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DOI:

[10.1002/chem.201903973](https://doi.org/10.1002/chem.201903973)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Magnall, R., Balazs, G., Lu, E., Kern, M., Van Slageren, J., Tuna, F., Wooles, A., Scheer, M., & Liddle, S. (2019). Photolytic and Reductive Activations of 2Arsaethynolate in a UraniumTriamidoamine Complex: Decarbonylative Arsenic GroupTransfer Reactions and Trapping of a Highly Bent and Reduced Form. *Chemistry – A European Journal*, 25(62), 14246-14252. <https://doi.org/10.1002/chem.201903973>

Published in:

Chemistry – A European Journal

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Photolytic and Reductive Activations of 2-Arsaethynolate in a Uranium-Triamidoamine Complex: Decarbonylative Arsenic Group-Transfer Reactions and Trapping of a Highly Bent and Reduced Form

Rosie Magnall,^[a] Gábor Balázs,^[b] Erli Lu,^[a] Michal Kern,^[c] Joris van Slageren,^[c] Floriana Tuna,^[d] Ashley J. Wooles,^[a] Manfred Scheer,^{*[b]} and Stephen T. Liddle^{*[a]}

Abstract: Little is known about the chemistry of the 2-arsaethynolate anion, but to date it has exclusively undergone fragmentation reactions when reduced. Here, we report the synthesis of $[U(\text{Tren}^{\text{TIPS}})(\text{OCAs})]$ (**2**, $\text{Tren}^{\text{TIPS}} = \text{N}(\text{CH}_2\text{CH}_2\text{NSiPr}^i_3)_3$), which is the first isolable actinide-2-arsaethynolate linkage. UV-photolysis of **2** results in decarbonylation, but the putative $[U(\text{Tren}^{\text{TIPS}})(\text{As})]$ product was not isolated and instead only $\{[U(\text{Tren}^{\text{TIPS}})]_2(\mu-\eta^2:\eta^2\text{-As}_2\text{H}_2)\}$ (**3**) was detected. In contrast, reduction of **2** with $[U(\text{Tren}^{\text{TIPS}})]$ gave the mixed-valence arsenido $\{[U(\text{Tren}^{\text{TIPS}})]_2(\mu\text{-As})\}$ (**4**) in very low yield. Complex **4** is unstable which precluded full characterisation, but these photolytic and reductive reactions testify to the tendency of 2-arsaethynolate to fragment with CO-release and As-transfer. However, addition of **2** to an electride mixture of potassium-graphite and 2,2,2-cryptand gives $\{[U(\text{Tren}^{\text{TIPS}})]_2(\mu-\eta^2(\text{OAs}):\eta^2(\text{CAs})\text{-OCAs})\}[\text{K}(2,2,2\text{-cryptand})]$ (**5**). The coordination mode of the trapped 2-arsaethynolate in **5** is unique, and derives from a new highly-reduced and -bent form of this ligand with the most acute O-C-As angle in any complex to date (O-C-As $\angle \sim 128^\circ$). The trapping rather than fragmentation of this highly reduced O-C-As unit is unprecedented, and quantum chemical calculations reveal that reduction confers donor-acceptor character to the O-C-As unit.

Introduction

Heavy valence isoelectronic 2-pnictaethynolate, OCE^- (E = P, As), analogues of the cyanate ion, OCN^- , are of growing fundamental interest.^[1] However, for many years investigations were hampered by a paucity of methods to routinely access the heavier 2-pnictaethynolates. This situation dramatically changed for 2-phosphaethynolate within the past decade^[1a,2] and thus the use of that anion is burgeoning,^[1a] but the 2-arsaethynolate anion was only introduced to the pantheon of ligands in coordination and organometallic chemistry in 2016^[1b,3] and therefore little is known of its chemistry.^[4] Nevertheless, from the few reports of reduction chemistry it is becoming clear that when OCAs^- is placed in reducing situations it always undergoes facile fragmentations like OCP^- , and often it cleaves by decarbonylation thus acting as an As-transfer reagent.^[3,4] One exception to this emerging reactivity paradigm is the only report of OCAs^- reactivity with an actinide where reducing $[U\{\text{N}(\text{OAr}^{\text{Ad,Me}})_3\}(\text{DME})]$ [$\text{N}(\text{OAr}^{\text{Ad,Me}})_3$ = tri-anion of tris(2-hydroxy-3-(1-adamantyl)-5-methylbenzyl)amine] was treated with one and two equivalents of $[\text{Na}(\text{OCAs}(\text{dioxane}))_3]$ to give cyaarside and 1,3-diarsallendiide products, respectively.^[4a]

In recent years, we have been investigating the coordination

chemistry of actinide triamidoamine complexes,^[5] and in particular complexes of the type $[U(\text{Tren}^{\text{TIPS}})\text{X}]^n$ or $\{[U(\text{Tren}^{\text{TIPS}})]_2(\mu\text{-X})\}^n$ [$\text{Tren}^{\text{TIPS}} = \text{N}(\text{CH}_2\text{CH}_2\text{NSiPr}^i_3)_3$; X = formally charged ligand; n = 0 or -1] which have proven proficient at stabilising unusual main group fragments.^[6] In particular, we recently reported a successful attempt to trap a reduced and bent form of 2-phosphaethynolate in the mixed-valence uranium(III/IV) complex $\{[U(\text{Tren}^{\text{TIPS}})]_2(\mu-\eta^2(\text{OP}):\eta^2(\text{CP})\text{-OCP})\}[\text{K}(2,2,2\text{-cryptand})]$ (**I**),^[7] thus defying the usual fragmentation or coupling reactions of this ligand when it is reduced.^[8] There are few structurally confirmed examples of U-As linkages, and they all involve derivatives of H_2As^- ,^[6g,h] $(\text{Me}_3\text{Si})_2\text{As}^-$,^[6a] and the above $\text{As}=\text{C}=\text{As}^-$ example.^[4a] Thus, we directed our attention to examining 2-arsaethynolate in a triamidoamine uranium environment because, given the established widely divergent natures of OCP^- and OCAs^- reduction chemistries, and the fact that arsenic chemistry often sharply digresses from that of phosphorus congeners, the likely outcomes could not be predicted. We were interested in determining whether under reducing conditions 2-arsaethynolate could act as an As-atom transfer reagent at uranium, and the isolation of **I** also prompted the question of whether a bent 2-arsaethynolate, clearly very susceptible to cleavage, could be trapped.

Here, we report the synthesis of the first actinide-2-arsaethynolate complex. Photolysis or reduction of this linkage can result in decarbonylation fragmentations with arsenido complexes of uranium either isolated or implicated as intermediates that go on to form a diarsane-1,2-diide. We also report that surprisingly a highly reduced and bent form of 2-arsaethynolate can indeed be trapped, despite the fact it seems to be even more reduced than the 2-phosphaethynolate linkage in **I** and so should be subject to facile fragmentation. Calculations suggest that reduction introduces donor-acceptor character to the bent O-C-As unit, thus introducing some degree of carbene character to this linkage. The reductive chemistry of 2-arsaethynolate reported here adds and contrasts to the emerging picture of decarbonylation chemistry for this anion, and presents reactivity that is distinct to the only other report of actinide reactivity with this ligand.

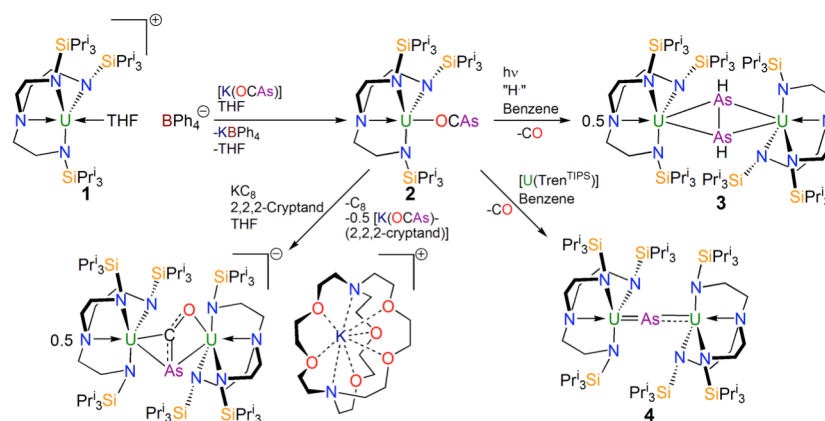
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Scheme 1. Synthesis of 2-5 from 1.

Results and Discussion

Synthesis and characterisation of a stable uranium(IV)-2-arsaethynolate complex

Noting the prior incompatibility of uranium(III) with OCAs^- ,^[4a] but that closely related OCP^- is stable with less reducing uranium(IV),^[7] we first targeted a uranium(IV)-Tren^{TIPS} derivative as a starting point. Accordingly, reaction of $[\text{U}(\text{Tren}^{\text{TIPS}})(\text{THF})][\text{BPh}_4]$ (**1**)^[6] with base-free $[\text{K}(\text{OCAs})]^{[9]}$ in THF afforded the uranium(IV)-2-arsaethynolate complex $[\text{U}(\text{Tren}^{\text{TIPS}})(\text{OCAs})]$ (**2**) as green crystals in 56% isolated yield after work-up and recrystallisation from pentane (Scheme 1).^[10]

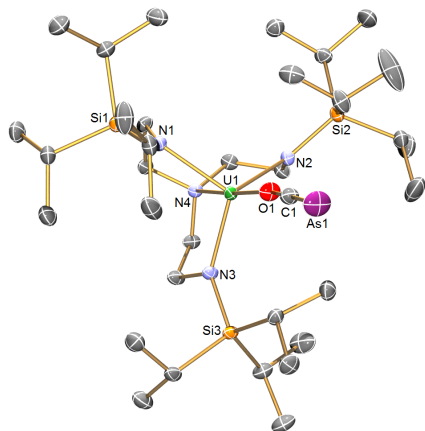


Figure 1. Molecular structure of **2** at 150 K. Displacement ellipsoids are set to 40%, and hydrogen atoms are omitted for clarity.

The crystal structure of **2** (Figure 1) reveals a terminal O-bound U-O-C-As linkage, with U-O, O-C, and C-As distances of 2.3007(16), 1.234(3), and 1.679(2) Å and U-O-C and O-C-As angles of 173.03(16) and 178.9(2)°, respectively; there are no actinide-OCAs examples to compare these data to, but the C-As distance is close to the sum of covalent triple bond radii for C and As (1.66 Å)^[11] and the O-C distance is close to the sum of double bond covalent radii for O and C (1.24 Å).^[11] The OCAs⁻ metrics compare well to reported MOCAs complexes (M = Na, Ge)^[3] and adjusting for the different covalent radii of P and As^[11] the structure of **2** is very similar to that of the closely related uranium(IV)-2-phosphaethynolate congener $[\text{U}(\text{Tren}^{\text{TIPS}})(\text{OCP})]$.^[7] The U-N_{amide} and U-N_{amine} distances in **2** are typical of uranium(IV)-Tren complexes.^[5]

The ¹H NMR spectrum of **2** ranges from 11 to -36 ppm and the optical spectrum exhibits weak ($\epsilon < 80 \text{ M}^{-1} \text{ cm}^{-1}$) absorptions across the NIR region. Variable-temperature SQUID magnetometry on powdered **2** (Figure 2) reveals a magnetic moment of 3.26 μ_B at 298 K and this decreases smoothly to 0.47 μ_B at 2 K; this is characteristic behaviour of a ³H₄ ion that is a magnetic singlet at low temperature with temperature independent magnetism.^[12] The data for **2** are similar to those of tetravalent $[\text{U}(\text{Tren}^{\text{TIPS}})(\text{OCP})]$,^[7] and dominance of the $\text{As}=\text{C}-\text{O}^-$, rather than $\text{O}=\text{C}=\text{As}^-$, resonance form of this complex.

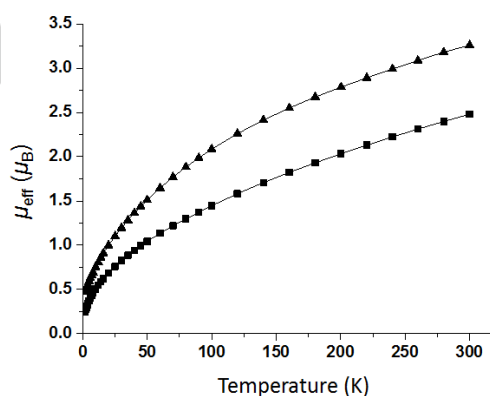


Figure 2. Variable-temperature SQUID magnetometry plots (per U ion) for powdered samples of **2** (triangles) and **5** (squares) over the temperature range 2-298 K. Solid lines are a guide to the eye only.

Photolysis reactivity of the uranium(IV)-2-arsaethynolate linkage

We examined the photolytic reactivity of **2** with a 125 W UV-lamp. Over one hour the green solution in benzene turns red-brown, and after work-up brown crystals were obtained that were verified by a single crystal unit cell check and spectroscopic techniques to be the previously reported diuranium(IV)-diarsane-1,2-diide complex $[\{\text{U}(\text{Tren}^{\text{TIPS}})\}_2(\mu-\eta^2-\eta^2-\text{As}_2\text{H}_2)]$ (**3**, Scheme 1).^[6,9] The isolation of **3** suggests that photolysis of **2** initially results in decarbonylation, in accordance with previous reports of the reactivity of OCAs⁻,^[3,4] to produce the putative uranium(VI)-arsenido complex $[\text{U}(\text{Tren}^{\text{TIPS}})(\text{As})]$. However, the $\text{U}=\text{As}$ bond would be expected to be polar and thus reactive and we postulate that it abstracts a H• from solvent. In support of this premise, we previously reported that when the uranium(IV)-arsenido complex $[\{\text{U}(\text{Tren}^{\text{TIPS}})(\text{AsK}_2)\}_4]$ is treated with K-sequestration reagents such as 2,2,2-cryptand the resulting U=As linkage is so destabilised this ultimately affords the uranium(IV)-

arsinidene complex $[\text{U}(\text{Tren}^{\text{TIPS}})\{\mu\text{-As}(\text{H})\text{K}(2,2,2\text{-crypt})\}]$,^[6h] and when the photolysis of **2** is carried out in C_6D_6 the As_2D_2 isotopologue of **3** is isolated.^[6g] We suggest that “[U(Tren^{TIPS})(AsH)]” transiently forms, but that this dimerises via U-As bond cleavage that would provide the requisite electrons to reduce the uranium(V) ions back to uranium(IV) and form the As-As bond.

It is germane to note that photolysis of [U(Tren^{TIPS})(OCP)] under identical conditions does not promote any reactivity, which may reflect the computed HOMO-LUMO gaps of OCP⁻ (4.11 eV, $\sim 33,150\text{ cm}^{-1}$) versus OCA^{s-} (3.791 eV, $\sim 30,580\text{ cm}^{-1}$), see below. Interestingly, there is no evidence for Tren^{TIPS} C-H activation chemistry when **2** is photolysed as is found to be the case for the nitride congener [U(Tren^{TIPS})(N)].^[6i] This may reflect the likely diminished ability of the softer arsenido to homolytically rupture C-H bonds, even under photolytic conditions, compared to the harder, more polarising nitride.

Reduction studies of the uranium(IV)-arsaethynolate linkage

Given our prior isolation of **1**, and that the HOMO-LUMO data above suggest OCA^{s-} is more reducible than OCP⁻, we treated **2** with [U(Tren^{TIPS})] in benzene directly since this uranium(III) complex is strongly reducing. However, instead of trapping the O-C-As unit between two uranium ions in a neutral version of **1**, we find that again decarbonylation occurs, but here the putative [U(Tren^{TIPS})(As)] is trapped by the reductant to give the mixed-valence diuranium-arsenido complex $[\{\text{U}(\text{Tren}^{\text{TIPS}})\}_2(\mu\text{-As})]$ (**4**, Scheme 1).^[10]

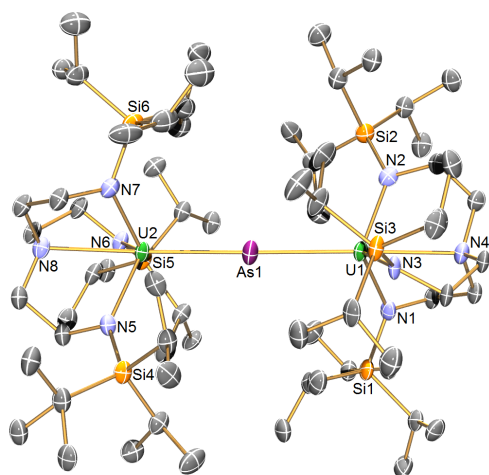


Figure 3. Molecular structure of **4** at 150 K. Displacement ellipsoids are set to 40%, and hydrogen atoms are omitted for clarity.

Complex **4** could only be obtained when the reaction is conducted on a small scale and even then it was obtained in very low crystalline yield. However, examination of several of the isolated brown crystals by single crystal X-ray diffraction (Figure 3) confirmed the identity of **4**. The structure of **4** is similar to the diuranium(IV)-phosphido anion $[\{\text{U}(\text{Tren}^{\text{TIPS}})\}_2(\mu\text{-P})]^{-}$,^[6c] except that we note with (3 σ) statistically distinct U-As distances of 2.943(4) and 2.889(4) Å the UAsU core in **4** is asymmetric whereas the UPU core is symmetrical, which may reflect the mixed-valence uranium(IV/V) nature of **4**. It should be noted that molecular actinide arsenido complexes are exceedingly rare^[6d,h] and indeed remain rare for transition metals.^[4f,13]

Unfortunately, like salts of $[\{\text{U}(\text{Tren}^{\text{TIPS}})\}_2(\mu\text{-P})]^{-}$,^[6c] when **4** is redissolved decomposition rapidly occurs, so this combined with the low isolated yield precluded further characterization. However, the identification of **4** is informative as it adds to the growing picture of the

prevalent decomposition mode of OCA^{s-} by decarbonylation,^[3,4] and also it demonstrates that even though the OCA^{s-} ligand is O-bound in **2** this complex can still extrude CO to generate arsenido derivatives, even if they convert into something else (*cf* **3**), which may have general implications for deliberate use of OCA^{s-} as an arsenido transfer reagent.

Since the use of trivalent uranium as a reducing agent ‘over-reduced’ the OCA^{s-} resulting in fragmentation and CO-release, we focused on an electride; although electrides are thermodynamically strongly reducing our qualitative experience is that they are often kinetically milder reducing agents overall than uranium(III). Addition of **2** to a preformed mixture of KC_8 and 2,2,2-cryptand in THF in a 1:1:1 ratio resulted in a dark green solution, from which brown $[\{\text{U}(\text{Tren}^{\text{TIPS}})\}_2\{\mu\text{-}\eta^2(\text{OAs})\text{:}\eta^2(\text{CAs})\text{-OCA}_s\}][\text{K}(2,2,2\text{-cryptand})]$ (**5**) was isolated from toluene in 33% crystalline yield (based on uranium content, Scheme 1).^[10] The presumed by-product of this reaction, $[\text{K}(\text{OCA}_s)(2,2,2\text{-cryptand})]$, could not be confirmed since despite several attempts only **5** could be isolated from the reaction mixtures.

Experimental characterisation of the trapped and highly bent form of arsaethynolate

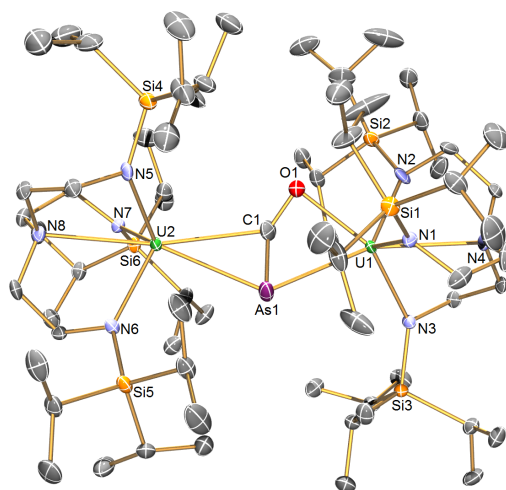


Figure 4. Molecular structure of the anion component of **5** at 150 K. Displacement ellipsoids are set to 40%, and hydrogen atoms, minor disorder components, and the K-2,2,2-cryptand cation are omitted for clarity. The O-C-As unit is disordered over two positions in a 50:50 ratio with only one component being shown.

The crystal structure of **5** (Figure 4) confirms its structure and the presence of a highly-bent As-C-O linkage bridging two [U(Tren^{TIPS})] units in the anion component. The $\mu\text{-}\eta^2(\text{OAs})\text{:}\eta^2(\text{CAs})\text{-OCA}_s$ coordination mode is unique for 2-arsaethynolate. The As-C and C-O distances are 1.742(10) and 1.30(2) Å, respectively; unfortunately disorder of the O-C-As unit over two locations reduces the precision of the bond metrics, but it is clear that the C-As bond is longer in **5** compared to **2** reflecting substantial charge transfer from the uranium ions to the OCA^{s-} ligand. Further reinforcing the notion of a highly-reduced form of the As-C-O linkage, the O-C-As angle in **5** is 128° (av.), which is a significant departure from linearity for the O-C-As unit. The U1-O1, U1-As1, U2-As1 bond distances are 2.294(7), 2.895(4), and 2.923(4) Å, respectively, and are unexceptional. The U1-C1 distance of 2.54(2) Å, is essentially the same as in **1**,^[7] and compares to distances of 2.576(12)-2.598(11) and 2.672(5) Å in the mesoionic and *N*-heterocyclic carbene complexes $[\text{U}\{\text{CN}(\text{Me})\text{C}(\text{Me})\text{N}(\text{Me})\text{CH}\}(\text{N}^{\text{M}})_3]$ and $[\text{U}\{\text{C}(\text{NMeCMe})_2\}(\text{N}^{\text{M}})_3]$ $[\text{N}^{\text{M}} = \text{N}(\text{SiMe}_3)_2]$,^[14] which together with the acute O-C-As angle suggests,

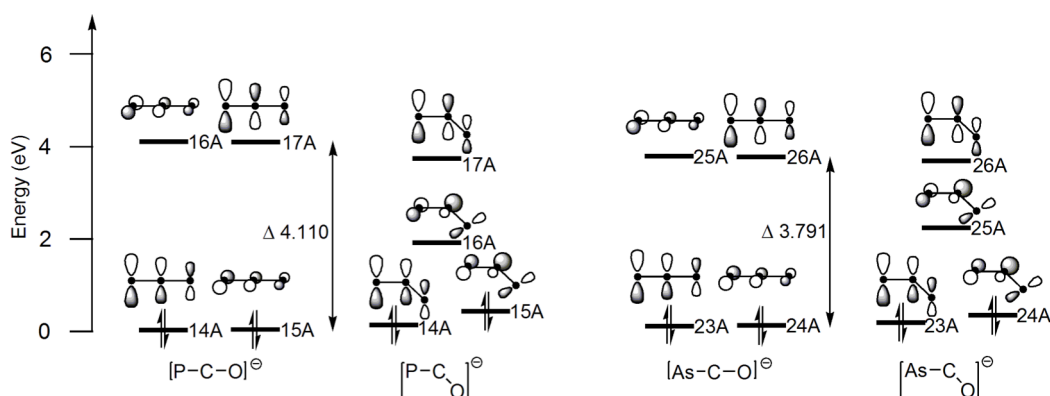


Figure 5. Computed frontier orbital regions of the linear OCP[−] anion, bent OCP[−] anion (130°), linear OCAs[−], and bent OCAs[−] anion (128°). The energy scale is arbitrarily set such that 14A and 15A of linear OCP[−] are 0 eV. The OCP[−] portion is adapted from reference 7.

analogously to some reduced CO₂ and CS₂ complexes,^[15] that the C-atom in **5** possess some carbene character when highly reduced. The U-N_{amide} (av. 2.324(9) Å) and U-N_{amine} (av. 2.776(7) Å) distances are averaged by the disorder, and towards the high end of such distances.^[5] This most likely reflects the overall anionic charge state of the diuranium component of **5**, but could also reflect the presence of uranium(III) character since the anion portion of **5** can be formulated as a ‘high spin’ diuranium(III)/AsCO-monoanion or a diuranium(IV)/AsCO-highly-reduced ‘low spin’ form. Which of these is the most appropriate electronic structure description is addressed below.

The ATR-IR spectrum of **5** exhibits two absorptions at 1771 and 1737 cm^{−1}, which can be attributed to ν₁-derived stretching modes of the O-C-As unit. This is consistent with charge accumulation on the O-C-As linkage and a lowering of the C-As bond order, and these absorptions are at a slightly lower range than **1**.^[7] There are no examples for comparison of side-on bound OCAs[−], but the IR data for **5** fall in the range of side-on η²- and μ-η²:η²-coordination modes of the OCP[−] anion (1890-1688 cm^{−1}).^[11]

The UV/Vis/NIR spectrum of **5** reveals moderately strong (ε ~1000 M^{−1} cm^{−1}) absorptions in the region 20,000-12,000 cm^{−1}, suggestive of Laporte-allowed 5f-6d transitions of uranium(III)^[16] along with multiple weak (ε ~ 50 M^{−1} cm^{−1}) f-f absorptions in the NIR region. These data are distinct to the uranium(IV) complex **2** and the 5f-6d absorptions of **5** are red-shifted by ~2,000 cm^{−1} compared to mixed-valence **1**,^[7] which overall implies that **5** has some Kramers uranium(III) character. However, the X-band EPR spectrum of powdered **5** at 5 K reveals only one sharp g-value absorption at g = 2.0026, suggesting spin density on the O-C-As unit, with no features with substantial g-value anisotropy attributable to uranium(III). This indicates a uranium(IV/IV)-radical formulation, which contrasts to the situation for **1** where the corresponding EPR spectrum exhibits clear resonance lines corresponding to uranium(III). However, there it was noted that those features were very weak and only observed due to the very sensitive nature of EPR spectroscopy. To help reconcile the apparently conflicting optical and EPR data, we examined the magnetism of **5**. Complex **5** exhibits a magnetic moment of 2.48 μ_B (per U ion) at 298 K and this decreases smoothly to 0.25 μ_B at 2 K and tending to zero (Figure 2). Interestingly, at 2 K the M vs H data reach 0.65 μ_B at 70 kOe but are still not saturated,^[10] and the magnetic moment data for **5** are on a like-for-like basis always lower than those of **1**, and indeed almost diamagnetic at 2 K. This suggests a dominance of diuranium(IV) character in **5**, and whilst we cannot rule out the presence of any uranium(III) character in **5** it would seem to be the case that there is less uranium(III) and more uranium(IV) character

than in **1**,^[7] which would be in-line with the superior computed acceptor capability of OCAs[−] compared to OCP[−]. In order to probe the electronic structure of **5** in more detail we turned to quantum chemical DFT calculations.

Computational characterisation of the trapped and highly bent form of arsaethynolate

In order to examine the electronic structure of **5** we first benchmark the computed frontier orbitals of the OCAs[−] anion itself against that of OCP[−] in linear and bent forms (Figure 5). As expected, on a like-for-like basis they are largely similar, though the HOMO-LUMO gap of linear OCAs[−] is noticeably smaller than that of OCP[−] suggesting that the former is easier to reduce. The top two occupied OCAs[−] MOs (23A and 24A) are a degenerate pair of π-bonds that are As-C bonding and C-O anti-bonding. The first two unoccupied MOs (25A and 26A) are a degenerate pair of π* character across the O-C-P unit that would be successively occupied if the OCAs[−] anion is reduced, hence the facile proclivity of OCAs[−] to fragment when reduced. Bending the OCAs[−] anion to an angle of 128° to match the O-C-As angle found in the crystal structure of **5** results in the degeneracy of 23A and 24A being lifted, such that 23A if occupied would form a σ-symmetry lone pair and 24A would present a vacant p-orbital at the C-atom for π-backbonding from a metal.

We geometry optimised the septet ‘high spin’ (**sept5**) and ‘low spin’ (**quin5**) formulations of the anion of **5**. The key difference between these two spin forms is that in the former the MO that derives from MO 23A of OCAs[−] is only occupied in the α-spin manifold, but in the latter both α- and β-spin orbitals are occupied. Interestingly, however, whilst the computed O-C-As angle (136.5°) is over-estimated for the former, for the latter it is under-estimated (120.0°). This suggests that **5** lies between these two electronic structure extremes, and so is not pure diuranium(IV) and has some diuranium(III/IV) character but less so than **1**.^[7] We note that **quin5** lies 21.3 kcal/mol lower in energy than **sept5**, and so the following discussion focuses on **quin5**. Inspection of 457a and 457b (which derives from orbital 25A, Fig. 5) of **quin5** reveals that overall they are composed of ~20:80 U-5f:C-2p character, thus equating to significant formal reduction of the OCAs[−] unit, and more extensively than **1** where 50:50 character was found. This suggests, consistent with the superior acceptor character of OCAs[−] compared to OCP[−] that the OCAs[−] linkage in **5** is indeed strongly reduced. This would also account for the absence of any observable uranium(III) character in the EPR spectrum of **5** since the more extensive the reduction of OCAs[−] the more non-Kramers diuranium(IV) character can be ascribed. In addition, interestingly MO 458a (which derives from orbital 26A, Fig. 5) of **quin5** does not

possess pure 5f-character, being mixed weakly with a OCA^s orbital of 26A-parentage to constitute a weak backbond (Figure 6b) further supporting the notion of the As-C-O linkage in **5** as having some carbene character and this is also consistent with the EPR data.

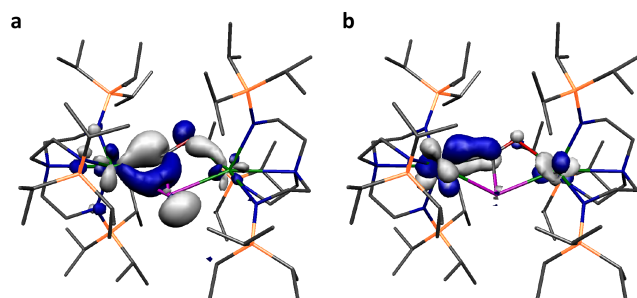


Figure 6. Selected computed α -spin molecular orbitals of **quin5⁻**. a) α -HOMO-4 (457a, -1.794 eV), b) α -HOMO-3 (458a, -0.651 eV).

The computed Mayer bond orders for the C-O, C-As, U1-As, U2-As, U2-C1, and U1-O1 bonds are 1.25, 1.03, 0.70, 0.79, 0.57, and 0.54, respectively. As would be expected, this shows that reduction of OCA^s results in lowering of the C-O and As-C bond orders. The computed MDC_q charges for **quin5⁻** are O (-0.37), As (-1.83), C (-0.97), U1 (2.88), and U2 (3.53), and the latter charge is consistent with extensive backbonding to the O-C-As linkage. Thus, the O-C-As unit in **quin5⁻** has a total computed charge of -3.17, which is \sim -0.2 more than the computed charge of the O-C-P unit in **I**.^[7] For comparison, the Tren-amides have average relative computed charges of -1.6 and so since an amide is formally a -1 charge ligand the O-C-As unit in **3** is somewhere on the continuum from the radical dianion to trianion forms of arsaethynolate. Lastly, analysis of the bonding topology with QTAIM shows polar U-O, -As, and -C bonds with 3, -1 bond critical point (BCP) ρ values of 0.08, 0.05 (av.), and 0.08, respectively. Most of these bonding interactions present roughly spherical charge ellipticity (ϵ) distributions around the inter-nuclear axes at their respective BCPs ($\epsilon = 0.02$ -0.19), but the U-C bond exhibits an ϵ value of 0.39 confirming the weak π -backbond and thus a two-fold U-C bonding interaction.^[17]

Conclusion

To conclude, by using uranium-Tren^{TIPS} we have prepared the first example of an actinide-2-arsaethynolate complex. Photolysis of this complex affords a diarsane-1,2-diide unit. We suggest this HASAsH unit originates from decarbonylative fragmentation of the O-C-As unit and As-transfer to U, followed by arsenide-mediated H[•] abstraction from solvent and dimerisation of the resulting arsinidene. This contrasts to the 2-phosphaethynolate congener where no reactivity under photolytic conditions was observed consistent with the HOMO-LUMO gaps of OCP[•] and OCA^s. In a similar vein, uranium(III)-mediated reduction affords a rare example of a bridging arsenido mixed-valence actinide complex by decarbonylation and As-transfer, which occurs even though the 2-arsaethynolate was O-bound to uranium. This could inform strategies to deliberately prepare metal-arsenido complexes and the decarbonylation fragmentations here add to the growing picture of the dominant fragmentation pathways of 2-arsaethynolate. However, by using an electronegative reductant a highly reduced, bent form of 2-arsaethynolate with a unique coordination mode has been trapped, thus defying the to date exclusive and facile

fragmentation reactions of this ligand when it is strongly reduced. The O-C-As unit in **5** is bent to an unprecedented degree due to extensive backbonding from uranium to this ligand. The combined experimental and computational characterisation data suggest a diuranium(IV)-form dominates with a O-C-As unit most likely best described as formally somewhere between di- and trianionic. This is consistent with the superior electron acceptor character of 2-arsaethynolate compared to 2-phosphaethynolate, which further underscores how different the chemistries of these two anions are and how surprising it is that a bent and highly reduced form of 2-arsaethynolate can be trapped. The bent O-C-As unit has donor-acceptor character, thus introducing some carbene character to this linkage.

Acknowledgements

We gratefully acknowledge the UK EPSRC (grants EP/M027015/1 and EP/P001286/1), ERC (grant CoG612724), Royal Society (grant UF110005), Leverhulme Trust (RF/2018-545\4), National Nuclear Laboratory, The Universities of Manchester and Regensburg, the Deutsche Forschungsgemeinschaft, COST Action CM1006, and the National EPSRC UK EPR Facility for generous funding and support.

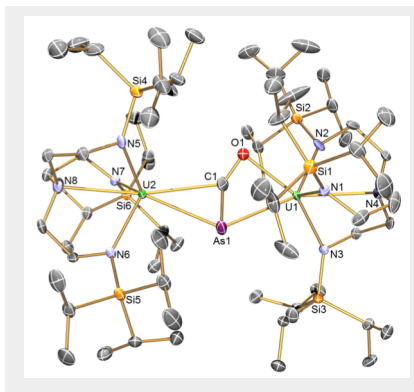
Keywords: uranium • 2-arsaethynolate • decarbonylation • carbene • density functional theory

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ToC Entry

In a triamidoamine uranium complex 2-arsaethynolate is shown to undergo decarbonylation and As-transfer under photolytic and reductive conditions, and also an unprecedented highly bent and reduced form has been trapped.



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