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f-Element Half-Sandwich Complexes: A Tetrasilylcyclobutadienyl-Uranium(IV)-Tris(tetrahydroborate) Anion Pianostool Complex

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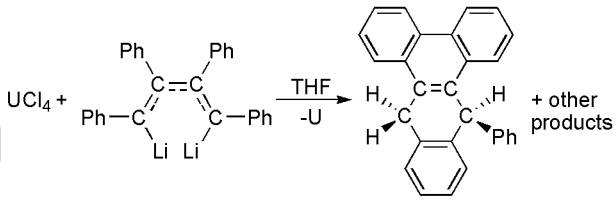
Abstract: *Despite there being numerous examples of f-element compounds supported by cyclopentadienyl, arene, cycloheptatrienyl, and cyclooctatetraenyl ligands (C_{5-8}), cyclobutadienyl (C_4) complexes remain exceedingly rare. Here, we report that reaction of $[Li_2\{C_4(SiMe_3)_4\}(THF)_2]$ (**1**) with $[U(BH_4)_3(THF)_2]$ (**2**) gives the pianostool complex $[U\{C_4(SiMe_3)_4\}(BH_4)_3][Li(THF)_4]$ (**3**), where use of a borohydride and preformed C_4-unit circumvents difficulties in product isolation and closing a C_4-ring at uranium. Complex **3** is an unprecedented example of an f-element half-sandwich cyclobutadienyl complex, and it is only the second example of an actinide-cyclobutadienyl complex, the other being an inverse-sandwich. The U-C distances are short (av. 2.513 Å), reflecting the formal 2- charge of the C_4-unit, and the $SiMe_3$ groups are displaced from the C_4-plane, which we propose maximises U-C_4 orbital overlap. DFT calculations identify two quasi-degenerate U-C_4 π-bonds utilising the ψ_2 and ψ_3 molecular orbitals of the C_4-unit, but the potential δ-bond using the ψ_4 orbital is vacant.*

The discovery of ferrocene in 1951 heralded a new age of organometallic chemistry,[1] and this resulted in the rapid proliferation of sandwich, half-sandwich, and inverse-sandwich η^n-bonded d-block and f-element-carbocyclic derivatives including cyclobutadienyl (C_4), cyclopentadienyl (C_5), arene (C_6), cycloheptatrienyl (C_7), and cyclooctatetraenyl (C_8).[2] The area is still burgeoning today due to its continuing impact on developing our understanding of bonding theory and its many applications in synthesis and catalysis.[3] Where f-element-η^n-carbocyclic derivatives, first initiated in 1954,[4] are concerned, although reports of C_{5-8} derivatives are numerous,[5] C_4 complexes remain rare with only two reports to date.[6] In actinide chemistry, in 2013 we reported the synthesis of the diuranium-cyclobutadienyl inverse-sandwich complex $[\{U(Ts^{Xy})\}_2(C_4Ph_4)]$ (**I**, $Ts^{Xy} = HC(SiMe_3NC_6H_3\text{-}3,5\text{-}Me_2)_3$),[6a] and in lanthanide chemistry the synthesis of 'ate' cyclometallated cyclobutadienyl sandwich complexes $[M\{C_4(SiMe_3)_4\}\{C_4(SiMe_3)_3(SiMe_2CH_2)K_2(toluene)]$ (M = Y, Dy) was described in 2018.[6b]

Complex **I** was formed by a [2 + 2]-cycloaddition reaction that takes over a month to complete, and it is mediated by two uranium ions to enforce the ring-closure which, unlike transition metals, usually does not occur at f-elements,[7,8] whereas the lanthanide examples feature cyclometallation. These observations perhaps underscore why there is such a paucity of f-element cyclobutadienyl complexes generally and that synthetic progress has been slow; (i) there are few C_4-ligand transfer reagents; (ii) it is difficult to promote C_4-ring formation at ions that little enforce orbital control of reactivity; (iii) the resulting $(C_4R_4)^{2-}$ dianions can be strongly reducing and basic, thus leading to undesirable redox and acid-base side-reactions.[8] Nonetheless, the dearth of f-element cyclobutadienyl derivatives demanded attention, and encouraged by our synthesis of **I** we set out to develop this chemistry further. We targeted a half-sandwich uranium complex, since the continued absence of any f-element half-sandwich cyclobutadienyl complex after seven decades of research on η^n-bonded f-element-carbocyclic complexes was conspicuous. Furthermore, the cyclobutadienyl ligand has long been considered an enigmatic ligand,[9] and a half-sandwich formulation would present the opportunity to study the U-C_4 interaction in isolation, free of the inherent *trans*-ligand or -metal effects in sandwich and inverse-sandwich motifs.

Herein, we report on our progress in this arena, describing how our synthetic strategy has evolved, to ameliorate the aforementioned synthetic challenges, in order to deliver a uranium-cyclobutadienyl pianostool complex. This is the first example of an f-element half-sandwich cyclobutadienyl complex, and only the second example of an actinide-cyclobutadienyl complex. The successful synthesis and characterisation of this half-sandwich complex underscores the importance of using appropriate starting material combinations, and how under-utilised reagents can succeed over more conventional approaches. The uranium-cyclobutadienyl bonding has been probed with quantum chemical calculations, revealing exclusively π-bonding utilising the ψ_2 and ψ_3 molecular orbitals of the C_4-unit, but the potential δ-bond using the C_4-unit ψ_4 orbital is absent.



Scheme 1. Synthesis of 9,14-dihydro-9-phenyldibenz[a,c]anthracene from UCl_4 and [LiC(Ph)C(Ph)C(Ph)C(Ph)Li].

Given our previous work in this area,[6a] we initially examined the potential for developing our reductive alkyne [2 + 2]-cycloaddition at uranium. Thus, we treated UCl_4[10] with one equivalent of acyclic [LiC(Ph)C(Ph)C(Ph)C(Ph)Li],[11] (Scheme 1) but isolated only elemental uranium along with concomitant formation and structural characterisation of the hydrocarbon product 9,14-dihydro-9-phenyldibenz[a,c]anthracene that derives from proton-transfer and intramolecular cyclisation of the butadiene.[12,13] Analogously to **I**, we deduced that the barrier to C_4-ring closure at uranium is significant in this scenario, and clearly facile phenyl-C-H activations add deleterious complications, and we so turned our attention to using the cyclic silyl cousin $[Li_2\{C_4(SiMe_3)_4\}(THF)_2]$ (**1**).[14] However, treatment of UCl_4 with **1** resulted in thus far intractable, darkly coloured solutions that are indicative of uncontrolled uranium reduction.[12] Thus, we switched to a halide-free salt elimination strategy using the generally under-utilised uranium(III)-borohydride complex $[U(BH_4)_3(THF)_2]$ (**2**),[15] since this would be unlikely to be reduced, and we report here the first crystal structure of **2**.[12]

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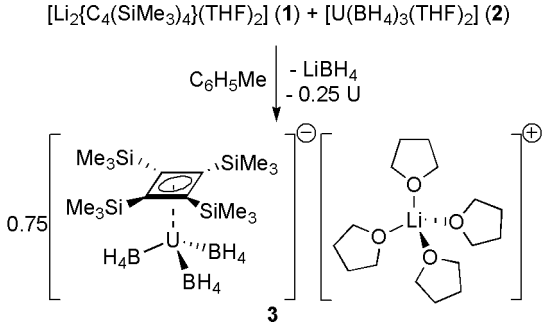

Scheme 2. Synthesis of complex **3**.

Addition of toluene to a cold (−196 °C) 0.9:1 mixture of **1** and **2** results in the formation of a dark brown solution and the precipitation of elemental uranium, suggesting that uranium(III/IV) disproportionation has occurred. Removal of solvent, washing with $SiMe_4$, extraction away from the elemental uranium and $LiBH_4$ solids, and finally recrystallisation from toluene afforded brown crystals formulated as $[U\{C_4(SiMe_3)_4\}(BH_4)_3][Li(THF)_4]$ (**3**) in 55% isolated yield by uranium content (Scheme 2).[12]

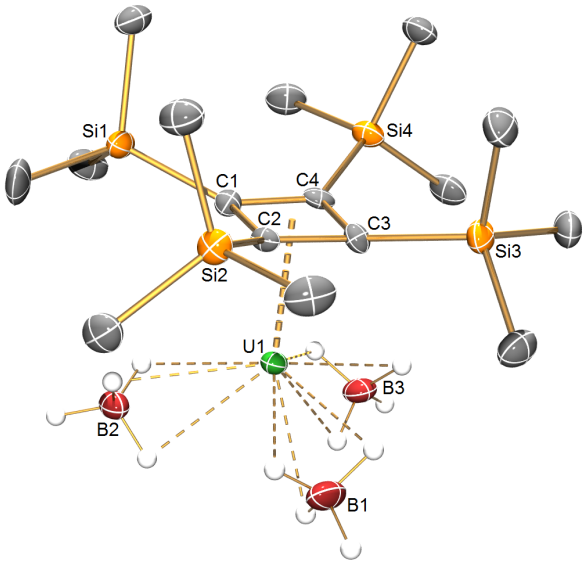

Figure 1. Molecular structure of the anion component of **3** at 150 K. Displacement ellipsoids are set at 40% with silyl-hydrogen atoms and the $[Li(THF)_4]^+$ cation omitted for clarity.

The solid-state structure of **3** (Figure 1) was determined, confirming its separated ion pair formulation. The salient features of the uranium anion component of **3** are the coordination of one η^4-cyclobutadienyl and three κ^3-tetrahydroborate ligands to uranium in a pianostool half-sandwich structure (the hydrides were located in the Fourier Difference Map but refined with restraints). The U-C distances in **3** span the range 2.477(11) to 2.549(12) Å, which is ~0.12-0.18 Å shorter than the U-C distances in **1**[6a] reflecting their terminal and bridging natures,[16] respectively, and the U-C_{cent} distance is 2.290(15) Å. It is instructive to compare the average U-C distances in **3** (2.513 Å) to those of $[U(\eta^5\text{-}C_5H_5)(BH_4)_3]$ (2.656 Å)[17] and $[U(\eta^6\text{-}C_6Me_6)(BH_4)_3]$ (2.927 Å)[18] since each complex features a $\{U(BH_4)_3\}$ unit in a pianostool half-sandwich structural motif; the trend of increasing U-C distances nicely illustrates the effect on moving from formally dianionic $(C_4R_4)^{2-}$ to monoanionic $(C_5R_5)^{1-}$ to neutral $(C_6R_6)^0$ ligands, adjusting for the increasing ring sizes and the fact that the uranium component of **3** is a charge-rich anion and the hexamethylbenzene complex incorporates uranium(III) rather than uranium(IV). The cyclobutadienyl ring C-C distances span the range 1.452(16) to 1.488(17) Å, which is typical of metal coordinated cyclobutadienyl ligands.[8] The four $SiMe_3$ groups are displaced out of the C_4 plane of the cyclobutadienyl core, and all bend away from the uranium ion with displacements ranging from 0.452 to 0.566 Å; this is comparable to the magnitude of out of plane displacements for methyl groups in sterically crowded *tris*(cyclopentadienyl) complexes,[19] but the anion component of **3** is not obviously sterically overloaded, and we address a possible electronic reason for this below. The U-H distances span the range 2.34(10) to 2.51(10) Å, but, as is inherent to X-ray diffraction, those bond metrics are not determined with great precision invalidating any detailed discussion, and so perhaps a more meaningful metric is the U···B distances (range: 2.537(19) to 2.594(17) Å), which compare well to the U···B distances in $[U(\eta^5\text{-}C_5H_5)(BH_4)_3]$ (range: 2.46(4) to 2.57(5) Å)[17] and $[U(\eta^6\text{-}C_6Me_6)(BH_4)_3]$ (range: 2.49(4) to 2.69(3) Å).[18] Lastly, the $[Li(THF)_4]^+$ cation is unremarkable so is not discussed any further.

The ^1H NMR spectrum of **3** exhibits only four resonances, spanning the range +16 to −5 ppm, suggesting a symmetrical species on the NMR timescale with no symmetry-lowering by cyclometallation. The $^{11}B\{^1H\}$ and $^7Li\{^1H\}$ NMR spectra exhibit single resonances at 132.67 and 5.93 ppm, respectively, again suggesting a symmetric species and the latter is consistent with the presence of a $[Li(THF)_4]^+$ cation.

The ATR-IR spectrum of **3** exhibits strong absorptions at 2452, 2193, 2119, and 1241 cm^{-1}, which are characteristic of κ^3-coordinated BH_4 ligands,[20] in-line with the crystallographic data. Specifically, the highest energy band is a terminal B-H A_1 stretching mode, the middle two are a doublet (Δ 74 cm^{-1}) bridging B-H A_1 and E stretching modes that characteristically occur within 80 cm^{-1} of one another, and the lowest energy absorption is a bridge deformation E mode. An absorption at 1307 cm^{-1} is tentatively assigned as a C_4-ring B_1 and/or E stretching mode.[21]

The UV/Vis/NIR spectrum of **3** is dominated by a charge transfer band across the UV and visible regions consistent with the brown colour of **3**, and the NIR region is populated with multiple weak (ε = 15-70 M^{-1} cm^{-1}) absorptions that are characteristic of intra-configurational transitions of $^3H_4$ uranium(IV).[22]

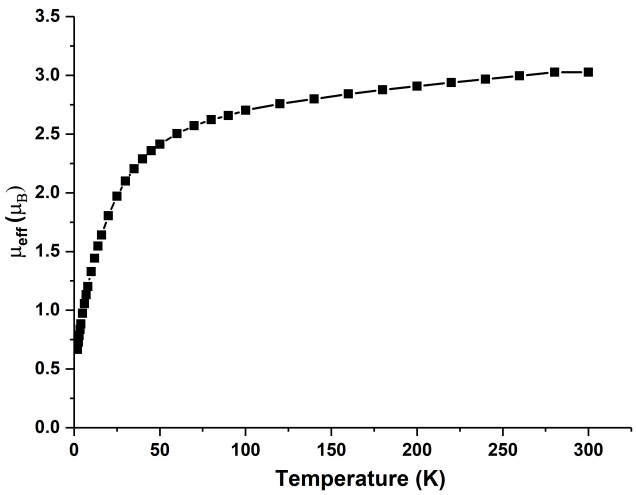

Figure 2. Variable temperature SQUID magnetometry plot for **3** over the temperature range 2-300 K. The line is a guide to the eye only.

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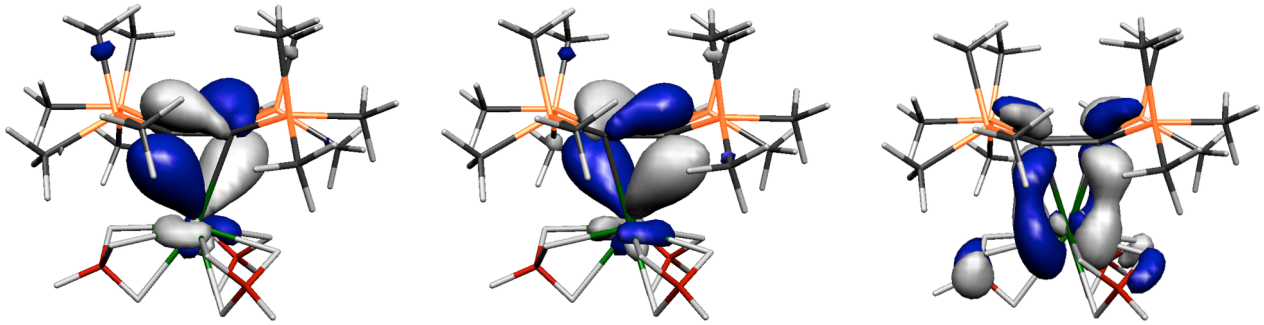

Figure 3. Frontier Kohn Sham Molecular Orbitals of **3'**. Left to right: α-HOMO-3 (152a, −1.577 eV); α-HOMO−2 (153a, −1.560 eV); α-LUMO+5 (161a, +1.910 eV).

To confirm the uranium(IV) formulation of **3** we recorded variable temperature SQUID magnetometric data on a powdered sample of **3** (Figure 2). At 300 K the magnetic moment of **3** is 3.03 μ_B and this decreases smoothly to a magnetic moment of 0.67 μ_B at 2 K which is characteristic of uranium(IV) that is a magnetic singlet at low temperature subject to temperature-independent paramagnetism.[23] However, we note that the magnetic moment of **3** does not decrease as rapidly as is usual for $^3H_4$ uranium(IV), which has been observed before when strongly donating, charge-rich ligands are bound to this ion,[24] which presumably here reflects the formally dianionic and charge-concentrated nature of the relatively small cyclobutadienyl ring. Thus, overall the structural, spectroscopic, and magnetic characterisation data are internally consistent and confirm the proposed formulation of **3**.

In order to gain a deeper understanding of **3**, we undertook quantum chemical unrestricted calculations on the uranium anion component of **3**, **3'**. The DFT geometry optimised structure of **3'** is in good agreement with the experimental structural data, with the computed U-C distances (av. 2.580 Å) slightly over-estimated (~0.07 Å) compared to experiment. We therefore conclude that the optimized structure of **3'** provides a qualitative model of the electronic structure of the uranium anion component in **3**.

The computed MDC-q charges for **3'** of +1.26 (U), −1.49 (C_4), 0.23 (B av.), −0.19 to −0.22 (hydrides), are consistent with donation of electron density from the ligands to uranium and the formal dianionic charge on the cyclobutadienyl ring. The uranium MDC-m spin density is computed to be 1.96, consistent with its $5f^2$ formulation. The U-C bond orders (Mayer) are computed to range from 0.47 to 0.5 and sum up to 1.94. The U-H bond orders average 0.25, reflecting the highly polar nature of those uranium-hydride interactions. The C-C bond orders for the C_4-ring average 1.0, presumably reflecting the π-donation to uranium depletes these delocalised bonds from the anticipated value of 1.5.

The α-spin, quasi-degenerate HOMO and HOMO−1 of **3'** are of essentially pure 5f-character, consistent with the uranium(IV) formulation. HOMO−2 and −3 represent the principal quasi-degenerate binding interactions between uranium and the cyclobutadienyl ring (Figure 3), and are of exclusively π-bonding character deriving from the ψ_2 and ψ_3 π-symmetry molecular orbitals of cyclobutadienyl and vacant 5f/6d hybrid acceptor orbitals of uranium.[16] HOMO−2 and −3 are each composed of 70:30 C_4:U character, respectively, and the latter component in each case is composed of 67:33 5f:6d character. Interestingly, the potential U-C δ-bonding combination involving the ψ_4 δ-symmetry molecular orbital of cyclobutadienyl is found in LUMO+5 (Figure 3), ~3.47 eV above HOMO −2/−3, and this virtual orbital is computed to have a 49:51 C_4:U composition with the U contribution being made up of 7:93 5f:6d character. Interestingly, the π-δ combination gap in **3'** is far larger than in **I** (1.395 eV),[6a] which is consistent with the absence of any significant δ-bonding in the former but its weak presence in the latter. This all-π-symmetric bonding in **3'** is similar that that observed in uranium-C_5 complexes, but contrasts to **I**,[6a] and uranium-$C_{6/7/8}$ complexes where δ-bonding dominates.[16] Lastly, HOMO−2/−3 suggest that the deviation of the silyl groups from the C_4 plane, both experimentally observed in **3** and reproduced in the calculations on **3'**, may possibly be driven, in part, by less strained and thus maximised U-C orbital overlap,[25] since the C_4-ring is quite small for uranium, and such bending of substituents out of the carbocyclic ring plane has been noted in cyclopentadienyl chemistry.[2,3,19]

Since DFT calculations produce an orbital-based bonding picture, we examined the bonding topology in **3'** with Bader's QTAIM method. This reveals computed average ρ, $\nabla^2\rho$, *H* (energy), and ε (ellipticity) 3,-1 bond critical point values for the four U-C interactions in **3'** of 0.06, 0.11, −0.02, and 0.67, which in gross terms compare well to computed data for $[U(\eta^5\text{-}C_5H_5)_4]$;[26] however, the ρ and *H* values for **3'** are slightly larger than $[U(\eta^5\text{-}C_5H_5)_4]$ which is consistent with the cyclobutadienyl ring in the former being bonded more strongly and covalently than the cyclopentadienyl rings in the latter.

To conclude,[27] we have prepared and characterised the first example of an f-element half-sandwich cyclobutadienyl complex, and indeed it is only the second example of an actinide-cyclobutadienyl complex. Whereas synthetic endeavours with UCl_4 have thus far been intractable, using the halide-free uranium(III)-*tris*(tetrahydroborate), itself an infrequently used class of complex in actinide chemistry, proved decisively fruitful. The U-C distances in this pianostool complex are short, consistent with the formal dianionic nature of cyclobutadienyl, and the silyl substituents are displaced from the C_4 plane in a manner that is reminiscent of sterically crowded cyclopentadienyl complexes. However, we suggest that the displacement of silyl groups is not due to steric demands but possibly to maximise orbital overlap between the size-mismatched frontier orbitals of uranium and cyclobutadienyl. Interestingly, the two U-C_4 bonding interactions are computed to be of π-bonding character with a significant contribution from uranium, and the potential U-C_4 δ-bonding interaction is absent, being a virtual, unoccupied orbital lying substantially above the π-bonds. This bonding pattern is similar to that of actinide-cyclopentadienyls, but contrasts to uranium derivatives of arenes, cycloheptatrienyl, cyclooctatetraenyl, and even an inverse-sandwich diuranium cyclobutadienyl complex, where δ-bonding is prevalent to varying extents. The results presented here, when placed in the wider context of uranium-ligand bonding, demonstrate the highly flexible nature of the chemical bonding of uranium, which can adapt its bonding patterns to match the frontier orbitals of ligands that are available to it.

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Keywords: uranium • cyclobutadienyl • tetrahydroborate • half-sandwich • density functional theory

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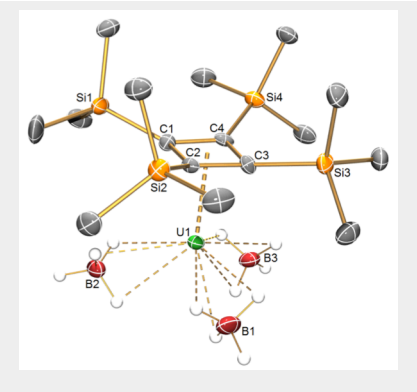
COMMUNICATION

We report the first example of an f-element half-sandwich cyclobutadienyl complex, which is only the second example of an actinide-cyclobutadienyl complex. Calculations suggest that U-C π-bonding dominates, with no δ-bonding component.



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f-Element Half-Sandwich Complexes: A Tetrasilylcyclobutadienyl-Uranium(IV)-Tris(tetrahydroborate) Anion Pianostool Complex

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