JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
Cite This: J. Am. Chem. Soc. 2018, 140, 17369−17373
pubs.acs.org/JACS

Synthesis and Characterization of a Neutral U(II) Arene Sandwich Complex

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Supporting Information

ABSTRACT: Reduction of IU(NHAr^{iPr6})$_2$ (Ar^{iPr6} = 2,6-(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$) results in a rare example of a U(II) complex, U(NHAr^{iPr6})$_2$, and the first example that is a neutral species. Here, we show spectroscopic and magnetic studies that suggest a 5f^{4}6d^0 valence electronic configuration for uranium, along with characterization of related U(III) complexes.

Recent exploration into the available oxidations states of uranium has led to discovery of U(II) complexes.[1−4] So far, two motifs have been reported, and surprisingly, these have had differing valence electron configurations. In the tris(cyclopentadienyl) systems reported by the Evans group, the geometry of the complex enforces a 5f^{3}6d^1 electron configuration.[1] In the tris(aryloxide)−arene system reported by Meyer, a 5f^{4}6d^0 electronic configuration was determined.[2]

It has been established that low valent uranium species can be stabilized through interactions with arenes.[2,5−14] Shown recently, steric bulk of terphenyl substituents might be ideal to protect the large radius of uranium.[15] We found that terphenyl substituents bound through an amide adopt an orientation that allows uranium−η^6-arene interactions. In fact, the complexes prepared are rare examples of uranium bis(arene) sandwich complexes.[16] In this study, investigations were done using the amide HNAr^{iPr6}, where Ar^{iPr6} = 2,6-(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$, as a ligand.[17,18]

Reaction of UI$_3$(THF)$_4$ with two equivalents of NaNHAr^{iPr6} in diethyl ether results in a dark purple solution of IU(NHAr^{iPr6})$_2$ (**1**). In the solid state, **1** is approximately C_2-symmetric (Figure 1). The two amide nitrogens, uranium, and iodide reside in a plane with the sum of the angles between these ligands totaling 359.9(1)°. Additionally, one triisopropylphenyl group from each amide substituent is η^6-bound to uranium along the axis of an approximate trigonal bipyramidal structure. The U−N−C bond angles and U−N bond lengths are all consistent with monoanionic amide ligands. The quality of the data obtained in the crystal structure allowed location and refinement of the N−H hydrogen positions.

The solid-state structure of **1** incorporates an equivalent of solvent of crystallization when prepared from either ether or n-hexane. From ether, the arene attached to N(1) has a U-centroid distance of 2.788(1) Å and the arene attached to N(2) 2.897(1) Å. Crystals grown from n-hexane have similar U-centroid distances at 2.790(1) and 2.776(1) Å. These relatively large changes due to solvent identity suggest shallow potential energy surfaces describing the U−arene interaction.

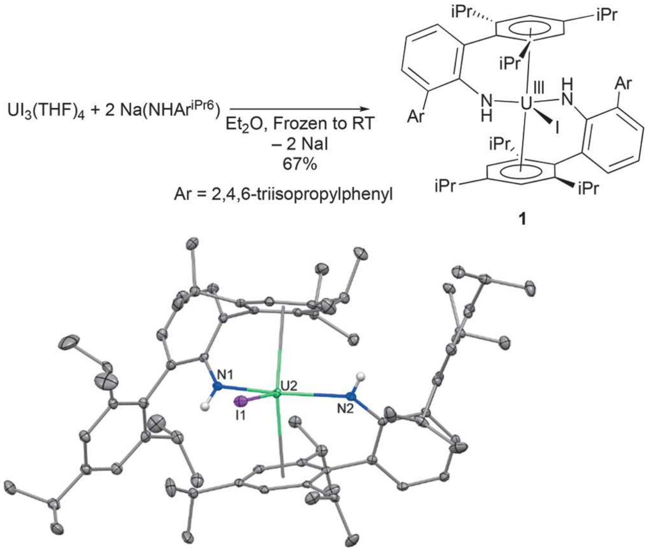

Figure 1. Synthesis of **1** and structure of IU(NHAr^{iPr6})$_2$·hexane from X-ray diffraction. Hydrogens on carbon are not shown. Solvent not shown for clarity. Selected metrical parameters: U−N distances (Å): 2.390(3), 2.372(3). U−Ar(centroid) (Å): 2.777(1), 2.790(1). U−N−C (deg): 137.5(2), 135.6(2).

Ambient temperature ^{1}H NMR spectroscopy only shows signals for solvent of crystallization. However, on cooling the solution to −30 °C, the expected number of signals for the C_2-symmetric molecule become distinguishable between +87 and −82 ppm, consistent with fluxionality of the arene substituents. Compound **1** was also investigated with absorption spectroscopy in the visible and near-infrared. A large absorption in the visible region along with broad but distinct f−f transitions in the near-infrared are consistent with the assignment of **1** as a U(III) species (vide infra).[19]

Abstraction of iodide from **1** with silver or sodium salts did not give clean products. However, reduction of **1** with excess

Received: October 9, 2018
Published: November 30, 2018

DOI: 10.1021/jacs.8b10888

KC_8 in THF (Figure 2) results in generation of a deep green solution of $U(NHAr^{iPr6})_2$ (**2**). Uranium(II) complex **2** is stable both in the solid-state and in solution, especially in comparison to previous U(II) reports.[1,2]

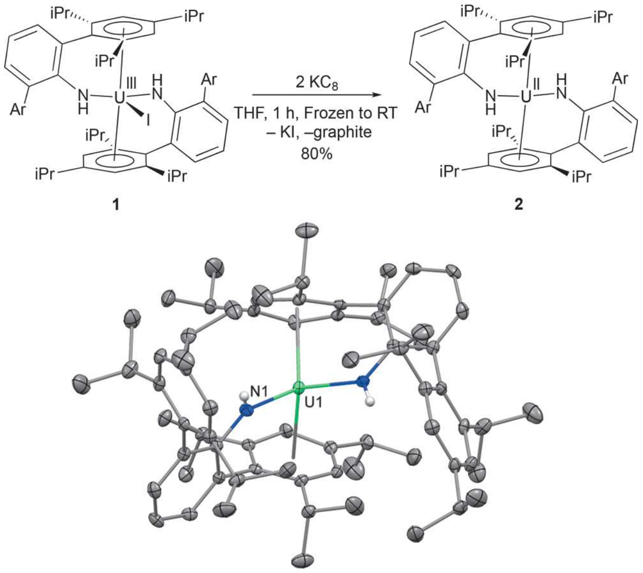

Figure 2. Synthesis of **2** and structure of $U(NHAr^{iPr6})_2 \cdot THF$ from X-ray diffraction. Hydrogens on carbon not shown. Solvent in the lattice is not shown for clarity. The molecule resides on a crystallographic 2-fold axis. Selected metrical parameters: U−N distance (Å): 2.330(2). U−Ar(centroid) (Å): 2.405(1). U−N−C (deg): 130.26(2).

The structural data of **2** were also of high enough quality to locate and refine the N−H hydrogen. The U−N−C angle is 130.2(2)°, consistent with an amide and more acute than any reported terminal uranium−imido bonds.[20] Further, the U−N bond distance of 2.330(2) Å is consistent with the assignment of N1 as a monoanionic amide ligand, $U{-}NHAr^{iPr6}$.

The geometries of **1** (Figure 1) and **2** (Figure 2) are substantially different. The U(II) compound **2** crystallizes as a C_2-symmetric molecule with only half of the molecule occupying the asymmetric unit. On reduction, the U−arene centroid bond distances shorten significantly, from an average of 2.843(1) Å in **1** to 2.405(1) Å in **2**. This contraction is consistent with increased backbonding between U(II) and arene. From **1** to **2**, the (arene centroid)−U−(arene centroid) angle decreases from 158.785(2)° to 134.240(9)°, respectively. Additionally, the N−U−N angle decreases from 149.92(7)° in **1** to 99.22(11)° in **2**. Analysis of the C−C bond lengths in the coordinated arene of **2** shows an avg. C−C bond length of 1.415(4) Å. This is essentially unchanged from both **1** (avg. C−C 1.402(5) Å) and from free H_2NAr^{iPr6}.[21]

The ^1H NMR of **2** displays sharp signals at room temperature, with no detectible fluxionality; this, too, is consistent with a stronger interaction between uranium and arene π-system in **2** relative to **1**. Complete assignment of the NMR spectrum of **2** was complicated by large paramagnetic shifts, but the number of peaks is consistent with a C_2-symmetric molecule with static U−arene bonds on the NMR time scale containing diastereotopic methyl groups within the *iso*-propyl substituents.

Absorption spectroscopy in the visible to near-infrared on **2** in ether is mostly featureless except for a strong absorption at 400 nm and a very broad absorption at ~600 nm. The spectrum of **2** is similar to that observed by the Meyer group for their uranium(II) species.[2] The absorptions in this region, when present, are generally assigned to f−f transitions. The absence of noticeable features in the near-infrared for the U(II) complex may be indicative of higher bonding participation of the f-orbitals in **2**, which would be expected to lead to peak broadening as the f-orbitals hybridize with other valence orbitals and interact with ligand orbitals. In addition, the Evans group notes intense transitions due to 6d to π^*/5f excitations consistent with their proposed $6d^15f^3$ configuration; these intense absorptions are absent from our spectrum of **2**.

Reaction of **2** in ether with $[FeCp_2][BArF_{24}]$ (Figure 3) results in a rapid color change from green to brown and production of uranium(III) $[U(NHAr^{iPr6})_2][BArF_{24}]$ (**3**), where $BArF_{24}^- = B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$. The metrical parameters of **3** are intermediate between **1** and **2**. The distances between the uranium and η^6-arene centroids are 2.570(3) and 2.583(3) Å. The (arene centroid)−U−(arene centroid) and N−U−N angles also fall between those of **1** and **2** at 145.8(1)° and 111.2(2)°, respectively. The uranium arene distances in **1** seem to be affected by the large radius of the iodide, which seems to pry apart the bulky Ar^{iPr6} groups when compared with the cationic **3** (Figure 3, bottom).

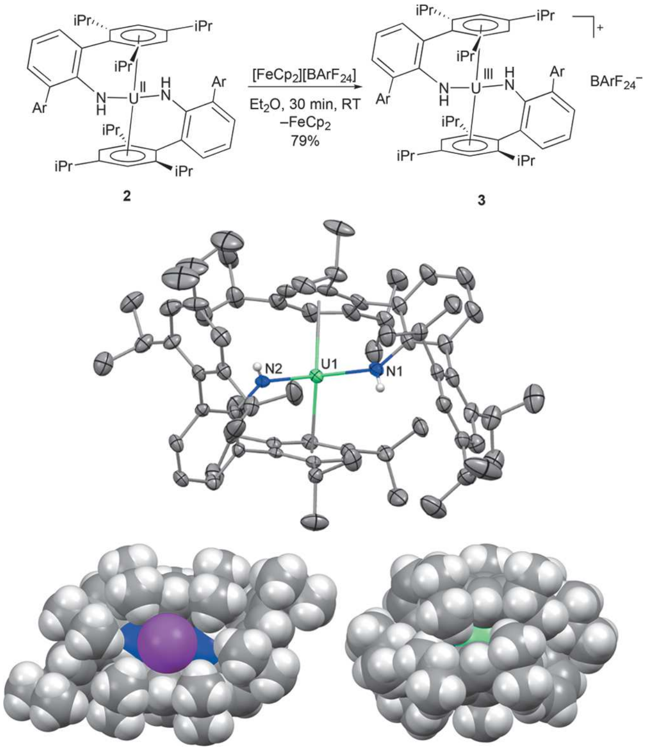

Figure 3. Synthesis **3** and structure of $[U(NHAr^{iPr6})_2][BArF_{24}] \cdot OEt_2$ from X-ray diffraction. Hydrogens on carbon are not shown. A solvent molecule in the lattice and counterion are not shown for clarity. At the bottom are space filling structures of uranium(III) complexes $IU(NHAr^{iPr6})_2$ (**1**) (left) and $[U(NHAr^{iPr6})_2]^+$ (**3**) (right). Selected metrical parameters for **3**: U−N distances (Å): 2.283(6), 2.282(6). U−Ar(centroid) (Å): 2.573(3), 2.583(3). U−N−C (deg): 133.5(5), 131.6(5).

The ^1H NMR spectrum of **3**, contrary to **1**, does not show fluxionality in the uranium−arene interactions. It is worth mentioning, however, that **3** was insoluble in many common solvents. To solubilize **3**, we used THF-d_8, and the compound reacts with this solvent slowly. Surprisingly, dissolving **3** in toluene resulted in a color change from brown to bright red. The uranium(III) cation apparently decomposes in this solvent; however, attempts at characterization of the products yielded colorless crystals containing the $BArF_{24}^-$ anion with an unresolvable cation, as well as crystals of H_2NAr^{iPr6}. In fact, **3** is unstable under most conditions. Even when isolated as crystals and kept in an inert atmosphere at 238 K, samples of **3** decompose in just a few days.

The X-band EPR spectrum of **1** collected at 6 K (Figure 4a) shows well-resolved peaks at g = 5.17 and g = 4.56 that are better shown in the inset. These were the only peaks resolved over a field range that extended from 50 to 850 mT (g = 13 to g = 0.8). While broad features at higher fields were observed in our spectra (Figure 4a), they could not be distinguished from typical baseline distortions that remain after subtracting background contributions.

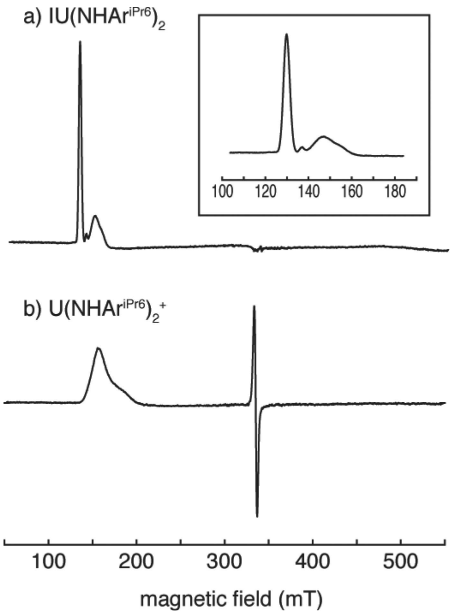

Figure 4. EPR spectra of (a) $IU(NHAr^{iPr6})_2$ (**1**) and (b) $[U(NHAr^{iPr6})_2][BArF_{24}]$ (**3**). Measurement parameters for both spectra were: microwave frequency = 9.40 GHz, microwave power = 0.79 mW; field modulation amplitude = 1 mT; and sample temperature = 6 K.

No EPR response was detected for **2** in either perpendicular or parallel detection modes at 6 K. Absence of a signal here supports our assignment of **2** as a U(II) species with neutral arene substituents.

The EPR spectrum of **3** collected at 6 K is provided in Figure 4b and shows a broad peak at g = 4.3 with a shoulder at g = 3.6. A resonance with a narrower line shape was also resolved at g = 2.003. The resonance at g = 2.003 is unusual because its narrow line shape makes it unlikely that it arises from the U(III) paramagnetic center. This signal was observed in three separate preparations of **3** that were carried out in two different solvents. It is possible that oxidation of **2** resulted in a species best described as a U(III) center, but with a small contribution of U(II) and ligand radical, or a small contribution from solvent radical. The EPR spectra of **1** and **3** bear a modest resemblance to those reported for a series of tris(cyclopentadienyl)U(III) complexes by Lukens and co-workers.[22] However, in that study, the low-field features of the EPR spectrum were resolved over a g-value range from 3.0 to 2.4, as opposed to the g = 5.2−4.3 range found for **1** and **3**. The significance of these differences in terms of the electronic structure of the actinide ion will require further investigation.

Solution state magnetic susceptibility studies were carried out on **2** using the Evans method. The resulting temperature dependent paramagnetism was determined in 10 K intervals from 299 to 219 K in d_8-toluene with hexamethyldisiloxane as a reference. At room temperature, the effective magnetic moment value of **2** is 0.78 cm^3 K mol^{-1} (μ_{eff} = 2.50), which decreases slightly to 0.72 cm^3 K mol^{-1} (μ_{eff} = 2.40) at 219 K.

Solid-state magnetic properties of **1**−**3** were also probed by SQUID magnetometry (Figure 5). While the magnetic moments for **1** and **3** are significantly different, both are in the range for previously reported U(III) complexes,[2,12,23] see the SI for more details. The magnetic susceptibility for the divalent species, **2**, at 300 K is $\chi_M T$ = 0.67 cm^3 K mol^{-1} (μ_{eff} = 2.32). Upon decreasing the temperature, the $\chi_M T$ value decreases monotonically until ~100 K, where the decrease becomes more dramatic; at 2 K, $\chi_M T$ = 0 cm^3 K mol^{-1} (μ_{eff} = 0). The temperature dependent profile of **2** tracks lower in the solid state than in solution. Differences observed between solution and solid-state behavior are common given the very different environments. For the one other U(II) species where magnetic studies were done in solution and the solid state, the solid state susceptibilities also tracked lower than the solution values.[2] The solid-state behavior is similar to what was observed for previously published U(II) complexes, although the downturns for the other U(II) complexes are observed at lower temperatures (~15−20 K) compared to **2**.[2,3] Similar to the other two complexes reported previously, the magnetic susceptibility approaches 0 cm^3 K mol^{-1} (μ_{eff} = 0) at low temperature, suggestive of an integer spin system where spin−orbit coupling leads to a ground state singlet. This agrees with the absence of an EPR signal in **2**. While not diagnostic, the temperature profile for **2** is qualitatively similar to Meyer's U(II) complex (Figure S14).[2]

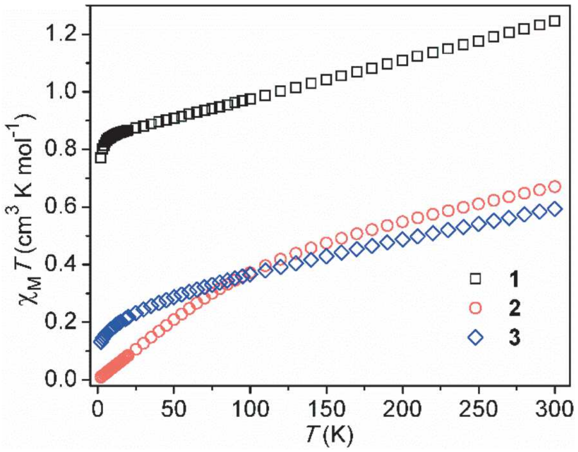

Figure 5. Temperature dependence of the magnetic susceptibility for **1**−**3**, collected at 5000 Oe.

In summary, the Ar^{iPr6} ligands allowed isolation of a neutral U(II) complex, $U(NHAr^{iPr6})_2$ (**2**), where the large arenes act as η^6-donors toward the metal center. Analysis of **2** by visible-NIR absorption spectroscopy, SQUID magnetometry, and EPR spectroscopy are consistent with a $5f^4 6d^0$ electron configuration. EPR spectroscopy and magnetometry studies clearly display integer spin properties expected from a U(II) center. This suggests that the 3-fold symmetrical tris(cyclopentadienyl) coordination environments employed by the Evan's group may impart the unexpected $5f^36d^1$ electronic configuration in $[U(Cp)_3]^-$.[1,3,4] In addition, two uranium(III) complexes with $NHAr^{iPr6}$ ligands were prepared, $IU(NHAr^{iPr6})_2$ (**1**) and $[U(NHAr^{iPr6})_2]^+$ (**3**). The uranium(II) complex has metrical parameters consistent with much stronger U−arene interactions than these U(III) complexes, presumably due to stronger metal−arene backbonding in the lower oxidation state.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b10888.

Synthetic details, spectra (NMR, absorption, EPR), and magnetic property details (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.
CCDC deposition numbers 1870051, 1870052, 1870053, and 1870054 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.

■ ACKNOWLEDGMENTS

B.S.B. acknowledges support from the DOE Office of Science Graduate Student Research (SCGSR) program. J.M.B. acknowledges support from the DOE Office of Science through the Heavy Element Chemistry program for X-ray crystallography and spectroscopy at LANL as well as Materials and supplies for B.S.B. We thank the National Science Foundation for financial support (CHE-1562140 for A.L.O. and B.S.B; CHE-1800554 for M.P.S. and B.N.L). We thank Dr. R. F. Higgins for helpful conversations on uranium magnetism. A.L.O. and B.S.B. thank Remi Beaulac for helpful discussion and use of his UV−vis-NIR instrument.

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DOI: 10.1021/jacs.8b10888
J. Am. Chem. Soc. 2018, 140, 17369−17373