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Uranium(III)-Mediated C−C-Coupling of Terminal Alkynes: Formation of Dinuclear Uranium(IV) Vinyl Complexes

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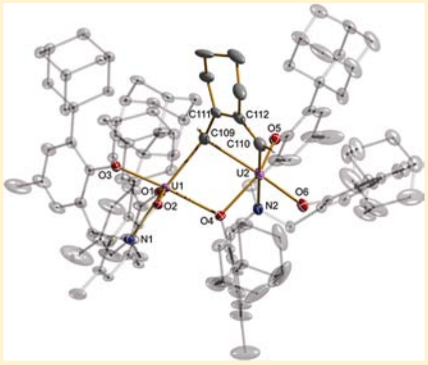
Ⓢ *Supporting Information*

ABSTRACT: The previously reported uranium(III) complex $[((^{Ad}ArO)_3N)U^{III}(DME)]$ (**1**; Ad = adamantane, DME = 1,2-dimethoxyethane) reacts with the terminal bis-alkynes 1,7-octadiyne or 1,6-heptadiyne in C−C-coupling reactions to form the uranium(IV) vinyl complexes $[\{((^{Ad}ArO)_3N)U^{IV}\}_2(\mu{-}\eta^2{:}\eta^1\text{-}1,2\text{-}(CH)_2\text{-cyclohexane})]$ (**2**) and $[\{((^{Ad}ArO)_3N)U^{IV}\}_2(\mu{-}\eta^2{:}\eta^2\text{-}1,2\text{-}(CH)_2\text{-cyclopentane})]$ (**3**). With the monoalkynes 1-hexyne or 4-^{t}butyl-phenylacetylene, the complexes $[\{((^{Ad}ArO)_3N)U^{IV}\}_2(\mu{-}\eta^2(C1){:}\eta^1(C4)\text{-}2\text{-}^n\text{Bu-1,3-octadiene})]$ (**4**) and $[\{((^{Ad}ArO)_3N)U^{IV}\}_2(\mu{-}\eta^2(C4){:}\eta^1(C1)\text{-1,3-di-}(p\text{-}^t\text{Bu-phenyl})\text{butadiene}))]$ (**5**), are formed. These are the first four examples of uranium vinyl complexes that are reported and crystallographically characterized. In addition, detailed DFT calculations are presented to establish a possible mechanism for their formation and explain the differences found for the coordination of the hydrocarbon fragments. In contrast to a previously proposed monometallic pathway for catalytic hydroamination of alkynes and alkyne dimerization involving a uranium vinyl intermediate at uranium(III) complexes, the calculations clearly support a bimetallic mechanism, since its transition states are energetically the most favored.



INTRODUCTION

The reaction of low-valent metal complexes with terminal alkynes forms isolable vinyl species or fleeting intermediates that often catalyze their C−C-coupling[1] and cycloisomerization.[2] The broad interest in this type of chemistry is well-documented in the extensively studied gold(I) chemistry. Complexes of this noble metal are known catalysts for C−X (X = C, N, O) bond formation chemistry,[3] for which vinyl complexes and intermediates have been isolated and characterized.[4] It is particularly interesting to note that a cooperative effect of a second metal center has been proposed,[5] suggesting a bimetallic mechanism in these catalytic reactions. Moreover, numerous rare-earth compounds with Ln−C σ-bonds have been investigated and found to exhibit interesting catalytic activity in Ziegler−Natta anionic polymerization as well as in, e.g. olefin hydrogenation, hydrosilylation, and alkyne dimerization.[6] The importance of this type of reactivity has led to the reinvestigation of the corresponding actinide organometallic chemistry,[7] which resulted in several catalytically active uranium species,[8] and other compounds with U−C σ-[9] or π-bonds.[10] Typically, uranium reacts with terminal alkynes in C−H-activation reactions to yield uranium acetylide[11] or μ-carbide complexes;[12] however, some of them have been shown to be active catalysts for the dimerization of alkynes or hydrosilylation reactions.[8a,c,e] In the late 1990s, Eisen et al. proposed a monometallic mechanism for the catalytic hydroamination of alkynes[8a] and alkyne dimerization, involving a uranium vinyl intermediate.[8b]

Nevertheless, to the best of our knowledge, the isolation and structural characterization of uranium vinyl complexes remained elusive, even though some examples of vinyl complexes have been reported for lanthanides.[13]

Herein, we present the synthesis and characterization of four dinuclear uranium(IV) complexes with bridging bis-vinyl ligands, derived from intra- or intermolecular C−C-coupling and cycloisomerization reactions of terminal mono- or bis-alkynes with trivalent $[((^{Ad}ArO)_3N)U^{III}(DME)]$[14] (**1**; Ad = adamantane, DME = 1,2-dimethoxyethane). Moreover, a DFT analysis is presented to rationalize a bimetallic mechanism for the formation of these compounds.

RESULTS AND DISCUSSION

$[((^{Ad}ArO)_3N)U^{III}(DME)]$ (**1**) reacts with one equivalent of the terminal bis-alkynes 1,7-octadiyne or 1,6-heptadiyne, undergoing intramolecular C−C-coupling and cyclization to form the uranium(IV) complexes $[\{((^{Ad}ArO)_3N)U^{IV}\}_2(\mu{-}\eta^2{:}\eta^1\text{-}1,2\text{-}(CH)_2\text{-cyclohexane})]$ (**2**) and $[\{((^{Ad}ArO)_3N)U^{IV}\}_2(\mu{-}\eta^2{:}\eta^2\text{-}1,2\text{-}(CH)_2\text{-cyclopentane})]$ (**3**) with bridging bis-vinyl cyclic hydrocarbons, forming C−C bonds between C2−C7 and C2−C6, respectively (Scheme 1).

Similarly, trivalent complex **1** reacts with 2 equiv of the terminal monoalkynes, 1-hexyne or 4-*tert*-butyl-phenylacetylene, in an intermolecular C−C-coupling reaction to yield the

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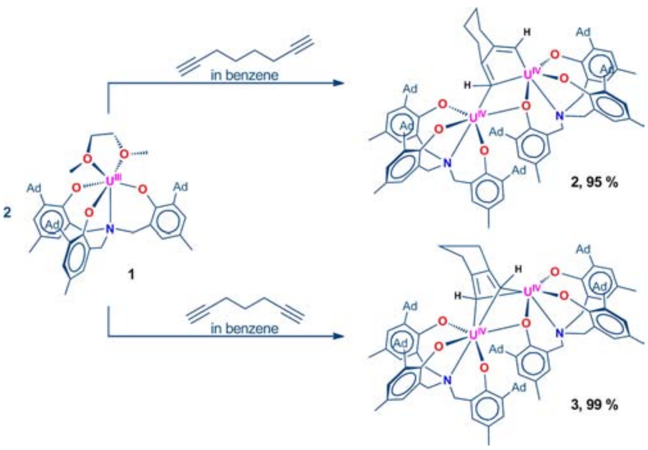
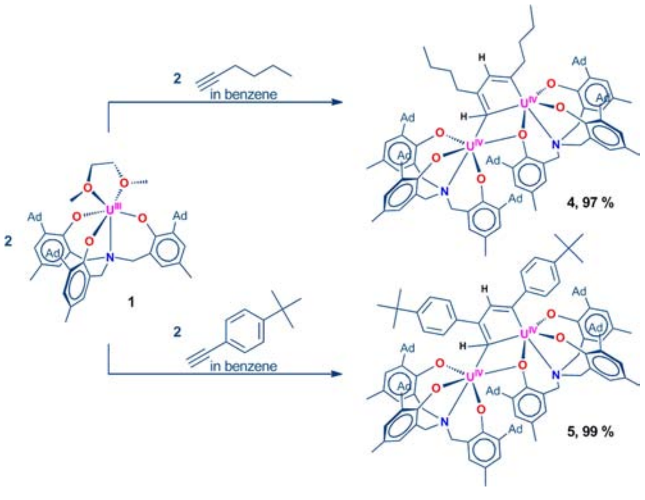
Scheme 1. Reaction of $[((^{Ad}ArO)_3N)U^{III}(DME)]$ (1) with 1 equiv of 1,7-octadiyne or 1,6-heptadiyne to form $[\{((^{Ad}ArO)_3N)U^{IV}\}_2(\mu-\eta^2:\eta^1\text{-}1,2\text{-}(CH)_2\text{-cyclohexane})]$ (2) and $[\{((^{Ad}ArO)_3N)U^{IV}\}_2(\mu-\eta^2:\eta^2\text{-}1,2\text{-}(CH)_2\text{-cyclopentane})]$ (3)



complexes $[\{((^{Ad}ArO)_3N)U^{IV}\}_2(\mu-\eta^2(C1):\eta^1(C4)\text{-}2\text{-}^n\text{Bu-}1,3\text{-octadiene})]$ (**4**) and $[\{((^{Ad}ArO)_3N)U^{IV}\}_2(\mu-\eta^2(C4):\eta^1(C1)\text{-}1,3\text{-di-}(p\text{-}^t\text{Bu-phenyl})\text{butadiene}))]$ (**5**), forming C−C bonds between C1 and C2 and thus leading to a different coordination mode (Scheme 2). This difference in C−C bond formation, as compared to the previous one, is due to a different mechanism that would, in principle, be possible for bis-alkynes as well, but is not observed due to higher energy of the relevant transition states (*vide infra*).

Scheme 2. Reaction of $[((^{Ad}ArO)_3N)U^{III}(DME)]$ (1) with 2 equiv of 1-hexyne or 4-^{t}Bu-phenylacetylene to yield $[\{((^{Ad}ArO)_3N)U^{IV}\}_2(\mu-\eta^2(C1):\eta^1(C4)\text{-}2\text{-}^n\text{Bu-}1,3\text{-octadiene})]$ (4) and $[\{((^{Ad}ArO)_3N)U^{IV}\}_2(\mu-\eta^2(C4):\eta^1(C1)\text{-}1,3\text{-di-}(p\text{-}^t\text{Bu-phenyl})\text{butadiene}))]$ (5)



In detail, adding one equivalent of a terminal bis-alkyne, such as 1,7-octadiyne or 1,6-heptadiyne, to a brown solution of $[((^{Ad}ArO)_3N)U^{III}(DME)]$ (**1**) in benzene leads to an immediate color change to yellow-brown and quantitative formation of the bis-vinyl complexes **2** and **3** (see Experimental Section). The molecular structures of these compounds are very similar to each other and show only slight differences (Figure 1).

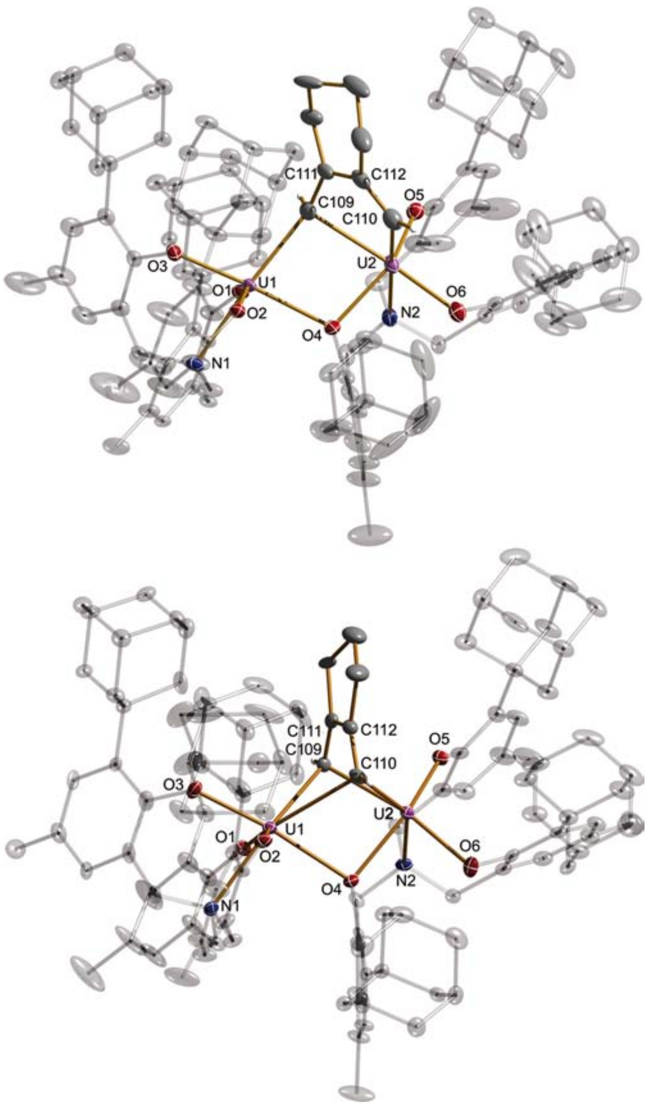


Figure 1. Molecular structure of $[\{((^{Ad}ArO)_3N)U^{IV}\}_2(\mu-\eta^2:\eta^1\text{-}1,2\text{-}(CH)_2\text{-cyclohexane})]\cdot3DME$ (**2**·3DME, top), and molecular structure of $[\{((^{Ad}ArO)_3N)U^{IV}\}_2(\mu-\eta^2:\eta^2\text{-}1,2\text{-}(CH)_2\text{-cyclopentane})]\cdot2DME$ (**3**·2DME, bottom). Co-crystallized solvent molecules and hydrogen atoms are omitted for clarity. Thermal ellipsoids are at 50% probability.

For steric reasons, both vinyl carbons C109 and C110 bridge the two uranium centers in the cyclopentyl-compound **3**, thus leading to a $\mu-\eta^2:\eta^2$-coordination mode of the bridging hydrocarbon ligand. In cyclohexyl-derivative **2**, however, one carbon is coordinated to both uranium atoms, while the other is bound to only one uranium center, resulting in a $\mu-\eta^2:\eta^1$ coordination mode. In both complexes, **2** and **3**, the aryloxide oxygen O4 of one of the N-anchored tris-aryloxide ligands bridges the two uranium(IV) centers, which places the aryloxides O3 and O5 trans to it. For **2**, both uranium centers are coordinated in a pseudo-octahedral fashion formed by the N-anchored tris-aryloxide, the additional aryloxide oxygen of the second chelator, and the vinyl carbon at U1; the U2 center is coordinated by the four heteroatoms of the second chelator and both vinyl carbons, C109 and C110. In complex **3**, U2 is coordinated in a similar fashion, while U1, due to the additional coordination of the second vinyl carbon, C110, is hepta-coordinated. The U1−O(1−3)$_{av}$ distances are 2.142 Å in **2** and

2.188 Å in **3**, while U1−O4 are long with 2.472(3) and 2.503(3) Å, respectively. The U2−O(5−6)$_{\mathrm{av}}$ distances are similar to the U1−O(1−3) distances with 2.151 Å in **2**, and 2.168 Å in **3**; the longest U−O distance is the bond to O4, which is the μ-aryloxide oxygen with 2.326(3) and 2.311(3) Å. U1−N1 and U2−N2 distances are 2.564(4) and 2.624(4) Å for **2** and 2.557(4) and 2.550(4) Å for **3**, respectively.

The most interesting metric parameters in these complexes are the uranium−carbon bond distances U1−C109/U2−C109 and U1−C110/U2−C110. For **2**, these are 2.511(5) and 2.632(5) Å for C109 and 4.476(5) and 2.434(5) Å for C110, clearly showing no bonding interaction of C110 to U1. In complex **3**, the distances are 2.613(5) and 2.549(4) Å for C109 and 2.839(5) and 2.503(5) Å for C110; both carbon centers are interacting with and bridging both U ions. In both instances, the vinyl C−ring−C bond distances, C109−C111 and C110−C112, are short with 1.378(7) and 1.349(8) for **2** and 1.372(6) and 1.360(6) Å for **3**, which supports the double bond character within this bridging unit. As expected, the newly formed C−C bonds upon ring-closure, C111−C112, are significantly longer with 1.470(8) in **2** and 1.477(7) Å in **3** and, thus, indicative of a normal C−C single bond.

Similar to the above-reported U(III)-mediated cyclomerization of bis-alkynes, monoalkynes also yield U(IV) μ-bis-vinyl complexes. Thus, adding one equivalent of 1-hexyne or 4-^{t}butyl-phenylacetylene to a brown solution of $[((^{\mathrm{Ad}}\mathrm{ArO})_3\mathrm{N})\mathrm{U}^{\mathrm{III}}(\mathrm{DME})]$ (**1**) in benzene leads to instant color change to yellow-brown and quantitative formation of the bis-vinyl complexes **4** and **5** (see Experimental Section). It is interesting to note, however, that the newly formed hydrocarbon ligands in **4** and **5** adopt identical coordination modes. This is despite the steric demand of the coordinated 1,3-di-(p-^{t}butyl-phenyl)-butadiene in complex **5**, compared to 2-^{n}butyl-1,3-octadiene in compound **4**. In both reactions, the C−C-coupling is an intermolecular C1−C2-coupling, and thus, the coordination occurs μ−η^2:η^1 in both complexes (Figure 2).

The coordination geometry is comparable to that found for complex **2**. The average U1−O(1−3)$_{\mathrm{av}}$ aryloxide distances in both complexes are 2.152 Å in **4** and 2.159 Å in **5**; the bridging aryloxide, U1−O4, is again the longest U−O$_{\mathrm{ArO}}$ bond with 2.462(2) and 2.495(3) Å for **4** and **5**, respectively. The aryloxide oxygen bond lengths to the second uranium center, U2−O(5−6)$_{\mathrm{av}}$, are 2.155 Å in **4** and 2.141 Å in **5**. The respective μ-aryloxide oxygen O4 has again a longer distance to U2 in both compounds with 2.331(2) and 2.334(3) Å. U1−N1 and U2−N2 distances are 2.556(3) and 2.572(3) Å for **4** and 2.555(4) and 2.592(3) Å for **5**, respectively. As in **2**, the bridging hydrocarbon ligand in complexes **4** and **5** is unsymmetrically coordinated. This results in the previously observed μ−η^2:η^1 coordination mode, in which C116 (**4**)/C118 (**5**) is bridging both uranium ions (μ−η^2) and C114 (**4**)/C116 (**5**) is bound η^1 to U2.

Accordingly, the U1/U2−C114 bond distances in **4** are determined to be 2.528(3) and 2.608(4) Å and the U2−C116 distance is 2.464(4) Å. In **5**, the corresponding U1/U2−C116 and U2−C118 distances are 2.535(4) and 2.643(4) Å for C116 and 2.474(4) Å for C118. The vinyl C−chain−C bonds C114−C113 (**4**) and C116−C115 (**5**) are found to be at 1.359(5) and 1.363(6) Å, characteristic for C═C double bonds, just like the chain C−C bonds C116−C115 (**4**) and C118−C117 (**5**) with 1.357(6) and 1.355(6) Å, while the chain C−C bonds C113−C115 (**4**) and C115−C117 (**5**) correspond to typical single bond distances with 1.475(6) and 1.484(6) Å, respectively. The conjugated π-system over the phenyl ring and the two conjugated double bonds in 1,3-di-(p-^{t}Bu-phenyl)butadiene should force the fragment to be planar. Regardless, the steric pressure exerted by the bulky adamantyl groups leads to a considerable twist in this coordinated hydrocarbon ligand. The central C$_4$ unit C116−C115−C117−C118 deviates significantly from planarity as is evidenced by its corresponding torsion angle of −26.4(7)°. The least-squares planes of the two adjacent phenyl rings C109−C114 and C119−C124 are twisted by 39.4(4)° and 37.3(4)° with respect to the planar C115−C117−C118 fragment.

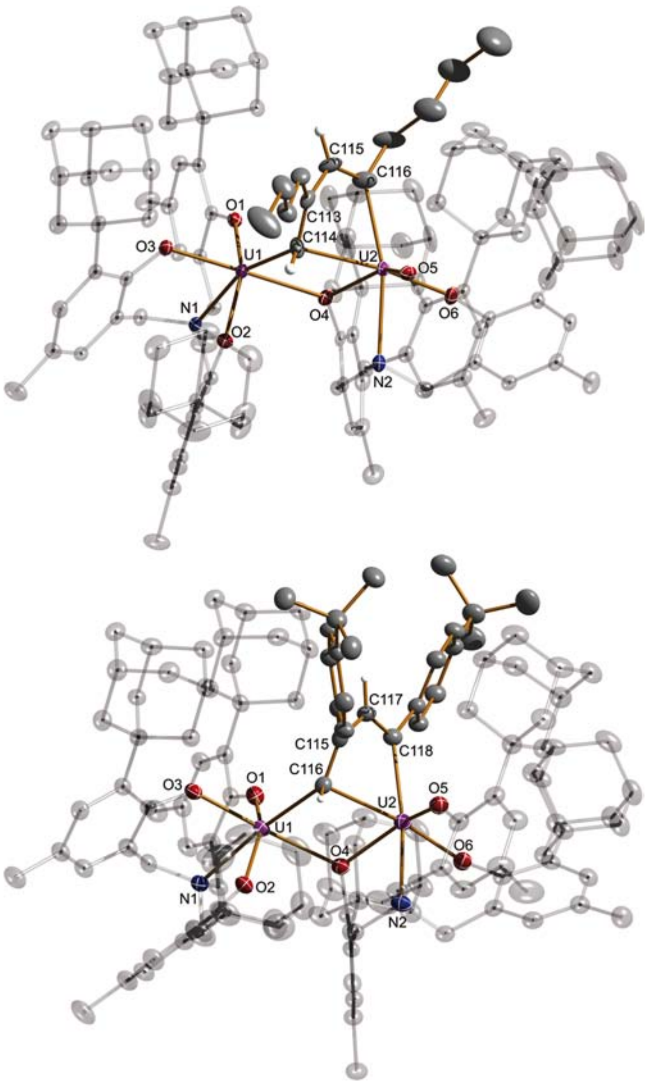


Figure 2. Molecular structure of $[\{((^{\mathrm{Ad}}\mathrm{ArO})_3\mathrm{N})\mathrm{U}^{\mathrm{IV}}\}_2$-($\mu$−$\eta^2$(C1):$\eta^1$(C4)-2-^{n}Bu-1,3-octadiene)]·DME (**4**·DME, top), and molecular structure of $[\{((^{\mathrm{Ad}}\mathrm{ArO})_3\mathrm{N})\mathrm{U}^{\mathrm{IV}}\}_2$($\mu$−$\eta^2$(C4):$\eta^1$(C1)-1,3-di-($p$-^{t}Bu-phenyl)butadiene)]·1.5DME (**5**·1.5DME, bottom). Co-crystallized solvent molecules and hydrogen atoms are omitted for clarity. Thermal ellipsoids are at 50% probability.

Variable-temperature SQUID measurements were carried out for all four vinyl complexes. The effective magnetic moment, μ_{eff}, at 2 K is low with approximately 0.5 μ_{B} for all compounds, and 3.4 μ_{B} at 300 K. As one example, the data for complex **5** are shown in Figure 3 (see SI for data for **2**, **3**, and **4**). The oxidation-state assignment of two, magnetically uncoupled uranium(IV) centers is in line with the observed magnetic properties.[15]

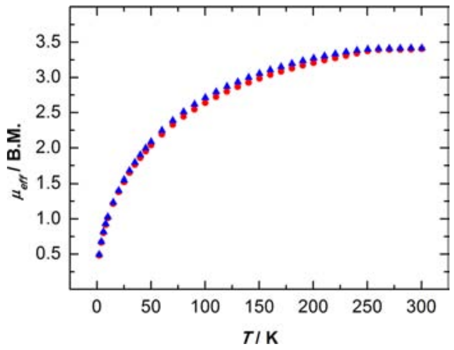


Figure 3. Temperature-dependent SQUID magnetization measurements for complex **5**. For reproducibility, three independently synthesized samples were measured.

A series of DFT (B3PW91) calculations were carried out to establish a possible reaction profile. In order to obtain a computationally convenient molecule size, models of **2** and **4** were calculated, in which the adamantyl groups of the ligand were replaced by methyl groups.[16] The most favorable mechanism, found by DFT computational analyses, is a bimolecular one (Figure 4, see SI for full calculation details and mechanism pathways). As already found in previous cases,[17] the oxidation of the U(III) to U(IV) is induced by the coordination of the substrate (here 1,7-octadiyne) that replaces the DME and leads to the formation of a dinuclear complex; the "key intermediate" (see boxed species in Figure 4). It should be noted that other dinuclear intermediates are found to be much higher in energy (see SI), especially, when each uranium center is disrupting a different triple bond (initial and terminal ones). As studied by Labouille et al.,[17d] the formation of the dinuclear complex occurs in one step, involving two subsequent one-electron oxidations (one for each uranium center). The stabilization energy is computed to be −22.8 kcal mol^{-1} with respect to the starting materials. This stabilization can be attributed to the existence of the aryloxide bridge, connecting the two U(IV) ions, and the formation of two U(IV)−C bonds *via* alkyne reduction. This intermediate further reacts to form the bis-vinyl complex, and it involves an ionic transition state, in which the second triple bond is polarized by one uranium center, allowing the formation of an empty sp^2-orbital at one of the two carbon centers and a lone-pair at the second carbon atom of the former triple bond.

This empty sp^2-orbital further interacts with the filled sp^2-orbital of one of the carbons interacting with one of the U(IV). The computed activation barrier for this transition is low at 12.3 kcal mol^{-1} (with respect to the key intermediate). The final product **2** is then formed after the cyclization step, and the overall reaction is strongly exergonic (−61.4 kcal mol^{-1}). It is noteworthy to mention that cyclization at a single uranium center is strongly disfavored. In fact, the transition state for such a transformation lies above the starting materials (see SI for further details). Similarly, α-C−H bond activation of the key intermediate has been investigated and was found to be kinetically less favorable than the cyclization by 10.5 kcal mol^{-1} and is endergonic by 17.9 kcal mol^{-1}, ruling out any kinetic formation of these products. These results are in line with the experimental observations (see SI). Finally, the addition of a second bis-alkyne molecule has been considered, which would result in a C−C-coupling product in either a 1,2- or a 2,2-fashion. However, the activation barriers are computed to be 10.0−13.0 kcal mol^{-1} higher than those of the cyclization route (22.6 and 23.9 kcal mol^{-1}, respectively). Consequently, these two reactions are disfavored under these conditions. Accordingly, the theoretical results are in excellent agreement with the experimental observation.

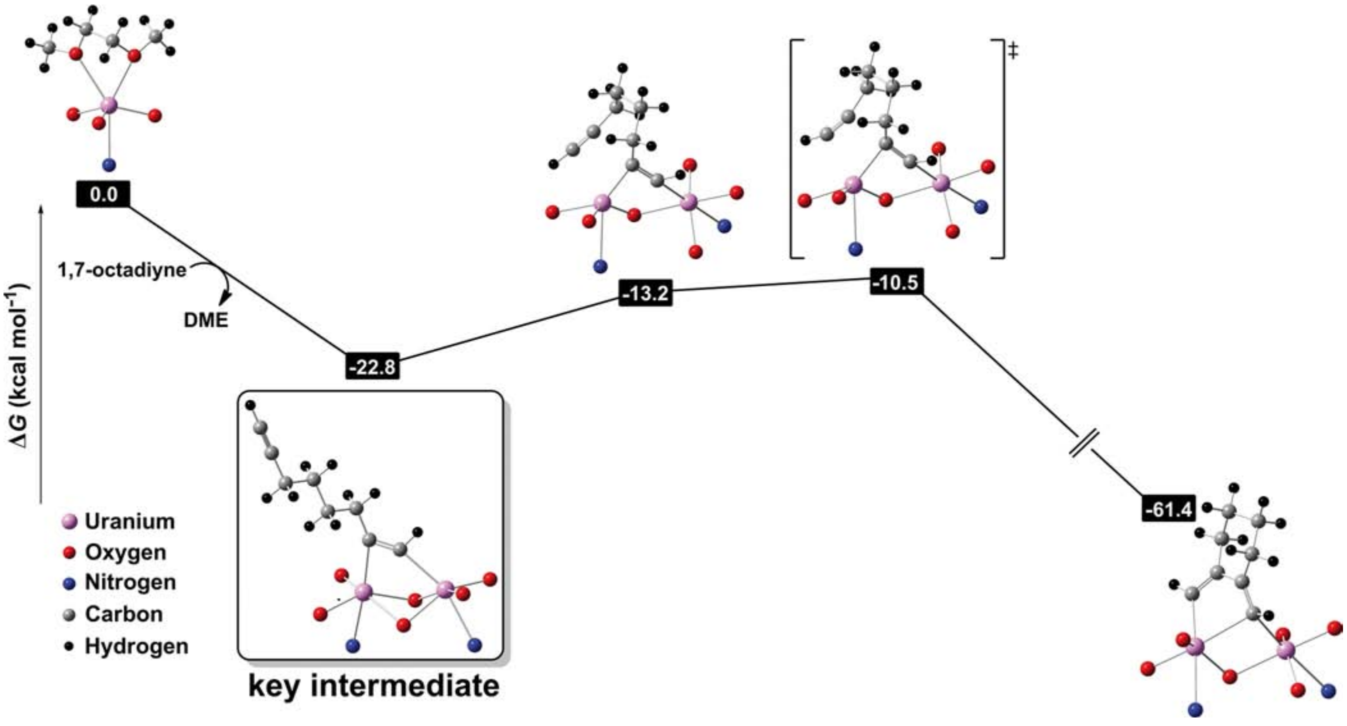


Figure 4. Gibbs free energy ΔG [kcal mol^{-1}] profile for the cyclization of 1,7-octadiyne (some atoms from the anchoring ligand $(^{Me}ArO)_3N^{3-}$ are omitted for clarity).

The use of terminal monoalkynes instead of bis-alkynes, as in cases **4** and **5**, experimentally leads to the intermolecular C−C-coupling products, since obviously no cyclization can occur. Computing the reaction profiles for the 1-hexyne case (see SI for the pathway), it is found that after the formation of the corresponding bimetallic key intermediate, C−C-coupling in 1,2- or 2,2-fashion can proceed, leading to the corresponding U(IV) bis-vinyl complexes. The activation barriers for the respective reactions were found to be 20.9 and 22.8 kcal mol^{-1}, respectively, while both reactions were found to be exergonic by 51.1 and 50.9 kcal mol^{-1}, in favor of the 1,2-C−C-coupling product. This result is also in line with the experimental observations. Although the C−H-activation reaction in this case is predicted to be kinetically accessible ($\Delta G^{\ddagger}$ = 21.8 kcal mol^{-1}) this reaction is computed to be endergonic by 16.5 kcal mol^{-1} (see SI for the whole pathway) and, thus, experimentally not observed.

CONCLUSION

In summary, reaction of $[((^{Ad}ArO)_3N)U^{III}(DME)]$ (**1**) with terminal mono- or bis-alkynes provided the first examples of uranium μ-vinyl complexes, which were fully characterized by NMR, UV/vis/NIR, SQUID magnetization, C/H/N elemental analysis, and X-ray diffraction. DFT computational analyses further provided detailed insight into the mechanisms of formation of these unique species. It is shown that U(IV) μ-vinyl complexes form via inter- and intramolecular C−C-coupling and cyclization reactions of terminal mono- or bis-alkynes with a reactive uranium(III) precursor **1**, involving a bimetallic key intermediate with one metal coordinated to each carbon of only one former C≡C triple bond. The results of this study can be translated to catalytic C−C bond-formation reactions of transition metals, rare earth, or actinides, where a bimetallic mechanism is suggested. The presented vinyl complexes can thus be seen as trapped intermediates in a catalytic C−C-coupling reaction of terminal alkynes, which has been shown with different uranium(III) catalysts by Eisen et al.[8b]

EXPERIMENTAL SECTION

Synthesis of $[\{((^{Ad}ArO)_3N)U^{IV}\}_2(\mu{-}\eta^2{:}\eta^1\text{-1,2-(CH)}_2\text{-cyclohexane})]$ (2). A 20 mL scintillation vial was charged with 0.1105 g (0.100 mmol) of $[((^{Ad}ArO)_3N)U^{III}(DME)]$ (**1**) in 5 mL of benzene. While the mixture stirred, 6.63 μL of 1,7-octadiyne [0.0053 g (0.050 mmol, 0.5 equiv)] was added with a Hamilton syringe to the dark-brown solution, resulting in a slight color change to yellow-brown. The reaction was stirred at RT overnight. The volatiles were removed *in vacuo* and dried to give 0.1019 g (0.048 mmol, 95%) of **2** as a yellow-brown solid. Elemental analysis for $C_{116}H_{142}N_2O_6U_2 \cdot 2C_4H_{10}O_2$, calc/found [%]: C: 64.29/64.28; H: 7.05/6.97; N: 1.21/1.32.

Synthesis of $[\{((^{Ad}ArO)_3N)U^{IV}\}_2(\mu{-}\eta^2{:}\eta^2\text{-1,2-(CH)}_2\text{-cyclopentane})]$ (3). A 20 mL scintillation vial was charged with 0.1105 g (0.100 mmol) of $[((^{Ad}ArO)_3N)U^{III}(DME)]$ (**1**) in 5 mL of benzene. While the mixture stirred, 5.72 μL of 1,6-heptadiyne [0.0046 g (0.050 mmol, 0.5 equiv)] was added with a Hamilton syringe to the dark-brown solution, resulting in a slight color change to yellow-brown. The reaction was stirred at RT overnight. The volatiles were removed *in vacuo* and dried to give 0.1055 g (0.050 mmol, 99%) of **3** as a yellow-brown solid. Elemental analysis for $C_{115}H_{140}N_2O_6U_2 \cdot 2C_4H_{10}O_2$, calc/found [%]: C: 64.16/64.11; H: 7.00/7.23; N: 1.22/1.08.

Synthesis of $[\{((^{Ad}ArO)_3N)U_2(\mu{-}\eta^2(C1){:}\eta^1(C4)\text{-2-}^n\text{Bu-1,3-octadiene})]$ (4). A 20 mL scintillation vial was charged with 0.1105 g (0.100 mmol) of $[((^{Ad}ArO)_3N)U^{III}(DME)]$ (**1**) in 5 mL of benzene. While the mixture stirred, 12.15 μL of 1-hexyne [0.0086 g (0.105 mmol, 1.05 equiv)] was added with a Hamilton syringe to the dark-brown solution, resulting in a slight color change to orange-brown. The reaction was stirred at RT overnight. The volatiles were removed *in vacuo* and dried to give 0.1066 g (0.049 mmol, 97%) of **4** as an orange-brown solid. Elemental analysis for $C_{120}H_{152}N_2O_6U_2$, calc/found [%]: C: 67.56/67.53; H: 6.87/6.96; N: 1.19/1.22.

Synthesis of $[\{((^{Ad}ArO)_3N)U^{IV}\}_2(\mu{-}\eta^2(C4){:}\eta^1(C1)\text{-1,3-di-(}p\text{-}^t\text{Bu-phenyl)butadiene}))]$ (5). A 20 mL scintillation vial was charged with $[((^{Ad}ArO)_3N)U^{III}(DME)]$ (**1**) [0.1105 g (0.100 mmol)] in 5 mL of benzene. While the mixture stirred, 18.7 μL of 4-^{t}Bu-phenylactylene [0.0166 g (0.105 mmol, 1.05 equiv)] was added with a Hamilton syringe to the dark-brown solution, resulting in a slight color change to dark yellow. The reaction was stirred at RT overnight. The volatiles were removed *in vacuo* and dried to give 0.1055 g (0.050 mmol, 99%) of **5** as a dark yellow-brown solid. Elemental analysis for $C_{132}H_{160}N_2O_6U_2$, calc/found [%]: C: 65.68/65.33; H: 6.98/6.78; N: 1.28/1.37.

ASSOCIATED CONTENT

Ⓢ Supporting Information

General considerations, spectroscopic details, crystallographic details and tables as well as computational details for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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