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Et_2SiH_2 assisted the selective dimerization of terminal alkynes catalyzed by $Cp^*_2UMe_2$

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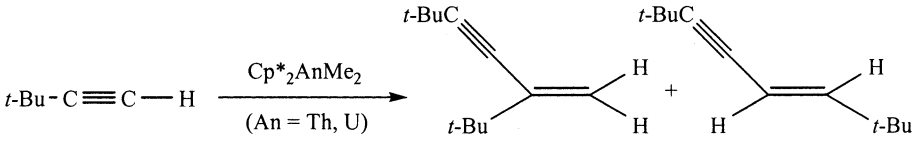
Abstract

A practical approach has been developed for the catalytic synthesis of short oligomers, dimers and/or trimers of terminal alkynes. The method allows control of the extent and, in some cases, the regiospecificity in the catalyzed oligomerization of terminal alkynes promoted by bis(pentamethylcyclopentadienyl)uranium dimethyl complex ($Cp^*_2U(CH_3)_2$, $Cp^* = C_5Me_5$). The metallocene precursor is known to promote the simultaneous production of a large number of differently sized oligomers in the presence of terminal alkynes. However, the addition of a specific secondary silane ensures the selective synthesis of short oligomers.

Keywords: Organoactinide; Alkyne complexes; Dimerization of alkynes; Oligomerization of alkynes; Catalysis; Silane

1. Introduction

Tailoring stoichiometric and catalytic reaction to obtain selective, and if possible regiospecific, products is a challenging goal in modern organometallic chemistry. In many cases, mild and easily controlled reactions have been obtained [1,2]. Besides the many successes, controlling the selectivity and regiospecificity of a catalytic oligomerization/polymerization remains a challenge [3]. Dihydrogen, for instance, is added to cut the growing polymeric chains in the catalytic Ziegler–Natta polymerization reaction [4]. In the polymerization of alkenes by cationic Group 4 metallocenes, the counterion affects the molecular weight of the observed polymers [5]. For the catalytic oligomerization of alkynes, the means to control the selectivity (extent of oligomerization) of the products has been to proceed through the addition of amines [6]. It is noteworthy to point out that catalysts (early and late transition metals) for the highly regioselective specific *dimerization* of terminal alkynes have been reported but provide no means to generate or to control the formation of higher oligomers [7,8]. Recently [9], we have shown that organoactinide complexes of the type $(C_5Me_5)_2AnMe_2$ (An = Th, U) were found effective precatalysts for the oligomerization of terminal alkynes. Bulky acetylenes, such as ^{t}BuC≡CH was dimerized (Eq. (1)) producing the head-to-tail dimer, whereas TMSC≡CH, was trimerized (Eq. (2)) specifically towards the head-to-tail-to-head trimer, respectively [10].



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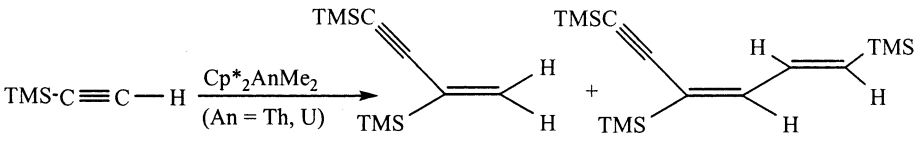
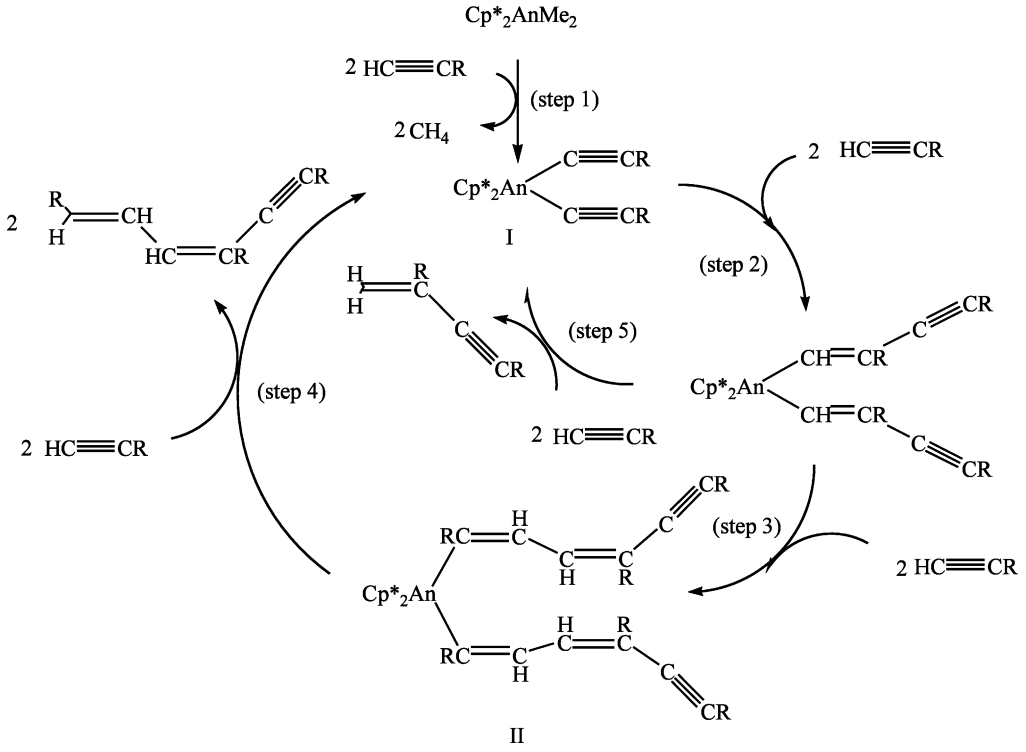


(2)

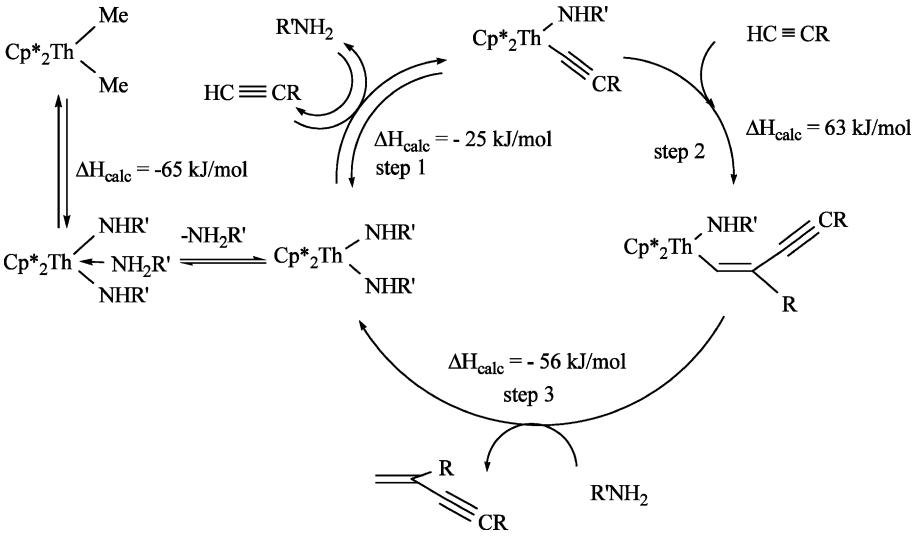
For non-bulky terminal alkynes, the oligomerization leads to a mixture of dimers to decamers with no chemo- or regioselectivity among different oligomers [10]. The proposed mechanistic scenario for the oligomerization of terminal alkynes is presented in Scheme 1. This mechanism is based on kinetic experiments and trapping intermediate species such as **I** and **II**. The rate-determining step, in the catalytic trimerization of TMSC≡CH was found to be the elimination of the trimer from the bis(dieneyne)thorium complex **II**. This result indicates that both rates: (i) σ-bond metathesis between the actinide-carbyls and the alkyne and (ii) insertion of the triple bond into the metal acetylide moiety (steps 1–3 in Scheme 1), are much faster than the rate for the protonolysis the metal–dialkenyl complex (step 4).

A fascinating conceptual question regarded the ability to tailor the proposed mechanism in such a fashion so as to induce the formation of a specific dimer or trimer and thus preventing the formation of higher oligomers. That is, to obstruct pathways 3 and 4 in Scheme 1, obligating the catalyst to follow routes 2 and 5. We recently reported a convenient principle for controlling the chemoselectivity in the oligomerization of terminal alkynes. The strategy uses an acidic chain-transfer agent that does not end-up in the product (in contrast to, e.g. H_2), and does not require subsequent elimination from the product to release the unsaturated oligomer (e.g. in contrast to ethene oligomerization by metallocene catalysts or magnesium reagents) [11]. Controlling the oligomerization was achieved by adding an amine into the catalytic cycle, without altering the turnover frequencies as compared with the non-controlled process [6]. The drawback of this strategy is that it worked satisfactorily with the thorium complex $Cp^*_2ThMe_2$, but it did not work satisfactorily with the corresponding uranium complex (besides for the bulky ^{t}BuC≡H), due to the differences in the corresponding enthalpies of the protonolysis reactions. The proposed mechanism, as proposed for the controlling oligomerization for the thorium complex with amines, is described in Scheme 2.

In addition to the reactivity of organoactinides as described above, we have recently shown that orga-

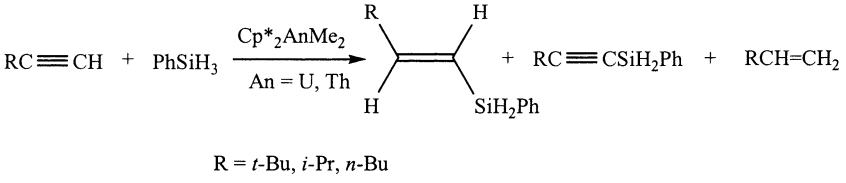


Scheme 1. Proposed scenario for the oligomerization of terminal alkynes promoted by organoactinide complexes.



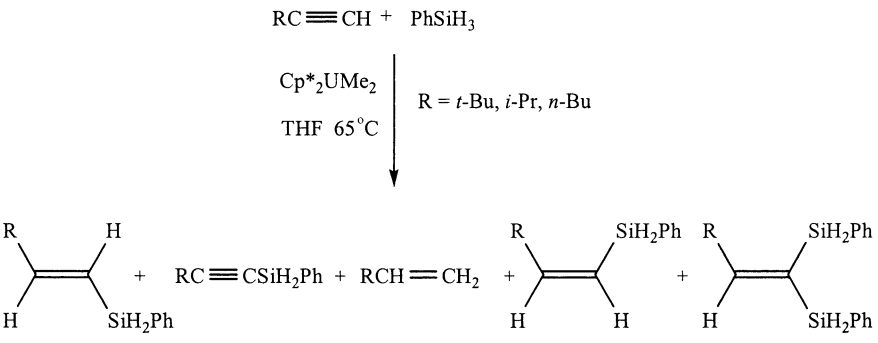
Scheme 2. Proposed mechanism for the controlled oligomerization of terminal alkynes promoted by the thorium complex $Cp^*_2ThMe_2$ in the presence of primary amines.

noactinides are active catalysts towards the hydrosilylation of terminal alkynes with primary silanes [12]. At room temperature, three major products were obtained as presented in Eq. (3):



(3)

Interestingly, regardless of the alkyl substituents and the metal center, the major product in the hydrosilylation reaction at room temperature was the *trans*-vinylsilane without any trace formation of the other two hydrosilylation isomers (*geminal* or *cis*). At high temperature (65 °C), however, the chemoselectivity and the regioselectivity of the vinylsilanes formed in the organoactinide-catalyzed hydrosilylation of terminal alkynes with $PhSiH_3$, were found to be different, as presented in Eq. (4):



(4)

Due to the fact that no hydrosilylation products of vinylsilanes were obtained, even under the presence of large excess amounts of $PhSiH_3$, it seems plausible to conclude that secondary silanes would be acidic enough to induce a rapid protonolysis of growing oligomers of terminal alkynes without inducing the corresponding additional hydrosilylation reaction. Therefore, here we present the activity of the organoactinide complex $Cp^*_2UMe_2$ in the presence of the secondary silane Et_2SiH_2 for the selective dimerization of terminal alkynes. The selectivity control, which refers to the number of the different oligomers obtained, could be achieved by considering the difference in the calculated bond-disruption energies between an actinide–alkenyl- and an actinide–silane-bond, and the combination of the non-selective catalytic pathways with individual stoichiometric reactions. This strategy provides an additional route to control, in principle, oligomerization–polymerization reactions of terminal alkynes producing specific enynes for further chemical transformations [13].

2. Experimental

2.1. Materials and methods

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 sieve column. Ether solvents were distilled under argon from sodium benzophenone ketyl. Hydrocarbon solvents (THF-d_8, benzene-d_6) were distilled under nitrogen from Na–K alloy. All solvents for vacuum line manipulations were stored in vacuo 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. Silane (Aldrich) was dried over Na–K alloy and stored over activated molecular sieves (4 Å). $Cp^*_2UMe_2$ [14] was prepared according to published procedures. NMR spectra were recorded on a Bruker AM 200 and Bruker AM 400 spectrometers. Chemical shifts for ^{1}H-NMR and ^{13}C-NMR are referenced to internal solvent resonances and are reported relative to tetramethylsilane. GC–MS experiments were conducted in a GC–MS (Finnigan Magnum) spectrometer. NMR experiments were conducted in Teflon valve-sealed tubes (J-Young) after vacuum transfer of the liquids in a high-vacuum line.

2.2. Controlled catalytic oligomerization of HC≡CR by $Cp^*_2UMe_2$ in the presence of Et_2SiH_2

2.2.1. General

In a typical procedure, alkyne and silane were added to an NMR tube containing 10 mg (0.0186 mmol) of the catalyst in ca. 0.6 ml of solvent (THF-d_8 or C_6D_6) by vacuum transfer in a high vacuum line. The sealed tube was heated in an oil bath (oil temperature = 100 °C) for 24 h. After 100% conversion of the alkyne (detected by ^{1}H-NMR), the organic products were vacuum transferred to another NMR tube and identified by ^{1}H, ^{13}C, Cosy, Noesy, C–H correlation NMR spectroscopy and GC–MS. Different geometrical isomers were identified by comparing the signals of clean isomers [6][8b][9,10].

2.2.2. Dimerization of 3-methyl-1-butyne by $Cp^*_2UMe_2$ and Et_2SiH_2

According to the general procedure described above, 0.08 ml (0.78 mmol) of 3-methyl-1-butyne was dimerized with 0.1 ml (0.76 mmol) of Et_2SiH_2 to a mixture of the *geminal* head-to-tail dimer (47.5%), *trans* head-to-head dimer, the alkene (23.7%) and the diethylsilyl isopropylacetylene (23.8%) as the major products. Additional trace amounts (5%) of a mixture of trimers up to pentamers were also observed.

2.2.3. Trimerization of 1-hexyne by $Cp^*_2UMe_2$ and Et_2SiH_2

As described above, 0.08 ml (0.68 mmol) of 1-hexyne was catalytically trimerized (100%) with 0.09 ml (0.86 mmol) of Et_2SiH_2 to the tail-to-head-to-tail trimer. Additional trace amounts (up to 1%) of ^{n}BuC≡CSiEt$_2$H and various trimers were observed in the GC–MS.

^{1}H-NMR (200 MHz, C_6D_6) $\delta = 6.02$ (s, 1H, H_2C=CCH=C), 5.21 (d, 1H, $^2J_{HH} = 1.95$ Hz, H_2C=CCH=C), 4.92 (d, 1H, $^2J_{HH} = 1.95$ Hz, H_2C=CCH=C), 2.10–2.50 (m, 6H, CH_2CH$_2$CH$_2$CH$_3$), 1.25–1.65 (m, 12H, CH$_2$CH_2CH_2CH$_3$), 0.85–1.03 (m, 9H, CH$_2$CH$_2$-CH$_2$CH_3).

^{13}C-NMR (50 MHz, C_6D_6) $\delta = 149.8$ (s, H_2C=CCH=C), 137.8 (d, $^1J_{CH} = 154.1$ Hz, H_2C=CCH=C), 125.8 (s, H_2C=CCH=C), 118.0 (t, $^1J_{CH} = 156.4$ Hz, H_2C=CCH=C), 99.9 (s, C≡CCH$_2$), 83.7 (s, C≡CCH$_2$), 43.0 (t, CH$_2$CH$_2$CH$_2$CH$_3$), 40.4 (t, CH$_2$CH$_2$CH$_2$CH$_3$), 38.4 (t, CH$_2$CH$_2$CH$_2$CH$_3$), 34.9 (t, CH$_2C$H$_2$CH$_2$CH$_3$), 34.4 (t, CH$_2C$H$_2$CH$_2$CH$_3$), 30.6 (t, CH$_2C$H$_2$CH$_2$CH$_3$), 25.7 (t, CH$_2$CH$_2C$H$_2$CH$_3$), 25.4 (t, CH$_2$CH$_2C$H$_2$CH$_3$), 22.6 (t, CH$_2$CH$_2C$H$_2$CH$_3$), 17.0 (q, CH$_3$), 16.9 (q, CH$_3$), 16.5 (q, CH$_3$).

High-resolution mass spectrum: Calc. for $C_{18}H_{30}$ [M$^+$]: 246.4398. Found: 246.4387.

2.2.4. Dimerization of 3,3 dimethyl-1-butyne by $Cp^*_2UMe_2$ and Et_2SiH_2

As described above, 0.08 ml (0.64 mmol) of ^{t}BuC≡CH was catalytically dimerized (100% conversion after 24 h) with 0.08 ml (0.64 mmol) of Et_2SiH_2 to a mixture of the *trans* head-to-head dimer (15.3%), *geminal* head-to-tail dimer (38.5%) and the corresponding alkene (44.2%) as the major products. Trace amounts of the silylalkyne and oligosilanes (2%) were also observed.

2.2.5. Trimerization of trimethylsilylacetylene by $Cp^*_2UMe_2$ and Et_2SiH_2

As described above, 0.08 ml (0.56 mmol) of TMSC≡CH was catalytically trimerized (100% conversion after 24 h) with 0.07 ml (0.56 mmol) of Et_2SiH_2 to the head-to-head-to-head trimer (TMS)CH_a=$CH_b$$CH_c$=C(TMS)C≡C(TMS) (95%), the corresponding TMSC≡$CSiEt_2H$ (0.5%) and the three possible *geminal* head-to-tail dimer (2.2%), *trans* head-to-tail dimer (0.7%) and *cis* head-to-tail dimer (1.6%).

(TMS)CH_a=$CH_b$$CH_c$=C(TMS)C≡C(TMS): ^{1}H-NMR (200 MHz, C_6D_6) $\delta = 7.34$ (dd, 1H, $^3J_{H_aH_b} =$ 14.1 Hz, $^3J_{H_cH_b} = 11.6$ Hz, H_b), 6.85 (d, 1H, $^3J_{H_cH_b} =$ 11.6 Hz, H_c), 5.87 (d, 1H, $^3J_{H_aH_b} = 14.1$ Hz, H_a), 0.18 (s, 9H, C≡CSiCH_3), 0.17 (s, 18H, C=CSiCH_3).

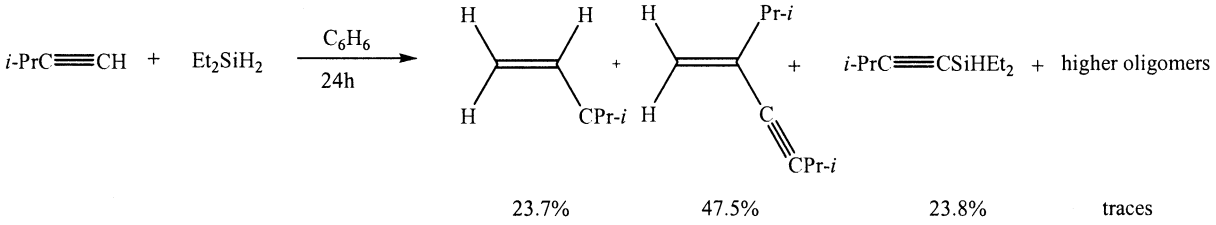
(TMS)CH_a=$CH_b$$CH_c$=C(TMS)C≡C(TMS): ^{13}C-NMR (50 MHz, C_6D_6) $\delta = 149.7$ (d, $^1J_{CH_a} = 154.8$ Hz, CH_a), 146.8 (d, $^1J_{CH_b} = 153.4$ Hz, CH_b), 139.9 (d, $^1J_{CH_c} = 135.5$ Hz, CH_a), 131.6 (s, C=C(TMS)C≡C), 108.2 (s, C=C(TMS)C≡C), 107.7 (s, C=C(TMS)C≡C(TMS)), 2.7 (q, $^1J_{CH} = 117.6$ Hz, ≡CTMS), 0.4 (q, $^1J_{CH} = 115.6$ Hz, 2 × C=C(TMS)).

3. Results and discussion

The goal of this investigation was to examine the scope, chemoselectivity and the regioselectivity for the oligomerization of terminal alkynes controlled by the addition of a secondary silane catalyzed by the uranium complex $Cp^*_2UMe_2$. This study represents an extension of, and comparison to, our previous investigation of the oligomerization of terminal alkynes promoted by organoactinides, and to the controlled oligomerization of alkynes promoted by $Cp^*_2ThMe_2$ in the presence of amines [6].

3.1. Reaction and scope of the controlled oligomerization

The organoactinide complex $(C_5Me_5)_2UMe_2$ reacts with terminal alkynes in the presence of secondary silanes, yielding small oligomers depending on the nature of the alkyne. In addition to the oligomers, the corresponding silylacetylene was always present at the end of the reaction in small amounts. These results, in general, are in contrast to the oligomerization chemo- and regioselectivity that have been observed under the same conditions in the absence of a controlling agent. The initial reaction of $(C_5Me_5)_2UMe_2$ with an alkyne, in the presence of the silane, yields the bis-acetylide complex. Neither mono- nor bis-silyl complexes were observed even when a large excess of silane was used. The chemo- and regioselectivity products of the controlled oligomerization of ^{i}PrC≡CH, ^{n}BuC≡CH, ^{t}BuC≡CH, and (TMS)C≡CH with Et_2SiH_2 are presented in Eqs. (5)–(8):



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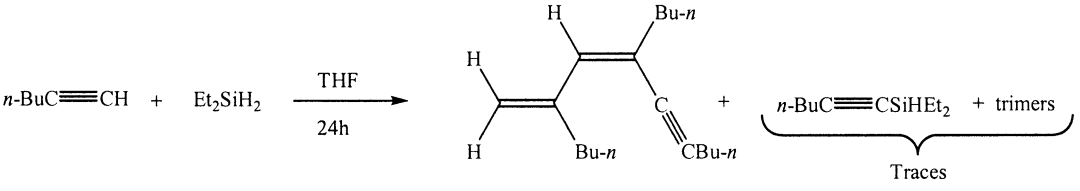

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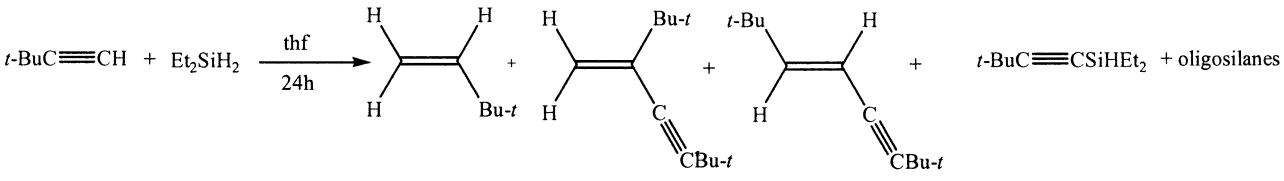

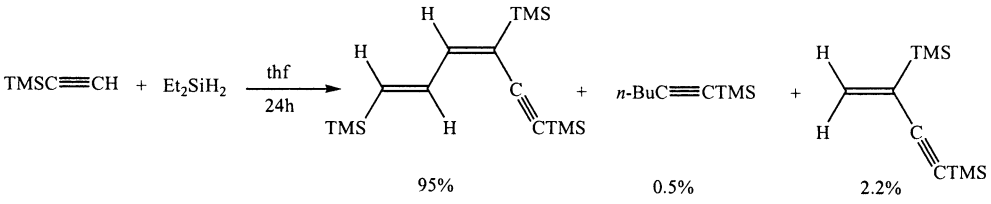

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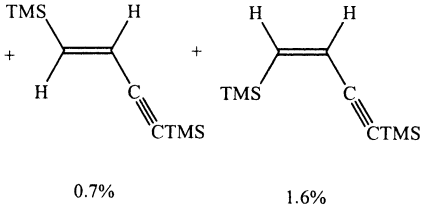
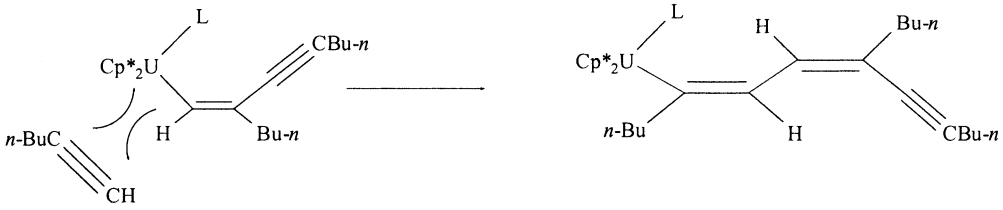
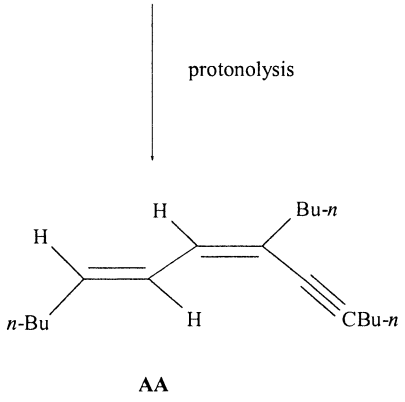


For ^{i}PrC≡CH (Eq. (5)), the controlling reaction is highly chemo- and regioselective affording the exclusive formation of the *geminal* dimer, in addition to the corresponding alkene and the silylalkyne. The formation of the alkene indicates that the secondary silane is acting as a source of hydrogen to reduce the triple bond, as already encountered in the hydrosilylation of terminal alkynes promoted by similar organoactinides [12]. Moreover, this result indicates the presence of a uranium-hydride intermediate species responsible for the catalytic reduction of the alkyne.

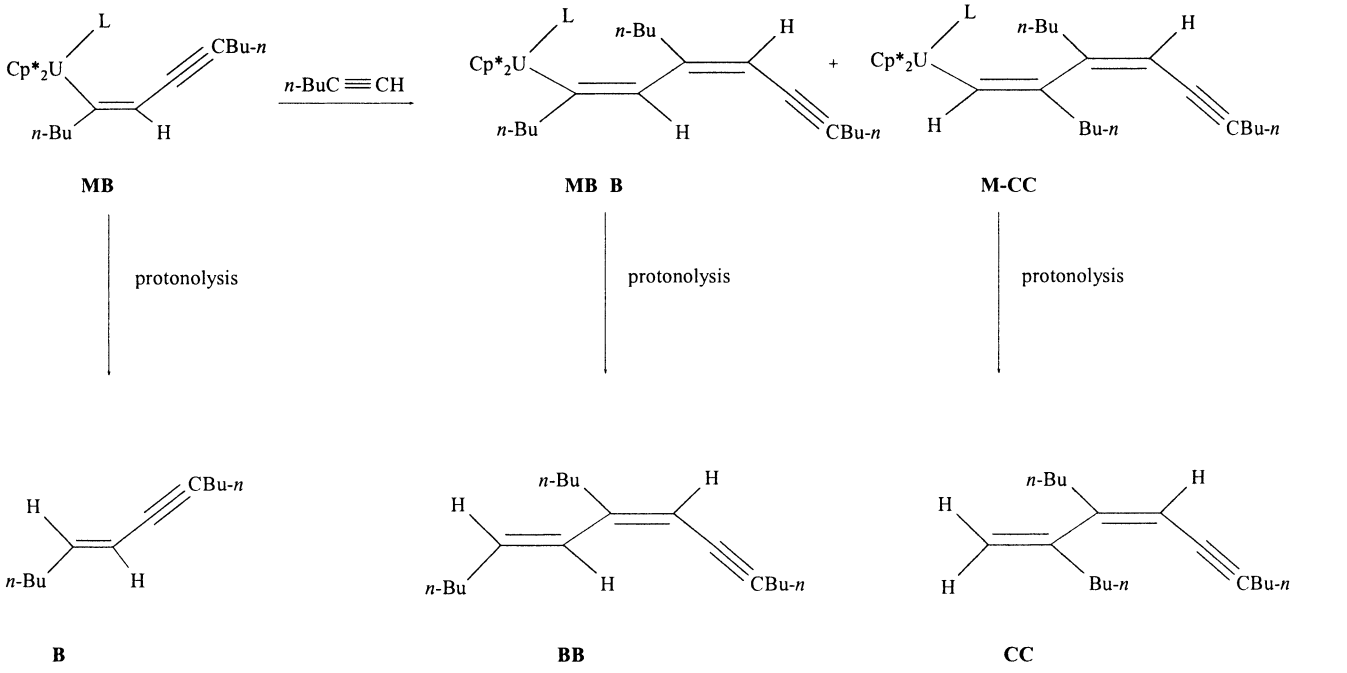
For ^{n}BuC≡CH (Eq. (6)), one exclusive trimer is formed. The specific trimer is formed through the regioselective addition of the terminal alkyne to the organometallic moiety (**M-A**), which theoretically is responsible for the formation of the *geminal* isomers (Eq. (9)):





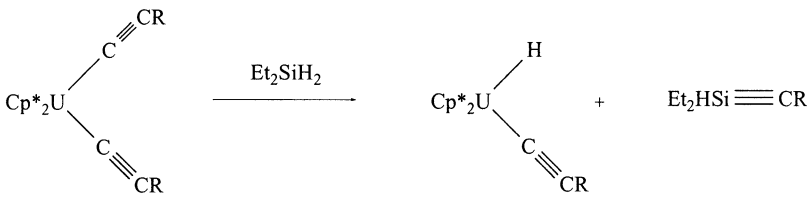
(9)

This result indicates that the insertion of the second alkyne into the metalla-eneyne complex **M-A** (which is presumably in the preferred stereochemistry due to the bulky substituent), and the subsequent trimer protonolysis, from the **M-AA** moiety to yield the trimer **AA**, are much faster than either the insertion of an alkyne into a possible intermediate complex **M-B** (yielding complexes **M-BB** and/or **M-CC**), and/or the protonolysis of any of the three complexes **M-B**, **M-BB** and **M-CC**, by either the alkyne or the silane, eliminating the dimer **B** or any of the two trimers **BB** or **CC**, respectively (see Eq. (10)) [15].



(10)

In the controlled reaction of the bulky ^{t}BuC≡CH (Eq. (7)), both the *geminal* and the *trans* dimers are obtained. Of interest is the comparison to the non-controlled reaction in which the *geminal* dimer was found to be the only product, whereas in the controlled process with primary amines, the *trans* isomer was the exclusively obtained compound. Since no trimers were obtained, it seems plausible to conclude that the protonolysis of the dimers are much faster than a second alkyne insertion. Therefore, the larger amount of the *geminal* dimer as compared with that of the *trans* isomer indicates that the insertion of the first alkyne into the uranium acetylide, forming the *geminal* organometallic moiety, is about twice as fast as the formation of the corresponding *trans* organometallic fragment. In addition to the dimers, alkene is obtained as the major product with the concomitant trace formation of the corresponding silylalkyne and oligosilanes. The formation of an alkene implies once more, the presence of a hydride organouranium complex that will be presumably obtained by the reaction between the starting bis-acetylide complex and the silane (Eq. (11)). Hence, equal amounts of the silylalkyne and alkene are theoretically expected as detected for ^{i}PrC≡CH. The formations of oligosilanes indicate that both Et_2SiH_2 and silylalkyne may act as the hydride source, reducing the final concentration of the latter [16]:



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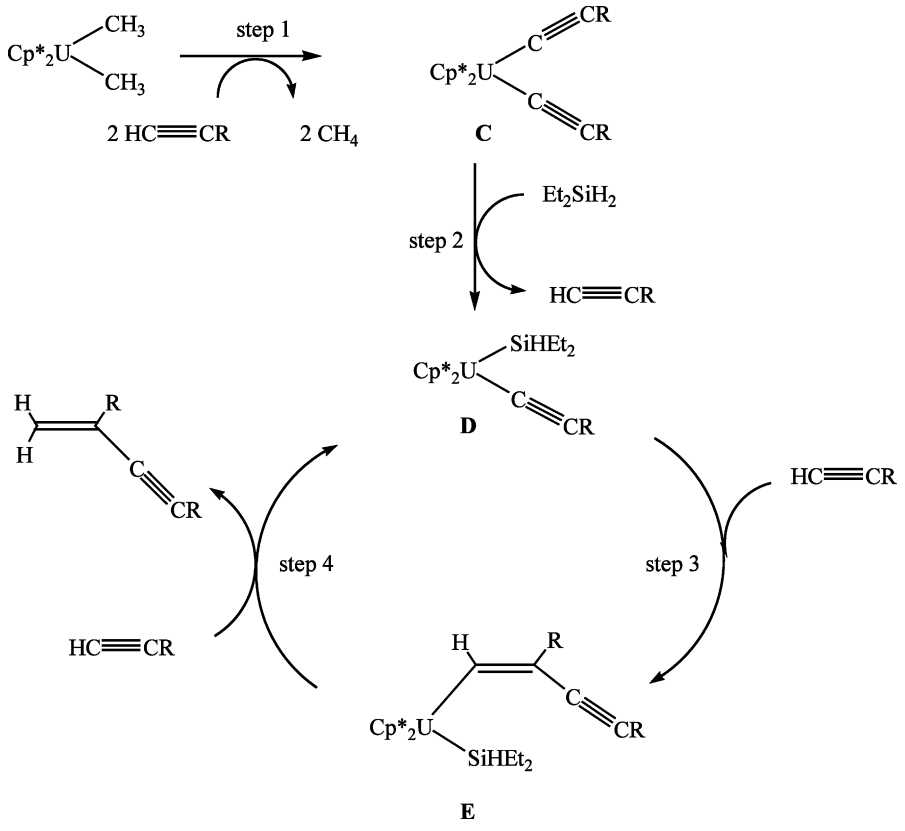
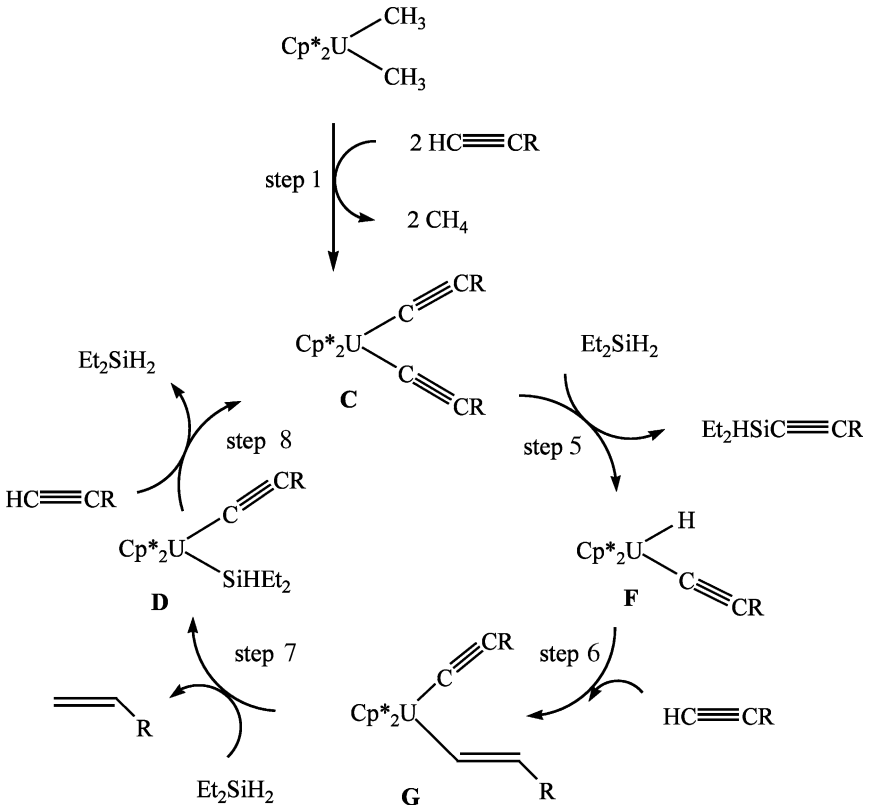
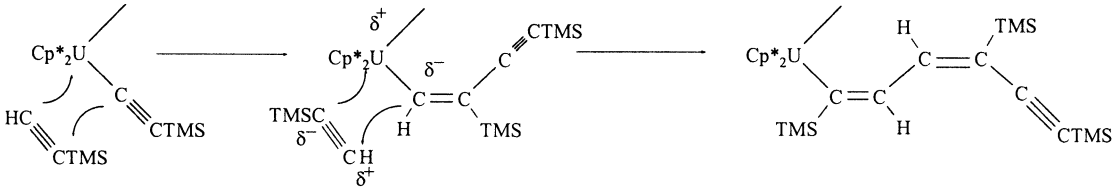


Scheme 3. Plausible scenario for the controlled oligomerization of terminal alkynes catalyzed by $Cp^*_2UMe_2$ in the presence of a secondary silane.



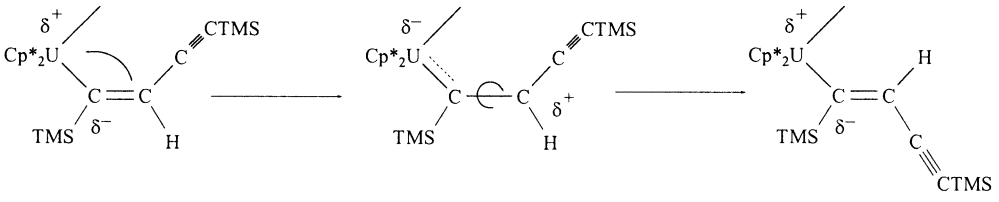
Scheme 4. Plausible mechanism for the hydrogenation of terminal alkynes by Et_2SiH_2 promoted by $Cp^*_2UMe_2$.

When performing the uranium-controlled oligomerization of TMSC≡CH (Eq. (8)), the head-to-head-to-head trimer was regioselectively formed, in addition to small amounts of the three possible dimers and the corresponding silylalkyne. As already observed for other alkynes, the first insertion of the alkyne prefers a *geminal* stereochemistry, presumably due to steric reasons. The second insertion for TMSC≡CH was found to be in opposite regiochemistry to that observed for ^{n}BuC≡CH. This result is expected and in agreement with the regiochemistry insertion of TMSC≡CH, as found in the non-controlled reaction or in the controlled oligomerization promoted by amines. This is due to the appreciable electronic character of the TMS group, stabilizing a partial carbanion charge at the α-position and a partial carbocation at the β-position (Eq. (12)) [9,17]:



(12)

Because of the stereochemistry of the insertion of olefins or alkynes into alkyl-organoactinide bonds are known to proceed through a four-centered transition state in the dimerization of terminal alkynes, the *geminal* and/or the *trans* isomers are expected (Eq. (12)). The formation of the *cis* isomer in the controlled oligomeriation of TMSC≡CH indicates that a fast isomerization of the *trans* isomer must occur before the protonolysis of the dimer (Eq. (13)). Interestingly, a similar isomerization has been observed in the oligomerization of terminal alkynes promoted by a cationic organouranium complex [18]:



(13)

3.2. Catalytic reaction scope and mechanism

The results presented here are for the catalytic oligomerization of terminal alkynes controlled by a secondary silane producing dimers or trimers with the absence of higher oligomers, as compared with the non-controlled catalytic cycle (tetramers–decamers), demonstrating the ability to tailor the extent of oligomerization catalyzed by the organouranium complex $Cp^{*}_{2}UMe_{2}$ [19]. This approach is based on an acidic chain-transfer mechanism as a competing reaction, modifying the non-selective oligomerization mechanism towards small oligomers. Using this strategy, the chain-transfer reagent does not end-up in the product (no hydrosilylation product) and, therefore, does not require subsequent elimination from the product to release the unsaturated oligomer. Interestingly, the formed trimers contain the same regiochemistry as the dimer complex before it was protonolyzed, indicating that the rate for releasing the dimer from the organometallic complex with the regiochemistry of **M-B** (Eq. (10)) is much slower than the rate of alkyne insertion into the metal complex with the regiochemistry **M-A** and subsequent protonolysis to the trimer (Eq. (9)). This result also corroborates that the insertion of the alkyne yielding, either **M-A** or **M-B** is not reversible [15].

Since the stereochemical approach of either silane or alkyne is by a side approach [20], it seems plausible that for bulky alkyne substituents, the steric hindrance

imparted by the pentamethylcyclopentadienyl rings prevents a second alkyne to insert, but allows the rapid protonolysis (the electronic effect of TMS is much stronger than the steric effect tolerating the trimer formation). A plausible scenario for the controlled oligomerization of terminal alkynes is described in Scheme 3.

The mechanism presented in Scheme 3 consists of a sequence of well-established elementary reactions, such as the insertion of acetylene into an M–C σ-bond and σ-bond metathesis. The precatalyst, $(C_5Me_5)_2UMe_2$, in the presence of a secondary silane and alkyne is converted to the bis-acetylide complex **C** (step 1). Complex **C**, which is the catalytic resting form of the complex under the catalytic conditions, reacts rapidly with one equivalent of silane, yielding the mono-acetylide mono-silane uranium complex **D** (step 2). Complex **D** reacts with an incoming alkyne, as the rate-limiting step, producing complex **E** (step 3). The formulation of complex **E**, instead of the bis-alkenyl complex (the insertion of two alkynes into complex **C**) is based on different ratios obtained for dimer formations in the non-assisted silane mechanism. This is confirmed by the fact that with silanes, the oligomerization of $^tBuC{\equiv}CH$ by $Cp^*_2UMe_2$ produced both dimers, whereas in the absence of silanes only the *geminal* dimer is formed arguing strongly for a coordination of the silane at the rate-determining step. The following step in the catalytic cycle is the rapid σ-bond protonolysis with an additional alkyne to yield the corresponding dimer and regenerating the silylacetylide complex **E** (step 4), or another insertion of an alkyne and concomitant σ-bond protonolysis by the silane, yielding the trimer and complex **D**. The protonolysis by another silane will produce the bis-silyl complex, which upon reaction with an alkyne will regenerate complex **C**.

The formation of the silylalkyne and the corresponding alkene corroborates the mechanism as shown in Scheme 3 and their formation is presented in Scheme 4. Complex **C** reacts with a silane, although in a different stereochemistry, producing the hydride complex **F** (step 5) and the corresponding silylalkyne. Rapid insertion of an alkyne into complex **F**, yields complex **G** (step 6), which reacts with a silane (or the silylalkyne) yielding the alkene and complex **D** (step 7). Complex **C** is regenerated by the reaction of and alkyne with the silylacetylide complex **D** (step 8).

4. Conclusion

In conclusion, we have shown that it is possible to control the extent of the oligomerization of terminal alkynes catalyzed by the organouranium complex $Cp^*_2UMe_2$, by using a selected silane. This has led to the possibility of ensuring catalysis by "recycling" the obtained organometallic silylacetylide. A detailed understanding of the thermodynamics of the single steps in the desired reactions was the key to "designing" the catalytic cycle. Studies using different protonolytic sources are under investigation.

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