ORGANOMETALLICS

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Selective Oligomerization and [2 + 2 + 2] Cycloaddition of Terminal Alkynes from Simple Actinide Precatalysts

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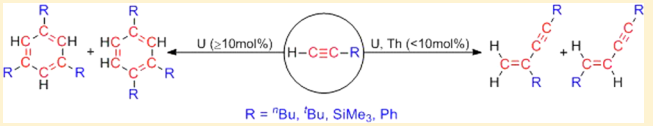
Supporting Information

ABSTRACT: A catalyzed conversion of terminal alkynes into dimers, trimers, and trisubstituted benzenes has been developed using the actinide amides $U[N(SiMe_3)_2]_3$ (**1**) and $[(Me_3Si)_2N]_2An[\kappa^2\text{-}(N,C)\text{-}CH_2Si(CH_3)N(SiMe_3)]$ (An = U (**2**), Th (**3**)) as precatalysts. These complexes allow for preferential product formation according to the identity of the metal and the catalyst loading. While these complexes are known as valuable precursors for the preparation of various actinide complexes, this is the first demonstration of their use as catalysts for C−C bond forming reactions. At high uranium catalyst loading, the cycloaddition of the terminal alkyne is generally preferred, whereas at low loadings, linear oligomerization to form enynes is favored. The thorium metallacycle produces only organic enynes, suggesting the importance of the ability of uranium to form stabilizing interactions with arenes and related π-electron-containing intermediates. Kinetic, spectroscopic, and mechanistic data that inform the nature of the activation and catalytic cycle of these reactions are presented.



INTRODUCTION

The reactivity of sp-hybridized carbon is a core aspect of organic chemistry. Alkynes have been extensively studied as adaptable synthons in modern synthesis,[1] and such reactions have given rise to a versatile array of organic products: for example, enynes,[2] ketones,[3] diynes,[4] metal acetylides,[5] and substituted benzenes.[6] In particular, organic enynes and trisubstituted benzenes have attracted considerable attention in recent years owing to their ubiquity in natural products,[7] supramolecules,[8] and medicinal compounds.[9] Since the first reports of the palladium-mediated dimerization of alkynes to enynes by Trost,[10] and the nickel-promoted cycloaddition of alkynes to benzenes by Reppe and Schweckendick,[11] several advancements have been made utilizing numerous metal complexes to catalyze these processes. To date, a vast array of transition metals have been applied to achieve alkyne catalysis toward enynes and substituted arenes, including metals from each group of the transition block and many main-group elements (Figure 1).[12]

Although many of these systems are highly developed, several shortcomings exist, including the use of expensive metal catalysts, elaborate ligand frameworks, and limited regio- and chemoselectivities. Moreover, no single system to our knowledge has been reported that is capable of switching catalytic activity to perform both oligomerization and cyclotrimerization selectively.

Some complexes of the f elements have emerged as adept catalysts in numerous organic transformations and have drawn considerable attention owing to their unique properties. The lanthanides have been shown to facilitate oligomerization of alkynes[13] and, in some rare examples, their cyclotrimerization;[14] however, the latter process requires heterobimetallic systems.[15] The organometallic chemistry of the early actinides has given rise to impressive and novel structures and reactivities[16] and has been further applied to effect challenging chemical transformations, including hydroaminations,[17] hydro-

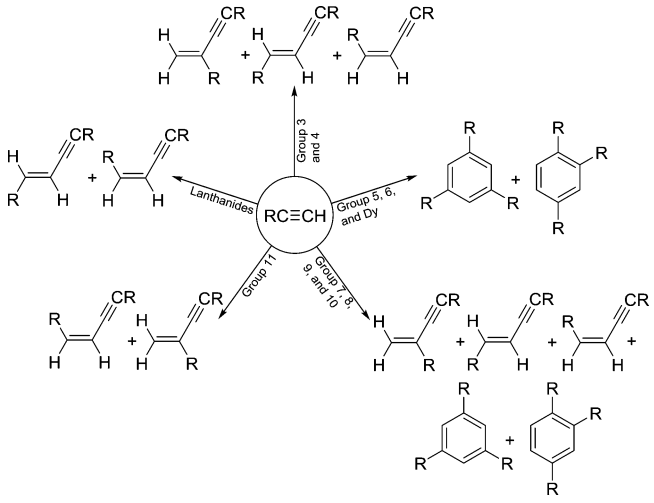


Figure 1. Previously reported oligomerization and cyclotrimerizations mediated by transition-metal, main-block-element, and lanthanide complexes.

Received: May 27, 2015

DOI: 10.1021/acs.organomet.5b00455
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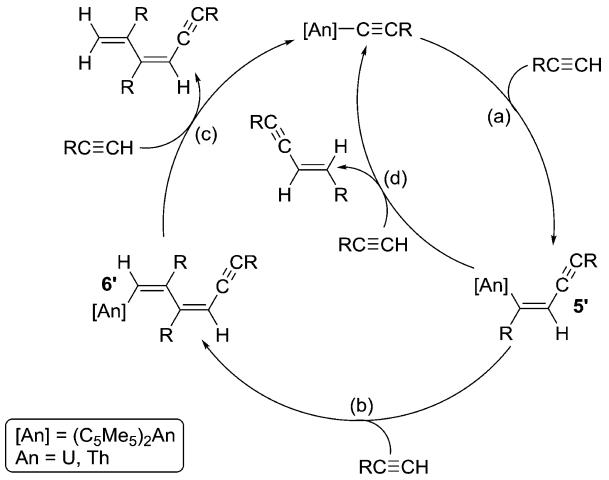
alkoxylations,[18] hydrosilylations,[19] the polymerization of dienes,[20] esters, and epoxides,[21] and various small-molecule activations.[22] Previously, the oligomerization of terminal alkynes has been shown to proceed when mediated by various organoactinide complexes, namely of the type $(C_5Me_5)_2AnMe_2$ (An = U, Th), and a mechanism was proposed for this process mediated by this class of catalyst (Scheme 1).[23] The mechanism

Scheme 1. Proposed Mechanism for the Catalytic Oligomerization of Terminal Alkynes Mediated by Organoactinide Complexes[a]



[a]Ligands are omitted, and only one of the two reactive sites is shown for clarity.

of oligomerization does not require reductive elimination to liberate the organic products, indicative of a conservation of the metal oxidation state for this cycle.

The selectivity of these complexes for the oligomerization process was further enhanced by the addition of a primary amine which serves as a proton source, enabling rapid cleavage of the metallodimer and thus improving control over the number of insertions of the alkyne. This resulted in a high chemoselectivity toward the formation of, chiefly, dimers for the majority of substrates studied. A similar chemoselectivity was found when the substrate was allowed increased access to the metal by the use of the *ansa*-bridged cyclopentadienyl ligand in $[Me_2Si(C_5Me_4)_2]Th^nBu_2$, rapidly and selectively yielding organic dimers. Investigation of the cationic uranium complex $[U(NEt_2)_3][BPh_4]$ in the oligomerization of terminal alkynes has given rise to comparable oligomerization products; however, the isolation of the π-alkynyl uranium complex $[(Et_2N)_2U(C{\equiv}C^tBu)(\eta^2\text{-}HC{\equiv}C^tBu)][BPh_4]$ represented the first example of such a species, raising the conceptual question as to whether other uranium complexes may exhibit this behavior (Scheme 2).[24]

The goal of this investigation was to study the combined effects of coordinative unsaturation and an open metal sphere and to examine the scope, chemoselectivity, regioselectivity, metal center influence, mechanism, and thermodynamic and kinetic parameters operative in the actinide-mediated oligomerization and cyclotrimerization of terminal alkynes. Herein, we have carried out a systematic study of the catalyzed oligomerization of a range of terminal alkynes using the actinide amides $U[N(SiMe_3)_2]_3$ (**1**) and $[(Me_3Si)_2N]_2An[\kappa^2\text{-}(N,C)\text{-}CH_2Si(CH_3)_2N(SiMe_3)]$ (An = U (**2**), Th (**3**)) as precatalysts.

RESULTS AND DISCUSSION

We present the reaction scope and selectivity of alkyne oligomerization and cyclization reactions catalyzed by the actinide amide complexes shown in Figure 2. In addition, experimentally derived mechanistic studies, as well as kinetic and thermodynamic calculations derived from experimental data, are provided.

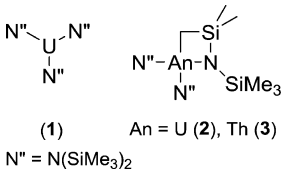


Figure 2. Amido actinide precatalysts used in the oligomerization and cyclotrimerization of terminal alkynes.

The actinide amido complexes $U[N(SiMe_3)_2]_3$ (**1**) and $[(Me_3Si)_2N]_2An[\kappa^2\text{-}(N,C)\text{-}CH_2Si(CH_3)_2N(SiMe_3)]$ (An = U (**2**), Th (**3**)) react with terminal alkynes to yield dimers, trimers, or trisubstituted benzenes as the major products, with small quantities of alkene being generated for selected experiments (Figure 3). The distribution of products was found to be strongly dependent on the nature of the metal center and the reacting alkyne (Table 1).

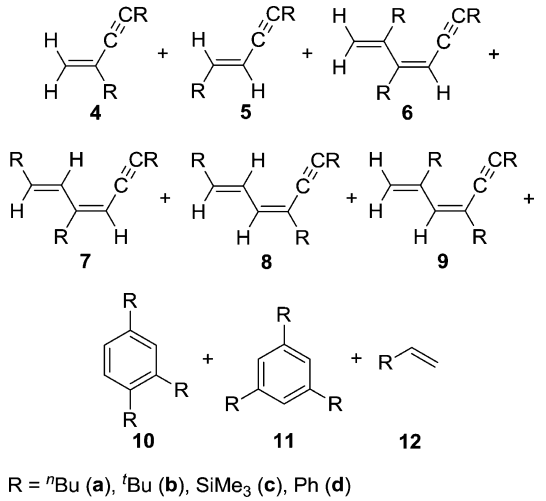
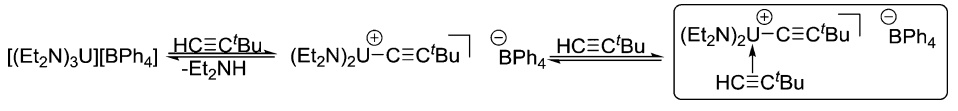


Figure 3. Accessible products from the catalytic reaction of actinide amides with terminal alkynes. The R substituent is *n*-butyl (**a**), *tert*-butyl (**b**), trimethylsilyl (**c**), or phenyl (**d**).

Scheme 2. Reaction of *tert*-Butylacetylene with a Cationic Uranium Complex Generating the π-Alkynyl Uranium



DOI: 10.1021/acs.organomet.5b00455
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Table 1. Results for the Catalytic Oligomerization/Cyclotrimerization of Terminal Alkynes by Complexes 1−3[a]

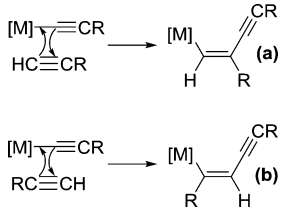
				yield (%)								
entry	catalyst (amt (mol %))	R[b]	conversion (%)	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
1	**1** (1)	^{n}Bu	88	91		5				2	1	
2	**1** (10)	^{n}Bu	100	13						29	42	15
3	**2** (1)	^{n}Bu	88	96		2				1	1	
4	**2** (10)	^{n}Bu	100							41	37	22
5[c]	**3** (1)	^{n}Bu	86	92		7						
6	**3** (10)	^{n}Bu	99	93		7						
7[c]	**1** (1)	^{t}Bu	87	22	40		21			8	1	7
8[c]	**1** (10)	^{t}Bu	100		55						22	23
9[c]	**2** (1)	^{t}Bu	77	60	22	9				3	1	5
10	**2** (10)	^{t}Bu	100		54	23				6	2	14
11[c]	**3** (1)	^{t}Bu	70	41	43		14					
12	**3** (10)	^{t}Bu	97	14	46		39					
13[c]	**1** (1)	$SiMe_3$	42	50	11					22	17	
14[c]	**1** (10)	$SiMe_3$	100							57	41	
15	**2** (1)	$SiMe_3$	97	32	8			19	38	2	2	
16	**2** (10)	$SiMe_3$	100	34	25					23	19	
17	**3** (1)	$SiMe_3$	64	22	43			35				
18	**3** (10)	$SiMe_3$	87	27	32			41				
19[d,e]	**1** (1)	Ph	92							25	63	
20[d,e]	**1** (10)	Ph	100							48	49	
21[d,e]	**2** (1)	Ph	96	2	17					35	40	
22[d,e]	**2** (10)	Ph	100							40	51	
23[d]	**3** (1)	Ph	99	91	9							
24[d]	**3** (10)	Ph	100	77	15							8

[a]Product percentages are ratios of converted substrate. Reactions were run for 72 h at 75 °C in C_6D_6. [b]R = substituent of the corresponding RC≡CH. [c]Traces of larger oligomers. [d]Products and distributions determined by HPLC-MS. [e]Remaining product contains dimers up to tetramers.

Reactivity and Selectivity of Alkyne Oligomerization and Cyclotrimerization Catalyzed by Complexes 1−3. Most notably, [2 + 2 + 2] cycloaddition is only observed when the uranium catalysts **1** and **2** are used. This is of particular interest, as the observed cycloaddition is largely found in late-transition-metal systems,[25] with few examples found in early-transition-metal chemistry and no previously reported instances in actinide systems.[26] A further unusual aspect of the results in Table 1 is the alkene product, arising formally from alkyne hydrogenation. The *in situ* generation of a uranium hydride is proposed to account for this result. In this study, the regioselectivity of the migratory insertion is described according to the disposition of the alkyne R substituent into the metal−carbon bond, with the head-to-head mode of insertion giving rise to a trans-configured enyne or a head-to-tail insertion producing the gem enyne (Scheme 3).

Oligomerization/Cyclotrimerization of 1-Hexyne by Complexes 1−3. In the reaction with 1-hexyne, the use of a low catalyst loading (1%) for each of the metal complexes gives rise to excellent conversion (≥86%) to yield the geminal dimer **4a** (Figure 3), produced from the head-to-tail insertion almost exclusively (≥91%) (Table 1, entries 1, 3, and 5), with a small amount of trisubstituted benzenes (≤3%) additionally being produced.

Scheme 3. Possible Pathways for Insertion of Terminal Alkyne into a Metal−Acetylide Bond Yielding (a) Head-to-Tail and (b) Head-to-Head Insertion Products



Conversely, and of particular note, when uranium catalysts **1** and **2** were used at high loading (10%) (Table 1, entries 2 and 4), the major products formed were found to be the trisubstituted benzenes. The oligomerization of 1-hexyne mediated by complex **1** results in a quantitative conversion of monomer to cyclotrimers, 29% of 1,2,4-tri-*n*-butylbenzene (**10a**) and 42% of 1,3,5-tri-*n*-butylbenzene (**11a**), involving the second migratory insertion of alkyne (Scheme 1, step c), followed by cyclization to give the arene product. Unexpectedly, the remaining 15% of the product was identified as 1-hexene (**12a**), a hydrogenation product. The uranium metallacycle **2** similarly gave a quantitative conversion, yielding cyclic trimers as the major products (41% of **10a** and 37% of **11a**), with the remaining 22% of product converted to 1-hexene (**12a**). The results for 1% catalyst loading with **1** and **2** were very similar to those for the use of thorium catalyst **3**, with **4a** and **5a** predominating, but with benzenes **10a** and **11a** completely absent. Unlike **1** and **2**, the product distribution was nearly identical at a 10% loading of **3**.

The observed preference toward the head-to-tail insertion shown by catalysts **1**−**3** is explained by the minimal steric hindrance imparted by the *n*-butyl group of the alkyne, allowing the terminal CH moiety to enter the coordination sphere of the metal toward the thermodynamically favored regioselectivity of insertion.[27] The high yield of dimer generated from this substrate illustrates the lower energetic pathway of protolytic

DOI: 10.1021/acs.organomet.5b00455
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cleavage in comparison to migratory insertion into the actinide−vinyl bond. This is corroborated by the small quantities of product formed from the additional insertion into this intermediate, evident by the formation of only small amounts of trimer **6a** (≤7%), similarly occurring from a head-to-tail insertion. At 10% catalyst loading in complexes **1** and **2**, it was seen that the [2 + 2 + 2] cycloaddition was favored. It is worth noting that the 1,3,5-trisubstituted benzenes are only accessible through two consecutive head-to-tail insertions toward the metallotrimer (Figure 3, **9′**) according to the proposed mechanism (Scheme 1), whereas the 1,2,4-trisubstituted benzene may be formed by a head-to-head insertion in either of the two migratory insertion steps, allowing for three possible intermediates to this product, (Figure 3, **6′**, **7′**, or **8′**). Furthermore, the higher degree of cyclization at high loading in uranium is proposed to arise from a bimetallic mechanism, owing to the larger ratio of metal to alkyne in solution (*vide infra*). A bimetallic cyclization is additionally lent credence by recent work describing a stoichiometric uranium-mediated bimetallic C−C coupling of alkynes, yielding [{((^{Ad}ArO)$_3$N)-U^{IV}}$_2$(μ-η^2:η^2-1,2-(CH)$_2$-cyclopentane)].[28] For complex **1**, the consecutive head-to-tail insertion is found to be prevalent, as made apparent by the larger amount of the symmetric arene **11a**, whereas complex **2** generates a larger quantity of the 1,2,4-tri-*n*-butylbenzene. This is indicative of different active catalytic species despite the remarkable similarity between the precatalyst structures.

Oligomerization/Cyclotrimerization of tert-Butylacetylene by Complexes 1−3. To investigate the steric effects of the substrate, *tert*-butylacetylene emerged as the obvious contrast to *n*-butylacetylene (ν_{eff} 1.24 and 0.68, respectively).[29] The reduction of alkyne to the corresponding alkene was observed to the greatest extent for this substrate (Table 1, entries 8 and 10). At 1 mol % loading, the uranium catalyst **1** gave an overall 87% conversion of *tert*-butylacetylene to both dimers **4b** and **5b** (22 and 40% yields, respectively) and trimer **7b** (21%) which is obtained by head-to-head insertion into **5′** and subsequent protonolysis (Table 1, entry 7). This precatalyst at 10 mol % loading follows a similar behavior, yielding a slightly larger quantity of cyclotrimerization product, providing the *trans* dimer **5b** as the major product (55%) (Table 1, entry 8).

Only a 77% monomer conversion was achieved using catalyst **2** at 1 mol % loading with a marked decrease in chemo- and regioselectivity; 60 and 22% of dimers **4b** and **5b**, respectively, were formed in the reaction mixture (Table 1, entry 9). Using the metallacycle **2** at 10% loading generated the lowest amount of the cycloaddition products for any of the uranium catalysts used at high loadings (8% total of arene) but did provide quantitative conversion of the terminal alkyne (Table 1, entry 10). This experiment yielded 54% of the *trans* dimer **5b**, as well as 14% of alkene **12b** and 23% of trimer **6b**; however, an interesting feature of this reaction is the observed reversal in regioselectivity on comparison of the dimers formed in the 1 and 10% catalyst loading runs using precatalyst **2**. Such a reversal in regioselectivity shows a previously unseen behavioral pattern in either f-group or transition-metal catalysis which is dictated by the applied catalyst loading. The change of regioselectivity is highly suggestive of migratory insertion into the uranium acetylide existing in an equilibrium process.

Use of the thorium metallacycle precatalyst **3** provided the greatest selectivity toward the oligomerization of *tert*-butylacetylene. At 1 and 10% catalyst loadings, the two possible dimers and trimer **7b** were produced as the major products (Table 1, entries 11 and 12, respectively). At 1 mol % loading, moderate conversions are observed (70%) with the production of equimolar amounts of dimers **4b** and **5b** (41 and 43%, respectively). Conversely, at high catalyst loading, the thorium metallacycle (**3**) provides a 97% conversion with 46% of *trans* dimer (**5b**) as the major product and an additional 14% of *gem* dimer (**4b**) with 39% of trimer (**7b**) from a head-to-head-to-head insertion.

In consideration of the reactivity with *tert*-butylacetylene, it is first apparent that the steric bulk of the alkyne inhibits sequential insertions during the catalytic cycle, as is shown by the modest conversions for these experiments (Table 1, entries 7, 9, and 11). In addition, the presence of the alkene **12b** in roughly equimolar amounts to the cyclotrimers, yet in considerable excess to catalyst, is informative that, while a uranium hydride species may be formed upon activation of the precatalyst, an additional mechanism must be operative in the catalytic cycle to regenerate the uranium hydride (*vide infra*). In addition, the catalytic reaction using complex **1** shows the propensity of the uranium complex to undergo rapid insertion into the *gem*-metallaenyne. Moreover, the absence of trimer **9b** indicates rapid cyclization of the metallatrimer being energetically favored over protonolytic cleavage.

Uranium complex **2** shows remarkable results in the catalysis with this substrate. At high catalyst loading, head-to-head insertion emerges as the dominant pathway to product **5b** and elucidates the rigidity of the metal acetylide moiety; however, after the first insertion has occurred, the resulting metal−vinylic bond provides less steric encumbrance, allowing for the head-to-tail mode of insertion for the incoming monomer. This can be assumed to be manifest from the flexibility imparted in moving from an sp to sp^2 hybridization on the coordinating carbon atom. Performing the reaction at a 1 mol % catalyst loading revealed interesting chemical reactivity; the uranium complex **2** at 10 mol % loading favors head-to-head insertion yielding dimer **5b**. However, at 1% loading, this experiment showed an obvious reversal in regioselectivity, yielding 60% of the *gem* dimer **4b** and only 22% of *trans* dimer **5b**. The reversal in regioselectivity is an outstanding feature in this reaction and, to the best of our knowledge, the first example of such a reversal arising from variable catalyst loading. We suggest that, at high concentration of the sterically cumbersome *tert*-butylacetylene, the formation of a π-alkynyl complex similar to one previously found in the literature is generated,[24] favoring head-to-tail insertion. While unexpected, this finding allows for the tuning of the regioselectivity of the oligomerization of *tert*-butylacetylene by simple alteration of the catalyst loading.

The study of the thorium metallacycle **3** in the oligomerization of *tert*-butylacetylene proved more straightforward, showing preference for head-to-head insertion. Interestingly, when the catalyst load is decreased to 1%, head-to-head insertion is still seen as the major mechanistic pathway; however, the approximate equimolar concentrations of *gem* and *trans* dimer (41 and 43%, respectively) suggests an equilibrium process of insertion into the thorium acetylide. Despite this product ratio, the head-to-head insertion remains the most favorable when the regioselectivity toward the production of trimer **7b** (14%) is considered.

Oligomerization/Cyclotrimerization of (Trimethylsilyl)-acetylene by Complexes 1−3. The trimethylsilyl moiety has been computationally and experimentally determined to be an approximate steric equivalent to methyl,[30] allowing for a predominantly electronic analysis of its reactivity. As the

DOI: 10.1021/acs.organomet.5b00455
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inductive effects of a trimethylsilyl moiety result in stabilization of α-carbanions and β-carbocations,[31] a head-to-head mode of insertion is expected to be favored. Given the considerable Lewis acidity of the metal center and the electronic nature of the substrate, a conceptual question was formed as to whether steric or electronic control would dominate in the observed regioselectivity (Figure 4).

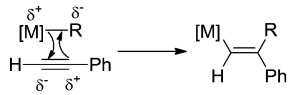
Figure 4. Expected polarization of (trimethylsilyl)acetylene toward an actinide catalyst in a migratory insertion step.

Furthermore, owing to the electron-rich nature of the alkyne, it was theorized that a π-alkynyl complex would be more likely to form to the metal center, resulting in a higher selectivity toward cyclization. Examination of the reactions shows that the average reactivity of the actinide complexes toward this monomer is the lowest of the alkynes studied (Table 1, entries 13−18), arising from the formation of a strong π-alkynyl complex to the metal center, in turn increasing the enthalpic barrier of insertion. However, this same π-bonding interaction is thought to give rise to the relatively high level of cycloaddition seen for the uranium complexes. Catalyst **1** at low loading (Table 1, entry 13) reveals thermodynamic control of insertion, reflected by the 50% of *gem* dimer (**4c**) produced. In addition, the formation of tris(trimethylsilyl)benzene and the absence of linear trimer implies that a rapid cyclization occurs with a lower energetic barrier in comparison to protonolysis. Increasing the catalyst loading to 10 mol % results in cyclotrimer formation as the dominant pathway (57 and 41% of 1,2,4- and 1,3,5-tris(trimethylsilyl)benzene, respectively), with less than 2% of larger oligomers formed according to GC-MS analysis (Table 1, entry 14). On consideration of the ratio of the arene products, the preference of head-to-tail insertion is still found to be substantial, as is illustrated by the quantity of symmetric cyclotrimer **11c** generated.

Complex **2** at 1% and 10% catalyst loadings shows a propensity toward a similar head-to-tail insertion, with superior regioselectivity to **1**, with dimer **4c**, trimer **9c**, and cycloaddition product **11c** observed as the dominant products (Table 1, entries 15 and 16). The degree of cyclization is significantly diminished in comparison to **1**. A 1% loading of complex **2** generated the *gem* dimer **5c** in 32% yield; however, a significant amount of trimer **9c** is generated (38%). With respect to **1**, complex **2** gives diminished selectivity at high catalyst loading. Although high chemoselectivity toward the formation of only dimers or cyclotrimers is apparent, the regioselectivity is less favorable on comparison of the product distributions. The lack of any linear trimer in this reaction informs us that, similar to the behavior seen using catalyst **1**, the metallotrimer intermediate cyclizes rapidly and preferentially.

The thorium metallacycle **3** catalysis of this substrate shows a product distribution suggestive of multiple, competitive processes. At low catalyst loading, **3** gives 64% conversion, yielding *gem* dimer **4c** as the minor product in 22% yield with *trans* dimer **5c** and trimer **8c** being generated in 43 and 35% yields, respectively (Table 1, entry 17). At 10% catalyst loading, a similar regioselectivity of products is observed; however, the trimer **8c** was produced instead as the major product in 41% yield (Table 1, entry 18). The presence of this trimer as the major product indicates the high level of electronic influence over the second insertion into the *gem*-dimer intermediate **4c′**. The observed activity for this catalyst−substrate combination, however, was one of the few examples in which a moderate substrate conversion was observed (87%) at high catalyst loading. These data show a marginal preference toward head-to-tail insertion into the active thorium−alkyne bond. Further insertions appear to be governed by the electronic properties of the alkyne, resulting in competitive head-to-head insertion and protonolysis.

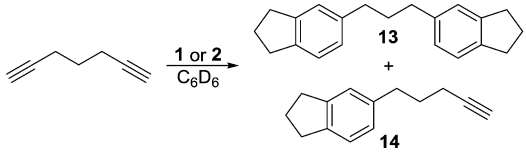
*Oligomerization/Cyclotrimerization of Phenylacetylene by Complexes **1**−**3**.* In order to study the behavior of comparatively electron-poor alkenes—in contrast to the examples detailed above—phenylacetylene was selected for study. Owing to the electron deficiency of the alkyne, a preference for cyclization is expected, owing to an increased π-back-bonding interaction. In addition, the minimal steric hindrance imparted by the phenyl ring (ν_{Ph} = 0.57)[29] would in theory pose a minimal steric barrier to this process. Equation 1 shows the anticipated preference for head-to-tail insertion, on the basis of the bond polarization of this substrate.



(1)

When either uranium catalyst was used, a minimum of 75% of cyclized product was observed (Table 1, entries 19−22), with up to 97% trisubstituted benzene being produced according to HPLC-MS (Table 1, entry 20). In addition, a strong preference toward head-to-tail insertion is evident by the production of the 1,3,5-triphenylbenzene species **11d** as the major product in the cyclizations. A 1% catalyst loading in thorium complex **3** achieved near-quantitative conversion of phenylacetylene, yielding 91% of *gem* dimer (Table 1, entry 23). Similarly, the 10% loading experiment generated the *gem* dimer as the major product, albeit with a notable decrease in regioselectivity. The results from the study of this substrate strongly support the previously stated hypothesis of the regioselectivity of insertion.

*Cyclotrimerization of 1,6-Heptadiyne Mediated by Uranium Complexes **1** and **2**.* The hypothesis of a bimetallic mechanism was probed by employing 1,6-heptadiyne in an effort to isolate the bis(indane) product **13** (eq 2).



(2)

Mechanistic Studies of Alkyne Oligomerization and Cyclotrimerization Catalyzed by 1−3. Comparative studies between complexes **2** and **3**, respectively, are highly evocative of the importance of the 5*f* electrons in the observed catalysis; however, the data from this study, as well as previous catalytic studies using Cp*AnMe$_2$, fail to provide sufficient information to dismiss effects which may arise from the difference in ionic radii. That the actinide-mediated oligomerization of terminal alkynes toward enynes is a sequential alkyne insertion into an An−acetylide bond has been well established.[23] However, given that the comparative reactivities between uranium(III) and

DOI: 10.1021/acs.organomet.5b00455
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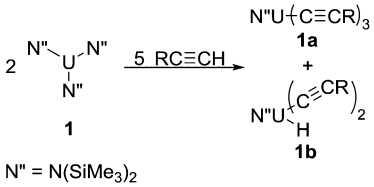
-(IV) were as yet unreported and that cyclotrimerization reactions are rare in early-transition-metal chemistry and are entirely absent from actinide chemistry, further studies were carried out to determine the activation pathway of complexes **1**−**3** and key steps in the mechanism of [2 + 2 + 2] cycloaddition.

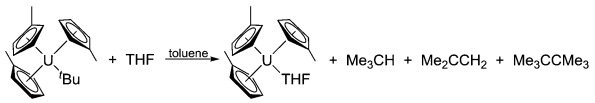
Mechanism of Activation. In order to ascertain the mechanism of activation, ^{1}H NMR, fluorescence, C_{60} radical trapping, and MALDI-TOF experiments were utilized. Further study was prudent when considering the observed reduction of the alkyne, a process rarely seen in actinide chemistry in the absence of a reducing agent.[32] In the study of the activation of catalyst **1** by 1-hexyne, it was observed by ^{1}H NMR spectroscopy that protonolysis of two of the available three bis(trimethylsilyl)amide ligands occurs, forming a bis(acetylide) uranium complex. Moreover, the presence of the alkene product **12**, arising from insertion of alkyne into an intermediate uranium hydride species, suggests that the initial activation involves a one-electron oxidation of two uranium centers across the C−H bond of alkyne substrate (eq 3), readily



(3)

accessible due to the low oxidation potential of uranium(III).[33] Accordingly, fluorescence data were used to ascertain the oxidation state of the metal after activation with alkyne. The emission spectrum obtained was found to be in agreement with recent studies characterizing the metal-based fluorescence of the uranium(IV) oxidation state (see Figure S1 in the Supporting Information).[34]

It was initially assumed that the uranium(IV) metallacycle would maintain the same formal charge; however, it has been previously established that uranium(IV) complexes can be reduced to U(III) through the homolytic cleavage of a U−alkyl bond such as from the *tert*-butyl group shown in eq 4.[35]



(4)

In order to substantiate the possibility of a radical reaction, EPR studies were utilized using C_{60} as a radical trapping agent. To a toluene solution of complex **2** with 2 equiv of fullerene was added an excess of 1-hexyne, and the EPR spectrum was acquired immediately after addition and after 3 h of heating at 75 °C. It was seen that, after the sample was heated, a monomeric fullerenyl radical was produced, as detected by EPR spectroscopy (see Figure S2 in the Supporting Information). Given this observation, accurate determination of the active catalytic species was not possible; however, it was additionally found that the +4 oxidation state is conserved.

Although the reaction of the thorium metallacycle **3** with stoichiometric amounts of phenylacetylene was previously studied,[36] no investigation had been performed when additional alkyne was introduced. After reaction with an excess of alkyne, it was seen by NMR spectroscopy that all amides were displaced, resulting in the formation of a homoleptic thorium-(IV) acetylide complex. The aforementioned studies have shown that the first equivalent of alkyne protolytically cleaves the thorium−carbon bond of the metallacyclobutane, resulting in the formation of a tris(amido)thorium acetylide complex. The remaining amides were subsequently protolytically cleaved by additional alkyne, producing the thorium(IV) acetylide and 3 equiv of bis(trimethylsilyl)amine as determined by NMR.

*Mechanistic Investigation of the Catalytic Oligomerization of 1-Hexyne by Complexes **1**−**3**.* The operative mechanism is proposed to occur in a manner analogous to that shown in Scheme 1. Activation of the precatalyst occurs to generate the active uranium or thorium acetylide complex (*vide supra*). Given the observed chemo- and regioselectivities, in conjunction with the occurrence of preferential formation of dimers or trimers on the basis of catalyst loading, the migratory insertion of alkyne is proposed to be an equilibrium process (Scheme 1, step a). The first insertion into the metal−alkyne bond generates the metallodimer; from this intermediate, two divergent pathways are accessible, either σ-bond metathesis to produce the organic dimer and regenerate the active catalyst (step d) or additional insertion to generate the metallotrimer intermediate (step b). Similar experiments with catalyst loadings in the range of 0.5−5 mol % provided comparable product distributions. If the mole ratio of precatalyst was increased to 10 mol % or greater (up to 20 mol % as was investigated in this study), the chemoselectivity tended toward the formation of cyclotrimers.

The kinetics of the oligomerization of 1-hexyne were studied using ^{1}H NMR spectroscopy at 75 °C and monitored by the appearance of one or both of the vinylic proton signals of the geminal dimer (δ 5.37 and 5.08 ppm). The rate equation for the oligomerization mediated by any of the three precatalysts was found to be first order in precatalyst and first order in alkyne, giving rise to the rate equation

$$\frac{\partial p}{\partial t} = k_{obs}[\text{catalyst}][\text{alkyne}] \quad (5)$$

Experimentally derived thermodynamic parameters from Eyring and Arrhenius plots (see Figures S3−S8 in the Supporting Information) were utilized to determine the enthalpy ($\Delta H^{\ddagger}$), entropy ($\Delta S^{\ddagger}$), and energy of activation (E_a) of oligomerization. From the derived data using catalyst **1**, relatively high enthalpy and energy of activation are observed (27.6(2) and 28.3(2) kcal mol^{-1}, respectively), and an approximately neutral entropy of activation of −0.5(6) eu is found. Use of deuterium-labeled alkyne (^{n}BuC≡CD) reveals a primary kinetic isotope effect (KIE = 2.85), corroborating the protonolysis as the rate-determining step of the catalytic cycle (Scheme 1, step d). The dimerization process mediated by complex **2** is similarly accompanied by high enthalpy (21.2(2) kcal mol^{-1}) and activation energies (21.9(2) kcal mol^{-1}), however, with a highly negative entropy of activation (−19.8(7) eu), indicating a highly ordered transition state, supporting a four-centered transition state of migratory insertion. These parameters mediated by the thorium metallacycle **3** lie between those of the two uranium complexes; the enthalpy and energy of activation were calculated as 26.1(3) and 26.8(3) kcal mol^{-1}, respectively, with a negative entropy supporting an ordered transition state (−8.5(8) eu).

*Mechanistic Investigation of the Catalytic Cyclotrimerization of (trimethylsilyl)acetylene by Complex **1**.* The novel actinide-mediated catalytic cyclotrimerization was thoroughly investigated in this study. The thermodynamic and kinetic data

DOI: 10.1021/acs.organomet.5b00455
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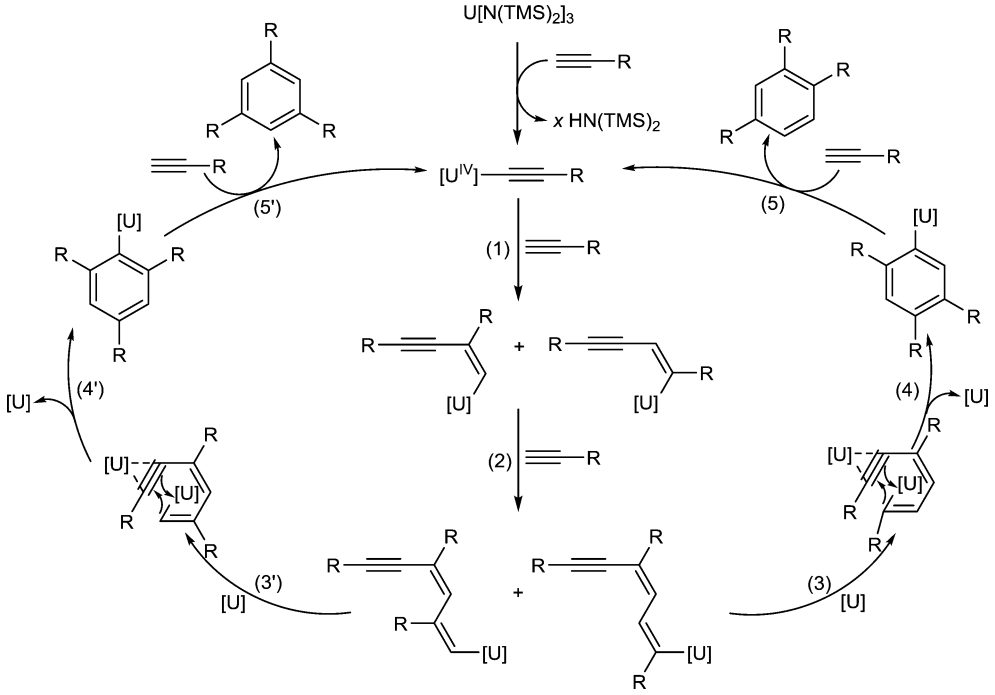
Scheme 4. Proposed Mechanism for the Catalytic Cyclotrimerization of Terminal Alkynes Promoted by Complexes 1 and 2[a]



[a]Ligands are omitted for clarity.

obtained here, as well as variable catalyst loading experiments, provide information which elucidates the mechanism of [2 + 2 + 2] cycloaddition (Scheme 4).

The ability of the uranium centers to cyclize the metallaoligomers, a reaction absent from thorium catalysis, shows the variability in reactivity of these two metals arising from the differing electronic structures.[37] The high catalyst loading of **1** and **2** required to effect cyclization suggests that arene formation likely occurs by a bimetallic process, yielding a uranium-arene intermediate. The catalytic cycle shown retains the +4 oxidation state of the uranium center. Protonolysis by an external alkyne yields the substituted benzene and regenerates the active uranium acetylide catalyst. When experiments were performed with 20 mol % catalyst loading, cyclotrimer was still found to the major product in the reaction mixture; however, the reaction rate was accelerated proportionally owing to the first-order behavior of the catalyst. Similar to the experiments performed with 1-hexyne, decreasing the catalyst loading below 10 mol % (in the range of 0.5−5 mol %) increased the propensity of oligomer formation.

The experimental kinetic and thermodynamic data for the cyclotrimerization of (trimethylsilyl)acetylene mediated by complex **1** is first order in catalyst and alkyne, suggesting that the cyclization of the metallatrimer (Scheme 4, step 4) occurs rapidly and is not rate-limiting. Deuterium labeling of the alkyne ($Me_3SiC{\equiv}CD$) revealed a primary kinetic isotope effect (KIE = 2.77), identifying that the aryl−alkynide exchange protonolysis is the slow step of the reaction (Scheme 4, step 5). The experimentally derived thermodynamic parameters reveal a moderate enthalpy and energy of activation (11.3(1) and 12.0(1) kcal mol^{-1}, respectively); however, the large negative entropy ($\Delta S^{\ddagger}$ = −39.5(3) eu) is most notably in agreement with a highly ordered transition state which would be expected for the cyclization process.

An additional question which remained was the determination of the involvement of the conjugate acid ($HN(SiMe_3)_2$) arising from protonolysis of the actinide precatalyst. In previous studies, it was seen that the addition of external amine did not aid in improving the selectivity of uranium-mediated catalysis[38] but did result in control for short oligomers using the thorium analogue. To a 1 mol % catalyst solution (**1**−**3**) was added 30 equiv of $HN(SiMe_3)_2$, and the reaction was followed by monitoring product formation at 75 °C. It was observed that the addition resulted in no discernible difference in the product distribution, and therefore the amine is not an active component of the catalytic cycle.

The study of 1,6-heptadiyne cyclization further aided in supporting the proposed mechanistic cycle. According to Scheme 5, the migratory insertion of 1,6-heptadiyne occurs through a uranium acetylide intermediate (step a), followed by an intramolecular insertion into the resulting uranium−vinylic bond (step b). A critical step in the reaction is the cyclization of the internal alkyne, whereby an additional 1 equiv of the uranium catalyst is required to form a π complex and distort the alkyne toward sp^2 geometry to facilitate the insertion (steps c and d). Following this, protolytic cleavage generates the intermediate monoindane product (step e). This cycle is repeated on the terminal alkyne from this step to generate the desired bis(indane) product **14**.

In describing the formation of alkene, it was necessary to determine how uranium(III) is regenerated from the uranium(IV) active catalyst during the catalytic cycle from complexes **1** and **2**, as more reduction product was generated than is possible with the assumption of a stoichiometric activation pathway (eq 3). This recurring reactivity pattern can be found in Table 1 (entries 2, 4, 7, 8, and 10) and suggests a unforeseen side reaction; given the divergent activation pathways observed by complex **1** versus complex **2** and considerations of the catalytic mechanism, it is proposed that uranium(III) is

DOI: 10.1021/acs.organomet.5b00455
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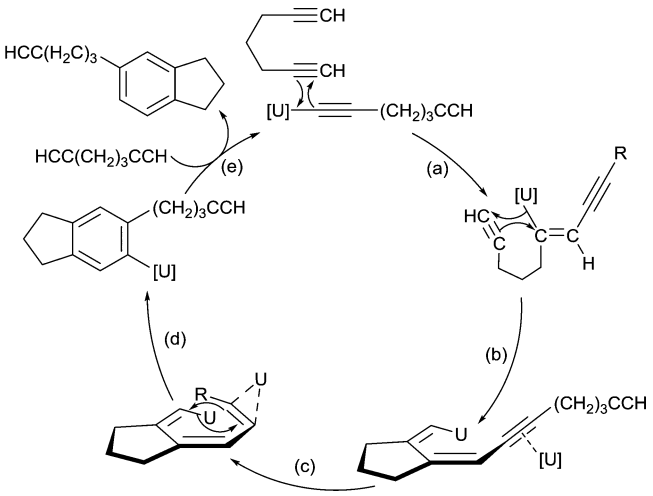
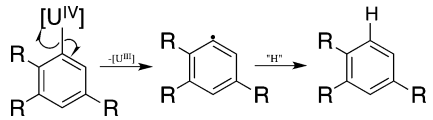
Scheme 5. Proposed Mechanism for the First Cyclization of 1,6-Heptadiyne[a]



[a]The final product is obtained by a repetition of this cycle.

produced by a minor reaction pathway by bond homolysis of the uranium(IV) arene intermediate, generating the uranium(III) complex and an arene radical which terminates at the neutral trisubstituted benzene (Scheme 6).

Scheme 6. Suggested Mechanism of Radical Formation of the Arene and Regeneration of Uranium(III)



The generated uranium(III) species may then undergo the previously proposed one-electron-oxidation process to generate the aforementioned uranium hydride **1b**, followed by insertion and protolytic cleavage by alkyne to generate alkene **12** and the uranium active catalyst. Radical trapping experiments were performed by the addition of a fullerene solution at the half-life of the reaction using both catalysts **1** and **2**. The formation of an organic fullerenyl radical was detected by EPR spectroscopy, consistent with the aforementioned process.

CONCLUSIONS

In this study we have introduced a class of actinide amide catalyst which allows for a control of regioselective oligomerization or cyclotrimerization of terminal alkynes. Of these, the latter [2 + 2 + 2] cycloaddition process is unprecedented, a surprising result given the large expected negative enthalpy of cyclization associated with the formation of aromatic species. In the linear oligomerization, a combination of migratory insertions and protolytic cleavages comprise the catalytic cycle. Mechanistic studies suggest a bimetallic cyclization of an intermediate metallatrimer, followed by protonolysis which liberates the organic arene product. Additionally, a radical cyclization is experimentally supported as a minor mechanistic pathway that generates a uranium(III) moiety capable of forming a uranium(IV) hydride, which results in the reduction of alkyne to alkene.

In addition, we have carried out systematic studies varying the steric and electronic effects of the substrate which has exposed a combination of metal center, catalyst loading, and substrate influences which allow for tuning of the regio- and chemoselectivity of the formed products. The electron-deficient and -rich alkynes phenylacetylene and (trimethylsilyl)acetylene, respectively, show a strong preference toward cyclization when either uranium catalyst is used. It is seen that the thorium metallacycle shows a high degree of regioselectivity, generating only two major oligomeric products when 1-hexyne or phenylacetylene is used, or three products when *tert*-butylacetylene or (trimethylsilyl)acetylene is used.

A comparative study between the two uranium catalysts used showed that, although the precatalysts share similar characteristics, the activation and nature of the active species are different in each case, giving rise to different regio- and chemoselectivities of oligomerization and cyclization products. The production of arenes as a result of catalytic cyclotrimerization by the uranium precatalysts **1** and **2** provides considerable evidence for the significance of the actinide 5f electrons in structure, bonding, and reactivity. The use of these simple amido actinide complexes in other new chemical transformations is under further investigation.

EXPERIMENTAL SECTION

Materials and Methods. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware or J. Young Teflon valve sealed NMR tubes on a dual-manifold Schlenk line interfaced to a high-vacuum (10^{-5} Torr) line or in a nitrogen-filled Innovative Technologies glovebox with a medium-capacity recirculator (1−2 ppm of O_2). Argon and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. The hydrocarbon solvents benzene-d_6 (Cambridge Isotopes), toluene (Bio-Lab), toluene-d_8 (Cambridge Isotopes), and THF (Aldrich) were distilled under nitrogen from Na/K alloy. 1-Hexyne, *tert*-butylacetylene, (trimethylsilyl)acetylene, and phenylacetylene were purchased from ABCR, degassed, and stored under nitrogen over 4 Å molecular sieves, and transferred under vacuum immediately prior to use. The actinide complexes $U[N(SiMe_3)_2]_3$ (**1**)[39] and $[(Me_3Si)_2N]_2An[\kappa^2\text{-}(N,C)\text{-}CH_2Si(CH_3)_2N(SiMe_3)]$ (An = U (**2**), Th (**3**))[55] were prepared according to published methods.

NMR spectra were recorded on a Bruker Avance 300, Bruker Avance III 400, or Bruker Avance 500 spectrometer. Chemical shifts for ^1H NMR are referenced to internal protio solvent and reported relative to tetramethylsilane. ESR spectra were recorded on a Bruker EMX-10/12 X-band (ν = 9.4 GHz) digital spectrometer. Spectra of fullerene radicals were recorded at a microwave power of 0.06 mW and 20 kHz magnetic field modulation of 0.02 G amplitude. Digital field resolution was 4096 points per spectrum, allowing all hyperfine splitting to be measured directly with an accuracy better than 0.01 G. Spectral processing and simulation were performed with Bruker WINEPR and SimFonia Software. MALDI-TOF LD+ and LD− experiments were performed on a Waters MALDI Micromass MX spectrometer using the standard Micromass 96-well matrix along with fullerene, which has a higher ability for light absorption and ionization than Ag. Mass analysis was performed in the reflectron mode in the region between m/z 300 and 3000. GC/MS analyses were carried out on a Thermo Scientific ITQ series GC-Ion Trap MS System or a single-quadrupole Waters ZMD instrument. LC/MS analyses were performed on a Thermo Scientific LCQ Fleet Ion Trap Mass Spectrometer with a reverse-phase octadecyl HPLC-MS column and acetonitrile/water as eluent, with a photodiode array detector. Electronic spectra were acquired on a Shimadzu UV-1800 spectrophotometer, and fluorescence measurements were performed on a Jobin Yvon (Fluorolog-3) Fluorometer.

General Procedure for Actinide-Mediated Alkyne Oligomerization/Cyclotrimerization. In a typical experiment, 0.5 mL of an ~30 mM solution of catalyst in benzene-d_6 was transferred to a J.

DOI: 10.1021/acs.organomet.5b00455
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Young Teflon-sealed NMR tube. Either 10 or 100 equiv of terminal alkyne was transferred to the same tube, which was then sealed, shaken, and heated to 75 °C for 72 h to ensure completion of the reaction. The samples were analyzed as crude reaction mixtures by ^{1}H, ^{13}C, and two-dimensional NMR spectroscopy, and the data were compared to literature values for the organic products. Following this, samples were quenched by the addition of a few drops of methanol, filtered through a short Celite plug, and analyzed by GC/MS or LC/MS methods on the reaction mixtures. Product ratios were determined by either ^{1}H NMR spectroscopy or UV−vis spectroscopy interfaced to the LC/MS system.

(a). Oligomerization of 1-hexyne by complex ***1*** *(1%):* 172 μL of 1-hexyne; 88% conversion; **4a** (91%);[41] **6a** (5%); ^{1}H NMR (300 MHz, C_6D_6) δ 6.39 (s, 1H), 5.00 (d, *J* = 1.0 Hz, 1H), 4.93 (d, *J* = 1.0 Hz, 1H), 2.54 (t, *J* = 6.0 Hz, 2H), 2.46 (t, *J* = 9.0 Hz, 4H), 1.41 (m, 2H), 1.34 (m, 6H), 1.22 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 9H); **10a** (2%);[42] **11a** (1%).[42]

(b). Oligomerization of 1-hexyne by complex ***1*** *(10%):* 17 μL of 1-hexyne; 100% conversion; **4a** (13%);[41] **10a** (29%);[42] **11a** (42%);[42] **12a** (15%); ^{1}H NMR (300 MHz, C_6D_6) δ 5.77 (ddt, 1H), 5.11−4.95 (m, 2H), 1.96 (q, *J* = 6.0 Hz, 2H), 1.41−1.27 (m, 4H), 0.88 (t, *J* = 6.0 Hz).

(c). Oligomerization of 1-hexyne by complex ***2*** *(1%):* 172 μL of 1-hexyne; 88% conversion; **4a** (96%);[41] **6a** (2%) (see reaction a); **10a** (1%);[42] **11a** (1%).[42]

(d). Oligomerization of 1-hexyne by complex ***2*** *(10%):* 17 μL of 1-hexyne; 100% conversion; **10a** (41%);[42] **11a** (37%);[42] **12a** (22%) (see reaction b).

(e). Oligomerization of 1-hexyne by complex ***3*** *(1%):* 172 μL of 1-hexyne; 86% conversion; **4a** (92%);[41] **6a** (7%) (see reaction a).

(f). Oligomerization of 1-hexyne by complex ***3*** *(10%):* 17 μL of 1-hexyne; 99% conversion; **4a** (93%);[41] **6a** (7%) (see reaction a).

(g). Oligomerization of tert-butylacetylene by complex ***1*** *(1%):* 185 μL of *tert*-butylacetylene ; 87% conversion; **4b** (22%);[43] **5b** (40%);[44] **7b** (21%); ^{1}H NMR (300 MHz, C_6D_6) δ 6.06 (d, *J* = 15 Hz, 1H), 5.63 (d, *J* = 15 Hz, 1H), 5.46 (s, 1H), 1.47 (s, 9H), 1.44 (s, 9H), 1.25 (s, 9H); **10b** (8%);[45] **11b** (1%);[46] **12b** (7%).[47]

(h). Oligomerization of tert-butylacetylene by complex ***1*** *(10%):* 19 μL of *tert*-butylacetylene; 100% conversion; **5b** (55%);[44] **11b** (22%);[46] **12b** (23%).[47]

(i). Oligomerization of tert-butylacetylene by complex ***2*** *(1%):* 185 μL of *tert*-butylacetylene; 77% conversion; **4b** (60%);[43] **5b** (22%);[44] **6b** (9%); ^{1}H NMR (300 MHz, C_6D_6) δ 5.90 (d, *J* = 1.8 Hz, 1H), 5.86 (d, *J* = 1.8 Hz, 1H), 5.80 (s, 1H), 1.23 (s, 18H), 1.18 (s, 9H); **10b** (3%);[45] **11b** (1%);[46] **12b** (5%).[47]

(j). Oligomerization of tert-butylacetylene by complex ***2*** *(10%):* 19 μL of *tert*-butylacetylene; 100% conversion; **5b** (54%);[44] **6b** (23%), (see reaction **i**); **10b** (6%);[45] **11b** (2%);[46] **12b** (16%).[47]

(k). Oligomerization of tert-butylacetylene by complex ***3*** *(1%):* 185 μL of *tert*-butylacetylene; 70% conversion; **4b** (41%);[43] **5b** (43%);[44] **7b** (16%), (see reaction g).

(l). Oligomerization of tert-butylacetylene by complex ***3*** *(10%):* 19 μL of *tert*-butylacetylene; 97% conversion; **4b** (14%);[43] **5b** (46%);[44] **7b** (39%), (see reaction g).

(m). Oligomerization of ethynyltrimethylsilane by complex ***1*** *(1%):* 214 μL of ethynyltrimethylsilane; 42% conversion; **4c** (50%);[48] **5c** (11%);[49] **10c** (22%);[42] **11c** (17%).[42]

(n). Oligomerization of ethynyltrimethylsilane by complex ***1*** *(10%):* 21 μL of ethynyltrimethylsilane; 100% conversion; **10c** (58%);[42] **11c** (42%).[42]

(o). Oligomerization of ethynyltrimethylsilane by complex ***2*** *(1%):* 214 μL of ethynyltrimethylsilane; 97% conversion; **4c** (32%);[48] **5c** (8%);[49] **8c** (19%);[50] **9c** (38%); ^{1}H NMR (300 MHz, C_6D_6) δ 7.03 (m, 1H), 6.90 (m, 1H), 6.84 (s, 1H), 0.10 (s, 27H); **10c** (2%);[42] **11c** (2%).[42]

(p). Oligomerization of ethynyltrimethylsilane by complex ***2*** *(10%):* 21 μL of ethynyltrimethylsilane; 100% conversion; **4c** (34%);[48] **5c** (25%);[49] **10c** (23%);[42] **11c** (19%).[42]

(q). Oligomerization of ethynyltrimethylsilane by complex ***3*** *(1%):* 214 μL of ethynyltrimethylsilane; 64% conversion; **4c** (22%);[48] **5c** (43%);[49] **8c** (35%), (see reaction o).

(r). Oligomerization of ethynyltrimethylsilane by complex ***3*** *(10%):* 21 μL of ethynyltrimethylsilane; 87% conversion; **4c** (27%);[48] **5c** (32%);[49] **8c** (41%), (see reaction o).

(s). Oligomerization of phenylacetylene by complex ***1*** *(1%):* 165 μL of phenyacetylene; 92% conversion; dimers (5%), MS (ESI+) *m*/*z* 205.16 ($[M + H]^+$), 126.94 ($H_2CC(Ph)(C{\equiv}C)^+$); trimers (7%), MS (ESI+) *m*/*z* 306.37 (M^+), 205.10 ($H_2CC(Ph)$ $(CHCPh)^+$); **10d** (25%), MS (ESI+) *m*/*z* 306.34 (M^+), 229.18 ($Ph_2C_6H_3^+$); **11d** (63%), MS (ESI+) *m*/*z* 306.33 (M^+), 229.12 ($Ph_2C_6H_3^+$).

(t). Oligomerization of phenylacetylene by complex ***1*** *(10%):* 17 μL of phenyacetylene; 100% conversion; dimers (2%), MS (ESI+) *m*/*z* 205.17 ($[M + H]^+$), 126.30 ($H_2CC(Ph)(C{\equiv}C)^+$); **10d** (48%), MS (ESI+) *m*/*z* 306.11 (M^+), 229.23 ($Ph_2C_6H_3^+$); **11d** (49%), MS (ESI+) *m*/*z* 306.39 (M^+), 229.26 ($Ph_2C_6H_3^+$).

(u). Oligomerization of phenylacetylene by complex ***2*** *(1%):* 165 μL of phenyacetylene; 96% conversion; dimers (19%), MS (ESI+): *m*/*z* 204.16 (M^+), 127.01 ($H_2CC(Ph)(C{\equiv}C)^+$); trimers (5%), MS (ESI +): *m*/*z* 306.34 (M^+), 204.16 (H2CC(Ph) $(CHCPh)^+$); **10d** (35%), MS (ESI+): *m*/*z* 306.30 (M^+), 229.23 ($Ph_2C_6H_3^+$); **11d** (40%), MS (ESI+): *m*/*z* 306.31 (M^+), 229.20 ($Ph_2C_6H_3^+$).

(v). Oligomerization of phenylacetylene by complex ***2*** *(10%):* 17 μL of phenyacetylene; 100% conversion; dimers (2%), MS (ESI+) *m*/*z* 205.25 ($[M + H]^+$), 126.91 ($H_2CC(Ph)(C{\equiv}C)^+$); **10d** (48%), MS (ESI+) *m*/*z* 306.30 (M^+), 229.25 ($Ph_2C_6H_3^+$); **11d** (49%), MS (ESI+) *m*/*z* 306.37 (M^+), 229.36 ($Ph_2C_6H_3^+$).

(w). Oligomerization of phenylacetylene by complex ***3*** *(1%):* 165 μL of phenyacetylene; 99% conversion; **4d** (91%);[51] **5d** (9%).[52]

(x). Oligomerization of phenylacetylene by complex ***3*** *(10%):* 17 μL of phenyacetylene; 100% conversion; **4d** (77%);[51] **5d** (15%);[52] **12d** (8%).[53]

Preparative Reaction of 1,6-Heptadiyne with Complexes 1. In a thick-walled Schlenk tube with a J. Young Teflon stopcock was placed 0.11 g (153 μmol) of complex **1** in 15 mL of toluene. A 175 μL portion (0.141 g, 1.53 mmol) of 1,6-heptadiyne was added to the reaction mixture, followed by sealing the tube, evacuating the head space, and heating to 75 °C for 24 h. The reaction mixture was then cooled to room temperature and quenched by the addition of water. The organic layer was separated, and the aqueous layer was extracted three times with 10 mL portions of ethyl ether and then three 10 mL portions of ethyl acetate. The organics were combined, dried over sodium sulfate (Na_2SO_4), filtered, and evaporated to dryness. The crude product was purified by preparative thin-layer chromatography with *n*-hexane as eluent, yielding the mono- and bis(indane) products (22% based on 1,6-heptadiyne). The ^{1}H NMR spectra of these compounds were found to be in agreement with previous literature data.[54]

Synthesis of ^{n}BuC≡CD. 1-Hexyne (20 mL, 174 mmol) was syringed into a thick-walled Schlenk tube containing a 1.6 M solution of ^{n}BuLi in hexane (90 mL, 144 mmol) at −95 °C. The mixture was warmed slowly to 0 °C and stirred for 30 min. The mixture was then warmed to room temperature, and the volatiles were removed in vacuo to yield a white solid. The flask was cooled to −85 °C, and a under nitrogen flush a large excess of D_2O (50 mL) was slowly added by syringe. The tube was sealed and slowly warmed to 0 °C and the mixture stirred vigorously for 10 min until all solids dissolved. The mixture was separated, and the organic layer was distilled under nitrogen. The distillate was run through a plug of $MgSO_4$, redistilled, and stored over 4 Å molecular sieves, yielding 18 mL of ^{n}BuC≡CD. ^{2}H NMR: δ 1.85 ppm. No signal for the terminal alkyne proton (C≡CH) was found in the ^{1}H NMR.

Synthesis of $Me_3SiC{\equiv}CD$. (Trimethylsilyl)acetylene (10 mL, 70 mmol) was syringed into a thick-walled Schlenk tube containing a 1.6 M solution of ^{n}BuLi in hexane (37 mL, 59 mmol) at −95 °C. The mixture was warmed slowly to 0 °C and stirred for 30 min. The mixture was then warmed to room temperature, and the volatiles were removed in vacuo to yield a white solid. The flask was cooled to −85 °C, and under a nitrogen flush an excess of D_2O (20 mL) was slowly

DOI: 10.1021/acs.organomet.5b00455
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added by syringe. The tube was sealed and slowly warmed to 0 °C and the mixture stirred vigorously for 10 min until all solids dissolved. The mixture was separated, and the organic layer was distilled under nitrogen. The distillate was run through a plug of $MgSO_4$, redistilled, and stored over 4 Å molecular sieves, yielding 8 mL of $Me_3SiC{\equiv}CD$. ^2H NMR: δ 2.32 ppm. ^1H NMR spectroscopy showed less than 1% of the terminal alkyne proton (C≡CH).

EPR Studies of Oligomerization of 1-Hexyne with Complexes 1 and 2. Preparation of samples was performed inside an inert-atmosphere glovebox. Stock solutions of reagents were prepared in vials within the glovebox and added to J. Young Teflon-sealed NMR tubes. A 1 mL portion of fullerene stock solution (2 mg mL^{-1} in toluene) was added to 45 μL of 1-hexyne followed by the addition of 100 μL of a 40 mM stock solution of complexes **1** or **2** or by the addition of the fullerene solution to a similar catalytic solution after the sample reacted with heating for 1 day. Samples were heated to 75 °C followed by acquisition of the EPR spectrum immediately after addition and after completion of the reaction, showing the presence of a fullerene-trapped organic radical. MALDI-TOF LD+ analysis was performed on the crude sample to determine the molecular weight of the fullerene-trapped species.

Kinetic Studies of 1-Hexyne Oligomerization and Trimethylacetylene Cyclotrimerization. In a typical experiment, an NMR sample was prepared as described above (see General Procedure for Actinide-Mediated Alkyne Oligomerization). Experiments for reagent-order determination were performed at variable concentrations of catalyst or alkyne, spanning 1 order of magnitude concentration differences while the other reagent concentration was constant. The sample tube was inserted into the probe of a Bruker Avance 300 spectrometer that had been previously set to the desired temperature (T = 75 ± 0.1 °C; checked with ethylene glycol temperature standard). Data were acquired every 5 min up to 1.5 h, and product concentrations were measured from the area of one or both vinylic protons of product **4a** (1-hexyne oligomerization) or the aromatic proton of **11c** ((trimethylsilyl)acetylene cyclotrimerization) and calibrated against the aromatic proton signal of mesitylene as internal standard. Reaction rates were determined by a least-squares fit of product concentration versus time, and the collective rate data were plotted to determine alkyne and catalyst orders.

Activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and E_a) were calculated from acquired kinetic data using Eyring and Arrhenius plots. In a typical experiment, an NMR sample was prepared as described above (see General Procedure for Actinide-Mediated Alkyne Oligomerization). The sample tube was inserted into the probe of the Bruker Avance 300 spectrometer which had been previously set to the desired temperature over the range of 55−100 °C (T ±0.1 °C; checked with ethylene glycol temperature standard). Data were acquired every 5 min up to 1.5 h, and product concentrations were determined from the area of one of the vinylic protons of product **4a** (1-hexyne oligomerization) or the aromatic proton of **11c** ((trimethylsilyl)acetylene cyclotrimerization) and calibrated against the aromatic peak of mesitylene as internal standard. Reaction rates were determined by a least-squares fit of product concentration versus time. Eyring plots were generated in the usual manner, and the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for activation were calculated from the slope and intercept of the least-squares fit, respectively. Energies of activation (E_a) were calculated as a function of slope of the respective Arrhenius plots.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00455.

Fluorescence data, EPR data, and experimentally derived Eyring and Arrhenius plots (PDF)

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Author Contributions

The manuscript was written through contributions of all authors./All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Israel Science Foundation administered by the Israel Academy of Science and Humanities under Contract No. 78/14, the Technion-Israel Institute of Technology, the University of Edinburgh, EaStCHEM School of Chemistry, and the EPSRC (U.K.). We also thank COST Action CM1006 for making this collaboration possible and Dr. Boris Tumanskii for his generous assistance with EPR spectroscopy.

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DOI: 10.1021/acs.organomet.5b00455
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