Arene-Bridged Diuranium Complexes: Inverted Sandwiches Supported by δ Backbonding

Paula L. Diaconescu, Polly L. Arnold, Thomas A. Baker,
Daniel J. Mindiola, and Christopher C. Cummins*

Department of Chemistry Room 2-227
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139-4307

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Treatment of $U(I)(N[R]Ar)_3$[1] ($R = C(CH_3)_3$, $Ar = 3,5\text{-}C_6H_3\text{-}Me_2$) with KC_8 in toluene has been found to provide an inverted sandwich compound in which a toluene molecule bridges two uranium bis-amido fragments in a symmetrical η^6,η^6 fashion. Compound **1**, $(\mu\text{-}C_7H_8)[U(N[R]Ar)_2]_2$, is obtained reproducibly in ca. 40% isolated yield on scales of ca. 500 mg as a dark brown crystalline substance. To facilitate assignment of the NMR spectrum of paramagnetic **1**, the deuterated variant **1**-d_8 was prepared by carrying out the synthesis in toluene-d_8. The four resonances for the bound toluene were thereby identified at +18.7, −65.0, −83.6, and −88.8 ppm in the ^2H NMR spectrum of the compound, the high-field resonances being assigned to the aryl deuterons and the downfield signal signifying the deuteriomethyl group.

It was found also that benzene-bridged diuranium compounds could be obtained by carrying out the KC_8 reaction in benzene or benzene-d_6. A single peak was observed at −81.5 ppm in the ^2H NMR spectrum of $(\mu\text{-}C_6D_6)[U(N[R]Ar)_2]_2$, in accord with the chemical shift assignments for **1**. Furthermore, an *N*-1-adamantyl derivative $(\mu\text{-}C_7H_8)[U(N[Ad]Ar)_2]_2$ (**1b**) likewise was obtained upon KC_8 treatment in toluene of uranium(IV) precursor $U(I)(N[Ad]Ar)_3$, or in low yield from the reaction of $UI_3(THF)_4$[2] with $Li(N[Ad]Ar)(OEt_2)$.[3,4]

Structural data were obtained for derivative **1b** by single-crystal X-ray crystallography. Accordingly the average C−C distance for the bridging toluene molecule was determined to be 1.438(13) Å. Thus the arene undergoes a slight (ca. 0.04 Å) increase in d_{C-C} upon complexation, relative to free toluene.[5] Noteworthy are the short uranium−carbon distances, averaging in the experimentally determined structure to 2.593(9) Å, the shortest such distance being U(2)−C(3) at 2.503(9) Å, and the longest being 2.660(8) Å for U(1)−C(3). The latter two outlying distances reflect the fact that C(3) is displaced slightly from the mean plane of the complexed toluene molecule.

Known uranium complexes of benzene or its derivatives tend to exhibit significantly longer U−C bond lengths. An example of this is $U(\eta^6\text{-}C_6Me_6)(BH_4)_3$,[6] a uranium(III) complex exhibiting a mean d_{U-C} value of 2.93(2) Å. The latter complex can be prepared from its benzene analogue $U(\eta^6\text{-}C_6H_6)(BH_4)_3$ by treatment with hexamethylbenzene, indicating that the more electron rich arene is the better ligand for uranium(III). The related tetrachloroaluminate derivative $U(\eta^6\text{-}C_6H_5Me)(AlCl_4)_3$ displays similarly long bonds involving its toluene ligand, the mean U−C bond length in this case being 2.94(1) Å.[7]

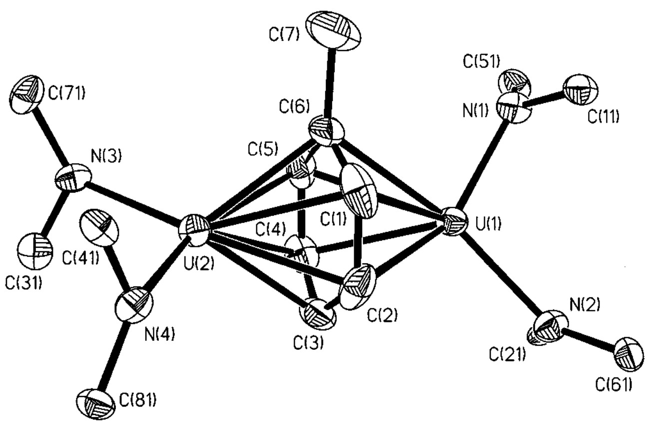

Figure 1. Structural drawing of complex **1b**. Bulky peripheral substituents are omitted for clarity. Selected bond distances (Å): U−C(av), 2.594(9); U−N(av), 2.334(6); C−C(μ-toluene, av), 1.438(13).

Shorter uranium−carbon distances are found in cases where a C_nH_n ring interacting with uranium carries a formal charge. For example, in uranocene the $\eta^8\text{-}C_8H_8^{2-}$ ligand exhibits an average d_{U-C} of 2.647(10) Å,[8] while in $U(\eta^5\text{-}C_5H_5)_4$ the $\eta^5\text{-}C_5H_5^-$ ligands evince an average d_{U-C} value of 2.807(18) Å.[9] In the latter two cases, the ligating ring requires negative charge to achieve Hückel aromaticity,[10] explaining on electrostatic grounds the relatively short U−C bond lengths.

Transition metal systems in which benzene or toluene bridges two metal centers in a symmetrical η^6,η^6 fashion are rare,[11] an example being $(\mu\text{-}C_6H_6)[V(\eta^5\text{-}C_5H_5)]_2$.[12]

Formulation of compound **1** as $(\mu\text{-}C_7H_8)[U(N[R]Ar)_2]_2$ suggests various possibilities for the uranium valency. One extreme requires a formally divalent uranium center[13,14] with a neutral arene bridge, while another invokes trivalent uranium with an arene dianion.[15] The chemical reactivity of compound **1** is consistent with the formality of divalent uranium, inasmuch as **1** behaves as a 4e reductant, giving rise to uranium(IV) derivatives and extruding neutral toluene upon reaction with appropriate substrates.

Treatment of **1** with Ph_2S_2 (2 equiv) in cold pentane led to a rapid color change to yellow. The yellow compound was isolated in 74% yield and was determined via X-ray crystallography to be the dimeric thiolate-bridged uranium(IV) derivative $[U(\mu\text{-}SPh)(SPh)(N[R]Ar)_2]_2$ (**2**). No gases were evolved in the reaction of **1** with Ph_2S_2, according to a Toepler pump experiment.[16]

Similarly, treatment of **1** with azobenzene (1 equiv) in cold *n*-hexane led to a reaction that was complete in less than 15 min. A red crystalline compound was thereby obtained in 67% isolated

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[15] Further studies employing techniques such as XANES will be of interest for determining the actual degree of oxidation of the uranium centers in complex **1**. See, for example: DenAuwer, C.; Madic, J.; Berthet, J. C.; Ephritikhine, M.; Rehr, J. *J. Radiochim. Acta* **1997**, *76*, 211.

[16] Although the formulation of compound **1** as indicated in the text and in Figure 2 is entirely consistent with the data in hand, it is difficult to rule out the possibility that compound **1** might contain unobserved hydride ligands. If such were the case, however, the reaction of **1** with Ph_2S_2 would be expected to occur with production of H_2. This is not the case, as evidenced by the Toepler pump experiment showing that no gases are evolved in the course of said reaction.

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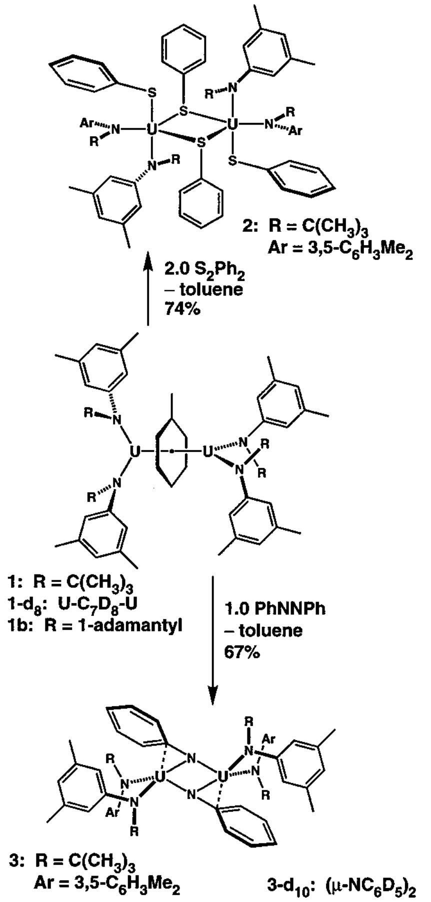

Figure 2. Reactions of compound **1** with azobenzene and diphenyl disulfide.

yield, formulated as the uranium(IV) phenylimido-bridged dimer $[U(\mu\text{-}NPh)(N[R]Ar)_2]_2$ (**3**) by virtue of a single-crystal X-ray diffraction study. When said reaction was carried out with azobenzene-d_{10}, NMR spectral assignment was facilitated, three signals being observed in the ^{2}H NMR spectrum of **3**-d_{10} at −6.45, −7.86, and −43.06 ppm. Toluene extrusion in the azobenzene reductive cleavage reaction was ascertained by treating **1**-d_8 with $[N(C_6H_5)]_2$ in hexamethyldisiloxane solvent with octane-d_{18} present as an internal integration standard. Integration of the ^{2}H NMR spectrum of the crude mixture indicated production of ca. 0.75 equiv of C_7D_8. Azobenzene reductive cleavage to form bis-phenylimido derivatives represents an intriguing N−N bond cleavage process, few examples of which have been reported previously.[13,17−19]

The calculated structure of $(\mu\text{-}C_6H_6)[U(NH_2)_2]_2$ (constrained to D_2 symmetry, see caption to Figure 3) reproduced the key features of the structure of **1b** quite closely.[20] Electrons 1−4, the four most energetic electrons in the system, were found to be uranium-based and nonbonding in character. Electrons 5−8, however, were found to be stabilized via bonding interactions involving uranium 6d and 5f orbital participation, and participation of the benzene LUMO. Stabilization of four electrons in this manner is consonant with two δ symmetry backbonds from the formal uranium(II) centers to the formally neutral benzene molecule. The δ backbonding molecular orbitals are of a and b_1 symmetry types. In the limit of complete transfer of electrons 5−8 from the two U centers to the bridging arene, uranium would attain the +4 oxidation state and the bridging ligand would be [arene]$^{4-}$. That the δ bonding interactions in question are expected to be quite covalent is indicated by the appearance of the contour plots in Figure 3. In related work, Bursten has implicated a metal−ring δ interaction in the bonding scheme for $[U(\eta^7\text{-}C_7H_7)_2]^-$,[21] while this type of interaction is seen also to be important for metal−ring binding in $Ti(\eta^8\text{-}C_8H_8)(N^tBu)$.[22] Similar electronic structure considerations presumably also apply to the inverse sandwich compounds reported by Ephritikhine and co-workers, compounds featuring two uranium centers bridged by a $[\eta^7\text{-}C_7H_7]$ ring.[23,24]

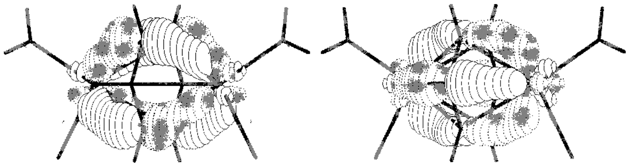

Figure 3. Two near-degenerate δ symmetry back-bonding orbitals, from an ADF geometry-optimization calculation on $(\mu\text{-}C_6H_6)[U(NH_2)_2]_2$ in idealized D_2 symmetry.[20] Selected calculated bond distances (Å): U−C, 2.569; U−N, 2.216; C−C, 1.461.

Because of their high nodality,[25] f orbitals can be construed as ill-suited for π-back-bonding, such a construct being in accord with the paucity of N_2[1,26−28] and CO[29−31] complexes of the early actinide elements. On the other hand, the results reported herein suggest that δ symmetry backbonding represents a vehicle for gaining access to a divalent uranium synthon in the context of arene binding.

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Supporting Information Available: Full synthetic details and spectroscopic data for all new compounds, full X-ray structural details for compounds **1b**, **2**, and **3**, and details of the computational study (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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