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A Heterobimetallic Complex With an Unsupported Uranium(III)–Aluminum(I) Bond: $(CpSiMe_3)_3U–AlCp^*$ ($Cp^* = C_5Me_5$)

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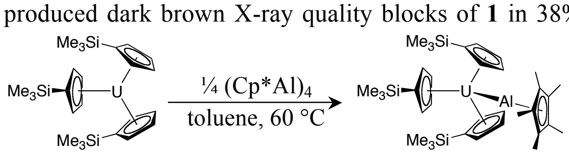
The discovery of molecular metal-metal bonds has been of fundamental importance to the understanding of chemical bonding.[1] For the actinides, examples of unsupported metal-metal bonds are relatively uncommon, consisting of $Cp_3U–SnPh_3$, and several actinide–transition metal complexes.[2] Traditionally, bonding in the *f*-elements has been described as electrostatic; however, elucidating the degree of covalency is a subject of recent research.[3] In carbon monoxide complexes of the trivalent uranium metallocenes, decreased ν_{CO} values relative to free CO suggest that the U(III) atom acts as a π-donor.[4] Ephritikhine and coworkers have demonstrated that π-accepting ligands can differentiate trivalent lanthanide and actinide ions, an effect that renders this chemistry of interest in the context of nuclear waste separation technology.[5]

Considering the propensity for the U(III) metallocenes to bind soft π-accepting ligands, we recently began exploring the reactivity of these complexes toward the Group 13 diyls Cp*M. The $(Cp^*Al)_4$ tetramer dissociates at elevated temperature into Cp*Al monomers which each possess a pair of electrons on the aluminum atom allowing it to act as a Lewis base.[6] As a ligand, Cp*Al is formally isolobal with singlet carbene, CO, and PR_3;[7] neverthless, DFT calculations have suggested that metal→aluminum π-backbonding is thwarted by the π-donating Cp*.[8] Group 13 diyls Cp*M (M = Al, Ga) have proven useful as starting materials in the discovery of some of the first examples of lanthanide–metal bonds, $Cp^*_2Ln–AlCp^*$ (Ln = Eu, Yb), $Cp^*_2Eu(GaCp^*)_2$, and $Cp^*_2Yb(THF)–GaCp^*$.[9] Herein, we report the synthesis and characterization of the first example of a complex with an unsupported bond between an actinide and Group 13 element.

Stirring a mixture of $(CpSiMe_3)_3U$ and $(Cp^*Al)_4$ in toluene at 60 °C for several hours resulted in a dark brown solution. Evaporation and crystallization from pentane at -80 °C produced dark brown X-ray quality blocks of **1** in 38% yield



(1)

(Eq 1). The crystal structure of **1** consists of two crystallographically inequivalent molecules **1A** and **1B** with nearly identical geometries (Figure 1).[10] The position and orientation of the U–Al bonds were carefully checked to confirm the absence of a crystallographic relationship. The uranium atom coordination environment in **1A** and **1B** is similar to the pseudotetrahedral geometry observed in other $(CpSiMe_3)_3UL$ complexes.[11] A slight distortion is observed in the Ct(1A)–Al(1A)–U(1A) (Ct(1A) = Cp* centroid) bond angle (164.2(4)°), which is expected due to the steric environment provided by the $CpSiMe_3$ ligands. Interestingly, the Ct(1A)–Al(1A) distance (1.886(5) Å) is *ca.* 0.1 Å shorter than that in $(Cp^*Al)_4$.[6a]

Though uranium binary alloys of aluminum are known,[12] there are no known molecular actinide—Group 13 bonds available for comparison. The uranium–aluminum bonds in **1** (U(1A)–Al(1A), 3.117(3) Å; U(1B)–Al(1B), 3.124(4) Å) are very close to the sum of the covalent radii recently reported by Alvarez and coworkers (U + Al = 3.17 Å).[13] In contrast, the U–C distances in $(C_5Me_4H)_3U(CO)$ (2.383(6) Å) and $(C_5Me_4H)U(CNC_6H_4\text{-}p\text{-}OMe)$ (2.464(4) Å) are both much shorter than the sum of the covalent radii (U + C = 2.65).[4a] The related aluminum lanthanide complexes $Cp^*_2Ln–AlCp^*$ (Ln = Yb, Eu) have Ln–Al distances (Eu–Al, 3.3652(10) Å; Yb–Al, 3.1981(11) Å) which are slightly longer than the sums of their covalent radii (Eu + Al = 3.19 Å; Yb + Al = 3.08 Å).[9a] These Ln–Al bonds are generally regarded as dative bonds,

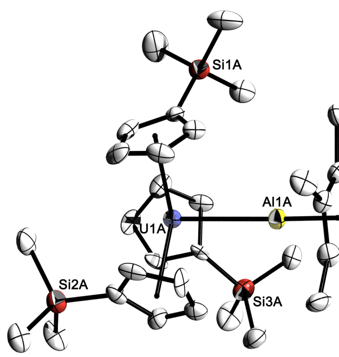


Figure 1. Molecular structure of **1A**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (deg): U(1A)–Al(1A), 3.117(3); Al(1A)–Ct(1A), 1.886(5); U(1A)–Ct(2A), 2.550(13); U(1A)–Ct(3A), 2.533(12); U(1A)–Ct(4A), 2.536(11); U(1A)–Al(1A)–Ct(1A), 164.1(4); Ct(2A)–U(1A)–Ct(3A), 115.4(5); Ct(3A)–U(1A)–Ct(4A), 119.6(4); Ct(2A)–U(1A)–Ct(4A), 119.8(5).

though a recently reported Nd–Ga bond (3.2199(3) Å) is closer to the sum of its covalent radii (Nd + Ga = 3.23 Å).[14]

Careful scrutiny of the geometric parameters observed in the X-ray crystal structure of **1**, including the U–Al bond lengths, η^5-coordination of the Cp* ligands, and a relatively linear Cp* centroid–aluminum–uranium bond angle, effectively rules out the presence of bridging hydrides. In addition, while not providing definitive evidence, the following observations support the formulation for **1** depicted in Equation 1: Signals attributable to a hydride were not detected in the ^1H NMR spectrum between -100 and 300 ppm, as have previously been observed in derivatives of $U(BH_4)_4$, or in $(CpSiMe_3)_3UH$.[15] Furthermore, no signals were detected in the IR spectrum of **1** between 1461 and 2665 cm^{-1}; in contrast, IR spectra of uranium–BH_4 complexes[15a] and Cp^*AlH_2[16] exhibited signals in this region. While the molecular ion of **1** was not seen in the EI mass spectrum, the highest mass peak corresponds to $[M^+ - SiMe_3]$ at 738 m/z (with the expected isotope envelope). The room-temperature magnetic moment of **1**, μ_{eff} = 3.0(1) μ_B, is lower than the calculated moment for a U(III) ion,[3c] but well within the range for reported U(III) complexes.[17] Finally, the room-temperature electronic absorption spectrum of **1** exhibits a series of Laporte-forbidden $f \rightarrow f$ bands between 500 and 1500 nm which are typical of the electronic "fingerprint" observed for trivalent uranium compounds.[17,18]

Further support for the absence of a bridging hydride in **1** was found in its reactivity toward CCl_4.[19] A sample of **1** in C_6D_{12} was analyzed by ^{1}H NMR spectroscopy before and after addition of 1 and 10 molar equivalents of CCl_4. No formation of $CHCl_3$ was observed.

Preliminary results from an ongoing DFT[20] study suggest that there is a degree of covalent character to the U–Al bond in **1**.[21] The model complex Cp_3U–AlCp was constructed using the crystallographic coordinates but replacing the silyl and methyl groups by H atoms (at 1.08 Å from the Cp carbon atoms). Unrestricted BPW91[22] and B3LYP[23] (values listed in parentheses) yielded similar results. Essentially all of the spin density is located in three non–bonding *f*-orbitals centered on uranium. Figure 2 depicts the α HOMO–4, which clearly displays a U–Al bonding interaction (the β HOMO–1 is nearly identical).[24] No occupied orbitals with any U–Al π–bonding character were observed.

A natural bond orbital (NBO)[25] analysis yielded natural charges of 1.899 (1.982) and 0.594 (0.651) for U and Al, respectively. A natural charge of 0.540 (0.560) was computed for the (geometry optimized) AlCp fragment, indicating that there is a net Al→U charge transfer, albeit small. However, the Wiberg bond index between U and Al is 0.487 (0.436), indicating the presence of a covalent bond of order *ca.* 0.5.

In summary, we have prepared the first complex with an unsupported bond between a 5*f* and Group 13 element. This complex is stable in solution and DFT calculations suggest that the U–Al bond exhibits some covalent character owing to charge transfer from the Cp*Al ligand onto uranium. The reactivity of **1**, physical measurements regarding the enthalpy and electronic structure of the U–Al bond, along with the synthesis of related complexes of other group 13, lanthanide and actinide congeners, are the subject of current work.

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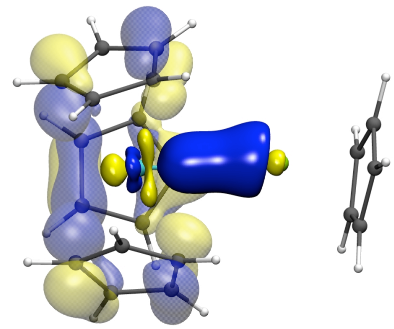

Figure 2. Molecular orbital diagram of the α HOMO-4 (BPW91). The Cp ligand contributions were rendered transparent to clarify the uranium-aluminum bonding interaction.

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