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Uranium(IV) cyclobutadienyl sandwich compounds: synthesis, structure and chemical bonding

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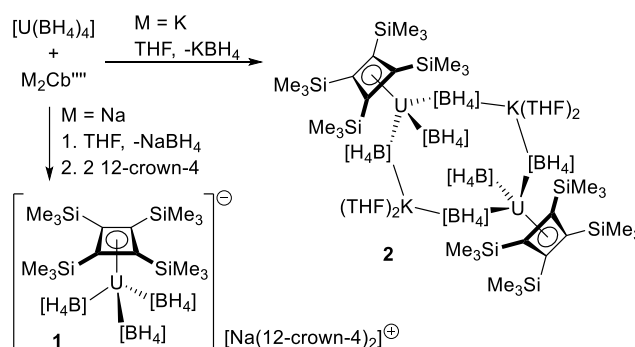
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Organometallic sandwich compounds have been central to developing an understanding of structure, bonding and reactivity in actinide chemistry. Since the discovery of the first well-defined actinide sandwich compounds in the 1950s, two ligand types have dominated the field, namely cyclopentadienyl (Cp) and cyclo-octatetraenyl (COT), both of which are capable of stabilizing actinide ions in a range of formal oxidation states. Actinide cyclopentadienyl chemistry is a well-developed field and has enabled many key advances in small-molecule activation and the stabilization of unusual ligand environments and oxidation states, such as the reductive coupling of carbon monoxide, stabilization of a terminal phosphinidene complex of thorium and, most recently, the divalent uranium metallocene $[(\eta^5\text{-C}_5\text{Pr}_5)_2\text{U}]$. Of the many members of the actinide COT family, none have captivated attention more than the iconic uranocene, i.e. $[(\eta^8\text{-C}_8\text{H}_8)_2\text{U}]$, a compound that ultimately became the main reference point for comparing models of chemical bonding in actinide sandwich compounds with those applied to their transition metal cousins.

In contrast to the prevalence of 5- and 8-membered carbocyclic rings in actinide chemistry, sandwich compounds containing ligands based other rings are less common, however several η^7 -cycloheptatrienyl and η^6 -arene actinide complexes are known. Notably, compounds containing four-membered η^4 -cyclobutadienyl (Cb) ligands are particularly rare in f-element chemistry, with the first lanthanide cyclobutadienyl compounds

being reported only recently. Consequently, a cyclobutadienyl analogue of uranocene with the formula $[(\eta^4\text{-C}_4\text{R}_4)_2\text{U}]$ emerged as an important target for synthesis. Since cyclobutadienyl and COT ligands have elements of four-fold symmetry in common, the frontier orbital structure of the former should, in principle, be well suited to interactions with uranium 5f orbitals. Furthermore, since so little is known about actinide cyclobutadienyl chemistry, it is also of interest to establish whether or not uranium complexes of these ligands are susceptible to the ligand activation processes observed for some lanthanide cyclobutadienyls, such as protonation to give allyl derivatives or formation of tuck-in interactions.

We now report two uranium(IV) half-sandwich complexes of the 1,2,3,4-*tetrakis*(trimethylsilyl)cyclobutadienyl ligand $[\text{C}_4(\text{SiMe}_3)_4]^{2-}$ (Cb'''), i.e. the ion-separated compound $[\text{Na}(\text{12-crown-4})_2][\text{U}(\eta^4\text{-Cb'''})(\text{BH}_4)_3]$ (**1**) and the contact ion-pair $[\text{U}(\eta^4\text{-Cb'''})(\mu\text{-BH}_4)_3\{\text{K}(\text{THF})_2\}]_2$ (**2**), the targeted syntheses of which was accomplished according to Scheme 1. In addition, an initial attempt at synthesizing $[(\eta^4\text{-C}_4\text{R}_4)_2\text{U}]$ revealed that ligand activation is indeed possible, as witnessed by formation of the complex anion $[\text{U}(\eta^4\text{-Cb'''})(\eta^3\text{-C}_4\text{H}(\text{SiMe}_3)_3\text{-}\kappa\text{-(CH}_2\text{SiMe}_2)(\text{BH}_4)]^-$ (**3**), as a salt of $[\text{Na}(\text{tBuOMe})_{3.6}(\text{THF})_{0.4}]^+$, in which one Cb ring has indeed been protonated and a trimethylsilyl substituent has been deprotonated (Scheme 2).

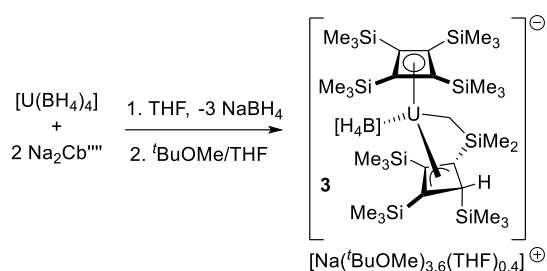
Scheme 1. Synthesis of $[\text{Na}(\text{12-crown-4})_2][\mathbf{1}]$ and **2**.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



Scheme 2. Synthesis of [Na(^tBuOMe)_{3.6}(THF)_{0.4}][3].

The 1:1 stoichiometric reactions of Na₂Cb^{'''} or K₂Cb^{'''} with uranium(IV) *tetrakis*(borohydride) produced, upon work-up, brown crystalline materials, which in the case of the potassium reaction directly yielded diffraction quality crystals. In the case of the sodium reaction, the initial microcrystalline material was subsequently identified to be [U(η⁴-Cb^{'''})(BH₄)₃Na(THF)₃] by multinuclear NMR spectroscopy (Figures SX-SX), and the addition of two equivalents of 12-crown-4 enabled the isolation of diffraction-quality single crystals. The molecular structures of the [U(η⁴-Cb^{'''})(BH₄)₃]⁻ complexes in **1** and **2** are qualitatively similar, with each consisting of uranium(IV) centres bound almost symmetrically to an η⁴-cyclobutadienyl ligand and to three borohydride ligands (Figure 1). The U–C distances in **1** are in the range 2.522(5)–2.556(4) Å, with an associated distance of 2.xxx(x) Å to the centroid of the Cb ring; the analogous U–C and U–Cb distances in **2** are 2.46(2)–2.56(2) and 2.xxx(x) Å, respectively. The trimethylsilyl substituents in **1** and **2** bend out of the cyclobutadienyl plane, away from uranium, by approximately 20°. In the structure of **1**, a κ³-coordination mode of the borohydride ligands was found. In contrast, the structure of **2** shows that two borohydride ligands per uranium bridge to potassium cations, which are also complexed by two THF ligands, resulting in a centrosymmetric dimer with a core geometry reminiscent of the chair conformation of cyclooctatetraene. The transannular U⋯U and K⋯K separations in **2** are 7.308(x) and 7.575(x) Å, respectively.

The NMR spectra of [Na(12-crown-4)₂][**1**] and **2** in THF-D₈ are similar and consistent with the solid-state structures (Figures SX-SX). Thus, resonances due to the SiMe₃ substituents occur in the ¹H NMR spectrum at δ = –5.06 and –4.87 ppm, respectively, and the borohydride protons occur as broad

resonances centred on δ = 15.57 and 15.64 ppm. The ¹¹B and ²⁹Si chemical shifts for **1** occur at δ = 124.69 and –208.46 ppm, respectively, and those for **2** occur at δ = 125.70 and –208.35 ppm. In addition, the ²³Na NMR spectrum for [Na(12-crown-4)₂][**1**] features a resonance at δ = –1.51 ppm.

Based on evidence from ¹H NMR spectroscopy, the 2:1 stoichiometric reaction of Na₂Cb^{'''} with U(BH₄)₄ in THF-D₈ at room temperature initially produces the half-sandwich complex **1**, and subsequent heating at 55°C overnight resulted in all starting materials being consumed. Work-up of the reaction yielded a brown microcrystalline material identified by NMR spectroscopy to contain one intact η⁴-Cb^{'''} ligand, another ligand corresponding to protonation of the Cb^{'''} ring and deprotonation of one of the trimethylsilyl substituents, and one borohydride ligand. By dissolving this material in ^tBuOMe containing a few drops of THF it was possible to obtain single crystals suitable for analysis by X-ray diffraction, which revealed the product to contain the complex anion [U(η⁴-Cb^{'''})(η³-C₄H(SiMe₃)₃-κ-(CH₂SiMe₂)(BH₄)]⁻ (**3**) as a salt of the mixed-ether solvated cation [Na(^tBuOMe)_{3.6}(THF)_{0.4}]⁺.

The structure of **3** features an asymmetrically bound η⁴-Cb ligand with U–C distances of 2.550(5)–2.650(6) Å and, hence, an average of 0.06 Å longer than those in **1**. The protonated η³-cyclobutenyl ligand displays the pattern of U–C distances typically associated with allylic ligands, with two relatively short distances to C(2) and C(4) of 2.638(5) and 2.635(6) Å, and a longer distance of 2.765(6) Å to C(3). One allylic carbon also carries a deprotonated trimethylsilyl substituent that engages in a tuck-in interaction with uranium, producing a U–C(23) distance of 2.534(6) Å. In addition to a change in the bonding mode of the Cb ligand upon protonation, the planarity of the C4 rings also changes appreciably, as witnessed by the C(1)–C(2)–C(3)–C(4) and C(5)–C(6)–C(7)–C(8) torsion angles of 8.7(4)° and 0.2(4)°, respectively. The bending angle subtended at uranium by the centroids of the η⁴-Cb and η³-Cb interactions is xxx.x(x)°.

The solution-phase structure of [Na(^tBuOMe)_{3.6}(THF)_{0.4}][**3**] is consistent with that determined crystallographically, whereby the ²⁹Si NMR spectrum shows five resonances in the range δ = +67.53 to –258.00 ppm in THF-D₈. A single resonance was observed in the ¹¹B NMR spectrum at δ = 41.60 ppm and 10 resonances due to complex **3** were observed in the ¹H NMR spectrum in the region δ = +12.65 to –148.77 ppm, in addition

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Figure 1. Molecular structures of **1**, **2** and **3**. For clarity, the hydrogen atoms, except those in the borohydride ligands, are not shown in the structures of **1** and **3**. In the structure of **2** it was not possible to locate the hydrogen atoms, hence only the boron atoms of the borohydride ligands are shown.

COMMUNICATION

to resonances for the ^tBuOMe ligands coordinated to sodium. Since the NMR spectra of $[\text{Na}(\text{}^t\text{BuOMe})_{3.6}(\text{THF})_{0.4}][\mathbf{3}]$ are essentially the same as those recorded for the brown microcrystalline material first isolated from the reaction of $\text{Na}_2\text{Cb}^{\text{IV}}$ with $\text{U}(\text{BH}_4)_4$, it is therefore possible to formulate this material as $[\text{U}(\eta^4\text{-Cb}^{\text{IV}})(\eta^3\text{-C}_4\text{H}(\text{SiMe}_3)_3\text{-}\kappa\text{-(CH}_2\text{SiMe}_2)(\text{BH}_4)\text{Na}(\text{THF})_3]$, which is fully consistent with the analytical carbon and hydrogen content of the compound.

The structural properties of the compounds described above demonstrate that, whilst it is possible to transfer an intact Cb^{IV} ligand from sodium to uranium(IV), the activation processes that we have previously observed in our studies of lanthanide cyclobutadienyl compounds are also possible with uranium. Since the synthesis of **3** was performed in deuterated THF at 55°C, and the ¹H NMR spectrum of this complex shows that the $\eta^3\text{-Cb}$ ligand has been protonated and not deuterated, the source of the proton should therefore be a trimethylsilyl substituent. As such, although the original target compound $[\text{U}(\eta^4\text{-Cb}^{\text{IV}})]_2$ was not isolated from the reaction, it may form as a fleeting intermediate only to undergo rapid ligand activation, leading ultimately to the formation **3**. Modification of the Cb substituents to derivatives less prone to C–H activation than SiMe_3 are currently under investigation in our laboratories.

To gain insight into the bonding between the uranium(IV) centre and the cyclobutadienyl ligands and its activated counterpart, complexes **1** and **3** were studied by density functional methods as implemented through the Amsterdam Density Functional (ADF) code. Full computational details are provided in the ESI. The valence orbitals of **1** and **3** are shown in Figure 1 and a decomposition of the orbitals onto fragment orbitals is given in Tables S2 and S3.

In **1**, the metal-ligand covalency is dominated by the U-Cb^{IV} interaction; the U-BH_4^- interaction is almost completely ionic. The occupied valence orbitals consist of two orbitals occupied by the unpaired 5f electrons (orbitals 152 α and 153 α) and two doubly occupied orbitals describing the covalent bonding contribution to the U-Cb^{IV} interaction (154 α , 155 α , 152 β and 153 β). The 5f orbitals have more than 88% 5f character each, with some ^{weak} ligand contributions. The orbitals 154 α and 155 α both have more than 11% 5f character and more than 9% 6d character. Thus, the overall metal contribution to the bonding α orbitals is more than 20%. In case of the 152 β and 153 β orbitals, the 5f contribution is over 5% and the 6d contribution over 9%. The covalency in the β orbitals is weaker but the metal contribution is still more than 15%, which is certainly significant. Our findings on **1** are qualitatively similar to those described for the same complex as the salt of $[\text{Li}(\text{THF})_4]^+$, which was reported during the course of this work.

The bonding situation in **3** is qualitatively similar to that in **1**.

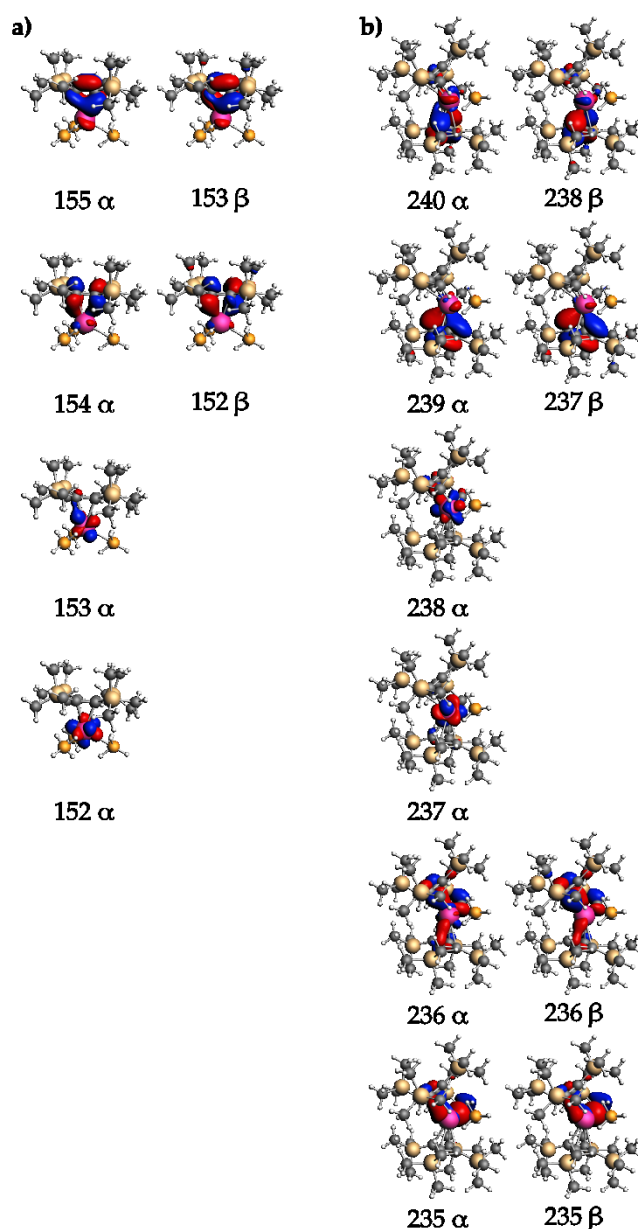


Figure 2. The valence MOs of: **1** (left) and **3** (right).

The covalent component of the U-BH_4^- interaction is again negligible. The unpaired 5f electrons occupy two orbitals (237 α and 238 α) with 5f contributions of 85% and 73%, respectively. This indicates strong metal-ligand covalency even in the orbitals with unpaired electrons and should lead to significant delocalization of the spin into the intact Cb^{IV} ligand and the doubly activated ligand. The U-Cb^{IV} and $\text{U-Cb}(\text{activated})$ interactions both contribute two bonding valence orbitals. The

5f contribution ranges between 4% and 16% and the 6d contribution between 4% and 15%.

In both **1** and **3**, the 5f and 6d contributions to the covalency are similar in magnitude. This is in stark contrast to previously characterized divalent $[(\eta^5\text{-C}_5\text{Pr}_5)_2\text{U}]$ and trivalent $[(\eta^5\text{-C}_5\text{Pr}_5)_2\text{U}]^+$ complexes, where the covalency was dominated by a ligand-to-6d contribution and the 5f was much weaker, although still not negligible. This is almost certainly a consequence of the larger charge difference between the metal and ligands in **1** and **3** as compared to $[(\eta^5\text{-C}_5\text{Pr}_5)_2\text{U}]$ and trivalent $[(\eta^5\text{-C}_5\text{Pr}_5)_2\text{U}]^+$. This leads to stronger electrostatic attraction, shorter metal-ligand distances and overlap that is more significant between the metal and ligand orbitals. This then leads to stronger covalency. Other significant differences between **1** and **3** as compared to $[(\eta^5\text{-C}_5\text{Pr}_5)_2\text{U}]$ and trivalent $[(\eta^5\text{-C}_5\text{Pr}_5)_2\text{U}]^+$, is that in the latter two, the geometries are much closer to an idealized D_{5d} symmetry. This reduces the mixing between the 5f and 6d orbitals, which is forbidden on symmetry grounds. Both $[(\eta^5\text{-C}_5\text{Pr}_5)_2\text{U}]$ and trivalent $[(\eta^5\text{-C}_5\text{Pr}_5)_2\text{U}]^+$ and have two (roughly) *gerade*-symmetric bonding orbitals resulting from the ligand-to-6d interaction and two (roughly) *ungerade*-symmetric orbitals resulting from the ligand-to-5f interaction. In **3** the geometry is so distorted from an ideal D_{4h} geometry, that the 5f and 6d orbitals become strongly mixed.

In summary, the sodium and potassium cyclobutadienyl compounds M_2Cb^{2-} are effective reagents for transferring the $[\text{Cb}^{2-}]$ ligand to uranium(IV), resulting in formation of the half-sandwich complex $[\text{U}(\eta^4\text{-Cb})(\text{BH}_4)_3]^-$, either as the ion-separated salt of $[\text{Na}(12\text{-crown-4})_2]^+$ or as the contact ion pair $[\text{U}(\eta^4\text{-Cb})(\mu\text{-BH}_4)_3\{\text{K}(\text{THF})_2\}]_2$ (**2**). An attempted synthesis of $[\text{U}(\eta^4\text{-Cb})_2]$ from M_2Cb^{2-} and $\text{U}(\text{BH}_4)_4$ resulted instead in the formation of the sandwich complex $[\text{U}(\eta^4\text{-Cb})(\eta^3\text{-C}_4\text{H}(\text{SiMe}_3)_3\text{-}\kappa\text{-(CH}_2\text{SiMe}_2)(\text{BH}_4))]^-$ (**3**). Double activation of the cyclobutadienyl ligand is seemingly a consequence of the reactive nature of $[\text{C}_4(\text{SiMe}_3)_4]^{2-}$, which is apparently capable of self-deprotonation when bound to the strongly Lewis acidic uranium(IV) centre. A computational study of the bonding in **1** and **3** revealed that uranium-Cb interactions to have a significant covalent component, which arises from electron donation from the two nearly degenerate ligand HOMOs to the uranium 5f and 6d orbitals.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

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under discussion, limited experimental and spectral data, and crystallographic data.

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