Oligomerization and Hydroamination of Terminal Alkynes Promoted by the Cationic Organoactinide Compound $[(Et_2N)_3U][BPh_4]$

Jiaxi Wang,[a] Aswini Kumar Dash,[a] Moshe Kapon,[a] Jean-Claude Berthet,[b] Michel Ephritikhine,[b] and Moris S. Eisen*[a]

Abstract: The three ancillary amido moieties in the cationic complex $[(Et_2N)_3U][BPh_4]$ are highly reactive and are easily replaced when the complex is treated with primary amines. The reaction of $[(Et_2N)_3U][BPh_4]$ with excess tBuNH$_2$ allows the formation of the cationic complex $[(t\text{BuNH}_2)_3(t\text{BuNH})_3U][BPh_4]$. X-ray diffraction studies on the complex indicate that three amido and three amine ligands are arranged around the cationic metal center in a slightly distorted octahedral *mer* geometry. The cationic complex reacts with primary alkynes in the presence of external primary amines to primarily afford the *unexpected cis* dimer and, in some cases, the hydroamination products are obtained concomitantly. The formation of the *cis* dimer is the result of an envelope isomerization through a metal–cyclopropyl cationic complex. In the reaction of the bulkier alkyne tBuC≡CH with the cationic uranium complex in the presence of various primary amines, the *cis* dimer, one trimer, and one tetramer are obtained regioselectively, as confirmed by deuterium labeling experiments. The trimer and the tetramer correspond to consecutive insertions of an alkyne molecule into the vinylic CH bond *trans* to the bulky *tert*-butyl group. The reaction of (TMS)C≡CH with the uranium catalyst in the presence of EtNH$_2$ followed a different course and produced the *gem* dimer along with the hydroamination imine as the major product. However, when other bulkier amines were used (iPrNH$_2$ or tBuNH$_2$) both hydroamination isomeric imines *Z* and *E* were obtained. During the catalytic reaction, the *E* (kinetic) isomer is transformed into the most stable *Z* (thermodynamic) isomer. The unique reactivity of the alkyne (TMS)C≡CH with the secondary amine Et$_2$NH is remarkable because it afforded the *trans* dimer and the corresponding hydroamination enamine. The latter probably results from the insertion of the alkyne into a secondary metal–amide bond, followed by protonolysis.

Keywords: alkynes · dimerization · homogeneous catalysis · hydroamination · uranium

Introduction

The catalytic chemistry of electrophilic d^0/f^n organometallic complexes is under intense investigation, reaching a high level of sophistication. Most studies are devoted to the functionalization of unsaturated organic molecules.[1–14] Among the numerous reactions, metal-mediated oligomerization of terminal alkynes is of substantial current interest, since it can lead to a diversity of organic enynes and oligoacetylene products[4–14] that are valuable synthetic precursors for the synthesis of natural products[15] and also a diversity of organic conducting polymers.[16] Enynes are the simplest oligomerization products of alkynes, and their formation involves the creation of a M–C≡CR acetylide moiety followed by the insertion of an additional alkyne to yield the alkenyl intermediate M–C(H)=C(R)C≡CR. Protonolysis by an additional alkyne releases the dimer and regenerates the M–C≡CR species. If higher oligomers are produced, those are formed by additional insertions of the alkyne into the M–C(H)=C(R)C≡CR species, usually lacking any regioselectivity. 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 properties of the alkyne substituents.[14] For example, bulky alkynes reacted with high regioselectivity towards dimers and/or trimers, whereas nonbulky alkynes were transformed into oligomers with a total lack of regioselectivity. The addition of primary amines to the catalytic cycle, for An = Th, permitted the chemoselective formation of dimers, whereas for An = U, this control was not accomplished.[14b] In contrast to the neutral organoactinide complexes, cationic d^0/f^n actinide

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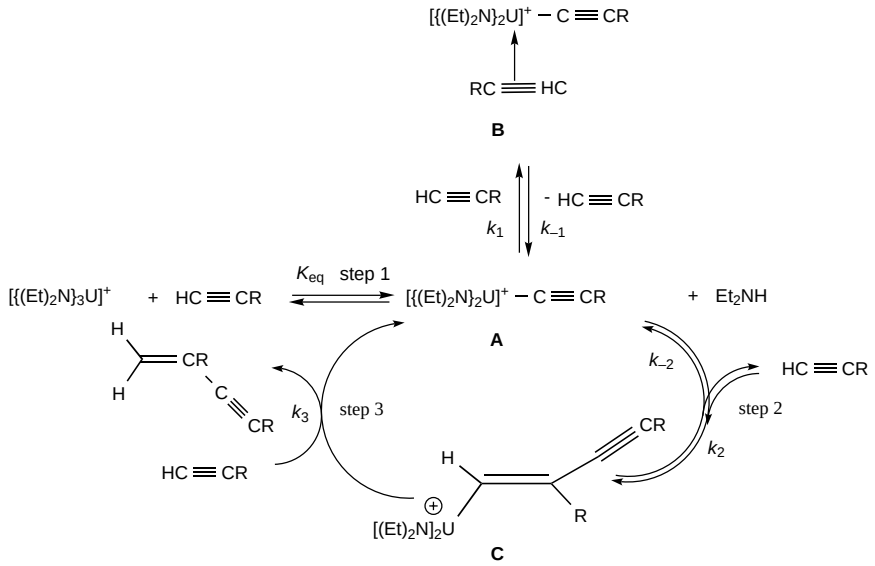
complexes have been used in homogeneous catalysis for the polymerization of α-olefins,[17] similar to the behavior of cationic Group 4 compounds. Regarding alkyne activations with such complexes, $[Cp^*_2ZrMe]^+$ dimerizes *t*BuC≡CH selectively to the head-to-tail dimer, although for the less bulky alkynes, such as *n*PrC≡CH and MeC≡CH, mixtures of dimers and trimers are obtained.[18] Thus, catalytic alkyne oligomerization is a convenient way to investigate insertion and σ-bond metathesis reactivity of complexes. We have recently shown that the reaction of terminal alkynes (RC≡CH) promoted by $[(Et_2N)_3U][BPh_4]$ in toluene efficiently produces the *gem* dimers (for R = Me, *i*Pr and *n*Bu) as the major products, whereas for bulky alkynes (R = TMS or *t*Bu) small amounts of the *cis* dimer were concomitantly obtained. A plausible mechanism was proposed for the dimerization of terminal alkynes; this was corroborated by kinetic, thermodynamic, equilibrium studies, and trapping experiments of the first f-element alkyne π-complex (Scheme 1).[19, 20]



Scheme 1. Plausible mechanism for the dimerization of terminal alkynes promoted by $[(Et_2N)_3U][BPh_4]$.

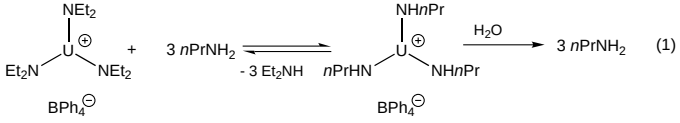
The initial step in the catalytic cycle is the equilibrium reaction between the alkyne and the cationic uranium amide complex forming the bisamido acetylide compound $[(Et_2N)_2U(C{\equiv}CR)][BPh_4]$ (**A**) along with Et_2NH (step 1). Complex **A** reacts with an alkyne molecule, being in equilibrium with a π-alkyne acetylide uranium complex **B**, which drives the active species out of the catalytic cycle, inducing an inverse rate dependence in alkyne, and concomitantly reacts with another alkyne in a head-to-tail fashion to yield the substituted uranium–alkenyl complex **C** (step 2). This complex undergoes a σ-bond metathesis reaction with an additional alkyne (step 3) leading to the corresponding dimer and regenerating the active acetylide complex **A**. The turnover-limiting step for the catalytic dimerization was found to be the insertion of the alkyne into the uranium–carbon bond of **A** (step 2). This result suggested that the σ-bond metathesis between the cationic complex $[(Et_2N)_3U][BPh_4]$ and the alkyne, and the protonolysis of **C** by the alkyne (or amine) are faster than the insertion of the alkyne into complex **A**. Since the formation of the cationic complex **A** is an equilibrium reaction, it seems plausible to tailor the regiochemistry of the oligomerization process by the use of external amines. It is expected that the amine will be bonded to the cationic metal center, probably causing a kinetic delay but also allowing a unique regiochemistry.

To expand the rich potential of the cationic organoactinide compounds as homogeneous catalysts, in this publication we report on the reactivity of the well-defined cationic uranium complex $[(Et_2N)_3U][BPh_4]$ as a catalytic precursor for the selective dimerization, oligomerization, or/and hydroamination of a variety of terminal alkynes. We also present the spectroscopic and crystallographic characterization of a cationic uranium intermediate.

Results and Discussion

We start the presentation of the results with the stoichiometric reactions of $[(Et_2N)_3U][BPh_4]$ with primary amines. We then describe the diverse catalyzed reactions of the alkynes, by following their order of substitution, and discuss the mechanism of these reactions as soon as they are presented.

Reaction of the cationic complex $[(Et_2N)_3U][BPh_4]$ with primary amines: At room temperature in benzene, the amido ligands of this complex are easily activated. Thus, its treatment with *n*-propylamine yields an organoactinide intermediate that upon consecutive quenching with water, when all volatiles have been removed, yields only *n*-propylamine with no traces of Et_2NH. This result indicates that all three amido groups were easily exchanged according to the transamination reaction depicted by [Eq. (1)].[21] The NMR spectra indicated that the complexes $[(R_2N)_3U][BPh_4]$ adopt a zwitterionic structure in non-coordinating solvents with two phenyl groups of BPh_4 coordinated to the uranium center.[20]



A similar reaction of $[(Et_2N)_3U][BPh_4]$ with excess *tert*-butylamine allows the formation of the complex $[(tBuNH_2)_3(tBuNH)_3U][BPh_4]$ [Eq. (2)], which crystallized

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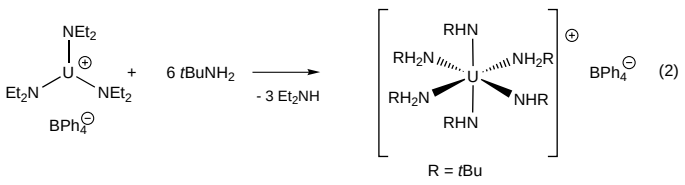

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from a toluene/hexane mixture. The X-ray diffraction study revealed that the crystals are composed of discrete cation–anion pairs. The structure of the cation is shown in Figure 1. The BPh_4 anion displays the expected geometry, whereas the

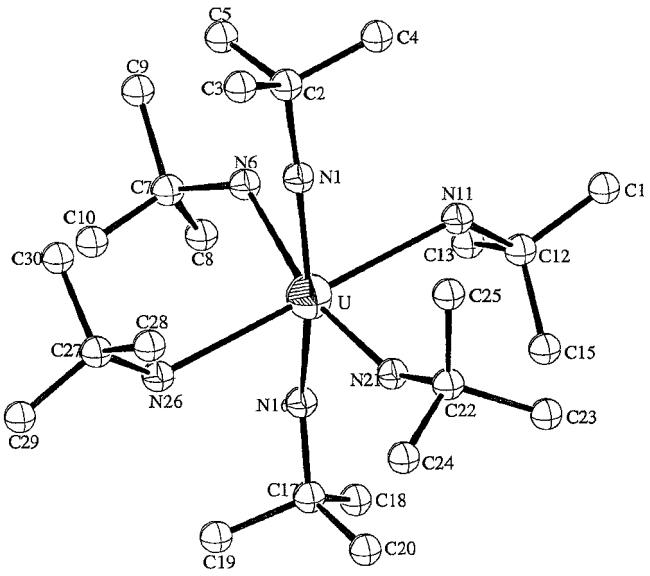
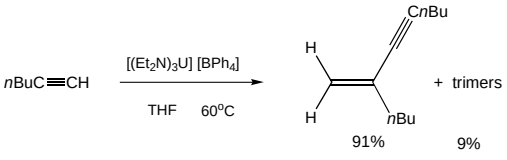


Figure 1. Perspective ORTEP drawing of the non-hydrogen atoms of the cation $[(t\mathrm{BuNH_2})_3(t\mathrm{BuNH})_3\mathrm{U}]^+$ (**1**) in the complex $[(t\mathrm{BuNH_2})_3(t\mathrm{BuNH})_3\mathrm{U}][\mathrm{BPh_4}]$. All atoms are represented by thermal ellipsoids drawn to encompass 50% of the electron density.

uranium atom is in a slightly distorted octahedral environment, with the three amido and three amine ligands arranged in a *mer* geometry. The U–N(amido) bond lengths average 2.20(2) Å and are similar to those determined in the distorted *fac* octahedral cation $[(\mathrm{Et_2N})_3(\mathrm{thf})_3\mathrm{U}]^+$ (mean value of 2.18(1) Å).[20] To our knowledge, $[(t\mathrm{BuNH_2})_3(t\mathrm{BuNH})_3\mathrm{U}][\mathrm{BPh_4}]$ is the only uranium(IV) complex with primary amine ligands to have been crystallographically characterized. The mean U–N(amino) bond length of 2.67(3) Å can be compared with the average U–N bond length of 2.79(2) Å in $[\mathrm{UCl_4}(\mathrm{Me_2NCH_2CH_2NMe_2})_2]$.[22] In this latter compound, the U–N bond lengths were 0.1 Å longer than those expected as a result of steric repulsions between the methyl groups on the nitrogen atoms and the chloride ligands. Interestingly, the shorter U–N(amido) bond length (U–N21 = 2.185(7) Å) and the larger U–N(amine) bond length (U–N6 = 2.705(8) Å) are those which are in the *trans* positions. The small octahedral distortion can be observed by the different angles between the amine–amido, amine–amine, and amido–amido groups: N21-U-N16 = 95.2(3), N21-U-N1 = 95.4(2), N21-U-N11 = 87.4(2), N21-U-N26 = 92.6(3), N21-U-N6 = 165.8(2), N16-U-N1 = 169.3(2), N16-U-N11 = 98.1(2), N16-U-N26 = 81.4(2), and N11-U-N26 = 179.50(18)°.

Distinct regioselectivity in the dimerization of propyne and 1-hexyne catalyzed by $[(\mathrm{Et_2N})_3\mathrm{U}][\mathrm{BPh_4}]$ in the presence of amines: The different reactivity of the precatalyst as a function of the solvent was investigated first in order to gain knowledge of the best experimental conditions. Thus, the reaction of 1-hexyne with a catalytic amount of the cationic complex $[(\mathrm{Et_2N})_3\mathrm{U}][\mathrm{BPh_4}]$, in toluene at 60 °C, produced only the geminal dimer **1**.[19] In contrast, the reaction in THF was much slower at the same temperature and gave, in addition to **1**, a mixture of trimers [Eq. (3)]. These results can be explained by the lower reactivity of the THF adduct $[(\mathrm{Et_2N})_3(\mathrm{thf})_3\mathrm{U}]^+$, which induced a slower protonolysis reaction of the alkenyl intermediate $[(\mathrm{Et_2N})_2(\mathrm{thf})_3\mathrm{U}(\mathrm{C{=}C(H)C{\equiv}CR})]^+$ (R = *n*Bu) and permitted an additional insertion of the alkyne and formation of trimers, with lack of regioselectivity.

The addition of equimolar amounts of the external amine $\mathrm{EtNH_2}$ (alkyne:amine = 1:1) to the reaction mixture in benzene impeded the dimerization process. In addition, no reaction was observed when propyne was treated with the cationic uranium complex in benzene in the presence of external $\mathrm{EtNH_2}$ [Eq. (4)]. The two alkynes RC≡CH (R = Me, *n*Bu) are thus unable to shift the equilibrium reaction (Scheme 1, step 1) toward the formation of the acetylide complex **A** in the presence of external $\mathrm{EtNH_2}$. It is also



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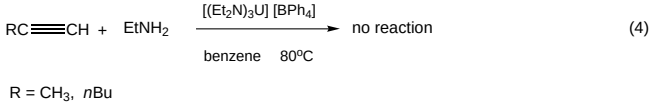

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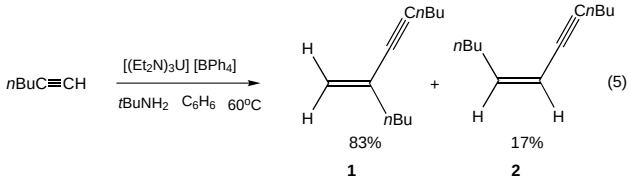
possible that these small alkynes favor the formation of an inactive π-alkyne complex, similar to **B** in Scheme 1. In contrast, when the same reaction of 1-hexyne was carried out in the presence of an equimolar amount of the bulkier amine $t\mathrm{BuNH_2}$, the *gem* dimer **1** and the unexpected *cis* dimer **2** were obtained [Eq. (5)]. This result indicates that the bulky amine does not impede the formation of the acetylide intermediate



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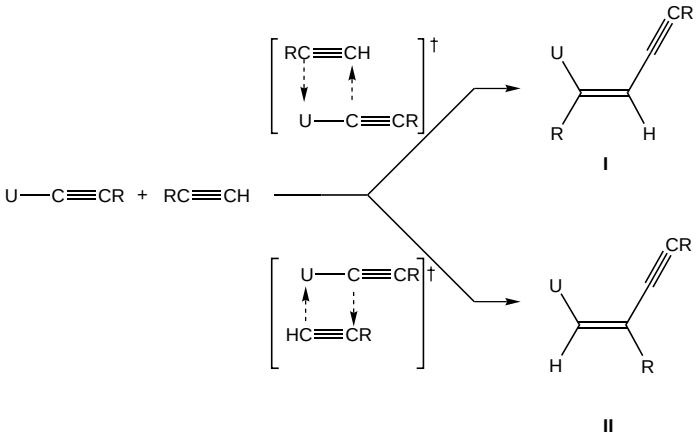
$[(t\mathrm{BuNH_2})_x(t\mathrm{BuNH})_2\mathrm{U}(\mathrm{C}{\equiv}\mathrm{C}n\mathrm{Bu})]^+$ by reaction of $n\mathrm{BuC}{\equiv}\mathrm{CH}$ and the trisamido cation $[(t\mathrm{BuNH_2})_3(t\mathrm{BuNH})_3\mathrm{U}]^+$, which, as seen before, is obtained by treatment of $[(\mathrm{Et_2N})_3\mathrm{U}]^+$ with $t\mathrm{BuNH_2}$. The acetylide would then undergo insertion of an alkyne molecule to give the corresponding alkenyl species and dimerization products. However, the regioselectivity of this insertion reaction is astonishingly different from that previously observed in the absence of external amines.

In view of the known reactivity of organoactinides with terminal alkynes, two different dimers are indeed expected, depending on the regiospecificity of the alkyne insertion into the metal acetylide intermediate. Thus, either the *trans*- or the *gem*-alkenyl species **I** and **II** are anticipated, based on a concerted *syn* four-centered transition pathway (Scheme 2).[14] The formation of the *cis* isomer indicates that



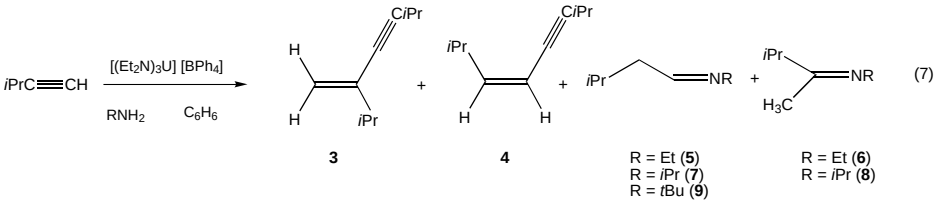
Scheme 2. Modes of activation of an actinide-acetylide complex with an alkyne through a *syn* four-centered transition state pathway towards the formation of the intermediates **I** or/and **II**.

I was isomerized before protonolysis.[19] It is essential that the rate of this protonolysis reaction is slower than that of the isomerization of the metal–alkenyl species. This pathway presumably takes place via a metal–cyclopropyl cation **D**, in a similar manner to the well-known "envelope isomerization" process [Eq. (6)].[23]

Reaction of the *trans* dimer of $n\mathrm{BuC}{\equiv}\mathrm{CH}$ or $t\mathrm{BuC}{\equiv}\mathrm{CH}$, which was synthesized by an alternative route,[14] with the cationic complex $[(\mathrm{Et_2N})_3\mathrm{U}][\mathrm{BPh_4}]$ in the presence or the absence of external amines did not induce the formation of the corresponding *cis* dimer, indicating that protonolysis and re-insertion of the enyne are not operative, and that isomerization should proceed by rearrangement of the alkenyl intermediate. Moreover, in the reaction of either the *cis* or *trans* dimer of $n\mathrm{BuC}{\equiv}\mathrm{CH}$ or $t\mathrm{BuC}{\equiv}\mathrm{CH}$ with $[(\mathrm{Et_2N})_3\mathrm{U}][\mathrm{BPh_4}]$ in the presence of $t\mathrm{BuND_2}$, no deuterium was found in the vinylic positions of the enynes. This corroborates the lack of reactivity of $[(\mathrm{Et_2N})_3\mathrm{U}][\mathrm{BPh_4}]$ towards the eneynes. The formation of the *cis* dimer **2** in the reaction of $n\mathrm{BuC}{\equiv}\mathrm{CH}$ and $[(\mathrm{Et_2N})_3\mathrm{U}][\mathrm{BPh_4}]$ in the presence of $t\mathrm{BuNH_2}$, while only the *gem* isomer was observed in the absence of the amine, would be a consequence of the distinct electronic and steric environment of the acetylide intermediate $[(t\mathrm{BuNH_2})_x(t\mathrm{BuNH})_2\mathrm{U}(\mathrm{C}{\equiv}\mathrm{C}n\mathrm{Bu})]^+$, which would favor the head-to-head insertion of the alkyne.

Dimerization and hydroamination of $i\mathrm{PrC}{\equiv}\mathrm{CH}$ catalyzed by $[(\mathrm{Et_2N})_3\mathrm{U}][\mathrm{BPh_4}]$ in the presence of amines: Unpredictably, the reactions of $i\mathrm{PrC}{\equiv}\mathrm{CH}$ and $t\mathrm{BuC}{\equiv}\mathrm{CH}$, under the same conditions, followed a quite distinct course. These alkynes were much more reactive than 1-hexyne or propyne in the presence of different amines, and the nature of the diverse products was found to be strongly dependent on the bulkiness of the amine. Thus, the reaction of $i\mathrm{PrC}{\equiv}\mathrm{CH}$ with $[(\mathrm{Et_2N})_3\mathrm{U}][\mathrm{BPh_4}]$ in the presence of $\mathrm{EtNH_2}$ or $i\mathrm{PrNH_2}$ afforded the unexpected *cis* dimer **4** as the major dimerization product and traces of the *gem* dimer **3** [Eq. (7)]. The two possible hydroamination products, **5** and **6** with $\mathrm{EtNH_2}$ and **7** and **8** with $i\mathrm{PrNH_2}$, were also observed in addition to the alkyne dimers. The relative proportions **5**+**6**:**3**+**4** and **7**+**8**:**3**+**4** were 74:26 and 34:66, respectively. The same reaction in the presence of $t\mathrm{BuNH_2}$ gave a mixture of **3** (40%) and **4** (24%), with **9** (26%) as the only hydroamination product.[5, 24]

Two mechanisms can be envisaged for the hydroamination reaction of $i\mathrm{PrC}{\equiv}\mathrm{CH}$. The first one (Scheme 3) involves the insertion of an alkyne molecule into the U–N(amido) bond of the cationic trisamido compound $[(\mathrm{RNH_2})_3(\mathrm{RNH})_3\mathrm{U}]^+$ (**E**), to give $[(\mathrm{RNH_2})_x(\mathrm{RNH})_2\mathrm{U}\{\mathrm{CH}{=}\mathrm{C}(i\mathrm{Pr})(\mathrm{NHR})\}]^+$ (**F**) or $[(\mathrm{RNH_2})_x(\mathrm{RNH})_2\mathrm{U}\{\mathrm{C}(i\mathrm{Pr}){=}\mathrm{CH}(\mathrm{NHR})\}]^+$ (**G**; step 4), followed by enamine–imine tautomerism to complexes **H** and **I**, respectively (step 5), and concomitant protonolysis release of the organic products (step 6 in Scheme 3).



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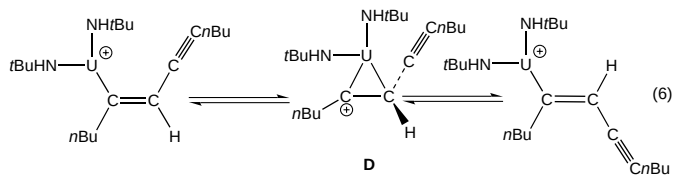
This protonolysis can be achieved either by the amine, to give back the trisamido uranium cation, or by the alkyne, leading to the acetylide complex (like complex **A** in Scheme 1), which is in equilibrium with the trisamido cation and is an intermediate in the formation of the oligomeric products. In the second mechanism (Scheme 4), elimination of



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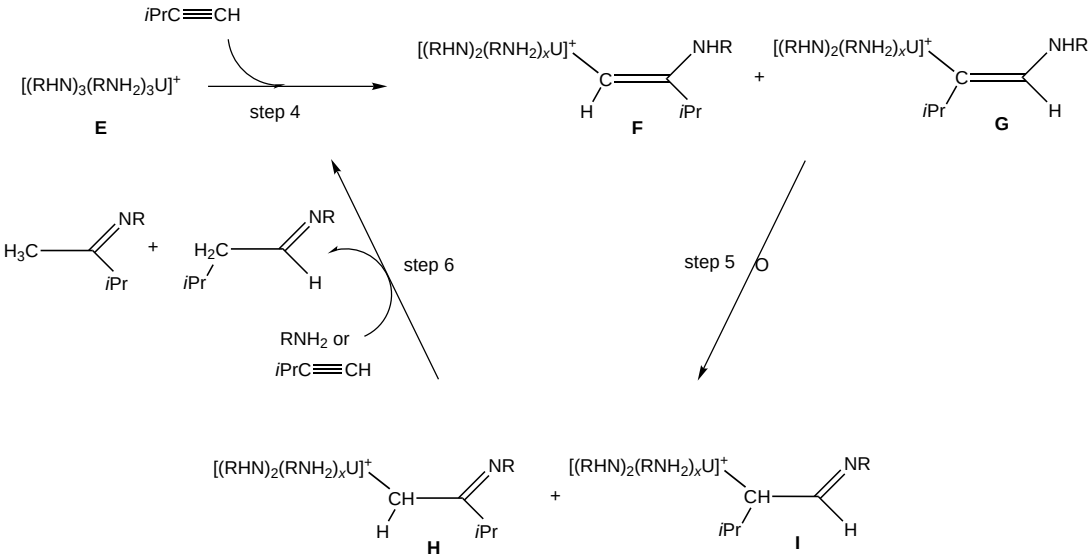
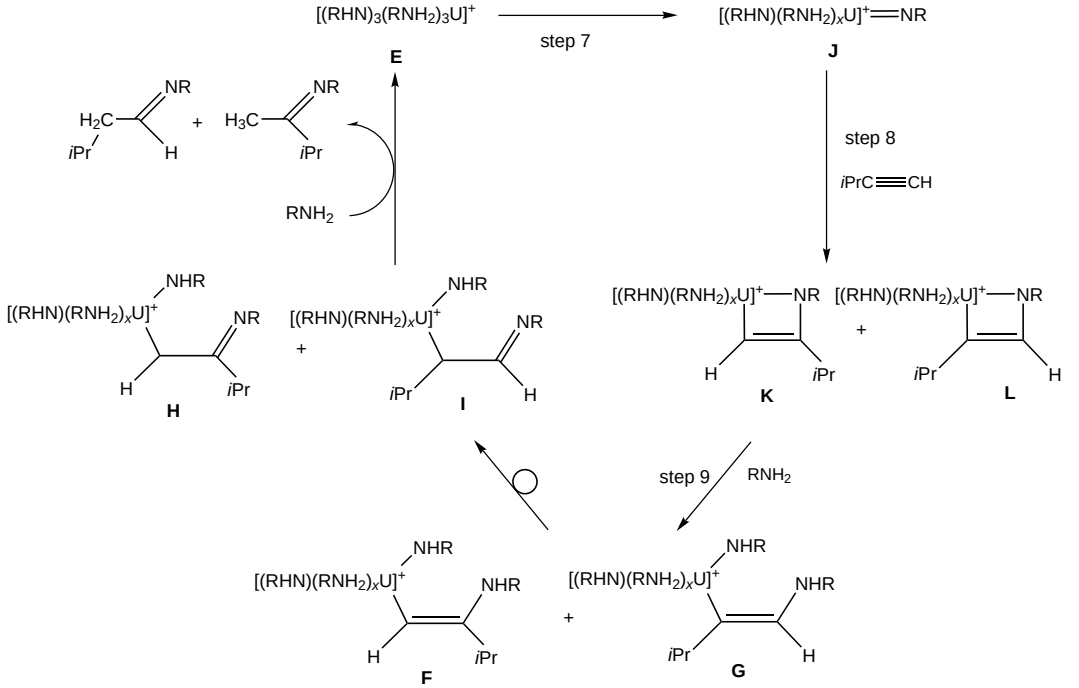


Scheme 3. Plausible mechanism for the intermolecular hydroamination of alkynes and primary amines through an activation of a metal-amido bond promoted by $[(Et_2N)_3U][BPh_4]$.



Scheme 4. Plausible mechanism for the intermolecular hydroamination of alkynes and primary amines through a metal-imido bond promoted by $[(Et_2N)_3U][BPh_4]$.

an amine molecule from the trisamido cation produces the imido complex $[(RNH_2)_x(RNH)U(=NR)]^+$ (**J**; step 7). The double bond of the latter compound undergoes a rapid metathesis reaction with an incoming alkyne to give the two possible metallacycles **K** and **L** (step 8), and their subsequent protonolytic ring-opening by the amine leads to the formation of **F** and **G**, respectively (step 9). Imine–enamine isomerization to the alkylimine complexes **H** and **I** with the subsequent protonolysis, as described above in Scheme 3, yield the expected organic products regenerating the active uranium complex **E**. It is important to point out that an additional route for the imine–enamine tautomerization is applicable in both proposed mechanisms. This route will take effect by protonolysis of the metal–enamine complex, eliminating the organic enamine that will tautomerize into the corresponding imine. We have recently shown that, with organoactinide complexes of the type $Cp^*_2AnMe_2$ (An = Th, U), the enamine is not eliminated but instead it undergoes the tautomerization reaction presented in Schemes 3 and 4.[12a] By considering the steric effect of the R group on the insertion of

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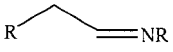
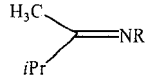
*i*PrC≡CH into the U–N bond of the trisamido cation $[(RNH_2)_3(RNH)_3U]^+$, or the addition of *i*PrC≡CH to the imido species $[(RNH_2)_x(RNH)U(=NR)]^+$, it is not surprising that the total yield of the hydroamination products, as well as the relative proportions of the branched imine *i*Pr(Me)C=NR, decrease with increasing steric hindrance of the amine.

To shed light on the applicability of which of the two above mentioned mechanisms for the hydroamination of alkynes is preferentially operative, we performed the reaction with deuterium-labeled amines. Interestingly, the use of the deuterated amine $tBuND_2$ (*i*PrC≡CH:$tBuND_2$ = 2:1; entry 4, Table 1) led to the formation of a mixture of mono- and nondeuterated dimers **3** (70%) and **4** (8%). The amount of the nondeuterated dimer is much larger (75%) than that of the monodeuterated dimer. This indicates that a small fraction of *i*PrC≡CH was transformed into *i*PrC≡CD following H/D exchange with $tBuND_2$. It is interesting to note that the deuterium atom is scrambled between the two geminal positions of **3**, revealing that it was introduced into the molecule either during the insertion of the alkyne into the acetylide intermediate or in the course of the protonolysis of the alkenyl species. Most notably, no deuterium incorporation was detected in the hydroamination product **9**. This result favors the mechanism shown in Scheme 4 for the hydroamination reaction which involves an imido intermediate, as already observed in organoactinide systems of the type $Cp^*_2AnMe_2$ (An = Th, U),[12] and implies that only the nondeuterated alkyne and amine are operative in the protonolysis steps of the catalytic cycle.[25] Moreover, the large effect of the amount of the alkyne on the product distribution is revealed by the relative proportions of the dimers **3** and **4**, which vary from 40:24 in the reaction of $tBuND_2$ with two equivalents of *i*PrC≡CH to 70:8 in the reaction of $tBuNH_2$ with one equivalent of *i*PrC≡CH. Interestingly, the larger the amount of the alkyne utilized, the larger the amount of the *gem* dimer obtained. These results corroborate again with a dimerization mechanism as indicated in Scheme 5. The mechanism consists in the formation of complex **M** by the reaction of the cationic complex **E** with the alkyne (step 10 in Scheme 5, similar to step 1 in Scheme 1). This acetylide complex reacts with an additional alkyne producing the mixture of alkenyl compounds **N** and **O** (step 11). Isomerization of complex **N** through an envelope mechanism (step 12) allows the formation of complex **P**, which upon protonolysis yields the unexpected *cis* dimer (step 13). The addition of a large amount of alkyne in combination with a source of deuterium (as $tBuND_2$) routes complex **O** towards the geminal product (step 14). This is found to be partially deuterated, since the alkyne can serve as well as a protonolytic reagent. It is important to point out that the rate-determining step in the reaction is the isomerization (step 12), allowing the formation of the *gem* dimer in the presence of larger amounts of the alkyne (step 14).

Regioselective oligomerization of *t*BuC≡CH promoted by $[(Et_2N)_3U][BPh_4]$ in the presence of amines: The reaction of the bulkier alkyne *t*BuC≡CH with the cationic uranium complex in the presence of ethylamine gave essentially the *cis* dimer **10** (98%) with a small amount of the *gem* isomer (2%). This result corroborates again the mechanism presented in Scheme 5, showing the remarkable influence of the nature of the amine on the dimerization reaction, by inverting the regioselectivity. With other primary or secondary amines, the *cis* dimer **10** was the major product, although the concomitant formation of one regiospecific trimer **11** and one regiospecific tetramer **12** was also observed. The most remarkable result, apart from the fact that only one trimer and one tetramer are produced, is that the regiochemistry of these oligomers is the unpredictable one, regardless of the amine used (entries 5–9, in Table 1) [Eq. (8)]. The trimer and the tetramer correspond to the consecutive insertions of an alkyne molecule into the vinylic CH bond *trans* to the bulky *tert*-butyl group.

To understand the role of the amine and to elucidate the possibility that the initially formed *cis* isomer was reactivated to yield the trimer and tetramer, the reactions with deuterated amine $tBuND_2$ and deuterated alkyne *t*BuC≡CD were performed at different reaction times, as described in Scheme 6. The reaction of *t*BuC≡CD with $tBuNH_2$ (alkyne/amine = 1.2:1) for 40 h at room temperature gave the products with *no* deuterium. This result indicates that *t*BuC≡CD was

Table 1. Product distribution for the reactions of $[(Et_2N)_3U][BPh_4]$ with terminal alkynes in the presence of amines

Entry	R group in RC≡CH	R′ in R′NH$_2$	*T* [°C]	*t* [h]	*cis* Dimer [%]	*gem* Dimer [%]	 [%]	 [%]	Trimer [%]	Tetramer [%]
1	*i*Pr	Et	20	40	22	4	27	47	–	–
2	*i*Pr	*i*Pr	80	6	63	3	30	4	–	–
3	*i*Pr	*t*Bu	80	37	24	40	26	–	7	3
4	*i*Pr	*t*Bu[a]	80	24	8	70	17	–	4	–
5	*t*Bu	Et	60	75	98	2	–	–	–	–
6	*t*Bu	*i*Pr	90	20	62	–	–	–	34	4
7	*t*Bu	*t*Bu	90	22	64	–	–	–	19	17
8	*t*Bu	*t*Bu	20	200	51	–	–	–	23	20
9	*t*Bu	*t*Bu[b]	20	10	60	–	–	–	15	20[d]
10	*t*Bu	Et_2NH[c]	60	21	46	–	–	–	34	16[d]

[a] $tBuND_2$. [b] The amount of catalysts is four times larger and the reaction was carried out at room temperature. [c] Et_2NH a secondary amine. [d] A small amount of pentamer was observed.

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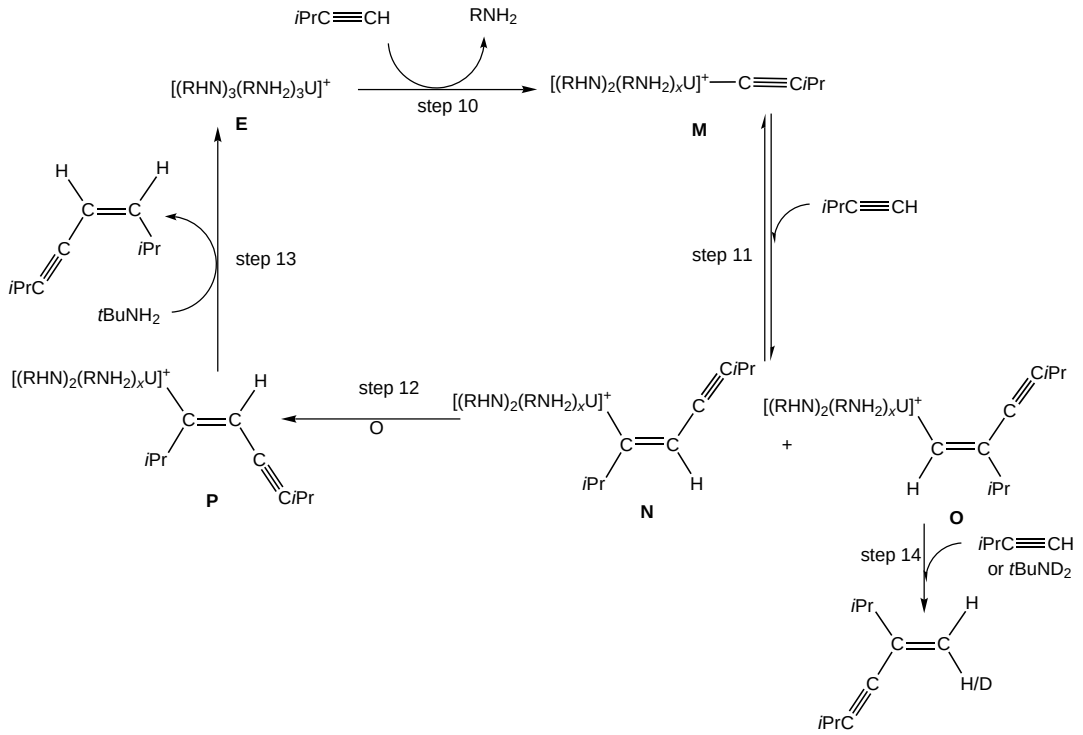
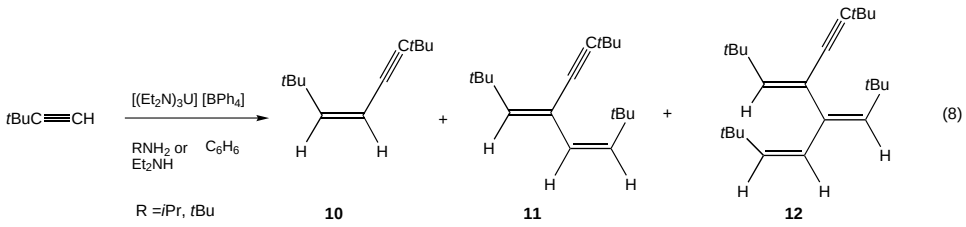


Scheme 5. Plausible mechanisms for the formation of the *gem* and *cis* dimers by the reaction of *i*PrC≡CH with primary amines promoted by the cationic precursor $[(Et_2N)_3U][BPh_4]$.



(8)

almost completely transformed into *t*BuC≡CH. The H/D exchange reaction between *t*BuC≡CH and $tBuND_2$ was found to occur rapidly in refluxing benzene, in the presence of the catalyst, to give *t*BuC≡CD and *t*BUNHD. These compounds were also observed at the early stage of the catalytic oligomerization of *t*BuC≡CH in the presence of $tBuND_2$, which afforded the *cis* dimer as a mixture of mono- and nondeuterated compounds, whereby the amount of the nondeuterated dimer was always larger (70%) than that of the monodeuterated dimer. The deuterium atom in **10** is found only in the *trans* position relative to the *t*Bu group. Mixtures of non- and monodeuterated compounds are also obtained for the trimer and tetramer, the deuterium atom always being found in the internal position, *trans* to the *t*Bu group. The presence of only one deuterium atom in compounds **10**–**12**, in unique positions, strongly suggests that this D atom was introduced during the protonolysis steps of the catalytic cycle. In agreement with this fact is the increasing proportion of the trimer and dimer, which probably results from the slower cleavage of the alkenyl intermediate by the deuterated amine or alkyne, permitting further insertion of an alkyne molecule into the U–C bond. Such a kinetic protonolysis delay was recently observed in the controlled oligomerization of terminal alkynes toward dimers using amines, when the reaction was promoted by organoactinide complexes of the type $Cp^*_2AnMe_2$ (An = Th, U).[14]

A plausible mechanism for the regiospecific formation of the trimer and tetramer is described in Scheme 7. The same intermediate **D**, which was proposed to explain the *trans*–*cis* isomerization of the alkenyl intermediate by the envelope mechanism [Eq. (6)] can conceptually explain the regiospecific formation of one trimer and one tetramer. The mechanism consists of a 1,2-hydride shift isomerization of the metal–alkenyl complex **D** leading to the isomeric compound **Q** (step 15).[26] Deuterolysis at this stage liberates the deuterated dimer **10** regioselectively (step 16). Insertion of an alkyne molecule into the U–C bond of **Q** leads to the formation of complex **R**. The regioselectivity of this insertion (step 17) would result from steric hindrance between the *tert*-butylacetylide group at the α-position of the metal–alkenyl chain and the incoming alkyne because of the rotation around the metal–carbon bond. The same isomerization process as above would convert complex **R** into the *syn* complex **S** (step 18). Protonolysis of **S** regenerates the catalyst and produces the specific trimer **11** (step 19), whereas additional insertion of an alkyne, envelope isomerization, and protonolysis would yield the specific tetramer **12**.

Selective hydroamination of (TMS)C≡CH catalyzed by $[(Et_2N)_3U][BPh_4]$: The reaction of (TMS)C≡CH with the uranium catalyst in the presence of $EtNH_2$ followed quite a

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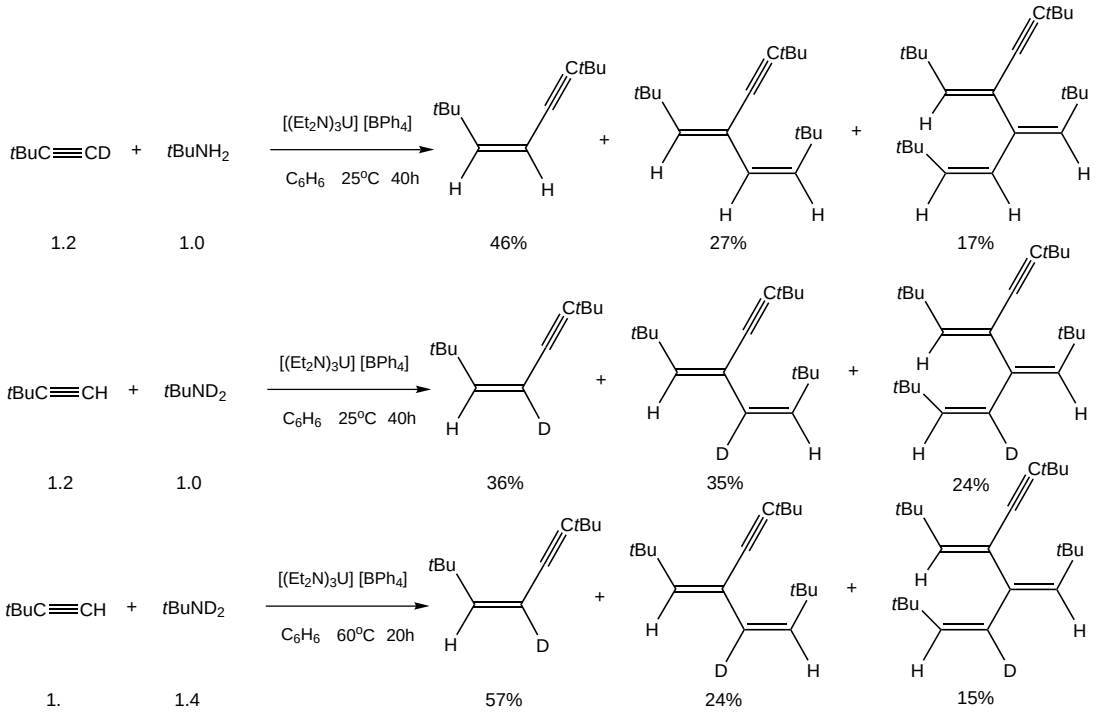
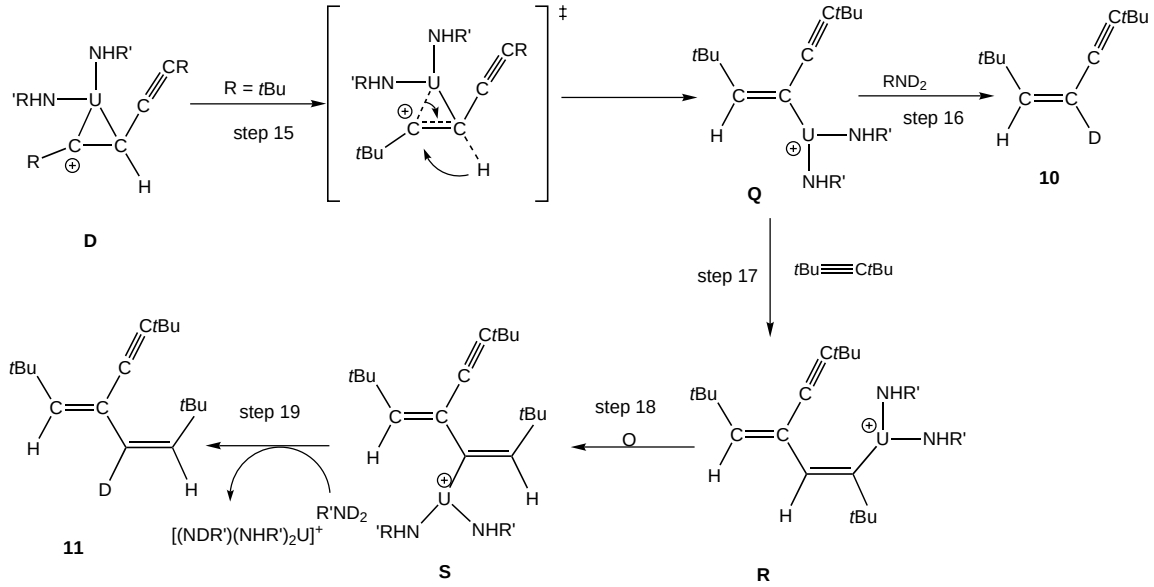
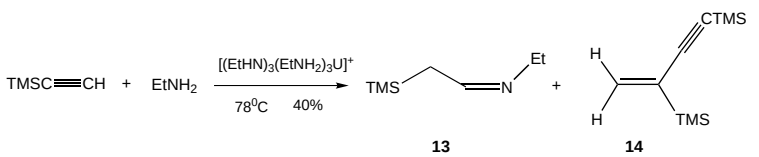


Scheme 6. Deuterium labeling experiments to study the oligomerization of *t*BuC≡CH with *t*BuND$_2$ and of *t*BuC≡CD with *t*BuNH$_2$ promoted by [(Et$_2$N)$_3$U][BPh$_4$] with compounds **10**, **11**, and **12**.

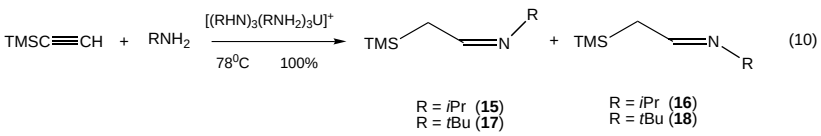


Scheme 7. Plausible mechanism for the regioselective dimerization and trimerization of *tert*-butylacetylene promoted by [(Et$_2$N)$_3$U][BPh$_4$] in the presence of *tert*-butylamine.

different course from that of *t*BuC≡CH, since imine **13** was the major product and the *gem* dimer **14** was obtained in 15% yield [Eq. (9)]. In the presence of *i*PrNH$_2$ or *t*BuNH$_2$, the reaction afforded the two hydroamination products, the *E* and *Z* isomers **15** and **16** or **17** and **18**, respectively [Eq. (10)]. As in the case of the hydroamination of *i*PrNH$_2$, the selective formation of these linear imines can be explained by the steric repulsion between the R and TMS groups during the approach of the alkyne molecule either to the trisamido or the imido intermediate. However, the reaction with EtNH$_2$ took 67 h to achieve a 40% alkyne conversion, whereas



(9)



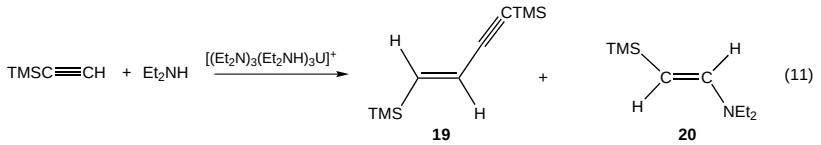
with the other primary amines, quantitative conversions (>99%) were obtained after 5 h (see entries 2–5 in Table 2). This result indicates again the prevalence of $EtNH_2$ to shift the equilibrium reaction (step 1, in Scheme 1) towards the starting material.

Table 2. Product distribution of the $[(Et_2N)_3U][BPh_4]$-catalyzed intermolecular hydroamination of TMSC≡CH with various amines.

Entry	R in $R'NH_2$	t[h]	T[°C]	Conversion [%]	TMS N R' [%]	TMS N R' [%]
1	Et	67	78	40		81
2	*i*Pr	5	78	100	52	48
3	*i*Pr	160	25	100	100	–
4	*t*Bu	5	50	100	8	91
5	*t*Bu	20	20	50	30	70
6	*t*Bu	42	20	100	35	65
7	*t*Bu	66	20	100	40	60
8	*t*Bu	90	20	100	72	28
9	*t*Bu	120	20	100	100	–

It was interesting to note that, during the hydroamination reaction of (TMS)C≡CH and $iPrNH_2$, the relative proportions of (*Z*)-**15** and (*E*)-**16** were 52:48 after 5 h, but after 160 h, the (*E*)-**16** isomer was fully transformed into the (*Z*)-**15** isomer (entries 2 and 3, Table 2). A similar observation was made for the reaction of (TMS)C≡CH with $tBuNH_2$ at 20 °C (at 50 °C, only small amounts of the thermodynamically stable product is observed after 5 h), indicating that the *E* isomer (kinetic product) was slowly isomerized to the *Z* isomer (thermodynamic product). The remarkable difference between the two alkynes (TMS)C≡CH and *t*BuC≡CH in their reactions with primary amines catalyzed by $[(Et_2N)_3U][BPh_4]$ can be related to the distinct electronic effects of the TMS and *t*Bu groups allowing mostly the formation of the hydroamination or oligomerization products.[27]

Also remarkable is the unique reactivity of the alkyne (TMS)C≡CH with the secondary amine Et_2NH, which afforded the trans dimer **19** (13%) and the enamine **20** (87%)[Eq. (11)]. Formation of the enamine most probably results from protonolysis of the intermediate $[(Et_2NH)_x(Et_2N)_2U\{C(TMS)=CH(NEt_2)\}]^+$, the analogue of **G** in Schemes 3 and 4; in that case, it is clear that the enamine–imine tautomerism could not be observed.



Conclusion

These results demonstrate that the cationic actinide complexes are active catalysts for the dimerization and intermolecular hydroamination of terminal alkynes through insertion and σ-bond metathesis mechanisms. The addition of external primary amines to the catalytic reaction induces the formation of the unexpected *cis* dimer, presumably formed by an envelope isomerization mechanism. For $tBuNH_2$, the complex $[(tBuNH_2)_3(tBuNH)_3U][BPh_4]$ was isolated as the first crystallographically characterized U^{IV} complex with a primary amine. The reactions of $tBuNH_2/D_2$ with *t*Bu≡CH/D produced regioselectively one dimer, trimer, and tetramer obtained through a common intermediate followed by a 1,2-hydride rearrangement. The regiochemistry of the oligomers is unpredictable and corresponds to the consecutive insertions of an alkyne molecule into the vinylic CH bond *trans* to the bulky *tert*-butyl group. The reactivity of TMSC≡CH relative to *t*BuC≡CH is thoroughly unique and allows the formation of the intermolecular hydroamination imine product. Moreover, when secondary amines were treated with TMSC≡CH, the corresponding hydroamination enamine was formed, which indicates that an alkyne inserts into a $U-NR_2$ bond. The use of these cationic organouranium complexes in new, demanding, chemical transformations is under investigation.

Experimental Section

General: All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line, or interfaced to a high vacuum (10^{-5} torr) line, or in a nitrogen-filled "Vacuum Atmospheres" glove box with a medium capacity recirculator (1–2 ppm O_2). Argon and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieves column. Hydrocarbon solvents and deuterated solvents ([D_6]benzene, [D_8]toluene, [D_8]THF) were distilled over Na/K alloy and under an atmosphere of nitrogen. All solvents for vacuum-line manipulations were stored in vacuum over Na/K alloy in resealable bulbs. Acetylenic compounds (Aldrich) were dried and stored over activated molecular sieves (4 Å), degassed and freshly vacuum-distilled. Deuterium oxide was purchased from Cambridge isotopes. Et_2NH (Fluka) and other RNH_2 (Aldrich) were dried over small amounts of Na/K alloy, stored over activated molecular sieves (4 Å), degassed, and freshly vacuum-distilled. For low boiling-point amines, the reactions were performed in thick-walled glass Schlenk flasks. $[(Et_2N)_3U][BPh_4]$ was prepared according to the literature.[20] NMR spectra were recorded on Bruker AM 200 and Bruker AM 400 spectrometers. Chemical shifts for ^1H NMR and ^{13}C NMR are

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referenced to internal solvent resonances and are reported relative to tetramethylsilane. GC/MS experiments were conducted with a GC-MS (Finnigan Magnum) spectrometer. The NMR experiments were conducted in Teflon valve-sealed tubes (J-Young) after vacuum transfer of the liquids in a high vacuum line.

Preparation of $[(t\text{BuNH}_2)_3(t\text{BuNH})_3\text{U}][\text{BPh}_4]$: A 50 mL Schlenk flask was charged in the glovebox with $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$ (50 mg, 0.065 mmol). The flask was connected to a high-vacuum line and benzene (2.5 mL) and *tert*-butylamine (0.07 mL, 0.666 mmol) were transferred under vacuum. The solution was stirred for 30 min at room temperature and all liquid components were evacuated under high vacuum. The residue was recrystallized from a toluene/hexane mixture at $-78\,^{\circ}\text{C}$ to give yellow crystals of $[(t\text{BuNH}_2)_3(t\text{BuNH})_3\text{U}][\text{BPh}_4]$ in almost quantitative yield. ^{1}H NMR (200 MHz, [D$_6$]benzene, 20 °C): $\delta = 1.00-1.50$ (m, 54H; C(CH_3)$_3$), 6.70–7.70 (m, 20H; Ph), 63.20, 17.57, and 15.20 (s, 3×1H; NH), 3.31 (s, 2H; NH_2), -33.82 ppm (s, 4H; NH_2); ^{13}C NMR (50 MHz, [D$_6$]benzene, 20 °C, DEPT): $\delta = 30.3$ ($3\,H_2NC(CH_3)_3$), 82.0 (HNC(CH_3)$_3$), 126.0 (*C*H), 128.7 (*C*H), 134.8 ppm (*C*H); ^{1}H NMR (200 MHz, [D$_8$]THF, 20 °C): $\delta = 0.80-1.30$ (br, 27H; $H_2NC(CH_3)_3$), 1.30–1.60 (m, 27H; HNC(CH_3)$_3$, 5.80–6.00 (br, 6H; NH_2), 6.00–6.50 (m, 10H; Ph), 7.10–7.65 (m, 10H; Ph), 93.72, 89.25, and -14.2 ppm (s, 3×1H; NH); ^{13}C NMR (50 MHz, [D$_8$]THF, 20 °C, DEPT): $\delta = 33.5$ ($H_2NC(CH_3)_3$), 33.6 ($H_2NC(CH_3)_3$), 34.5 (HNC(CH_3)$_3$), 35.9 (HNC(CH_3)$_3$), 36.8 (HNC(CH_3)$_3$), 124.3 (*C**H), 128.0 (*C**H), 139.2 (*C**H), 128.5 (*C*′H), 130.6 (*C*′H), 138.2 ppm (*C*′H) (*C** and *C*′ were assigned to the phenyl rings with proton signals at at $\delta = 6.00-6.50$ and $\delta = 7.10-7.65$ ppm, respectively); elemental analysis calcd (%) for $C_{48}H_{83}BN_6U$ (993.05): C 58.05, H 8.42, N 8.46; found: C 58.59, H 7.92, N 9.03.

Synthesis of $t\text{BuND}_2$: D_2O (8.50 g, 0.425 mol) was added to a Schlenk flask that contained *tert*-butylamine (3.00 g, 41 mmol). The mixture was stirred for 30 min. The amine was distilled at 46 °C and the same procedure was repeated for a second time. The distilled amine was transferred into a flask that contained anhydrous magnesium sulfate. The mixture was filtered and redistilled to obtain 1.05 g (13.4 mmol) of $t\text{BuND}_2$. ^{2}H NMR $\delta = 1.676$ ppm. No signal for the NH proton was observed in the ^{1}H NMR spectrum.

Synthesis of $t\text{BuC}\equiv\text{CD}$: 3,3-Dimethyl-1-butyne (1.1 mL, 9.9 mmol) was syringed into a thick-walled Schlenk tube that contained a 1.6 M solution of *n*BuLi in hexane (4.5 mL, 7.2 mmol) at $-100\,^{\circ}\text{C}$. The mixture was allowed to warm slowly to 0 °C and stirred for 30 min. The temperature was then allowed to rise to room temperature and the excess alkyne was removed by means of a bubbler connected to a well-ventilated hood. Evaporation of the solvent gave a white solid in quantitative yield. The tube was cooled to $-85\,^{\circ}\text{C}$ and, under an argon flush, D_2O (0.16 mL, 8 mmol) was added by syringe. The Schlenk tube was sealed and warmed slowly to $-20\,^{\circ}\text{C}$, and the mixture was stirred for 10 min. The product was distilled into a new Schlenk tube containing activated molecular sieves to dry the alkyne, and redistilled to obtain 0.4 g of $t\text{BuC}\equiv\text{CD}$. ^{2}H NMR $\delta = 2.65$ ppm. No signal for the terminal alkyne proton (C≡CH) was found in the ^{1}H NMR spectrum.

General procedure for the catalytic oligomerization of alkynes: In a typical procedure, the amount of the specific alkyne was transferred under a vacuum into a Schlenk tube containing $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$ (10 mg, 0.013 mmol) in benzene (6 mL). The precise amount was measured by vacuum transfer of the alkyne into a microburette connected in line to the high-vacuum line and then transferred to the Schlenk flask. The sealed tube was thermostated at the respective temperature. The organic products were vacuum-transferred (10^{-6} mmHg) into a Schlenk tube and both residue and volatiles were characterized by ^{1}H, ^{13}C, and 2D NMR spectroscopy, GC-MS, and by comparison with known compounds. For spectroscopic data of compounds, see the corresponding references: **1**, **2**,[28] **3**,[14b] **4**,[29a] **5**,[29b] **8**,[29c, 29d] **10**,[19] **13**,[12] **14**,[14] and **19**.[12]

Oligomerization of 1-hexyne in THF promoted by $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$: Following the typical experimental procedure, the reaction of 1-hexyne (0.083 mL, 0.73 mmol) in THF (0.33 mL) at 60 °C for 64 h gave the *gem* dimer **1** (91%), and some non-regiospecific trimers (9% based on GC-MS). The conversion of 1-hexyne was 50%.

Catalytic dimerization of 1-hexyne in the presence of *tert*-butylamine: Following the typical experimental procedure, 1-hexyne (0.083 mL, 0.73 mmol) was dimerized in the presence of *tert*-butylamine (0.76 mL, 0.73 mmol) in benzene (3.0 mL) at 60 °C for 6 h to yield 83% of the *gem* dimer **1** and 17% of the corresponding *cis* isomer **2**. The precise amount of the amine and the alkyne were measured by vacuum transfer of the alkyne into a microburette connected in line to the high-vacuum line and then transferred to the Schlenk flask. The conversion of 1-hexyne was 95%.

Reaction of 3-methyl-1-butyne in the presence of EtNH_2 promoted by $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$: As described in the typical experimental procedure, the reaction of ethylamine (0.056 mL, 1.0 mmol) with 3-methyl-1-butyne (0.051 mL, 0.50 mmol) at 20 °C for 40 h gave the *cis* dimer **4** (22%) and the two hydroamination products *i*PrCH$_2$CH=NEt (**5**, 27%) and *i*PrC(CH$_3$)=NEt (**6**, 47%). Traces of the *gem* dimer **3** (4%) were also observed. The conversion of 3-methyl-1-butyne was 73%.

***cis* Dimer 4**: ^{1}H NMR (200 MHz, [D$_6$]benzene, 20 °C): $\delta = 0.90$ (d, ^3J(H,H) = 6.7 Hz, 6H; CH_3), 1.01 (d, ^3J(H,H) = 4.6 Hz, 6H; CH_3), 2.45–2.55 (m, 1H; C*H*), 2.90–3.10 (m, 1H; C*H*), 5.29 (dd, ^3J(H,H) = 10.7 Hz, ^4J(H,H) = 1.5 Hz, 1H; C*H*=), 5.41 ppm (dd, ^3J(H,H) = 10.7 Hz, ^3J(H,H) = 8.8 Hz, 1H; C*H*); ^{13}C NMR (50 MHz, [D$_6$]benzene, 20 °C): $\delta = 22.4$ (CH_3), 23.7 (CH_3), 27.7 (*C*H), 29.8 (*C*H), 77.2 (R*C*≡), 99.9 (*C*≡CR), 108.1 (R*C*H=), 149.1 ppm (=*C*HC≡); GC-MS: *m*/*z* (%): 135 (9) [$M^+ - H$], 121 (70) [$M^+ - CH_3$], 105 (45) [$M^+ - CH_3 - CH_4$], 93 (95) [$M^+ - C_3H_7$], 91 (100) [$M^+ - C_3H_9$], 79 (95) [$M^+ - C_4H_9$], 77 (75) [$M^+ - C_4H_{11}$].

***i*PrC(CH$_3$)=NEt (6)**: ^{1}H NMR (200 MHz, [D$_6$]benzene, 20 °C): $\delta = 1.16$ (d, ^3J(H,H) = 6.7 Hz, 6H; CH_3), 1.30 (t, ^3J(H,H) = 7 Hz, 3H; CH_3), 1.72 (s, 3H; CH_3), 2.67 (m, 1H; C*H*), 3.34 ppm (q, ^3J(H,H) = 7 Hz, 2H; CH_2); ^{13}C NMR (50 MHz, [D$_6$]benzene, 20 °C):$\delta = 14.7$ (CH_3), 17.2 (CH_3), 20.8 (CH_3), 30.6 (*C*H), 46.1 (CH_2N), 158.9 ppm (=*C*); GC-MS: *m*/*z* (%): 113 (15) [M^+], 98 (50) [$M^+ - CH_3$], 71 (100) [$M^+ - C_3H_6$].

Reaction of 3-methyl-1-butyne in the presence of *i*PrNH$_2$ promoted by $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$: Following the typical experimental procedure, 100% conversion of the alkyne was obtained for the reaction of isopropylamine (1.10 mL, 12.7 mmol) with 3-methyl-1-butyne (1.30 mL, 12.7 mmol) at 80 °C for 6 h with the uranium catalyst (100 mg, 0.13 mmol) in benzene (6 mL) yielding the *cis* dimer **4** (63%), and the hydroamination product *i*PrCH$_2$CH=N*i*Pr (**7**) (30%). Trace amounts of the *gem* dimer **3** (4%) and the second hydroamination product *i*PrC(CH$_3$)=N*i*Pr (**8**, 3%) were also obtained.

***i*PrCH$_2$CH=N*i*Pr (7)**: B.p.$_{25}$ 75–80 °C; ^{1}H NMR (200 MHz, [D$_6$]benzene, 20 °C): $\delta = 0.76$ (d, ^3J(H,H) = 6.5 Hz, 6H; CH_3), 1.03 (d, ^3J(H,H) = 6.4 Hz, 6H; CH_3), 1.62 (sept, ^3J(H,H) = 6.4 Hz, 1H; CH), 1.87–1.93 (m, 2H; CH_2), 3.00–3.15 (m, 1H; CH), 7.36 ppm (t, ^3J(H,H) = 8.3 Hz, 1H; CH=); ^{13}C NMR (50 MHz, [D$_6$]benzene, 20 °C):$\delta = 22.7$ (CH_3), 24.2 (CH_3), 44.2 (*C*H), 44.8 (*C*H), 68.0 (CH_2), 159.7 ppm (*C*H); GC-MS: *m*/*z* (%): 128 (25) [$M^+ - H$], 112 (22) [$M^+ - CH_3$], 85 (53) [$M^+ - C_3H_6$], 70 (100) [$M^+ - C_4H_9$].

Reaction of 3-methyl-1-butyne in the presence of $t\text{BuNH}_2$ promoted by $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$

Procedure A: As described in the typical experimental procedure. 100% conversion of the alkyne was obtained for the reaction of *tert*-butylamine (1.14 mL, 10.9 mmol) with 3-methyl-1-butyne (1.11 mL, 10.9 mmol) at 80 °C with the uranium catalyst (100 mg, 0.13 mmol) in benzene (6 mL) for 37 h yielding the *cis* dimer **4** (24%), the *gem* dimer **3** (40%), and the hydroamination product *i*PrCH$_2$CH=N*t*Bu (**9**, 26%). Trace amounts of different trimers (7%) and tetramer (3%) were also obtained.

***i*PrCH$_2$CH=N*t*Bu (9)**: B.p.$_{25}$ 85–90 °C; ^{1}H NMR (200 MHz, [D$_6$]benzene, 20 °C): $\delta = 0.90$ (s, 9H; CH_3), 1.15 (d, ^3J(H,H) = 7 Hz, 6H; CH_3), 2.00 (m, 2H; CH_2), 2.45 (m, 1H; C*H*), 7.37 ppm (t, ^3J(H,H) = 4.9 Hz, 1H; C*H*); ^{13}C NMR (50 MHz, [D$_6$]benzene, 20 °C): $\delta = 21.8$ (CH_3), 26.4 (*C*H), 29.8 (CH_3), 45.3 (CH_2), 56.7 (*C*), 156.5 ppm (*C*H); GC-MS: *m*/*z* (%): 141 (4) [M^+], 125 (18) [$M^+ - CH_4$], 98 (30) [$M^+ - C_3H_7$], 84 (100) [$M^+ - C_4H_9$], 70 (35) [$M^+ - C_5H_{11}$], 57 (60) [$C_4H_9^+$].

Trimer: GC-MS: *m*/*z* (%): 203 (10) [$M^+ - H$], 189 (8) [$M^+ - CH_3$], 161 (80) [$M^+ - C_3H_7$], 147 (18) [$M^+ - C_4H_9$], 133 (66) [$M^+ - C_5H_{11}$], 119 (100) [$M^+ - C_6H_{13}$], 105 (86) [$M^+ - C_7H_{15}$], 91 (73) [$M^+ - C_8H_{17}$], 77 (43) [$M^+ - C_9H_{19}$].

Tetramer: GC-MS: *m*/*z* (%): 272 (35) [M^+], 257 (25) [$M^+ - CH_3$], 229 (95) [$M^+ - C_3H_7$], 187 (40) [$M^+ - C_6H_{13}$], 173 (90) [$M^+ - C_7H_{15}$], 159 (80) [$M^+ - C_8H_{17}$], 145 (100) [$M^+ - C_9H_{19}$], 131 (81) [$M^+ - C_{10}H_{21}$], 105 (48), 91 (67), 77 (50).

Procedure B: As described in the typical experimental procedure, full conversion of the alkyne was observed by the reaction of $t\text{BuND}_2$ (0.07 mL, 0.69 mmol) with 3-methyl-1-butyne (0.137 mL, 1.38 mmol) at 80 °C for 24 h to yield the *gem* dimer **3** (70%), the hydroamination product **9** (17%),

small amounts of the *cis* dimer **4** (8%), and traces of a mixture of trimers (4%). The ^{2}H NMR spectrum showed that in the *gem* dimer the deuterium atom is scrambled between the two *gem* positions with no equal populations. In addition, some of the *gem* dimer (65%) is nondeuterated. For the *cis* dimer, the ^{1}H and ^{13}C NMR spectra show also a mixture of mono- and nondeuterated isomers. The amount of the nondeuterated *cis* isomer is larger (75%) than that of the monodeuterated *cis* isomer. No CD_2 moiety for neither the geminal isomer nor the hydroamination product was observed.

Reaction of 3,3-dimethyl-1-butyne in the presence of ethylamine promoted by [$(Et_2N)_3U$][BPh_4]: Following the typical experimental procedure, 42% conversion of the alkyne was obtained by the reaction of 3,3-dimethyl-1-butyne (0.08 mL, 0.65 mmol) with ethylamine (0.05 mL, 0.9 mmol) at 60 °C for 75 h giving the *cis* dimer **10** (98%) and traces of the *gem* dimer (2%).

Reaction of 3,3-dimethyl-1-butyne in the presence of *i*PrNH$_2$ promoted by [$(Et_2N)_3U$][BPh_4]: Following the typical experimental procedure, 100% conversion of the alkyne was obtained for the reaction of 3,3-dimethyl-1-butyne (1.4 mL, 11.4 mmol) with *i*PrNH$_2$ (0.97 mL, 11.4 mmol) at 90 °C for 20 h to produce the *cis* dimer **10** (62%), trimer **11** (34%), and a small amount of tetramer **12** (4%). The dimer was distilled, whereas the trimer and tetramer were separated by chromatography on silica gel with petrol ether. The full characterization of the isomers was possible based on COSY, CH-correlation, and NOESY NMR spectroscopy showing NOE effects between the signals at $\delta = 5.20$ and 5.60 ppm with the *tert*-butyl groups for the trimer, and NOE correlation signals at $\delta = 5.24$, 5.44, and 5.66 ppm with the *t*Bu groups of the tetramer.

Trimer (11): ^{1}H NMR (200 MHz, [D$_6$]benzene, 20 °C): $\delta = 1.20$ (s, 9H; CH_3) 1.25 (s, 9H; CH_3), 1.35 (s, 9H; CH_3), 5.20 (d, ^3J(H,H) = 12.4 Hz, 1H; C*H*), 5.60 (d, ^4J(H,H) = 1.55 Hz, 1H; C*H*), 5.82 ppm (dd, ^3J(H,H) = 12.4 Hz, ^4J(H,H) = 1.55 Hz); ^{13}C NMR (50 MHz, [D$_6$]benzene, 20 °C):$\delta = 29.6$ (*C*H$_3$), 30.7 (*C*H$_3$), 31.8 (*C*H$_3$), 33.0 (*C*-CH$_3$), 34.1 (*C*-CH$_3$), 34.2 (*C*-CH$_3$), 79.1 (C≡), 105.4 (C≡, 119.4 (C=), 131.3 (*C*H corresponding to the hydrogen at $\delta = 5.82$), 141.1 (*C*H corresponding to the hydrogen at $\delta = 5.20$), 148.4 ppm (CH corresponding to the hydrogen at $\delta = 5.60$); GC-MS: *m*/*z* (%): 246 (5) [M^+], 231 (10), 189 (80), 175 (40), 147 (50), 133 (100), 119 (70), 105 (45), 91 (50).

Tetramer (12): ^{1}H NMR (200 MHz, [D$_6$]benzene, 20 °C): $\delta = 1.20$ (s, 9H; CH_3), 1.25 (s, 9H; CH_3), 1.30 (s, 9H; CH_3), 1.35 (s, 9H; CH_3), 5.24 (d, ^3J(H,H) = 12.4 Hz, 1H; C*H*), 5.44 (br, 1H; C*H*), 5.66 (s, 1H; C*H*), 5.85 ppm (dd, ^3J(H,H) = 12.4 Hz, ^4J(H,H) = 1.55 Hz, 1H; CH); ^{13}C NMR (50 MHz, [D$_6$]benzene, 20 °C):$\delta = 29.6$ (*C*H$_3$), 30.7 (*C*H$_3$), 31.8 (*C*H$_3$), 32.4(*C*H$_3$), 33.8 (*C*-CH$_3$), 34.1 (C-CH$_3$), 34.5 (*C*-CH$_3$), 35.1 (*C*-CH$_3$), 85.1 (*C*≡), 105.4 (*C*≡), 119.4 (*C*=), 121.6 (*C*=), 132.1 (CH corresponding to the hydrogen signal at $\delta = 5.85$), 139.4 (CH corresponding to the hydrogen signal at $\delta = 5.44$), 139.9 (CH corresponding to the hydrogen signal at $\delta = 5.25$), 147.7 ppm (CH corresponding to the hydrogen signal at $\delta = 5.66$); GC-MS: *m*/*z* (%): 313 (5) [$M^+ - CH_3$], 271 (50), 257 (10), 215 (60), 187 (20), 173 (45), 159 (50), 57 (100).

Reaction of 3,3-dimethyl-1-butyne in the presence of *t*BuNH$_2$ promoted by [$(Et_2N)_3U$][BPh_4]

Procedure A: Following the typical experimental procedure, 100% conversion of the alkyne was observed after 22 h at 90 °C for the reaction of *t*BuNH$_2$ (0.7 mL, 6.66 mmol) with 3,3-dimethyl-1-butyne (0.82 mL, 6.66 mmol) to give the *cis* dimer **10** (64%), the regiospecific trimer **11** (19%), and the specific tetramer **12** (17%).

Procedure B: Following the typical experimental procedure, 100% conversion of the alkyne was observed for the reaction of *t*BuNH$_2$ (0.7 mL, (6.66 mmol) with 3,3-dimethyl-1-butyne (0.82 mL, 6.66 mmol) promoted by [$(Et_2N)_3U$][BPh_4] (40 mg, 0.052 mmol) at room temperature for 10 h yielding the *cis* dimer **10** (60%), regiospecific trimer **11** (15%), regiospecific tetramer **12** (20%), and small amounts of a pentamer (4%).

Procedure C: Following the typical experimental procedure, 90% conversion of the alkyne was obtained for the reaction of *t*BuNH$_2$ (0.7 mL, 6.66 mmol) with 3,3-dimethyl-1-butyne (0.82 mL, 6.66 mmol) at room temperature for 200 h yielding the *cis* dimer **10** (51%), regiospecific trimer **11** (23%), and regiospecific tetramer **12** (20%). In addition, trace amounts of a pentamer (5%) were also observed.

Procedure D: Following the typical experimental procedure, 100% conversion of the alkyne was obtained for the reaction of *t*BuNH$_2$ (0.07 mL, 0.666 mmol) with 1-deuterium-3,3-dimethyl-1-butyne (0.098 mL, 0.799 mmol) at room temperature for 40 h to give the *cis* dimer **10** (46%), trimer **11** (27%), tetramer **12** (17%), and small amounts of a pentamer (10%). The ^{2}H NMR spectra show that all products contain no deuterium.

Procedure E: Following the typical experimental procedure, 100% conversion of the alkyne was obtained for the reaction of *t*BuND$_2$ (0.083 mL, 0.80 mmol) with 3,3-dimethyl-1-butyne (0.07 mL, 0.57 mmol) at 60 °C for 20 h to give the *cis* dimer (57%), the trimer (24%), the tetramer (15%), and small amounts of a pentamer (4%). The ^{1}H and ^{2}H NMR spectra show that each oligomer contains either only one or no deuterium atom. The ^{2}H NMR spectrum shows a signal at $\delta = 5.43$ ppm for the *cis* dimer, 5.82 ppm for the trimer, and 5.85 ppm for the tetramer. The amount of the nondeuterated alkyne is always larger (70%) than the amount of the corresponding monodeuterated isomer.

Procedure F: Following the typical experimental procedure, 100% conversion of the alkyne was obtained for the reaction of *t*BuND$_2$ (0.097 mL, 0.93 mmol) with 3,3-dimethyl-1-butyne (0.148 mL, 1.21 mmol) at room temperature for 40 h yielding the *cis* dimer (36%), the regiospecific trimer (35%), the regiospecific tetramer (24%), and trace amounts of a pentamer (4%). GC-MS and ^{1}H and ^{2}H NMR spectroscopy show that each oligomer contains only one deuterium atom at an internal position. The ^{2}H NMR spectrum shows a signal at $\delta = 5.43$ ppm for the *cis* dimer, 5.82 ppm for the trimer, and 5.85 ppm for the tetramer. The distribution of D atoms in the products is similar to that observed in Procedure E.

Reaction of *i*PrC≡CH and *t*BuND$_2$: Following the typical experimental procedure, 40% conversion of the amine was obtained for the reaction of *t*BuND$_2$ (0.097 mL, 0.93 mmol) with 3-methyl-1-butyne (0.148 mL, 1.21 mmol), without catalyst at 60 °C for 48 h to yield *i*PrC≡CD and *t*BuNHD.

Reaction of 3,3-dimethyl-1-butyne in the presence of Et$_2$NH promoted by [$(Et_2N)_3U$][BPh_4]: Following the typical experimental procedure, 100% conversion of the alkyne was obtained after 21 h at 60 °C for the reaction of Et$_2$NH (0.83 mL, 8.0 mmol) with 3,3-dimethyl-1-butyne (0.90 mL, 8.0 mmol) yielding the *cis* dimer **10** (46%), the trimer **11** (34%), the tetramer **12** (16%), and small amounts of a pentamer (4%).

Reaction of trimethylsilylacetylene with EtNH$_2$ promoted by [$(Et_2N)_3U$][BPh_4]: Following the typical experimental procedure, 40% conversion of the alkyne was obtained after 67 h at 78 °C for the reaction of trimethylsilylacetylene (0.9 mL, 6.4 mmol) with EtNH$_2$ (0.53 mL, 9.6 mmol) to give (*Z*)-TMSCH$_2$CH=NEt (**13**) (81%) and the *gem*-alkyne dimer **14** (19%).

Reaction of trimethylsilylacetylene with *i*PrNH$_2$ promoted by [$(Et_2N)_3U$][BPh_4]: Following the typical experimental procedure, 100% conversion of the alkyne was obtained after 5 h at 50 °C for the reaction of trimethylsilylacetylene (0.9 mL, 6.4 mmol) with *i*PrNH$_2$ (0.82 mL, 9.6 mmol) to yield (*Z*)-TMSCH$_2$CH=N*i*Pr (**15**, 52%) and (*E*)-TMSCH$_2$CH=N*i*Pr (**16**, 48%). In addition, trace amounts of the alkyne dimer were observed. After 160 h at room temperature, the *E* isomer was transformed into the *Z* product. The full characterization of the *E* isomer was performed by subtracting the NMR data of the clean *Z* isomer from that of the mixture. The configuration of the *Z* isomer was confirmed by NOE experiments.

(*Z*)-TMSCH$_2$CH=N*i*Pr (15): ^{1}H NMR (200 MHz, [D$_6$]benzene, 20 °C): $\delta =$ 0.05 (s, 9H; CH_3), 0.90 (d, ^3J(H,H) = 8 Hz, 6H; CH_3), 1.59 (d, ^3J(H,H) = 4.8 Hz, 2H; CH_2), 2.80 (m, 1H; C*H*), 7.30 ppm (t, ^3J(H,H) = 4.8 Hz, 1H; C*H*=); ^{13}C NMR (50 MHz, [D$_6$]benzene, 20 °C): $\delta = -0.06$ (Si*C*H$_3$), 21.7 (*C*H$_2$ ^1J(C,H) = 128.2 Hz), 27.9 (CH*C*H$_3$), 61.4 (*C*H-N), 155.5 ppm (*C*H=N, ^1J(C,H) = 151 Hz).

(*E*)-TMSCH$_2$CH=N*i*Pr (16): ^{1}H NMR (200 MHz, [D$_6$]benzene, 20 °C): $\delta =$ -0.10 (s, 9H; CH_3), 1.00 (d, ^3J(H,H) = 7 Hz, 6H; CH_3), 1.57 (d, ^3J(H,H) = 4.8 Hz, 2H; CH_2), 2.90 (m, 1H; C*H*), 7.45 ppm (t, ^3J(H,H) = 4.8 Hz, 1H; C*H*=); ^{13}C NMR (50 MHz, [D$_6$]benzene, 20 °C): $\delta = -1.7$ (Si*C*H$_3$), 27.6 (*C*H$_2$), 29.7 (CH*C*H$_3$), 55.9 (*C*H-N), 154.1 ppm (*C*H=N).

Reaction of trimethylsilylacetylene with *t*BuNH$_2$ promoted by [$(Et_2N)_3U$][BPh_4]:

Procedure A: Following the above procedure, 100% conversion of the alkyne has been observed after 5 h at 50 °C for the reaction of trimethylsilylacetylene (0.9 mL, 6.4 mmol) with *t*BuNH$_2$ (0.82 mL, 9.6 mmol) to give (*Z*)-TMSCH$_2$CH=N*t*Bu (**17**) (8%) and (*E*)-TMSCH$_2$CH=N*t*Bu (**18**)

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(91%) along with trace amounts of the alkyne dimer. After 120 h at room temperature, the (*E*)-**18** product was completely isomerized into the (*Z*)-**17** product.

Procedure B: Following the typical experimental procedure, 50% conversion of the alkyne was obtained after 20 h at 20 °C for the reaction of trimethylsilylacetylene (0.09 mL, 0.64 mmol) with *t*BuNH$_2$ (0.082 mL, 0.96 mmol) to yield (*E*)-TMSCH$_2$CH=N*t*Bu (**18**) (70%) and (*Z*)-TMSCH$_2$CH=N*t*Bu (**17**) (30%). The molar ratios of (*E*)-**18**:(*Z*)-**17** were 65:35, 40:60, 28:72, and 0:100% after 42, 66, 90, and 120 h, respectively.

(*Z*)-TMSCH$_2$CH=N*t*Bu (17): ^{1}H NMR (200 MHz, [D$_6$]benzene, 20 °C): $\delta = 0.05$ (s, 9H; CH_3), 1.07 (s, 9H; CH_3), 1.67 (d, ^3J(H,H) = 5.9 Hz, 2H; CH_2), 7.25 ppm (t, ^3J(H,H) = 5.9 Hz, 1H; C*H*=); ^{13}C NMR (50 MHz, [D$_6$]benzene, 20 °C): $\delta = 2.3$ (*C*H$_3$), 22.3 (*C*H$_2$), 33.5 (*C*H$_3$), 56.5 (CH-N), 152.1 ppm (CH=N).

(*E*)-TMSCH$_2$CH=N*t*Bu (18): ^{1}H NMR (200 MHz, [D$_6$]benzene, 20 °C): $\delta = -0.10$ (s, 9H; CH_3), 1.10 (s, 9H; CH_3), 1.68 (d, ^3J(H,H) = 5.9 Hz, 2H; CH_2), 7.50 ppm (t, ^3J(H,H) = 5.9 Hz, 1H; C*H*=); ^{13}C NMR (50 MHz, [D$_6$]benzene, 20 °C): $\delta = -1.7$ (*C*H$_3$), 27.6 (*C*H$_2$), 29.7 (CH$_3$), 55.9 (CH-N), 154.1 ppm (CH=N).

Reaction of trimethylsilylacetylene with Et$_2$NH promoted by [(Et$_2$N)$_3$U][BPh$_4$]: Following the above procedure, 20% conversion of the alkyne was obtained after 87 h at 50 °C for the reaction of trimethylsilylacetylene (0.09 mL, 0.64 mmol) with Et$_2$NH (0.132 mL, 1.28 mmol) to give the *trans* dimer of trimethylsilylacetylene (**19**; 13%) and the corresponding enamine (*E*)-TMSCH=CHNEt$_2$ (**20**; 87%); the latter compound was characterized by ^{1}H, ^{13}C, and 2D NMR (COSY, CH-correlation and NOESY) spectroscopy.

(*E*)-TMSCH=CHNEt$_2$ (20): ^{1}H NMR (200 MHz, [D$_6$]benzene, 20 °C): $\delta =$ 0.17 (s, 9H; CH_3), 0.74 (t, ^3J(H,H) = 7 Hz, 6H; CH_3), 2.65 (q, ^3J(H,H) = 7 Hz, 4H; CH_2), 3.84 (d, ^3J(H,H) = 16.5 Hz, 1H; C*H*=), 6.14 ppm (d, ^3J(H,H) = 16.5 Hz, 1H; C*H*=); ^{13}C NMR (50 MHz, [D$_6$]benzene, 20 °C): $\delta = -0.27$ (*C*H$_3$), 15.7 (*C*H$_3$), 44.3 (*C*H$_2$), 94.2 (*C*H-N), 147.2 ppm (CH=N).

X-ray crystallography of [(*t*BuNH$_2$)$_3$(*t*BuNH)$_3$U][BPh$_4$]: A dark single-crystal prism immersed in Parathone-N oil was quickly removed with a capillary tube and mounted on a Kappa CCD diffractometer under a stream of cold nitrogen at 230 K. Data was collected with monochromatized Mo$_{K\alpha}$ radiation by omega and phi scans to cover the Ewald sphere.[30] Accurate cell parameters were obtained with 17580 reflections.[3] The U atom was located by SHELXS-97 direct methods, and the remaining non-hydrogen atoms by successive Fourier difference maps. The structure was refined anisotropically for the U atom and only isotropically for the non-hydrogen atoms by using SHELXL-97 program package. Hydrogen atoms were totally ignored as their contribution to the structure was found to be negligible. At the final stages of refinement, difference maps also revealed a benzene solvent molecule, which was refined isotropically as an idealized ring. In addition, two peaks were found in the vicinity of the benzene ring that were attributed to an additional solvent molecule of methyl amine. It shared the same site as the benzene molecule with occupancies of 0.47 and 0.53% respectively. The structure was solved by SHELXL97 direct methods[32] and refined with the SHELXL97 program package.[33] Software used for molecular graphics: ORTEP, TEXRAY Structure Analysis package.[34]

Crystal data and structure refinement for [(*t*BuNH$_2$)$_3$(*t*BuNH)$_3$U][BPh$_4$]: Formula $C_{51.63}H_{80.18}BN_{6.47}U$, crystal size $0.1 \times 0.15 \times 0.17$ mm, $M_r = 1040.42$, $T = 200(2)$ K, $\lambda = 0.71073$ Å. Crystal system: monoclinic, space group: $P2_1/n$, $a = 12.7589(4)$, $b = 18.2907(4)$, $c = 24.5579(7)$ Å, $\alpha = 90$, $\beta = 97.8630(10)$, $\gamma = 90°$, $V = 5677.2(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.217$ Mg m^{-3}, $\mu = 2.894$ mm^{-1}, $F(000) = 2129$, θ range = 1.39–25.50°. Limiting indices: $0 \le h \le 15$, $0 \le k \le 22$, $-29 \le l \le 29$; reflections collected/unique = 10563/10563 [R(int) = 0.0000]; completeness to $\theta = 25.50 = 100.0$%; data/restraints/parameters = 10563/0/239; goodness-of-fit on $F^2 = 0.941$; final R indices [$I > 2\sigma(I)$]: $R1 = 0.0529$, $wR2 = 0.1560$; R indices (all data): $R1 = 0.1253$, $wR2 = 0.1687$; largest difference peak/hole: 0.822/ −1.964 e Å^{-3}.

CCDC-177698 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

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