Selective Dimerization of Terminal Alkynes Promoted by the Cationic Actinide Compound $[(Et_2N)_3U][BPh_4]$. Formation of the Alkyne π-Complex $[(Et_2N)_2U(C{\equiv}C^tBu)(\eta^2\text{-}HC{\equiv}C^tBu)][BPh_4]$

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Summary: The cationic actinide complex $[(Et_2N)_3U][BPh_4]$ is an active catalytic precursor for the selective dimerization of terminal alkynes. The regioselectivity is mainly toward the geminal dimer, but for bulky alkyne substituents the unexpected cis dimer is also obtained. Mechanistic NMR studies show that a η^2-π-complex is formed between a terminal alkyne and an uranium−acetylide intermediate. This latter complex has been characterized spectroscopically. A plausible mechanistic scenario is proposed for the dimerization process.

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Organometallic complexes of d^0/f^n-block elements proved to be active catalysts for the oligomerization of terminal alkynes. Such transformation is of considerable current interest because it can lead to a variety of organic enynes and oligoacetylene derivatives[1,2] that are useful synthetic precursors for the synthesis of natural products[3] and also for organic conducting polymers.[4] Enynes are the simplest oligomerization products of alkynes, and the key step in their formation involves the generation of a M−C≡CR carbyl moiety, insertion of alkyne to yield the M−C(H)=C(R)C≡CR alkenyl intermediate, and σ-bond metathesis with additional alkynes to release the dimer and regenerate the MC≡CR species. Lately, we have demonstrated that organoactinide complexes of the type $Cp^*_2AnMe_2$ ($Cp^* = C_5Me_5$; An = U, Th) are active catalysts for the linear oligomerization of terminal alkynes, and the extent of oligomerization was found to be strongly dependent on the electronic and steric hindrance of the alkyne substituents. For example, bulky alkynes reacted with high regioselectivity toward dimer and/or trimers, whereas for nonbulky alkynes, the oligomerization afforded dimers to heptamers with total lack of regioselectivity. The addition of primary amines, for An = Th, allowed the chemoselective formation of dimers, but this control could not be achieved with An = U.[5]

Virtually nothing is known for cationic actinide complexes regarding their reactivity toward terminal alkynes, while it was reported that $Cp^*_2ZrMe^+$ selectively dimerizes ^{t}BuC≡CH to the head-to-tail dimer but converts ^{n}PrC≡CH and MeC≡CH to mixtures of dimers and trimers.[6] In this communication we report on the reactions of the well-defined cationic actinide complex $[(Et_2N)_3U][BPh_4]$ with various monosubstituted alkynes. We found that this complex is an efficient catalytic precursor for the selective dimerization of terminal alkynes; we present the spectroscopic characterization of the first uranium−alkyne π-complex as the key organometallic intermediate in the catalytic cycles, as well as the kinetics and their mechanistic implications.

Reaction of $[(Et_2N)_3U][BPh_4]$[7] with an excess of terminal alkyne (RC≡CH, R = Me, ^{i}Pr, ^{n}Bu; toluene-d_8, alkyne/$[(Et_2N)_3U][BPh_4]$ ratio 50:1) results in the chemo- and regioselective catalytic formation of the head-to-tail dimers (**1**−**3**) with no formation of the *trans* isomer or major oligomers (eq 1). For PhC≡CH, the reaction is

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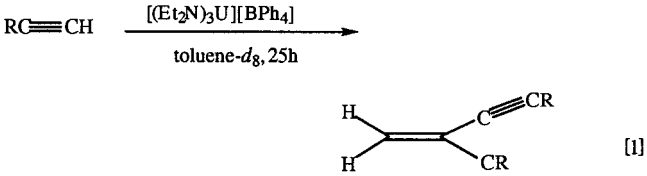
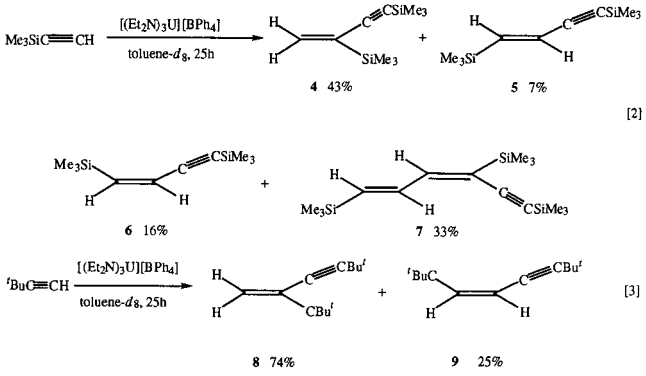


[1]

R = Me, 94% (**1**)
R = ^{i}Pr, 75% (**2**)
R = ^{n}Bu, 94% (**3**)

less chemoselective, allowing the formation of trimers (geminal dimer:trimers ratio = 32:58). For TMSC≡CH, besides the formation of the geminal head-to-tail dimer (**4**), the *trans*-head-to-head dimer (**5**), and the regioselective head-to-tail-to-head-trimer (*E*,*E*)-1,4,6-tris(trimethylsilyl)-1,3-hexadien-5-yne (**7**), the *unexpected* head-to-head *cis* dimer (**6**) is also formed (eq 2).[8] Likewise, for ^{t}BuC≡CH, the geminal dimer (**8**) and the *unexpected cis* dimer (**9**) are formed (eq 3).[8]



[2]

[3]

Mechanistically, the presence of relatively low-lying empty σ-bonding orbitals, the relatively polar metal−ligand bonds, and the absence of energetically accessible metal oxidation states for oxidative addition/reductive elimination processes[9] would implicate a "four-center" heterolytic transition state in the metal−carbon bond cleavage, suggesting that the *cis*-stereochemistry in the formation of the alkenyl intermediate should be preserved after the σ-bond metathesis step. Thus, the formation of dimers **6** and **9** argues for an isomerization pathway before the product is released from the metal center. It is noteworthy that in the oligomerization of terminal alkynes promoted by the cationic complexes [Cp*$_2$AnMe] [B(C_6F_5)$_4$] (An = Th, U) only the geminal dimer is formed with no trace formation of the *trans* or *cis* dimers.[2] Also, in the oligomerization promoted by Cp*$_2$AnMe$_2$, the *cis* dimer has not been observed.[2]

In the reaction of [(Et_2N)$_3$U][BPh_4] with terminal alkynes, 1 equiv of the Et_2NH amine is released to the solution, as observed in the NMR, with the likely formation of the bisamido acetylide cationic complex [(Et_2N)$_2$UC≡CR][BPh_4]. This seems to be a slow equilibrium process, and the addition of different equimolar amounts of Et_2NH to the reaction mixture leads to a lowering of the reaction rate linearly.[10] A second plausible equilibrium which may yield the same result will be the coordination of the amine to the organometallic cationic center. To get some insight regarding which of these two equilibrium processes is responsible for the lowering of the reaction rate, we have followed the Et_2-NH signals in the ^{1}H NMR as a fuction of the different equimolar additions of alkyne and amine. The addition of 1 equiv of alkyne to the starting complex induced the formation of 1 equiv of amine, which has very broad signals in the ^{1}H NMR spectrum, indicating that the latter equilibrium takes place when no excess of alkyne is present. However, by reacting the starting complex with two or more equivalents of alkyne, the signal of the amine becomes very sharp, indicating that under the catalytic conditions there seems to be no amine in equilibrium with the acetylide complex. In addition, since the amount of the free amine formed, in the catalytic reaction, is stoichiometric, it is clear that the major protonolytic agent releasing the dimer from the metal−alkenyl complex is the free terminal alkyne.

Kinetic measurements on the oligomerization reaction of *n*-BuC≡CH were undertaken by in situ ^{1}H NMR spectroscopy.[10] The reaction of excess *n*-BuC≡CH was monitored with constant catalyst concentration until complete substrate consumption. The disappearance of the C≡CH (δ = 2.28 ppm) ^{1}H resonance was normalized. The turnover frequency of the reaction was calculated from the slope of the kinetic plots of substrate-to-catalyst ratio vs time. When the initial concentration of the terminal alkyne is held constant and the concentration of the catalytic precursor is varied over a ~5-fold concentration range, a plot of reaction rate vs precatalyst concentration indicates that the reaction is first-order dependent in precatalyst, in analogy with the oligomerization of terminal alkynes promoted by Cp*$_2$-AnMe$_2$.[2] This result indicates that the best formulation of the active species should be monomeric. When the concentration of the catalyst is maintained constant and the concentration of the alkyne is varied over a 10-fold concentration range, a plot of the rate of the reaction vs alkyne concentration exhibits two-domain behavior. At low concentrations, an inverse proportionality is observed, indicating that the reaction is in an inverse first order, and at higher concentrations, the reaction exhibits a zero order in alkyne. An inverse proportionality in catalytic systems is well-known and consistent with an equilibrium before the rate-limiting step. The change from an inverse rate to a zero rate is consistent with two equilibrium processes. One of these equilibrium processes is routing the complex *out of the catalytic cycle (inverse order)*, whereas the second equilibrium, only at higher concentrations, is the rate-determining step toward the dimer formation.

A plausible reaction mechanism for the dimerization of ^{n}BuC≡CH is given in Scheme 1. This mechanism consists of a sequence of well-established elementary reactions such as acetylene insertion into a M−C σ-bond and σ-bond metathesis. The first step in the catalytic cycle involves the protonolysis of the cationic uranium amide by the alkyne and the formation of the bisamido carbyl complex **A** together with Et_2NH. Complex **A** may either be in equilibrium with an alkyne, forming the uranium−alkyne π-complex **B**, driving the active species out of the catalytic cycle (inverse rate dependence),[11] or undergo head-to-tail insertion of the alkyne into the uranium−carbon σ-bond, yielding the substituted uranium alkenyl complex **C**. This complex reacts with an incoming alkyne to give the corresponding dimer and regenerate the active carbyl complex.

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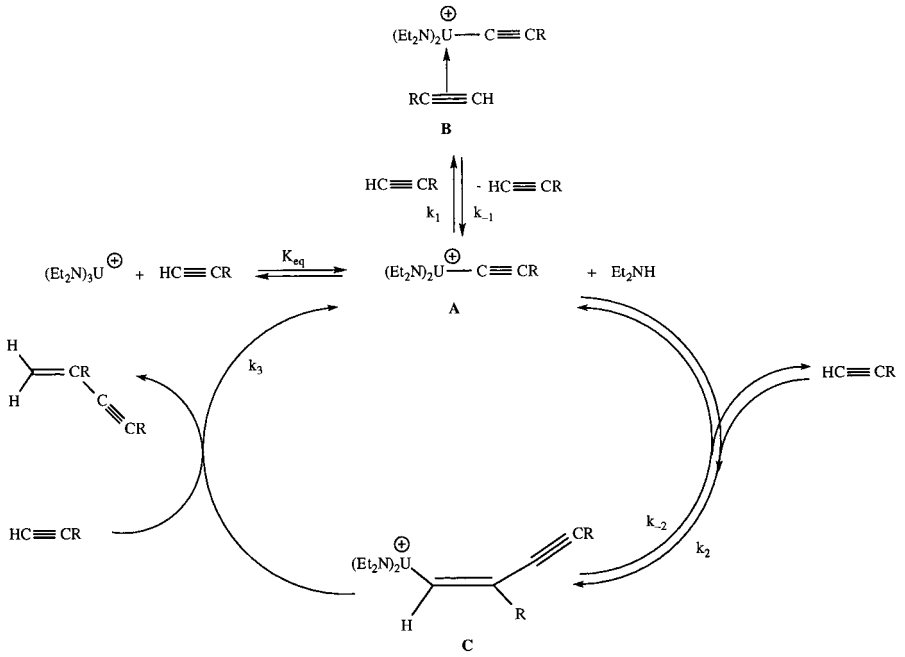
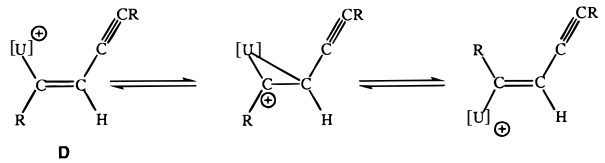
Scheme 1. Plausible Mechanism for the Dimerization of Terminal Alkynes Promoted by $[(Et_2N)_3U][BPh_4]$



Complex **B** (for R = ^{t}Bu) has been trapped ($\tau_{1/2}$ = 6 h) and its structure determined spectroscopically.[10] The NMR spectra (^{1}H and ^{13}C) of complex **B** exhibit sharp lines as found for other actinide-IV complexes. The ^{1}H NMR spectroscopy shows one acetylide signal (C−H) at −2.14 ppm, which correlated in the DEPT and 2D C−H correlation to a carbon at −19.85 ppm with a coupling constant of ^1J = 250 Hz. In addition, two ^{t}Bu group signals have been found in the ^{1}H and ^{13}C NMR, DEPT, and C−H correlation spectroscopy. This result clearly indicates that a free acetylene is attached to the organometallic cationic complex. An indication of an alkyne η^2-complex, as compared with an acetylide complex or just a free alkyne, has been obtained by FT-IR spectroscopy. The C≡C stretching of the free alkyne (2108 cm^{-1}) dissappeared, giving rise to two signals at lower frequencies as expected for η^2-transition metal complexes, one at 2032 cm^{-1} similar to acetylide lanthanides, and the second one at 2059 cm^{-1}.[12] To the best of our knowledge, this is the first example of a η^2-π-complex between an alkyne and an actinide compound.

The turnover-limiting step for the catalytic dimerization is the insertion of the alkyne into the uranium−carbyl complex **A**.[13] This result argues that the rate for σ-bond metathesis between the cationic uranium−amido and the alkyne and the protonolysis of the dimer by the alkyne are faster than the rate of insertion into complex **A**. In addition, this result argues that trimers are only expected if a kinetic delay in the protonolysis is induced, in agreement with our observations.

For the bulky alkyne substituents (TMS, ^{t}Bu), it seems necessary that the isomerization of the alkenyl complex **D** occurs at a rate that is greater than that of its protonolysis, allowing the formation of the unexpected *cis* dimer. This pathway takes place presumably through a metallacyclopropyl cation, similarly to the well-known "envelope isomerization" process (eq 4).[14]



(4)

These results demonstrate that cationic actinide complexes are active catalysts for the dimerization of terminal alkynes. A delicate balance between alkyne insertion and alkyne CH σ-bond metathesis steps determines the dimer:trimer:oligomer ratio and the *geminal*:*cis*:*trans* isomer ratio. The trapped π-acetylide complex is, to the best of our knowledge, the first characterized actinide−alkyne π-complex. The incorporation of these transformations into efficient and novel catalytic cycles is presently under investigation.

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Supporting Information Available: Text giving the experimental procedures and spectroscopic data for compounds **1**−**9** and **B** and kinetic data plots, and the derived rate law and the activation parameters for the dimerization of ^{n}BnC≡CH. This material is available free of charge via the Internet at http://pubs.acs.org.

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