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Uranium Chemistry

Comparison of the Reactivity of 2-Li-$C_6H_4CH_2NMe_2$ with MCl_4 (M = Th, U): Isolation of a Thorium Aryl Complex or a Uranium Benzyne Complex**

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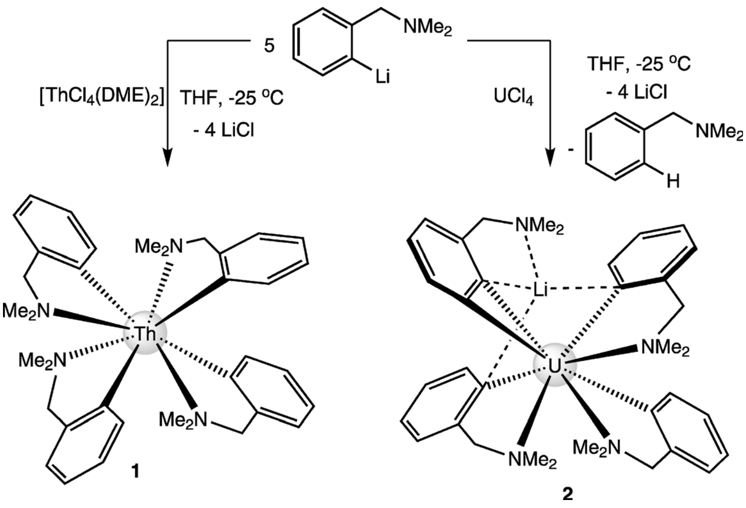
Transition-metal benzyne complexes exhibit a rich small-molecule chemistry, with potential application in organic synthesis.[1] For example, the prototypal benzyne complex, $[Cp_2Zr(\eta^2\text{-}C_6H_4)]$ ($Cp = \eta\text{-}C_5H_5$), formed by benzene elimination from $[Cp_2Zr(C_6H_5)_2]$,[1a,2] undergoes insertion reactivity with a wide variety of unsaturated substrates, including nitriles,[3] ketones,[2b] alkenes,[4] and alkynes.[5] Other transition-metal benzyne complexes can also participate in insertion chemistry[6] or mediate C–H activation.[7] In contrast to the transition metals, however, the reactivity of actinide benzyne complexes is essentially unknown, and the synthesis of an isolable f element benzyne has remained elusive.[8] For example, Marks and co-workers observed diphenylacetylene insertion into the ortho position of a phenyl ligand, via the proposed benzyne intermediate, $[Cp^*_2U(\eta^2\text{-}C_6H_4)]$ ($Cp^* = \eta\text{-}C_5Me_5$),[8b] while Evans and co-workers invoked the same benzyne intermediate in the coupling of a carbodiimide to a phenyl group.[8a] However, in both cases the benzyne intermediate was generated in situ and could not be isolated. Even actinide aryl complexes are rare,[8,9] and those that have been isolated often feature aryl ligands stabilized by chelating interactions.[9f,g] Given this observation, we endeavored to synthesize an actinide aryl complex by employing a chelating arylamine ligand derived from *N*,*N*-dimethylbenzylamine. This moiety has been used to stabilize aryl complexes containing a variety of metals, including several transition-metals and lanthanides.[9d,10] Herein, we report the synthesis, characterization, and computational study of a rare thorium aryl complex and a uranium benzyne complex. The uranium benzyne complex is the first isolable benzyne complex of the f elements.

Reaction of $[ThCl_4(DME)_2]$ with 5 equivalents of 2-Li-$C_6H_4CH_2NMe_2$ in cold THF results in the formation of the neutral homoleptic aryl complex, $[Th(2\text{-}C_6H_4CH_2NMe_2)_4]$ (**1**), which is isolated as a white crystalline solid in 61% yield (Scheme 1).[11] Complex **1** is insoluble in nonpolar solvents, such as hexanes, but quite soluble in THF and aromatic solvents. Complex **1** is stable in solution for up to 24 h and is indefinitely stable as a solid at −25 °C. No doubt, the stability of **1** relates to the coordination of the σ-donating dimethylamino group, which provides kinetic stabilization of the Th–C bond. Interestingly, its $^{13}C\{^1H\}$ NMR spectrum in C_6D_6 exhibits a resonance at $\delta = 230.79$ ppm, assignable to the thorium-bound carbon nuclei. The large chemical shift observed for these nuclei may be due to spin orbit coupling, which is significant in the actinides.[12]



Scheme 1. Syntheses of complexes **1** and **2**.

Complex **1** crystallizes in the monoclinic space group *C*2/*c* (Figure 1). Complex **1** exhibits a dodecahedral coordination geometry, in which the two orthogonal trapezoids are defined by N1-C1-N2-C2 and N1*-C1*-C2*-N2*.[13] The Th–C bond lengths are 2.550(2) Å and 2.548(2) Å, which are similar to reported Th–C_{aryl} bonds (2.59(1) Å–2.654(14) Å).[9a,b] Interestingly, there are only three other structurally characterized

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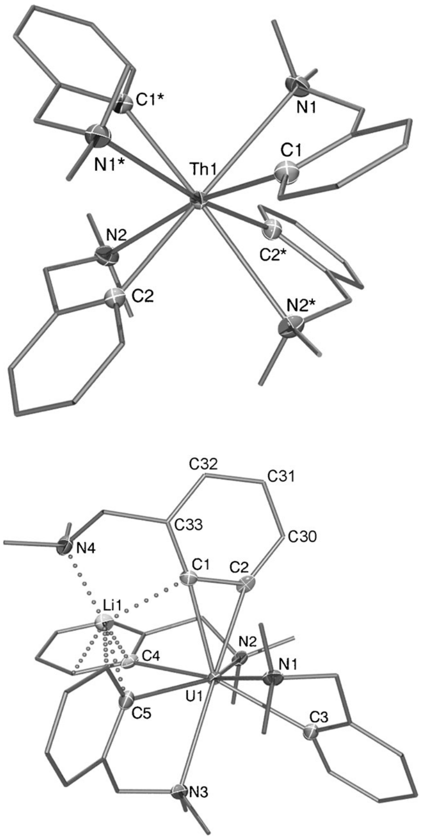

Figure 1. ORTEP diagram of **1** (top) and **2** (bottom), thermal ellipsoids set at 50% probability for selected atoms. Asterisks denote symmetry related atoms. Selected bond lengths [Å] and angles [°]: **1**: Th1-C1 2.548(2), Th1-C2 2.550(2), Th1-N1 2.972(2), Th1-N2 3.009(2); C1-Th1-N1 62.96(6), C2-Th1-N2 63.10(6). **2**: U1-C1 2.473(4), U1-C2 2.340(5), U1-C3 2.604(4), U1-C4 2.650(7), U1-C5 2.615(8), U1-N1 2.758(6), U1-N2 2.674(5), U1-N3 2.801(5), C1-C2 1.388(7), C2-C30 1.415(7), C30-C31 1.392(8), C31-C32 1.397(8), C32-C33 1.385(7), C33-C1 1.425(6); C1-U1-C2 33.4(2).

thorium aryl complexes, and like **1**, each contains thorium–aryl interactions supported by chelating ligands.[9a,b]

We also explored the reactivity of 2-Li-$C_6H_4CH_2NMe_2$ with UCl_4. Thus, addition of 5 equivalents of 2-Li-$C_6H_4CH_2NMe_2$ to a cold THF suspension of UCl_4 results in the formation of a red solution and an orange solid. Surprisingly, workup of the red solution results in the isolation of the uranium benzyne complex, [Li][U(2,3-$C_6H_3CH_2NMe_2$)(2-$C_6H_4CH_2NMe_2$)$_3$] (**2**), as a red crystalline solid in 26% yield (Scheme 1). We have also isolated a second benzyne product from this reaction, in comparable yields, which we have identified as [Li][Li(THF)$_2$][UCl_2(2,3-$C_6H_3CH_2NMe_2$)(2-$C_6H_4CH_2NMe_2$)$_3$] (**3**; see the Supporting Information for structural details).

The benzyne ligand in **2** likely results from the deprotonation of a uranium-bound aryl ligand by 2-Li-$C_6H_4CH_2NMe_2$, which acts as a sacrificial base, forming *N*,*N*-dimethylbenzylamine as a by-product. In support of this mechanism, monitoring the reaction of UCl_4 with 2-Li-$C_6H_4CH_2NMe_2$ in C_6D_6/[D_8]THF reveals rapid formation of *N*,*N*-dimethylbenzylamine in the reaction mixture. Complex **2** can also be formed by addition of 4 equivalents of 2-Li-$C_6H_4CH_2NMe_2$ to UCl_4; however, the yield of material isolated under these conditions is substantially lower. No evidence for the formation of a tetra(arylamine) uranium complex analogous to **1** is observed in either the 4:1 or 5:1 ligand-to-metal ratio reactions.

Comparative reactivity studies of thorium and uranium organometallics are relatively rare;[14] however, in their investigations of [$Cp^*_2M(C_6H_5)_2$] (M = Th, U), Marks and co-workers observed that the uranium analogue was more thermally sensitive than the thorium analogue,[8b] forming a benzyne intermediate upon heating to 45 °C. In contrast, the thorium complex required heating to 100 °C before benzene elimination was observed. These results are consistent with our observations, and suggest that uranium benzyne formation is, in general, more favorable than thorium benzyne formation (see also below).

Complex **2** crystallizes in the monoclinic space group $P2_1$. The solid-state molecular structure of complex **2** (Figure 1) reveals an eight coordinate geometry about the uranium center. Three of the arylamine ligands coordinate to the uranium center in the expected N,C-κ^2 fashion, while one of the aryl rings coordinates through two carbon atoms in a C,C-η^2 fashion, forming a benzyne ligand. The U$-C_{benzyne}$ bond lengths are U1$-$C2 2.340(5) Å and U1$-$C1 2.473(5) Å, and are much shorter than the U$-C_{aryl}$ bond lengths found in **2** (2.604(4) Å–2.650(7) Å). Additionally, they are on the lower end of U$-$C distances observed in other U$-C_{aryl}$ (2.342(7) Å–2.582(5) Å) and U$-C_{alkyl}$ (2.40(2) Å–2.658(6) Å) complexes.[8a,9d,f,g,15] Notably, the U1$-$C1 bond length of the benzyne ligand is longer than the U1$-$C2 distance, owing to the coordination of the lithium cation to the C1 atom. The C$-$C bond lengths within the benzyne ring are suggestive of a dianionic resonance form of the benzyne ligand, as there is no alternation of the C$-$C distances (C1$-$C2 1.388(7), C2$-$C30 1.415(7), C30$-$C31 1.392(8), C31$-$C3 1.397(8), C32$-$C33 1.385(7), and C33$-$C1 1.425(6) Å). These parameters are similar to those of the Group 4 benzynes, which also exhibit the dianionic resonance form.[2]

Complex **2** exhibits a complicated ^{1}H NMR spectrum in C_6D_6, exhibiting 31 resonances ranging from $\delta = 55.43$ ppm to $\delta = -60.15$ ppm. This pattern is consistent with a paramagnetic complex exhibiting C_1 symmetry, suggesting that the solid-state structure is retained in solution. Complex **2** features an effective magnetic moment of 3.47 μ_B, which drops to 0.78 μ_B upon cooling to 4 K (Supporting Information, Figure S16), as determined by SQUID magnetometry. This behavior is fully consistent with the proposed 4+ oxidation-state assignment.[16] The NIR spectrum of **2** is also consistent with the presence of the U^{IV} ion.[15a,17] Interestingly, complex **2** exhibits considerable thermal sensitivity, which partially explains the low yield isolated. Left standing, red C_6D_6 solutions of **2** turn deep blue over 24 h. Efforts to characterize the resulting products are underway.

To better understand the electronic structures of complexes **1** and **2** we undertook their computational study, as well as the computational study of their complementary complexes, that is, the thorium benzyne, [Li][Th(2,3-$C_6H_3CH_2NMe_2$)(2-$C_6H_4CH_2NMe_2$)$_3$] (**2′**), and the uranium tetra(arylamine), [U(2-$C_6H_4CH_2NMe_2$)$_4$] (**1′**). While **1′** and **2′**

were not observed experimentally, comparison of their electronic structure with **1** and **2** provides insight into the similarities and differences in the bonding of uranium and thorium with benzyne and arylamine ligands. The spin multiplicities of the ground states were found to be singlet for thorium complexes (**1** and **2′**) and triplet for uranium complexes (**1′** and **2**). The calculated bond lengths and angles are in a good agreement with those obtained from the crystal structure measurements (Tables S2 and S3).

To better understand similarities and differences in the bonding of U and Th complexes, we carried out natural localized molecular orbital analysis of the An−C bonds. The results are summarized in Table 1. In general, bonding in these complexes can be described as sigma bonds resulting from interactions between the occupied lone-pair orbitals of C atoms (with largely p orbital character) and empty lone pair orbitals of An ions with mostly d and f orbital character. Based on the percent contributions by atoms (Table 1), the binding has a slightly more covalent character in case of the U complexes. Interestingly, f orbitals also play a more important role in the U complexes. In the homoleptic arylamine complexes, the percent contribution of f orbitals to An−C(arylamine) bonds is substantially larger in the uranium complex **1′** than in the corresponding Th complex **1** (36.4% for **1′** vs. 21.8% for **1**). The difference is even more clear in case of the benzyne complexes **2** and **2′**, where the contribution of f orbitals to U−C(benzyne) bonds is 44.1%, while only 25.6% to Th−C(benzyne) bonds.

Table 1: Natural localized molecular orbital analysis of An−C (arylamine) and An−C (benzyne) bonds.[a]

		1	**1′**	**2′**	**2**
arylamine	%An	6.9	13.1	7.8	12.5
	%s	20.6	12.8	24.3	16.8
	%p	3.6	1.0	0.5	0.2
	%d	54.08	49.8	56.8	55.9
	%f	21.8	36.4	18.4	27.1
	%C	89.9	84.8	88.1	83.2
	%s	27.0	26.3	27.4	27.6
	%p	73.0	73.7	72.6	72.4
benzyne	%An			9.3	16.4
	%s			13.3	7.3
	%p			1.0	0.2
	%d			60.1	48.4
	%f			25.6	44.1
	%C			86.5	79.1
	%s			25.0	24.0
	%p			75.0	76.0

[a] The contributions by atom and orbital are averaged over all the ligands of the same character (complexes of U and Th) and over alpha and beta orbital contributions (complexes of U).

The change from an almost ideal tetrahedral geometry (with respect to the An−C bonds) in homoleptic arylamine complexes (**1**, **1′**) to a severely distorted tetrahedral geometry in the heteroleptic arylamine benzyne complexes (**2**, **2′**) also influences the character of An−C (arylamine) bonds. In the benzyne complexes, two of the arylamine ligands (C4, N2; C5, N3) and the benzyne ligand (C1, C2) take on pseudo-octahedral like geometry around the An center (see Figure S19 for numbering scheme). This change increases the overlap of the C4 and C5 lone-pair orbitals with the d orbitals of An. As a result, the contribution of d orbitals to An−C4 and An−C5 bonds increases on average from 55% to 59% for **2′**, and from 51% to 59% for **2** (Table S5), in comparison to the An homoleptic arylamine complexes (Table S4). On the other hand, there is no significant change in the character of the d and f orbital contributions to the An−C3 sigma bonds. The binding of this ligand is, however, weakened in comparison to the homoleptic complexes.

The population analysis performed for the An–benzyne bonds highlights the differences in the participation of the f orbitals between uranium and thorium. This change in f orbital participation in going from Th to U has been observed previously,[18] and tentatively suggests that the f orbitals play a role in stabilizing the uranium-benzyne linkage. Similarly, the f orbitals have been found to play important roles in the stabilization of the first terminal actinide nitride,[19] and in the manifestation of the inverse *trans* influence (ITI).[20] However, a binding-energy analysis suggests that the benzyne interaction in the Th complex **2′** is similar to that of **2** (Tables S6 and S7). As a result, the formation of a benzyne ligand for uranium is likely a kinetic and not thermodynamic effect. Accordingly, we suggest that the increased 5f orbital participation observed for uranium may instead play a role in reducing the kinetic barrier of benzyne formation.

In conclusion, we report the synthesis and characterization of the first actinide benzyne complex, $[Li][U(2,3\text{-}C_6H_3CH_2NMe_2)(2\text{-}C_6H_4CH_2NMe_2)_3]$. The isolation of the benzyne product prompted us to undertake a computational study to understand the bonding contributions to the U−$C_{benzyne}$ bond. Comparison of the orbitals involved in the U−$C_{benzyne}$ interaction versus the hypothetical thorium benzyne complex, reveals a significant increase in f-orbital character in the uranium case. In this regard, the postulated kinetic preference for uranium benzyne formation may be attributable to this increased f-orbital participation, and suggests that the f orbitals can play a critical role in determining reaction outcomes.

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