Uranium Arenes

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A Formal High Oxidation State Inverse-Sandwich Diuranium Complex: A New Route to f-Block-Metal Bonds**

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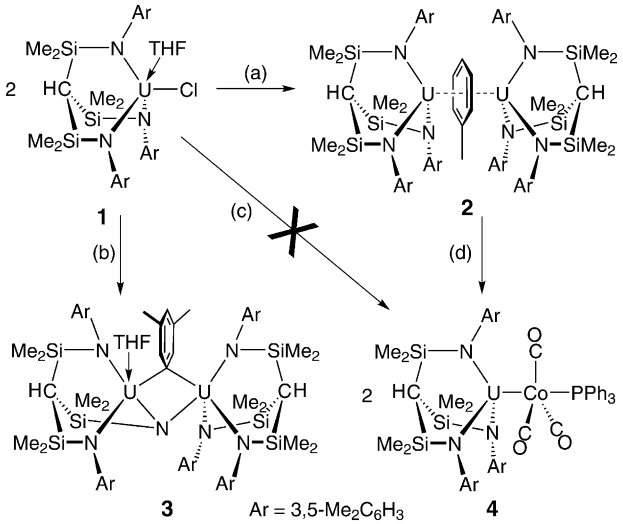
Although uranium–π-arene interactions were once viewed as essentially ionic with little metal–based orbital contributions,[1] covalent δ-backbonding is now recognized as a key contribution to the bonding. Three classes of uranium arene complex are known: 1) a neutral arene η^6-bound to uranium(III);[2] 2) a neutral arene η^6-coordinated to uranium(IV) in cationic complexes;[3] 3) a μ-η^6:η^6-arene bridging two uranium centers in $[(L_2U)_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-arene})]$.[4] The latter group is particularly intriguing since, at one extreme, two U^{II} centers and a neutral arene can be invoked to describe these systems, whereas at the other extreme two U^{IV} atoms with an arene tetraanion can be postulated. However, on the basis of experimental and computational data these type (3) complexes are best described as two U^{III} centers bridged by an arene dianion.[4] Thus, uranium arene complexes exclusively involve low-valent uranium or employ the additional coulombic stabilization afforded in cationic complexes. The paucity of neutral, high oxidation state uranium arene complexes poses fundamental questions as to their viability and the likely extent of δ-backbonding.

We have been investigating the use of triamido uranium complexes to probe their reactivity and access uranium–metal bonds.[5] Routes to uranium–metal bonds include salt, amine, and alkane elimination,[5,6] but new methods are desirable to expand the limited range. We sought to prepare and establish the properties of a triamido $[(L_3U)_2(\text{arene})]$ compound as this formulation represents a new class of neutral, high oxidation state inverse-sandwich diuranium complex and could provide new synthetic routes to uranium–metal bonds. Here, we show that reduction of $[U(Ts^{Xy})(Cl)(thf)]$ [**1**, $Ts^{Xy} = HC(SiMe_2NAr)_3$; $Ar = 3,5\text{-}Me_2C_6H_3$] in toluene gives the inverse-sandwich diuranium complex $[\{U(Ts^{Xy})\}_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_5Me)]$ (**2**). Data for **2** suggest the presence of a toluene tetraanion and two U^{V} centers rather than the anticipated toluene dianion/U^{IV} formulation. In contrast, reduction of **1** in hexane gives $[U\{HC(SiMe_2Ar)_2(SiMe_2\text{-}\mu\text{-}N)\}(\mu\text{-}\eta^1\text{:}\eta^1\text{-Ar})U(Ts^{Xy})]$ (**3**) as a result of reductive C–N bond activation, and magnetization data for this complex suggest it exhibits an unusual example of ferromagnetic coupling between uranium centers. In a preliminary reactivity study, the synthetic redox utility of **2** is demonstrated by the synthesis of the first example of a molecular U–Co bond in $[U(Ts^{Xy})Co(CO)_3(PPh_3)]$ (**4**) (Scheme 1).

Treatment of green **1** with KC_8 in toluene immediately afforded a dark red solution from which red-brown crystals of **2** were isolated in 65% yield following work-up.[7] The ^{1}H NMR spectrum of **2** spans the range +35 to −38 ppm; the methine protons resonate at −38.1 ppm (cf. −65.3 ppm for **1**) and the toluene resonances were identified at +34.2, −16.7, −32.6, and −37.0 ppm. The upfield resonances correspond to the aryl protons and the downfield resonance to the methyl group.



Scheme 1. Synthesis of **2**–**4**. Reagents: a) toluene, $2\,KC_8$, $-2\,KCl$; b) hexane, $2\,KC_8$, $-2\,KCl$; c) THF, diethyl ether, DME, or toluene, $2\,Na[Co(CO)_3(PPh_3)]$; d) toluene, $[Co_2(CO)_6(PPh_3)_2]$, −toluene.

The structure of **2** was determined by X-ray diffraction and this is illustrated in Figure 1.[7] Each uranium center is coordinated by a tridentate triamido Ts-ligand and in an η^6-mode to the bridging toluene molecule which is essentially planar. The U–C bonds are long and span the range 2.651(4)–2.698(4) Å, which compares to U–C_{arene} ranges of 2.503(9)–2.660(8) and 2.553(7)–2.616(7) Å reported for $[\{U[N(R)Ar]_2\}_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_5Me)]$ (R = adamantyl; Ar = 3,5-dimethylphenyl)[4a] and $[\{U(BIPM^{TMS}H)(I)\}_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_5Me)]$ [$BIPM^{TMS}H = CH(PPh_2NSiMe_3)_2$].[4e] The average toluene C–C distance was determined to be 1.440(6) Å. Thus, the arene undergoes a modest (0.024 Å) increase in the

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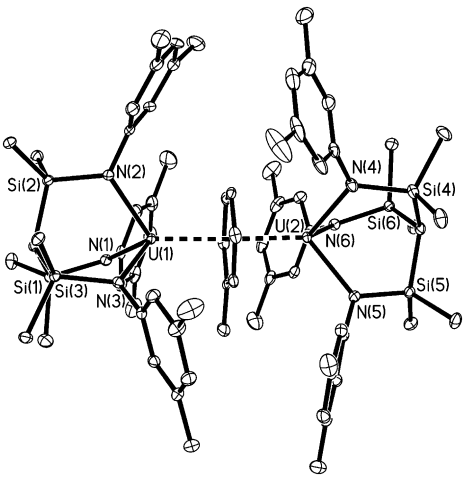

Figure 1. Molecular structure of **2**. Displacement ellipsoids set to 30% with selective labeling and hydrogen atoms omitted for clarity. Selected bond lengths [Å]: U(1)–N(1) 2.239(3), U(1)–N(2) 2.223(3), U(1)–N(3) 2.216(3), U(2)–N(4) 2.226(4), U(2)–N(5) 2.212(3), U(2)–N(6) 2.233(3), U(1)–C(33_{ipso}) 2.689(4), U(1)–C(34_{orth}) 2.666(4), U(1)–C(35_{meta}) 2.668(4), U(1)–C(36_{para}) 2.652(4), U(1)–C(37_{meta}) 2.672(4), U(1)–C(38_{ortho}) 2.690(4), U(2)–C(33_{ipso}) 2.698(4), U(2)–C(34_{orth}) 2.673(4), U(2)–C(35_{meta}) 2.651(4), U(2)–C(36_{para}) 2.681(4), U(2)–C(37_{meta}) 2.686(4), U(2)–C(38_{ortho}) 2.686(4).

average C–C distance upon complexation, compared to free toluene,[8] and, therefore, its charge cannot be inferred from these data alone. The U–N bonds average 2.225(3) Å which can be considered short, assuming a U^{IV} oxidation state.[9]

To gain further insight into the nature of **2** we carried out unrestricted DFT calculations on the whole molecule (Figure 2). The α-spin HOMO and HOMO−1 of **2** are each singularly occupied essentially pure f-orbitals which are delocalized across both uranium centers. The α-spin HOMO−2 and HOMO−3 orbitals, and their β-spin counterparts, are δ-backbonding with respect to the uranium and toluene carbon ring atoms. The α-spin HOMO−2 (411*a*) comprises 35.9% carbon 2p, 44.2% uranium 5f and 5.5% uranium 6d character, whilst the α-spin HOMO−3 (410*a*) is composed of 40.0% carbon 2p, 42.5% uranium 5f and 6.7% uranium 6d contributions. These compositions suggest a covalent interaction between the uranium fragments and the bridging toluene ligand. The Nalewajski–Mrozek U–C bond indices average 0.40 and span the range 0.32–0.48. Charge donation to the uranium centers by the ligands is suggested by an average uranium computed Mulliken charge of +3.00. The computed charge on the bridging toluene molecule is −4.47, consistent with significant U→arene charge transfer. This computed charge is considerably larger than calculated for type (3) arene complexes (ca. −2.2).[4] In addition, the computed spin densities for each U center in **2** are 1.18. Thus, DFT calculations of **2** suggest a formal description of two f^1 U^V centers bridged by a toluene tetraanion.

In order to corroborate the DFT calculations we examined the electronic absorption spectrum of **2** in toluene over the range 5000–25000 cm^{-1}.[7] The spectrum is dominated by strong bands between 25000 to 7500 cm^{-1} which are most likely derived from charge transfer or π–π*/π*–π* transitions.[10] A clearly separated sharp peak at 6815 cm^{-1} ($\varepsilon = 120\,M^{-1}cm^{-1}$) is characteristic of U^V,[11] and is assigned to a $\Gamma_7 \rightarrow \Gamma_7'$ transition, assuming effective C_s symmetry at each uranium center. The extinction coefficient for this transition is larger than for O_h UBr_6^- ($22\,M^{-1}cm^{-1}$)[12] and pseudo O_h [U{C(PPh$_2$NSiMe$_3$)$_2$}(Cl)$_2$(I)] ($\varepsilon = 35\,M^{-1}cm^{-1}$),[11h] but lower than observed for the approximately C_s symmetric metallocenes [(η^5-C$_5$Me$_5$)$_2$U(X)(NAr)] (X = halide; Ar = bulky aryl; $\varepsilon = 200$–$400\,M^{-1}cm^{-1}$).[11c,d]

Variable temperature magnetic moment measurements of **2** (Figure 3) showed a magnetic moment of 3.39 μ_B at 300 K, which decreases to 0.84 μ_B at 1.8 K, and this behavior is typical for U^V.[11] The moment of **2** at 300 K is below the theoretical value of 3.59 μ_B for two independent $^2F_{5/2}$ uranium centers. However, a clear-cut trend linking U^V orbital magnetism with ligand donor/acceptor properties has yet to emerge.[13] The magnetic moment of **2** does not tend to zero, which would be the case if **2** contained U^{IV}.[11]

Taken together, the structural, DFT, spectroscopic, and magnetic data are in agreement with each other and suggest the surprising conclusion that **2** contains two formal U^V centres bridged by a toluene tetraanion through two δ-bonds, rather than U^{IV} bridged by a toluene dianion.

In an attempt to trap the putative trivalent [U(Ts^{Xy})] intermediate in the formation of **2** we carried out the reduction of **1** in hexane (Scheme 1). However, complex **3** was consistently isolated in 65% yield as red crystals and has been fully characterized.[7] Complex **3** is the product of reductive C–N bond activation where one amide-*ipso*-carbon

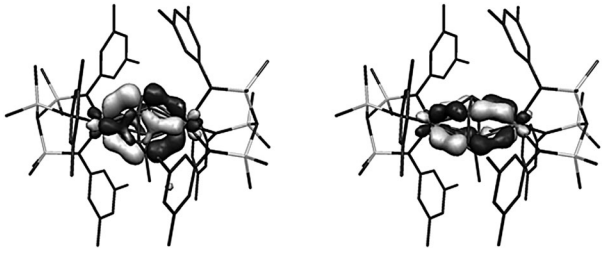

Figure 2. α-Spin Kohn–Sham orbital representations of the two δ-bonds in **2** of: a) HOMO−2 (411*a*, −3.670 eV); b) HOMO−3 (410*a*, −3.766 eV).

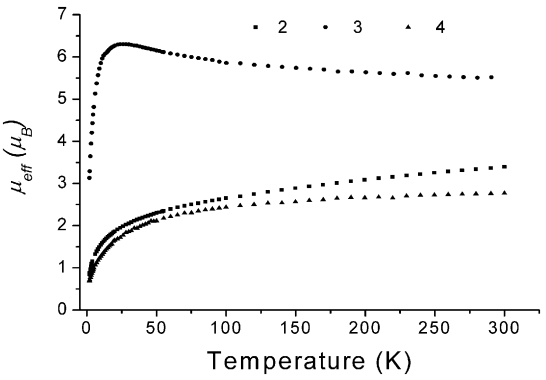

Figure 3. Variable-temperature magnetic moment data for **2**–**4** in the range 1.8–300 K.

linkage is cleaved resulting in a novel dinuclear complex that exhibits bridging aryl[14] and imido groups.[15] Whilst the mechanism of this transformation remains unclear, the facile C–N cleavage in the formation of **3** serves to underscore the high reactivity of uranium(III) and the stabilizing effect of the arene bridge in **2**. Notably, SQUID magnetometry of **3** shows that on cooling from 300 to 1.8 K the magnetic moment rises from 5.52 μ_B to a maximum of 6.30 μ_B at 26 K before falling to 3.13 μ_B at 1.8 K. The moment at 300 K is higher than that expected for two independent $^3H_4$ moments (5.06 μ_B). The Curie and Curie–Weiss constants for **3** are 3.63(2) $cm^3 K mol^{-1}$ and +15.5(9) K, respectively, from which we extracted a tentative exchange coupling constant of $J = +20\ cm^{-1}$.[16] These constants suggest that the uranium centers in **3** exhibit ferromagnetic coupling,[15d,17] and contrast with corresponding values of 2.40(2) and 1.107(4) $cm^3 K mol^{-1}$ and −203(4) and −48.4(7) K for **2** and **4**, respectively.[7]

In a preliminary study to establish the redox utility of **2**,[4,18] we targeted a U–Co bond. Our previous attempts to isolate this linkage using salt elimination failed and reactions between **1** and $Na[Co(CO)_3(PPh_3)]$ under a variety of conditions resulted in decomposition (Scheme 1). This contrasts to a related Zr–Co complex which was straightforwardly prepared using salt elimination.[19] Therefore, we examined the reaction of **2** with $[Co(CO)_3(PPh_3)]_2$ and obtained red blocks of the target U–Co complex **4** in 59% yield (Scheme 1). The formation of **4** results from the reductive cleavage of the cobalt dimer by **2**,[7] whereas polarized-covalent f-block-metal bonds are usually prepared by salt, amine, or alkane elimination.[5a,b,e,f,6,20]

The ^1H NMR spectrum of **4** spans the range +42 to −70 ppm and the methine resonance was observed at −69.9 ppm. The magnetic moment of **4** (Figure 3) was found to be 2.77 μ_B at 298 K. This decreases to 0.69 μ_B at 1.8 K and is consistent with the presence of a U^{IV} center in **4**. The FTIR spectrum of **4** exhibits one υ_{CO} band at 1903 cm^{-1} which reflects Co–CO backbonding that is tempered by polarization of charge within the cobalt anion towards uranium.[19]

Crystals of **4** suitable for X-ray diffraction were obtained from hexane and the structure is depicted in Figure 4a.[7] The uranium center in **4** is coordinated to the triamido Ts^{Xy} ligand and the cobalt atom of the $[Co(CO)_3(PPh_3)]^-$ ion and thus adopts a distorted tetrahedral geometry. Complex **4** exhibits crystallographic three-fold symmetry along the C(1)-U(1)-Co(1)-P(1) vector. The three carbonyl groups are tilted towards the uranium center [U-Co-C $\sphericalangle = 81.0(2)°$] but the U···$C_{CO}$ distances [3.183(7) Å] do not suggest any significant interactions. The U–Co bond length is 2.9450(9) Å. There are no other molecular U–Co distances with which to compare this value to, but the sum of the covalent radii for uranium and cobalt is 2.81 Å.[21] The formal shortness ratio (FSR_{UCo}),[22] defined as $FSR_{UCo} = D_{UCo}/(R_U + R_{Co})$ (where D_{UCo} is the U–Co bond length and the R values are the atomic radii of uranium and cobalt), of **4** is 1.05. This is comparable to the FSR_{ZrCo} value of 1.00 for $[ICo\{\mu\text{-}RNP(iPr)_2\}_3ZrCl]$ (R = 2,4,6-$Me_3C_6H_2$ or *i*Pr) which exhibit single, dative Co→Zr interactions.[23] The U(1)–N(1) bond of 2.153(7) Å is shorter than the corresponding U–N bonds in **2** but this may reflect the low-coordinate nature of the uranium center in **4**.

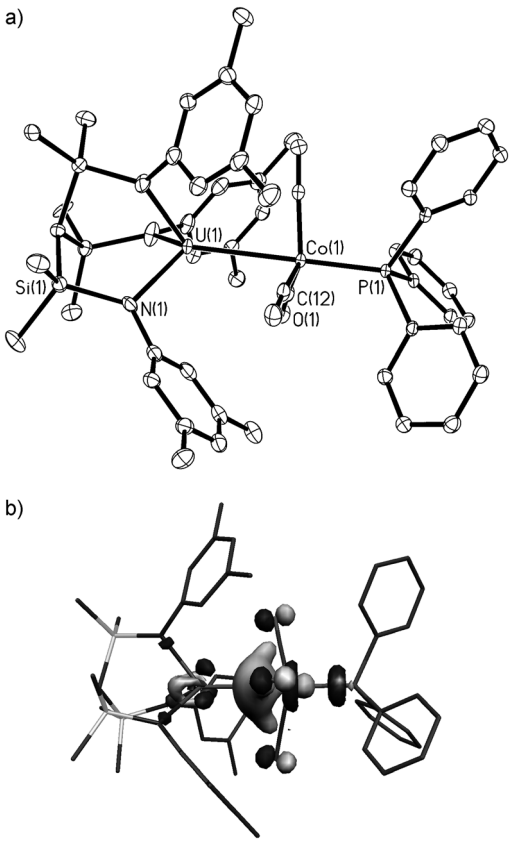

Figure 4. a) Molecular structure of **4**. Displacement ellipsoids set to 30% with selective labeling. Hydrogen atoms and disorder components omitted for clarity. Complex **4** resides on a crystallographic three-fold rotation axis intersecting the C(1)-U(1)-Co(1)-P(1) axis. Selected bond lengths [Å]: U(1)–N(1) 2.153(7), U(1)–Co(1) 2.9450(9), Co(1)–P(1) 2.1892(17), Co(1)–C(12) 1.753(4), C(12)–O(1) 1.166(5). b) α-Spin Kohn–Sham orbital representation of the HOMO−2 of **4** (296*a*, −4.645 eV).

An unrestricted DFT study of **4** revealed the HOMO and HOMO−1 to be singularly occupied, essentially pure f-orbitals as expected for a U^{IV} formulation. The HOMO−2 (Figure 4b) constitutes the primary U–Co interaction and is derived from 27.6% Co $3d_{z^2}$ and 10.3% Co $4p_z$, and 5.0% U $6d_{z^2}$, 2.5% U f_x, 1.6% U 7s, and 1.2% U $7p_z$. The rest of this molecular orbital (28%) is delocalized over the Co–CO, C–O, and Co–P bonds and is bonding with respect to the Co–C bonds but antibonding with respect to the C–O bonds. This orbital interaction most likely provides the mechanism for depleted Co–CO backbonding on coordination to uranium.[24] The Nalewajski–Mrozek U–Co, Co–C, C–O, and Co–P bond indices are 0.45, 0.92, 2.38, and 0.43, respectively, and suggest that electrostatic interactions dominate the U–Co bonding in **4**.[25] This is supported by the calculated U and Co spin densities of 2.30 and 0.02 and Mulliken charges of +1.87 and +0.31, respectively, which show modest charge transfer to uranium.

An energy decomposition analysis of the U–Co bond in **4** yielded Pauli repulsion, electrostatic, steric, and orbital terms of +303.9, −507.1, −203.1, and −197.7 kJ mol^{-1}, respectively. This gives a total U–Co bond interaction energy (BIE) of

$-400.8\,kJ\,mol^{-1}$, which compares to BIEs of ca. $-600\,kJ\,mol^{-1}$ for reported U–Re bonds.[5b,e,f] We employed Bader's Atoms in Molecules to analyze the topological electron density [$\rho(\mathbf{r})$] in the U–Co bond in **4**. For closed-shell interactions the Laplacian of the electron density [$\nabla^2\rho(\mathbf{r})$] is typically positive. The electronic energy density $H(\mathbf{r})$ of the charge distribution is defined as $H(\mathbf{r}) = G(\mathbf{r}) + V(\mathbf{r})$ where $G(\mathbf{r})$ is the kinetic energy density and $V(\mathbf{r})$ is the potential energy. For **4**, the U–Co bond critical point (BCP) values for $\rho(\mathbf{r})$, $\nabla^2\rho(\mathbf{r})$, $G(\mathbf{r})$, $V(\mathbf{r})$, and $H(\mathbf{r})$ are 0.0332, 0.0516, 0.0185, −0.0241, and −0.0056, respectively. These BCP values are typical of a predominantly closed-shell interaction with a largely ionic U–Co interaction.[26]

To summarize, we have reported the first example of a formal high oxidation state inverse-sandwich diuranium complex. The characterization data for **2** suggest the presence of a toluene tetraanion and two U^{V} centers rather than the anticipated toluene dianion/U^{IV} formulation. Despite the formal pentavalent nature of the uranium centers in **2**, two covalent δ-bonds are apparent in the uranium–arene orbital manifold which demonstrates that high valent uranium–arene complexes are accessible with suitable ancillary ligands. Attempts to prepare the putative trivalent [$U(Ts^{Xy})$] resulted in isolation of **3** as a consequence of reductive C–N bond activation and the magnetization data for this complex suggest a very rare ferromagnetic coupling between the two uranium centers. The formation of **3** underscores the high reactivity of U^{III} and the stabilizing effect of the bridging arene in **2**. Preliminary assessment of the synthetic utility of **2** has facilitated a new way to construct f-block-metal bonds by the synthesis of **4** which contains the first example of a molecular uranium–cobalt bond. Notably, **4** could not be prepared by salt elimination and the facile synthesis of **4** using **2** underscores the novelty of the new redox chemistry which **2** presents. We are currently investigating the full scope of the reactivity of **2** and will report on this in due course.

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