportionation product and to other unknown species (Figure S17), despite the presence of $-\text{OSiPh}_3$ ligands with arene substituents, which can stabilize reduced species as observed for the previously reported U(III) complex of TDA (TDA = *N*-(2,6-di-isopropylphenyl)pivalamido).^[6h]

Dinuclear complexes of uranium(III) were recently obtained by reduction of oxide bridged diuranium(IV) complexes.^{1f} In order to probe the possibility of stabilizing U(II) and U(I) synthons in dinuclear compounds, we set out to synthesize U(IV)/U(IV) oxo-bridged complex supported by $-\text{OSiPh}_3$ ancillary ligands using the recently developed strategy.

The reaction of **3** with the N_2O adduct of the *N*-heterocyclic carbene 1,3-dimesitylimidazol-2-ylidene (IMesN_2O)^[18, 1f] in dimethoxyethane (DME) led to the isolation of the U(IV)/U(IV) bridging oxo complex $[\{(\text{Ph}_3\text{SiO})_3(\text{DME})\text{U}\}_2(\mu\text{-O})]$, **4**, in 83% yield (Scheme 3 and Figure S51). The addition of reagents was performed on a thawing suspension/solution of IMesN_2O and **3** in DME, to avoid the formation of undesirable bis-oxo species. Teal crystals suitable for X-Ray diffraction were obtained from a concentrated solution of DME at -40°C . The solid-state molecular structure of **4**^[13] shows the presence of a diuranium(IV) complex where two $[\text{U}(\text{OSiPh}_3)_3(\text{DME})]$ moieties are bridged by an oxide ligand. Both U1 and U1' ions are six-coordinate, with three $-\text{OSiPh}_3$ ligands and one DME solvent molecule in an octahedral geometry. The values of the U–O_{siloxide} (2.160(3) -

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Scheme 3. Synthesis and reactivity of complexes **4**, **5**, and **6** with reducing and oxidizing agents.

2.181(2) Å) and the U-O_{bridgingoxo} (2.1116(1) Å) bond lengths in **4** are similar to those found in the previously reported oxide bridged U(IV)/U(IV) complex supported by the $-\text{OSi}(\text{O}^t\text{Bu})_3$ ligands [U(OSi(O^tBu)₃)₂(μ-O)].^[17] The ¹H NMR spectrum of **4** in [D₈]THF at -40°C (Figure S23) shows seven resonances between 35 ppm and -3 ppm assigned to the $-\text{OSiPh}_3$ ligands and the bound DME.

With the U(IV)/U(IV) complex **4** in hand, we next pursued the two and three electron reduction reactions. The reduction of **4** with 2.0 equiv. KC_8 in THF at -40°C led to the isolation of the two-electron reduction product, [(THF)₄K₂{(Ph₃SiO)₂U}(μ-O)(μ-κ²:η⁶-PhO-PhSiPh₂O)-U(THF)(Ph₃SiO)₃], **5** in 69% yield (Scheme 3 and Figure 1). The ¹H NMR spectrum of complex **5** in [D₈]THF at -40°C (Figure S26) shows nineteen resonances between 28 ppm and -90 ppm, in line with the presence of highly asymmetric solution species. In the solution state (THF) complex **5** is stable for at least one week at -40°C (Figure S27) and at least three days at room temperature (Figure S29). While in the solid state at -40°C , complex **5** is stable for at least a month.

The molecular structure of complex **5**^[13] shows the presence of a dinuclear complex where the two uranium centers present a different coordination environment with U1 and U2 binding two and four $-\text{OSiPh}_3$ ligands, respectively. The two uranium centers are bridged by an oxo moiety alongside an η⁶-arene from a OSiPh₃ ligand binding the U2 ion. The U–O–U bond angle (146.36(15)°) in **5** deviates significantly from the linearity (180°) found in complex **4**, most likely to accommodate the bridging arene in the asymmetric solid-state structure of **5**.

The molecular structure of **5** shows that upon the two-electron reduction of **4**, one of the $-\text{OSiPh}_3$ ligands migrates from one uranium, namely U1, to the other uranium center U2. The ligand migration results in what could be formally seen as a “U(II)/U(IV)” oxo complex (the bond valence sum calculation for U2 indicates a +4 oxidation state, and a +2 oxidation state for U1; refer to Table S4) where the low valent uranium moiety is stabilized by a U-arene interaction, rather than yielding the anticipated U(III)/U(III) analogue of **4**. The ligand migration was also observed when carrying out the reduction at a lower temperature (-80°C). It should be noted that when the reduction of **4** is carried out with 1.0 equiv. KC_8 in THF at -40°C only the signals assigned to complex **5** and unreacted **4** are observed in the ¹H NMR spectrum (Figure S38) indicating that a stable “U(III)/U(IV)” species cannot be formed.

The mean value of 2.227(6) Å for the U2-O_{siloxide} bond distance in complex **5** compares well with those found and in other

U(IV) tetrakis siloxide complexes.^[14, 2c] and are in agreement with the assignment of the oxidation state of U2 as a U(IV).

Analysis of the C_{arene}–C_{arene} bond distances (refer Table S3 and Figure S54) of the phenyl ring bound to U1 in an η⁶-fashion revealed the presence of a cyclohexadiene-like geometry (two short bonds and four long bonds) and the high torsion angles (14.0(7)° and 19.3(7)°) points towards the presence a reduced arene^[19] similar to what Arnold and coworkers observed in the Th(IV)-(arene)²⁻ complex, [K[2.2.2]cryptand][Th(TDA)₃(THF)] (torsion angles: 17.4(4)° and 24.2(4)°) and in the U(II)-(arene⁻¹) complex, [K[2.2.2]cryptand][U(TDA)₂](torsion angles: 11.5(4)° and 15.5(4)°) (TDA = *N*-(2,6-di-isopropylphenyl)pivalamido).^[6h] Deviations from planarity were also found in inverse sandwich complexes of uranium assigned as U(III)-(arene²⁻) previously reported by the groups of Cummins and Evans.^[12a, 20, 12g] In the [U(N(adamantyl)(C₆H₃-3,5-Me₂))₂(μ:η⁶-η⁶-C₆H₅Me)] example of Cummins and coworkers the arene is puckered due to the ipso carbon of the complexing toluene being slightly out of plane; with the C_{arene}–C_{arene} bond lengths (1.415(13)–1.461(13) Å) only ~ 0.04 Å longer than free toluene.^[12a] In comparison, the [U(η⁵-C₅Me₅)₂(μ:η⁶-η⁶-C₆H₆)] example of Evans and coworkers also features a puckered ring with torsion angles of 18° and 12.5°, but the C_{arene}–C_{arene} bond lengths (1.42(2)–1.462(18) Å) of the complexing benzene were indistinguishable from that of free benzene.^[20] In contrast, significant distortions could not be detected in previously reported U(II) complexes bearing arene donors.^[6b, 6d]

Considering the observed ability of the phenyl ring to stabilize low valent species in dinuclear complexes we explored the possibility of accessing lower oxidation states. We found that when increasing the amount of KC_8 from 2.0 to 3.0 equiv., further reduction of complex **5** could be observed leading to the isolation of the three-electron reduced species [K(THF)₂(18c6)]₂[K{(Ph₃SiO)U}(μ-O)(μ-κ²:η⁶-Ph,O-PhSiPh₂O)(μ-κ²:η⁶-Ph,O-PhSiPh₂O)-U(Ph₃SiO)₃], **6** in 53 % yield (Scheme 3 and Figure 1) after addition of 18-crown-6 ether (18c6) to the reaction mixture. Dark purple crystals of complex **6** were obtained from a concentrated reaction mixture in DME at -40°C .

In the solution state (THF), complex **6** is stable for at least one week at -40°C (Figure S34). In contrast, complex **6** completely decomposes after one week at room temperature (Figure S35). In the solid state, complex **6** is stable for at least a month at -40°C and at least one day at room temperature.

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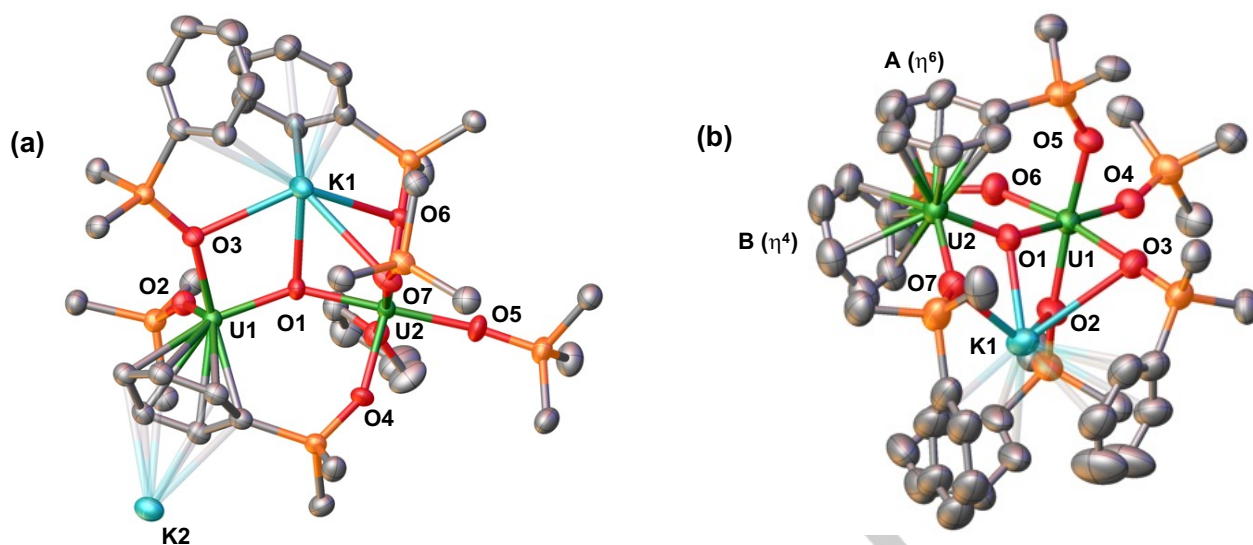


Figure 1. Molecular structures of complexes (a) **5** and (b) **6** with thermal ellipsoids drawn at the 50 % probability level. Hydrogen atoms, some phenyl groups, potassium (K2 in complex **6**), bound THF molecules (complex **5**), and $[K(THF)_2(18c6)]^+$ counter ions (complex **6**) have been omitted for clarity.

The molecular structure of complex **6**^[13] shows an oxo bridged dinuclear complex where an additional $-OSiPh_3$ ligand has migrated from U2 to U1 compared to complex **5**. As a result of this controlled migration, the U1 ion is coordinated by five $-OSiPh_3$ ligands and one bridging oxo with a pseudo-octahedral geometry. In contrast, U2 is coordinated by one siloxide ligand oxygen, by a η^6 -phenyl ring (ring **A**) and a η^4 -phenyl ring (ring **B**) from two different U1-bound $-OSiPh_3$ ligands. The coordination environment of U2 resulted in a rare uranium bis-arene complex.

The mean value of 2.264(11) Å for the U1–O_{siloxide} bond distance in complex **6** compares well with those found in other U(IV) tetrakis siloxide complexes.^[14, 2c] The bond valence analysis (refer Table S6) of U1 in **6** yielded a formal oxidation state of +4 for U1. The assignment of the oxidation state of the U2 center is more ambiguous.

The values of the C_{arene}–C_{arene} bond distances (refer Table S5 and Figure S55) of the two phenyl rings interacting with U2 did not reveal any obvious/significant deviations from planarity for either ring, unlike what was observed in **5** which could suggest the presence of neutral arenes and therefore the presence of U(I).

To further elucidate the electronic structure and bonding in the highly unusual complexes **5** and **6** EPR (refer Section D in SI) and SQUID magnetometry (Figure 2 and Section E in SI) studies were undertaken. The X-band EPR spectrum of **5** was silent in both the solid state and in frozen solution (30 mM in toluene) state at all the temperature measured (6K, 15 K, 30 K, 50 K and 100 K). A silent EPR spectrum could be due to the presence of either an f^4 or an f^2 ion corresponding to a U(II)-arene⁰ or to a U(IV)-arene²⁻ system.

In contrast, compound **6** exhibits an EPR spectrum (Figure S57) in the solid state (at 6 K) with g -values 2.83 and 0.97 fitted for an axial system. The observed EPR signal could be interpreted in terms of the presence of a U(III)-(arene)²⁻ or a U(III)-(arene²⁻)(arene⁰). The presence of a U(I)-(arene⁰) could not be completely ruled out due to the scarce information on this species, although a very different EPR spectrum was reported for the only known U(I) compound (g -values of 4.7, 1.6, and 1.2).^[7]

In comparison, the U(III) precursor **3** shows a similar well-defined EPR spectrum (Figure S56) in frozen solution state (30 mM in 1:1 THF/Et₂O) with g -values 2.71, 1.01 and 0.75 corresponding to a pseudo axial system. Similar g -values were reported for several U(III) complexes.^[21a-c, 12h, 21d]

Variable temperature magnetic susceptibility data were collected for complexes **3**, **4**, **5** and **6** under an applied magnetic field of 1 T (data were collected only up to 250 K for **3** due to the low thermal stability). The temperature dependence of **3** in the μ_{eff} vs T plot is similar to previously reported U(III) complexes with a $^4I_{9/2}$ ground state for the f^3 ion, where the magnetic moment decreases with decreasing the temperature to approach a non-zero value at 2 K associated with a doublet state for the Kramers ion.^[22] The magnetic moment and molar magnetic susceptibility values of **3** at 2 K ($\mu_{\text{eff}} = 1.55 \mu_B$, $\chi_M = 0.15 \text{ emu/mol}$) and 250 K ($\mu_{\text{eff}} = 3.16 \mu_B$, $\chi_M = 0.28 \times 10^{-2} \text{ emu/mol}$) are within the range of previously reported U(III) complexes.^[23, 22b] The μ_{eff} vs T behavior for **4** is characteristic of magnetically independent U(IV) ions possessing a singlet ground state, where the value of the magnetic moment decreases rapidly from around 50 K to approach zero towards 2 K. Once again, the magnetic moment and molar magnetic susceptibility values per uranium for complex **4** at 2 K ($\mu_{\text{eff}} = 0.35 \mu_B$, $\chi_M = 0.58 \times 10^{-2} \text{ emu/mol}$) and 300 K ($\mu_{\text{eff}} = 3.04 \mu_B$, $\chi_M = 0.22 \times 10^{-2} \text{ emu/mol}$) are consistent with values reported previously for diuranium complexes bridged by chalcogenides.^[24, 1f] The μ_{eff} vs T curve measured for complex **5** indicates the presence of a non-Kramers system in a singlet ground state, with the rapid decrease of magnetic moment from approx. 50 K on decreasing the temperature.

This behavior has been well documented for many U(IV) complexes, and also observed for the few U(II) complexes that have been characterized by SQUID magnetometry.^[6b-d, 6g] However, the values of the magnetic moment and molar magnetic susceptibility per complex measured for **5** at room temperature ($\mu_{\text{eff}} = 4.01 \mu_B$, $\chi_M = 0.33 \times 10^{-2} \text{ emu/mol}$) and above 30 K are similar and only slightly lower than those of the U(IV)/U(IV) precursor **4** ($\mu_{\text{eff}} = 4.29 \mu_B$, $\chi_M = 0.45 \times 10^{-2} \text{ emu/mol}$ at 300 K), which seems to point to the presence of a U(IV)/U(IV) complex.

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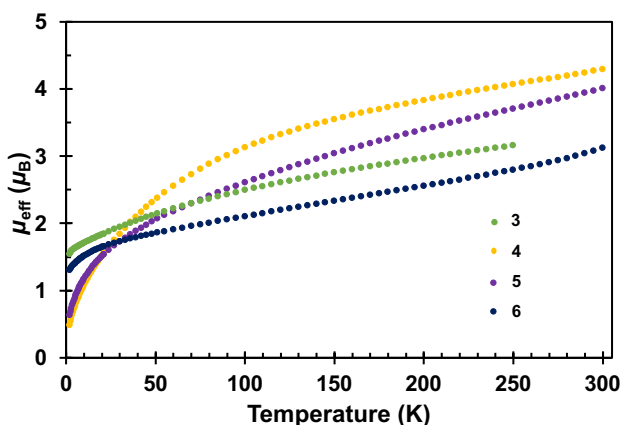


Figure 2. Temperature dependent SQUID magnetization data plotted as a function of μ_{eff} vs. temperature for complexes **3**, **4**, **5** and **6** (measured under an applied field of 1 T)

In the case of **6**, the μ_{eff} vs T curve suggests the presence of a Kramers ion and is very similar to that measured for the U(III) complex **3** discussed above. The magnetic data are in line with the EPR data and support the assignment of U2 as a U(III) ion. The magnetic moment of **6** at 2 K ($\mu_{\text{eff}} = 1.31 \mu_{\text{B}}$, $\chi_{\text{M}} = 0.10 \text{ emu/mol}$) is higher than that of **4** and **5**, but lower than that of **3**. The magnetic moment of **6** at 250 K ($\mu_{\text{eff}} = 2.80 \mu_{\text{B}}$, $\chi_{\text{M}} = 0.12 \times 10^{-2} \text{ emu/mol}$) is also slightly lower than that of **3** at 250 K ($\mu_{\text{eff}} = 3.16 \mu_{\text{B}}$, $\chi_{\text{M}} = 0.28 \times 10^{-2} \text{ emu/mol}$).

To gain insight into the bonding and electronic structures of complexes **5** and **6**, DFT calculations (B3PW91), including dispersion corrections, were carried out (see SI Section H for details). A full geometry optimization of complex **5** was carried out without symmetry constraints for different spin states, namely septet ($S=3$), quintet ($S=2$), triplet ($S=1$) and singlet ($S=0$) states. The quintet state ($S=2$) was found to be the ground state with both the septet and triplet states close in energy (7.4 and 7.6 kcal mol⁻¹ higher in energy, respectively), whereas the singlet state is 32.7 kcal mol⁻¹ higher in energy. This is consistent with the magnetic data for complex **5**, and the unpaired spin density, with two unpaired spins per uranium, overall suggesting the presence of two U(IV) centers, with an arene ring that has been formally reduced by two-electrons (a, Figure 3). Further scrutinization of the Molecular Orbitals (MO) shows the presence of two *f*-electrons per uranium, with the presence of a doubly occupied uranium-arene δ -bond. This further supports the formal oxidation assignment of U(IV) and a two-electron reduction of the arene. However, another possible description of complex **5** is a formal U(II)/U(IV), where two electrons from one of the uranium centers are stored in the δ -bond (see SI).

A similar analysis was carried out on complex **6**. Four different spin states were optimized, namely an octet ($S=7/2$), a sextet ($S=5/2$), a quartet ($S=3/2$) and a doublet ($S=1/2$). The ground state is found to be the sextet ($S=5/2$) with the quartet and the doublet only 4.7 and 4.9 kcal mol⁻¹ higher in energy, respectively, whereas the octet is 12.4 kcal mol⁻¹ higher. This is again consistent with the magnetic data, suggesting the presence of a formal U(III)/U(IV) complex (b, Figure 3). A CASSCF calculation

on this system for $S=5/2$ ($2S+1=6$) spin state distributing 5 electrons onto 5 *f* orbitals per uranium center and two arene π^* in the active space.

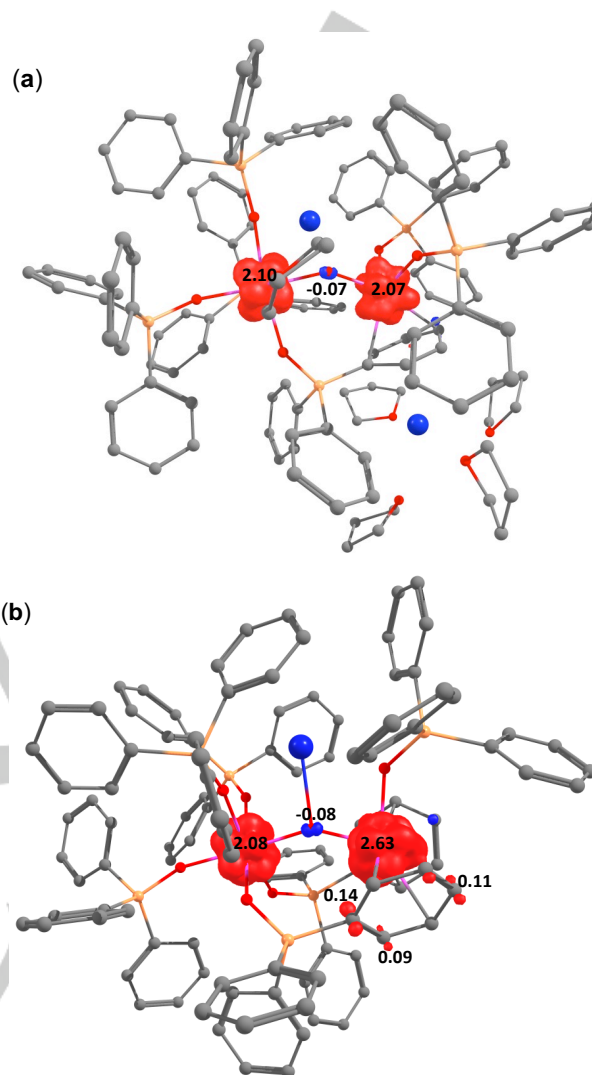
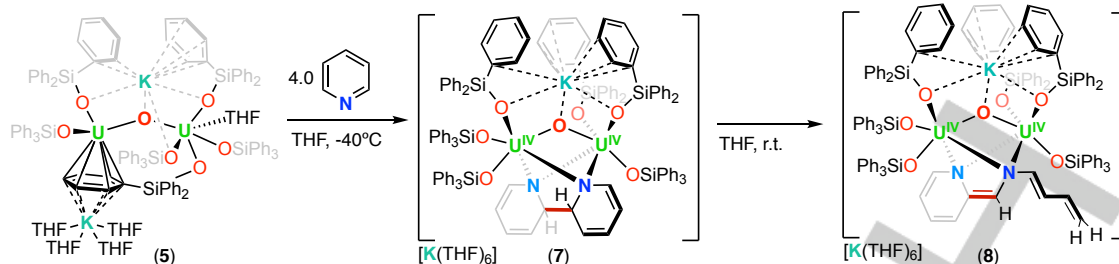


Figure 3. Unpaired spin density plots for the (a) quintet ground state of complex **5** and the (b) sextet ground state of complex **6**.

The final wavefunction shows slight contributions from the U(I)-U(IV) and U(II)/U(IV) systems (6% and 3%, respectively), whereas 91% stems from the U(III)/U(IV), with two-electrons located on the η^6 -arene **A**. At the DFT level, the MOs indicate that three electrons are stored in two δ -bonds, in which one δ -bond (Table S17) is 80% uranium and 20% arene π^* . Therefore, complex **6** can be described as a U(I)/U(IV) synthon where two-electrons of the U(I) center are stored in a uranium-arene δ -bond, similar to complex **5**.

To explore the availability of the electrons stored in these complexes, we studied their chemical reactivity. At first the relatively strong oxidizing agent AgBPh₄ was used (Ag⁺, $E^{\circ} = 0.41 \text{ V vs } [(\text{C}_5\text{H}_5)_2\text{Fe}]^{+/0}$ couple in THF).^[25] Chemical oxidation of complexes **5** and **6** with AgBPh₄

RESEARCH ARTICLE



Scheme 4. Reactivity of complex **5** to form **7** and subsequently **8**.

(2.0 equiv. and 3.0 equiv., respectively) and analysis by ^1H NMR spectroscopy (Figure S45 and Figure S46 respectively), indicated that oxidation leads to the formation of complex **4**. These reactions clearly show that two and three electrons are available in complexes **5** and **6** respectively for reduction of substrates. Moreover, these reactions indicate that the ligand migration resulting from reduction of **4** is reversible upon oxidation and allows the regeneration of complex **4**.

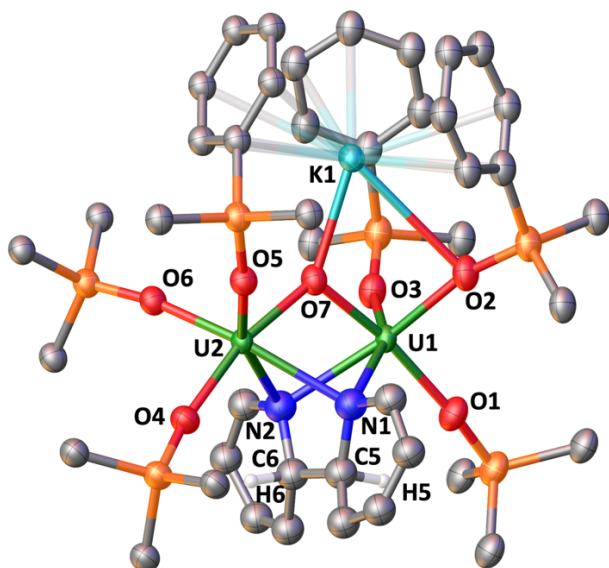


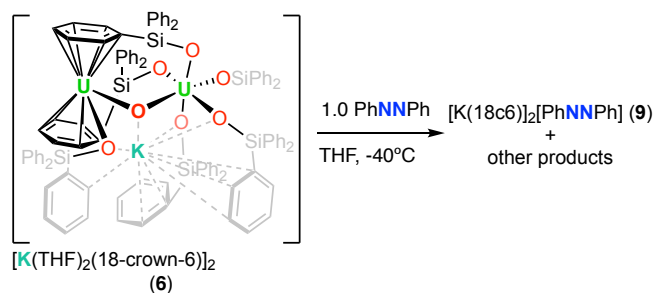
Figure 4. Molecular structure of **7** with thermal ellipsoids drawn at the 50 % probability level. Hydrogen atoms (except H5 and H6), some phenyl groups and the $[\text{K}(\text{THF})_4]^+$ counter ion have been omitted for clarity.

We then explored less-oxidizing substrates. Upon addition of pyridine (4.0 equiv.) to a solution of **5** in $[\text{D}_8]\text{THF}$ a new set of signals could be immediately observed in the ^1H NMR spectrum (Figure S39) at -40°C and the presence of **5**. However, after 18 hours, the reaction mixture showed the presence of a new set of signals and the complete consumption of **5**, accompanied by a color change from dark red brown to orange. Single crystals were obtained by slow diffusion of hexane into a THF solution of **7** and X-ray diffraction studies revealed the presence of the U(IV)/U(IV) complex, $[\text{K}(\text{THF})_6][\text{K}\{(\text{Ph}_3\text{SiO})_3\text{U}\}_2(\mu\text{-O})\mu\text{-}(\text{o-pyr})_2]$ (Scheme 4 and Figure 4) containing a dianionic reductively coupled pyridinyl moiety bridging the two uranium centers resulting from the reductive coupling of two pyridine moieties at the *ortho* position. The ^1H NMR spectrum of **7** (Figure S40) in $[\text{D}_8]\text{THF}$ at -40°C features six broad resonances between 40 and -10 ppm and five sharper resonances between -35 and -143 ppm, assigned to the $-\text{OSiPh}_3$ and $(\text{o-pyr})_2$ ligands, respectively. Complex **7** is stable in

a THF solution at -40°C for at least 5 days (Figure S42). At room temperature in a THF solution, the signals corresponding to **7** decrease rapidly over time and disappear after 4 hours, while new signals appear and a color change from orange to dark brown could be observed (Figure S43). Slow diffusion of hexane into the THF reaction mixture, afforded crystals of $[\text{K}(\text{THF})_6][\text{K}\{(\text{Ph}_3\text{SiO})_3\text{U}\}_2(\mu\text{-O})\mu\text{-}(\text{o-pyr})_2]$, **8** (Scheme 4 and Figure S52). The molecular structure of **8** shows that the dearomatized coupled pyridine ($(\text{o-pyr})_2$) bridging the two uranium centers in **7** has undergone a rare example of metal mediated C-C cleavage^[26] resulting in ring opening of one of the pyridine rings, probably as a result of steric bulk in the bridging $(\text{o-pyr})_2$ moiety. The conversion of **7** into **8** was followed over time by ^1H NMR spectroscopy at temperatures ranging from 15 to 30°C , from which ΔH^\ddagger and ΔS^\ddagger were calculated to be $22.0\text{ kcal mol}^{-1}$ and $3.44\text{ cal mol}^{-1}\text{ K}^{-1}$, respectively, resulting in a ΔG^\ddagger activation barrier of 22.0 kcal/mol at 298 K (See SI Section G). Overall, the reaction of **5** with pyridine provides a rare example of metal mediated C-C cleavage of an unstrained aromatic ring in ambient condition. The examples of metal mediated pyridine ring opening reported so far were all involving C-N cleavage.^[27]

The solid state molecular structure of complex **7** shows a diuranium(IV) complex where each uranium center is six-coordinated in a distorted octahedral geometry by three $-\text{OSiPh}_3$ ligands, one bridging oxygen atom, and the bridging dianionic $(\text{o-pyr})_2$ molecule. Both the $\text{U}-\text{O}_{\text{siloxide}}$ ($2.176(9) - 2.221(8)\text{ \AA}$) and the $\text{U}-\text{O}_{\text{oxo}}$ bond lengths ($2.127(8), 2.151(8)\text{ \AA}$) are similar to those found in **4**, albeit slightly elongated, most likely due to the presence of the $(\text{o-pyr})_2$ ligand. In contrast, the $\text{U}\dots\text{U}$ distance ($3.5205(6)\text{ \AA}$) is considerably shorter due to the decrease of the $\text{U}-\text{O}-\text{U}$ angle ($110.8(4)^\circ$) required to accommodate the $(\text{o-pyr})_2$ molecule. Interestingly, in contrast to the reactivity observed for the previously reported U(III)-O-U(III) complex supported by $\text{N}(\text{SiMe}_3)_2$ ligands,^[26] the pyridine molecules couple in the *ortho* position instead of the *para* position. Coupling of pyridine at the *ortho* position was reported previously, but was always coupled with hydrogen loss to afford the 2,2'-bipyridine ligand.^[28] In **7** on the other hand, the hydrogen atoms remain bound, as evidenced by the ^1H NMR spectrum of **7** (Figure S41).

RESEARCH ARTICLE



Scheme 5. Reactivity of complex **6** to form $[\text{K}(18\text{c6})]_2[\text{PhNNPh}]$.

The C–C bond distance (1.45(2) Å) in the $(o\text{-pyr})_2$ molecule is slightly shorter than those observed in previously reported examples of pyridine molecules reductively coupled in the para position (1.50(17) – 1.563(6) Å).^[29, 5b] Quite remarkably, during the reaction of **5** with pyridine (4.0 equiv.) to form the reductively coupled $(o\text{-pyr})_2$ product **7**, the 2:4 arrangement of the $-\text{OSiPh}_3$ ligands in **5** reverts back to the 3:3 arrangement found in **4**. This reactivity is in line with what was observed in the oxidation of **5** with AgBPh_4 (2.0 equiv.) which also results in the regeneration of complex **4** following ligand migration.

Complex **6** also reacts with pyridine but the resulting complex could not be isolated. We also failed to isolate the product of the reaction of **6** with cycloheptatriene (a three-electron acceptor). In contrast, we were able to characterize the reduction product obtained from the reaction with azobenzene. Addition of 1.0 equiv. of azobenzene (PhNNPh) to a solution of **6** in THF at -40°C , resulted in a color change from purple to orange-brown, and the precipitation of a red crystalline solid. XRD analysis of the red crystals isolated from the reaction mixture revealed the formation of $[\text{K}(18\text{c6})]_2[\text{PhNNPh}]$ (**9**) in 93% yield (Scheme 5 and Figure S53). The N–N bond length (1.40(3) Å) is elongated compared to PhNNPh (1.25 Å) and to the singly reduced derivative, $[\text{K}[2.2.2]\text{cryptand}][\text{PhNNPh}]$ (1.34(3) Å), obtained from the reaction of the only isolated U(I) complex with azobenzene^[7], indicating that a two-electron reduction of azobenzene has occurred. Although we could not isolate the underlying uranium species, these results show that complex **6** can transfer two electrons to PhNNPh.

Conclusion

In summary, we investigated the reduction of U(IV) complexes supported the $-\text{OSiPh}_3$ ligand. We showed that reduction of the mononuclear U(IV) complex **1** results only in the isolation of the penta-ligated U(IV) complex **2**, most likely due to the disproportionation of a putative U(III) intermediate and ligand scrambling. In contrast, the two- and the three-electron reductions of the dinuclear oxo bridged U(IV)/U(IV) complex, **4**, proceed in a controlled fashion, allowing access to low valent uranium synthons that can release two- and three-electrons to oxidizing substrates. The reduction proceeds via an unprecedented intramolecular ligand migration, affording two new complexes that can be formally described as the “U(II)/U(IV) (**5**)” and “U(I)/U(IV) (**6**)” complexes. Complexes **5** and **6** show one and two bridging arenes, which bind the “U(II)” and “U(I)” centers, respectively. Spectroscopic and computational data support the formal oxidation assignment of a U(IV)/U(IV) and U(III)/U(IV), resulting in a two-electron reduction of the arene for **5** and **6**, respectively. However, according to the computational studies, another possible description of complex **5** is a formal “U(II)/U(IV), where

two electrons from one of the uranium centers are stored in the δ -bond. Complex **6** can be described as a “U(I)/U(IV) synthon where two-electrons of the “U(I)” center are stored in a uranium-arene δ -bond, similar to complex **5**.

Remarkably, complex **5** effects the reductive coupling of pyridine affording complex **7**, which shows that the two electron-transfer is accompanied by ligand migration, restoring the 3:3 ligand arrangement found in **4**. Complex **7** reacts further at room temperature to yield an unprecedented metal mediated pyridine C–C cleavage and ring opening complex **8**.

Finally, the results presented provide a new method to control the redox reactivity in molecular complexes of unstable low-valent metal centers and should lead to the further development of *f*-elements redox reactivity.

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Keywords: redox-active ligands • uranium • siloxides • arenes • low valent uranium

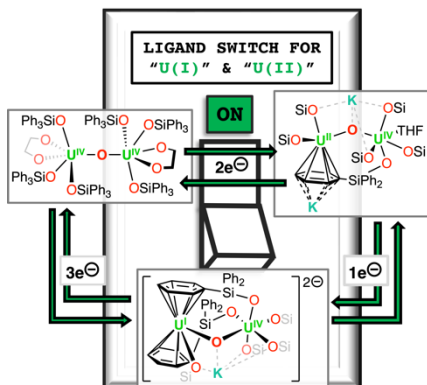
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RESEARCH ARTICLE

Entry for the Table of Contents



Low valent uranium can be stabilized via an unprecedented mechanism involving intramolecular ligand migration: the two- and three-electron reduction of the oxo-bridged U(IV)/U(IV) complex, $[(\text{Ph}_3\text{SiO})_3(\text{DME})\text{U}]_2(\text{O})$, yields formal "U(II)"/U(IV) and "U(I)"/U(IV) complexes, via ligand migration and formation of uranium-arene δ -bond interactions, that can transfer up to three electrons to substrates by restoring the original ligand arrangement.

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