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Diverse catalytic activity of the cationic actinide complex $[(Et_2N)_3U][BPh_4]$ in the dimerization and hydrosilylation of terminal alkynes. Characterization of the first f-element alkyne π-complex $[(Et_2N)_2U(C{\equiv}C^tBu)(\eta^2\text{-}HC{\equiv}C^tBu)][BPh_4]$

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Abstract

The cationic actinide complex $[(Et_2N)_3U][BPh_4]$ is an active catalytic precursor for the selective dimerization of terminal alkynes. The regioselectivity is mainly towards the *geminal* dimer but for bulky alkyne substituents, the unexpected *cis*-dimer is also obtained. Mechanistic studies show that the first step in the catalytic cycle is the formation of the acetylide complex $[(Et_2N)_2UC{\equiv}CR][BPh_4]$ with the concomitant reversible elimination of Et_2NH, followed by the formation of the alkyne π-complex $[(Et_2N)_2UC{\equiv}CR(RC{\equiv}CH)][BPh_4]$. This latter complex (R = ^{t}Bu) has been characterized spectroscopically. The kinetic rate law is first order in organoactinide and exhibits a two domain behavior as a function of alkyne concentration. At low alkyne concentrations, the reaction follows an inverse order whereas at high alkyne concentrations, a zero order is observed. The turnover-limiting step is the C≡C bond insertion of the terminal alkyne into the actinide–acetylide bond to give the corresponding alkenyl complex with $\Delta H^{\ddagger} = 15.6(3)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -11.4(6)$ eu. The following step, protonolysis of the uranium–carbon bond of the alkenyl intermediate by the terminal alkyne, is much faster but can be retarded by using $CH_3C{\equiv}CD$, allowing the formation of trimers. The unexpected *cis*-isomer is presumably obtained by the isomerization of the *trans*-alkenyl intermediate via an envelope mechanism. A plausible mechanistic scenario is proposed for the oligomerization of terminal alkynes. The cationic complex $[(Et_2N)_3U][BPh_4]$ has been found to be also an efficient catalyst for the hydrosilylation of terminal alkynes. The chemoselectivity and regiospecificity of the reaction depend strongly on the nature of the alkyne, the solvent and the reaction temperature. The hydrosilylation reaction of the terminal alkynes with $PhSiH_3$ at room temperature produced a myriad of products among which the *cis*- and *trans*-vinylsilanes, the alkene and the silylalkyne are the major components. At higher temperatures, besides the products obtained at room temperature, the double hydrosilylated alkene, in which the two silicon moieties are connected at the same carbon atom, is obtained. The catalytic hydrosilylation of (TMS)C≡CH and $PhSiH_3$ with $[(Et_2N)_3U][BPh_4]$ was found to proceed only at higher temperatures. Mechanistically, the key intermediate seems to be the uranium–hydride complex $[(Et_2N)_2U\text{–}H][BPh_4]$, as evidenced by the lack of the dehydrogenative coupling of silanes. A plausible mechanistic scenario is proposed for the hydrosilylation of terminal alkynes taking into account the formation of all products.

Keywords: Organoactinide; π-Complexes; Alkyne complexes; Dimerization of alkynes; Hydrosilylation; Catalysis

1. Introduction

In recent years, the catalytic aspects of the organometallic complexes of d^0/f^n-block have attracted a major attention and have been in particular the focus of numerous investigations for the functionalization of

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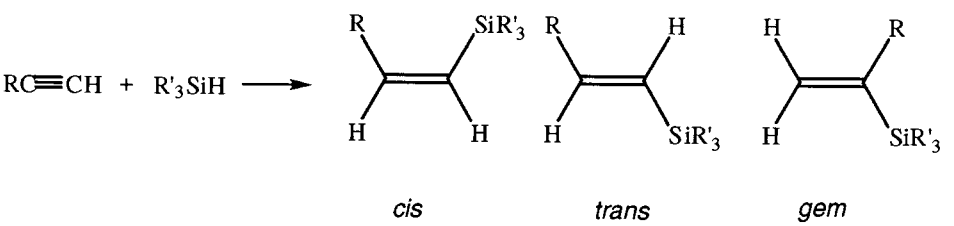
unsaturated organic molecules [1–14]. Metal-mediated oligomerization of terminal alkynes is currently of considerable interest because it can lead to a variety of organic enynes and oligoacetylene products [4,14] that are useful synthetic precursors for the synthesis of natural products [15] and also for organic conducting polymers [16]. Enynes are the simplest oligomerization products of alkynes and the key steps in their formation involve the generation of a M–C≡CR carbyl moiety, insertion of the alkyne to yield the M–C(H)=C(R)C≡CR alkenyl intermediate and protonolysis with additional alkyne to release the dimer and regenerate the MC≡CR species. Higher oligomers are formed by further insertion of alkyne into the M–C(H)=C(R)C≡CR species. Lately, we have demonstrated that organoactinides 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 [17]. For example, bulky alkynes reacted with high regioselectivity towards dimers and/or trimers whereas for non-bulky alkynes, the oligomerization yielded dimers to decamers with total lack of regioselectivity. The addition of primary amines, for An = Th, allowed the chemoselective formation of dimers whereas for An = U this control was not achieved [14b].

The metal-catalyzed hydrosilylation reaction, which is the addition of a Si–H bond across a carbon–carbon multiple bond, is one of the most important reactions in organosilicon chemistry and has been studied extensively for half a century [18]. The hydrosilylation reaction is used in the industrial production of organosilicon compounds (adhesives, binders and coupling agents), and in research laboratories as an efficient route to a variety of organosilicon compounds, silicon-based polymers and new type of dendrimeric materials [18]. Since the discovery of Speier's catalyst (H_2PtCl_6/^{i}PrOH) in 1957, [19] catalytic asymmetric hydrosilylation and new reactions related to hydrosilylation have been discovered and developed [18–20]. Interestingly, most of the research has been devoted to late-transition metal complexes [18–21]. More recently, metallocene complexes of either Group 3, 4, lanthanides and actinides, which exhibit distinctive features from those of the late transition complexes, have been reported to catalyze the hydrosilylation reaction of unsaturated hydrocarbons very effectively [22].

Considerable attention has been paid in recent years to the versatile and rich chemistry of vinylsilanes, which are considered as important building blocks in organic synthesis [23]. The synthesis of vinylsilanes has been extensively studied and one of the most convenient and straightforward methods is the hydrosilylation of alkynes [23–25]. In general, hydrosilylation of terminal alkynes produces the three different isomers, *cis*, *trans* and *geminal*, as a result of both 1,2 (*syn* and *anti*) and 2,1 additions, respectively, as shown in Reaction (1). The distribution of the products is found to vary considerably with the nature of the catalyst, substrates and also the specific reaction conditions [23–25].



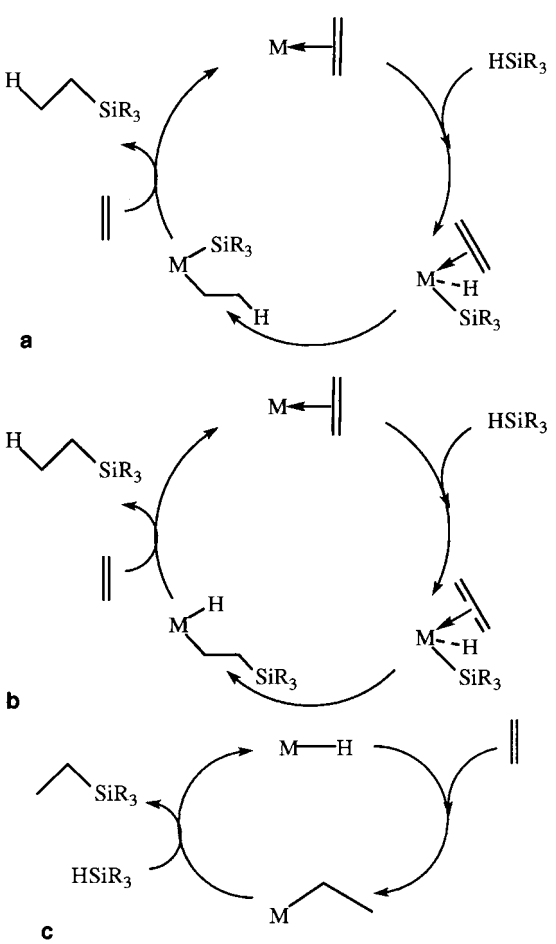
(1)

A number of mechanisms have been presented for the hydrosilylation process and one of the most widely accepted was first proposed by Chalk and Harrod in 1965 for the Pt-catalyzed hydrosilylation of alkenes [26]. The main feature of this mechanism (Scheme 1(a)) is the insertion of a coordinated alkene into a metal–hydrogen bond, followed by reductive elimination of the alkyl and silyl ligands. If the intermediate alkyl complex undergoes reversible β-hydride elimination and reinsertion with opposite regiochemistry, then the Chalk–Harrod mechanism provides an explanation for the olefin isomerization and deuterium scrambling during the hydrosilylation reactions [18a]. However, this mechanism is unable to explain the production of vinylsilanes from the hydrosilylation reaction of alkenes. In some cases vinylsilanes are produced more readily than the hydrosilylation product [27]. To account for this competing process, a number of different mechanisms, so called modified Chalk–Harrod mechanisms, have been proposed [28]. In the basic mechanism (Scheme 1(b)), an alkene inserts into a metal–silicon bond and the reductive elimination of the resulting β-silaalkyl and hydride ligands leads to the hydrosilylation product. A competing β-hydride elimination from the β-silaalkyl moiety permits the formation of the vinylsilane.

For organolanthanides and organoyttrium complexes, in the hydrosilylation of alkenes and for organoactinides, in the hydrosilylation of alkynes, the processes are proposed to proceed via the Chalk–Har-

rod mechanism (insertion of an olefin into a metal–hydride bond) with the classical oxidative addition–reductive elimination steps replaced with σ-bond metathesis reactions (Scheme 1(c)) [6,22].

In contrast to the neutral organoactinide complexes, homogeneous cationic d^0/f^n actinide complexes have been used as catalysts for the polymerization of α-olefins [29], similarly to their isolobal Group 4 complexes. Some heterogeneous complexes have been used for the rapid hydrogenation of aromatic molecules and C–H activation of alkanes [30]. Regarding alkyne activations with cationic Group 4 complexes, $Cp_2^*ZrMe^+$ selectively dimerizes ^{t}BuC≡CH to the head-to-tail dimer but converts ^{n}PrC≡CH and MeC≡CH into mixtures of dimers and trimers [31]. The less bulky Cp_2ZrMe^+ cation reacts with these alkynes to form catalytically inactive dinuclear compounds [32]. Thus, catalytic alkyne oligomerization is a useful probe of insertion and σ-bond metathesis reactivity of complexes. For cationic actinide complexes, virtually nothing is known regarding their reactivity with terminal alkynes [33]. Expanding their rich potential as homogeneous catalysts, in this publication we report the reactivity and selectivity of a well defined cationic actinide complex $[(Et_2N)_3U][BPh_4]$ as a catalytic precursor for the selective dimerization of a variety of terminal alkynes. In addition we have shown with as well as the spectroscopic characterization of the first uranium–alkyne π-complex as the key organometallic intermediate in the catalytic cycles; we present here a thorough kinetic, thermodynamic and mechanistic study. In addition, we present a comprehensive study on the reactivity of this cationic uranium complex in the hydrosilylation of terminal alkynes; This reaction seems to follow the hydride pathway rather than the silane route, as evidenced by the lack of dehydrogenative coupling of silanes.



Scheme 1. Proposed mechanisms for the hydrosilylation of alkenes: Chalk–Harrod (**1a**), modified Chalk–Harrod (**1b**) and modified Chalk–Harrod for early-transition metal complexes (**1c**).

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 4Å molecular sieve column. Hydrocarbon solvents (toluene-d_8, benzene-d_6, THF-d_8) 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 and phenylsilane (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) was dried over Na/K alloy and stored over activated molecular sieve (4 Å), degassed and freshly vacuum-distilled. $[(Et_2N)_3U][BPh_4]$ was prepared according to the literature [34]. NMR spectra were recorded on Bruker AM 200 and Bruker AM 400 spectrometers. Chemical shifts for ^{1}H- and ^{13}C-NMR are referenced to internal solvent resonances and are reported relative to tetramethylsilane. For ^{29}Si-NMR, $Si(TMS)_4$ was used as internal standard ($SiMe_3 = -7.80$ ppm), and the experiments were measured using either the INEPT or DEPT programs. GC–MS experiments were conducted with a GCMS (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.

2.2. General procedure for the catalytic oligomerization of alkynes

In a typical procedure, the amount of the specific alkyne was vacuum transferred into a J. Young NMR

tube containing 18 mg (0.0233 mmol) of $[(Et_2N)_3U][BPh_4]$ in 0.6 ml of toluene-d_8. The sealed tube was then heated in an oil bath to 110°C for 24 h. The organic products were vacuum transferred (10^{-6} mmHg) to another J. Young NMR tube, sealed and both residue and volatiles were characterized by ^{1}H-, ^{13}C- and 2D-NMR, GC–MS spectroscopy and by comparing with literature known compounds. Spectroscopic data of compounds **1b**, **1c**, **1d**, **2d**, **3d**, **4d**, **1e**, **3e**, **1g** are described in references [14] and [35].

2.2.1. Catalytic dimerization of MeC≡CH

As described above, 48 mg (1.2 mmol) of MeC≡CH (measured at low temperature, −40°C, where the alkyne is a liquid) were catalytically dimerized to head-to-tail dimer $H_2C{=}C(Me)C{\equiv}CMe$ (**1a**) in 94% yield (the remaining 6% was found to be starting material). ^{1}H-NMR (200 MHz, toluene-d_8), δ 5.30 (s, 1 H, H*H*C=C), 5.06 (s, 1 H, *H*HC=C), 1.83 (s, 3 H, C=CC*H*$_3$), 1.65 (s, 3 H, C≡CC*H*$_3$). ^{13}C-NMR (50 MHz, toluene-d_8), δ 136.4 (s, $H_2C{=}C$), 119.7 (t, $J = 159.5$ Hz, $H_2C{=}C$), 84.7 (s, *C*≡CMe), 81.5 (s, C≡*C*Me), 23.3 (q, $J = 127.6$ Hz, $H_2C{=}CCH_3$), 3.2 (q, $J = 131.3$ Hz, C≡C*C*H$_3$).

2.2.2. Catalytic dimerization of ^{n}BuC≡CH

As described above, 0.13 ml (1.1 mmol) of ^{n}BuC≡CH were catalytically dimerized into the head-to-tail *geminal* dimer $H_2C{=}C(^nBu)C{\equiv}C^nBu$ (**1b**) in 94% yield.

2.2.3. Catalytic dimerization of ^{i}PrC≡CH

As described above, 0.13 ml (1.248 mmol) of ^{i}PrC≡CH were catalytically dimerized into the *gem*-$H_2C{=}C(^iPr)C{\equiv}C^iPr$ (**1c**) in 75% yield.

2.2.4. Catalytic oligomerization of TMSC≡CH

As described above, 0.13 ml (0.903 mmol) of TMSC≡CH were catalytically oligomerized to a mixture of the *gem*(**1d**):*trans*(**2d**):*cis*(**3d**) dimers = 43:7:16, respectively, and the head-to-tail-to-head trimer, TMSC(H)=C(H)–C(H)=C(TMS)C≡CTMS (**4d**) in 33% yield.

2.2.5. Catalytic dimerization of ^{t}BuC≡CH

As described above, 0.13 ml (1.036 mmol) of ^{t}BuC≡CH were catalytically oligomerized to a mixture of *gem*-$H_2C{=}C(^tBu)C{\equiv}C^tBu$ (**1e**) in 74% yield, and the *cis*-^{t}BuC(H)=C(H)C≡C^{t}Bu (**3e**) in 25% yield.

2.2.6. Catalytic oligomerization of MeC≡CD

An excess of propyne (~5 ml) was condensed at −100°C into a Schlenk tube containing 3.13 ml (5.0 mmol) of a 1.6 M solution of ^{n}BuLi in hexane. The mixture was stirred for 30 min and then the temperature was allowed to rise to room temperature (r.t.). Evaporation of the solvent gave a white solid. The Schlenk tube was cooled to −85°C and under argon flush 0.1 ml (5.5 mmol) of D_2O was added. After stirring for 10 min, the mixture was warmed to r.t. and the evolved gas, MeC≡CD, was transferred and trapped into a J. Young NMR tube containing 10 mg (0.013 mmol) of $[(Et_2N)_3U][BPh_4]$ in 0.6 ml of toluene-d_8. The sealed tube was heated in an oil bath at 110°C for 24 h. The volatiles were vacuum transferred to another J. Young NMR tube and characterized by NMR methods to be the *gem*-$D_2C{=}C(Me)C{\equiv}CMe$ [1f] in 92% yield with 8% of trimers. ^{1}H-NMR: (200 MHz, toluene-d_8): δ 1.83 (s, 3 H, C=CC*H*$_3$), 1.64 (s, 3 H, C≡CC*H*$_3$). ^{13}C-NMR: (50 MHz, toluene-d_8): δ 119.5 (quintet, $J = 35$ Hz, $D_2C{=}C$), 118.0 (s, $D_2C{=}C$), 84.6 (s, *C*≡CMe), 81.2 (s, C≡*C*Me), 23.3 (q, $J = 127.6$ Hz, C=C*C*H$_3$), 3.3 (q, $J = 131.3$ Hz, C≡C*C*H$_3$).

2.2.7. Catalytic oligomerization of PhC≡CH

As described above, 0.13 ml (1.162 mmol) of PhC≡CH were catalytically oligomerized to a mixture of *gem*-dimer (**1g**) (32%) and trimers (58%).

2.3. Preparation of $[(Et_2N)_2U(C{\equiv}C^tBu)(HC{\equiv}C^tBu)][BPh_4]$

In a typical procedure, 61.6 mg (7.97×10^{-2} mmol) of $[(Et_2N)_3U][BPh_4]$ was charged in an NMR tube and dissolved in 0.5 ml of benzene-d_6 which was added by vacuum transfer through a greaseless vacuum line. The solution was transferred in the glovebox by a gas-tight syringe into another NMR tube containing 0.0196 ml (15.9×10^{-2} mmol) of ^{t}BuC≡CH in 0.5 ml of benzene-d_6. The mixture was stirred at r.t. for 12 h, leading to the formation of the complex $[(Et_2N)_2U(C{\equiv}C^tBu)(HC{\equiv}C^tBu)][BPh_4]$ and traces of the *gem*-dimer $H_2C{=}C(^tBu)(C{\equiv}C^tBu)$. The complex $[(Et_2N)_2U(C{\equiv}C^tBu)(HC{\equiv}C^tBu)][BPh_4]$ decomposes totally in 24 h.

^{1}H-NMR (200 MHz, benzene-d_6): δ −2.14 (s, 1H, *H*C), 1.24 (s, 9H, C(C*H*$_3$)$_3$), 1.26 (b, 6H, CH$_2$C*H*$_3$), 1.28 (b, 6H, CH$_2$C*H*$_3$), 1.30 (s, 9H, C(C*H*$_3$)$_3$), 7.19–7.31 (m, 20H, *Ph*), 25.07 (b, 8H, C*H*$_2$CH$_3$). ^{13}C{H}-NMR (200 MHz, benzene-d_6): δ −19.85 (d, $J = 250$ Hz, H*C*≡C), 15.25 (q, $J = 119$ Hz, *Me*$_3$CC≡CH), 24.33 (s, *C*Me$_3$), 27.54 (q, $J = 115$ Hz, *Me*$_3$CC≡C), 31.26 (q, $J = 122$ Hz, *C*H$_3$CH$_2$), 31.76 (q, $J = 122$ Hz, *C*H$_3$CH$_2$), 44.51 (t, $J = 144$ Hz, CH$_3$*C*H$_2$), 57.76 (bs, Me$_3$*C*–C≡CH), 104.96 (bs, Me$_3$C–*C*≡CU), 123.06 (bs, Me$_3$C–C≡*C*U), 139.4–151.97 (m, *Ph*). IR (dry parathone oil) cm^{-1}: 3079, 2967, 2934, 2908, 2875, 2059 (C≡C str), 2032 (C≡C str), 1486, 1368, 1275, 1210, 1157, 1045, 1005, 742, 709 (the IR of the free ^{t}BuC≡CH alkyne under the same condition is: 3313(C–H str), 2978, 2048, 2036, 2820, 2108 (C≡C str), 1484, 1465, 1370, 1250, 1212, 638.

2.4. Kinetic study of controlled oligomerization

In a typical experiment, a NMR sample was prepared as described in the typical NMR scale catalytic reactions section but maintained at −78°C until kinetic measurements were initiated. The sealed tube was heated in a temperature controlled oil bath and at time intervals NMR data were acquired using eight scans per time interval with a long pulse delay to avoid saturation of the signal. The kinetics were usually monitored by the intensity changes in the substrate resonances and in the product resonances over three or more half-lives. The substrate concentration (C) was measured from the area (A_s) of the ^{1}H-normalized signal of the solvent (A_b). All the data collected could convincingly fit ($R > 0.98$) by least-squares to Eq. (1) where C_o ($C_o = A_{so}/A_{bo}$) is the initial concentration of substrate, $C(A_s/A_b)$ is the substrate concentration at time t.

$$mt = \log(C/C_0) \quad (1)$$

The ratio of catalyst to substrate was accurately measured by calibration with internal $FeCp_2$. Turnover frequencies (N_t, h^{-1}) were calculated from the least-squares determined slopes (m) of the resulting plots. Typical initial alkyne concentrations were in the range 0.052–5.92 M and typical catalyst concentrations were in the range 9.7–35 mM.

2.5. General procedure for the catalytic hydrosilylation of terminal alkynes

In a typical procedure, the amount of the specific alkyne and $PhSiH_3$ were vacuum transferred in a high vacuum line into a J. Young NMR tube containing 10 mg of $[(Et_2N)_3U][BPh_4]$ in 0.6 ml of THF-d_8 or benzene-d_6. The sealed tube was then heated in an oil bath or kept at r.t. until 100% conversion of the alkyne was detected by the disappearance of the acetylenic hydrogen by ^{1}H-NMR spectroscopy. The organic products were vacuum transferred (10^{-6} mm Hg) to another J. Young NMR tube, sealed and both residue and volatiles were identified by ^{1}H-, ^{13}C-, ^{29}Si-, 2D-NMR (COSY, C–H correlation, Si–H correlation, NOESY), GC–MS spectroscopy and by comparing with literature known compounds. Spectroscopic data for compounds **5b–e**, **6b–e** and **7b–e** are described in the literature [22q].

2.5.1. Hydrosilylation of ^{i}PrC≡CH with $PhSiH_3$ catalyzed by $[(Et_2N)_3U][BPh_4]$

(a) According to the general procedure described above, 100% conversion was obtained by the reaction of 0.098 ml of ^{i}PrC≡CH (0.96 mmol) and 0.092 ml of $PhSiH_3$ (0.75 mmol), catalyzed by $[(Et_2N)_3U][BPh_4]$ (0.013 mmol) in benzene-d_6 at r.t., for 48 h, producing *trans*-^{i}PrCH=CHSiH_2Ph (**5c**) (27.5%), *cis*-^{i}PrCH=CHSiH_2Ph (**6c**) (10.4%), ^{i}PrC≡CSiH_2Ph (**7c**) (21.8%), ^{i}PrCH=CH_2 (**8c**) (28.4%), *gem*-H_2C=C(^{i}Pr)C≡C^{i}Pr (**1c**) (9.5%) and Et_2NSiH_2Ph (**9**) (2.4%).

(b) According to the general procedure described above, 100% conversion was obtained by the reaction of 0.098 ml of ^{i}PrC≡CH (0.96 mmol) and 0.092 ml of $PhSiH_3$ (0.75 mmol), catalyzed by $[(Et_2N)_3U][BPh_4]$ (0.013 mmol) in benzene-d_6 at 78°C, for 6 h, producing *trans*-^{i}PrCH=CHSiH_2Ph (**5c**) (20.5%), *cis*-^{i}PrCH=CHSiH_2Ph (**6c**) (16.9%), ^{i}PrC≡CSiH_2Ph (**7c**) (26.4%), ^{i}PrCH=CH_2 (**8c**) (20.5%), *gem*-H_2C=C(^{i}Pr)C≡C^{i}Pr (**1c**) (7.7%) and traces of *gem*-H_2C=C(^{i}Pr)CH=C(^{i}Pr)C≡C(^{i}Pr) (1.5%), *trans*-^{i}PrCH=CHSi(H)(Ph)C≡C^{i}Pr (1.5%), ^{i}PrCH=C(SiH_2Ph)$_2$ (1.9%) and Et_2NSiH_2Ph (**9**) (2.4%) as observed from GC–MS measurements.

(c) According to the general procedure described above, 100% conversion was obtained by the reaction of 0.078 ml of ^{i}PrC≡CH (0.768 mmol) and 0.092 ml of $PhSiH_3$ (0.75 mmol), catalyzed by $[(Et_2N)_3U][BPh_4]$ (0.013 mmol) in THF-d_8 at 65°C, for 12 h, producing *trans*-^{i}PrCH=CHSiH_2Ph (**5c**) (16.0%), *cis*-^{i}PrCH=CHSiH_2Ph (**6c**) (4.3%), ^{i}PrC≡CSiH_2Ph (**7c**) (29.9%), ^{i}PrCH=CH_2 (**8c**) (31.0%), *gem*-H_2C=C(^{i}Pr)C≡C(^{i}Pr) (**1c**) (15.5%) and Et_2NSiH_2Ph (**9**) (3.2%).

2.5.2. Hydrosilylation of ^{t}BuC≡CH with $PhSiH_3$ catalyzed by $[(Et_2N)_3U][BPh_4]$

(a) According to the general procedure described above, 100% conversion was obtained by the reaction of 0.098 ml of ^{t}BuC≡CH (0.79 mmol) and 0.098 ml of $PhSiH_3$ (0.79 mmol), catalyzed by $[(Et_2N)_3U][BPh_4]$ (0.013 mmol) in benzene-d_6 at r.t. for 48 h, producing *trans*-^{t}BuCH=CHSiH_2Ph (**5e**) (53.8%), *cis*-^{t}BuCH=CHSiH_2Ph (**6e**) (10.5%), ^{t}BuC≡CSiH_2Ph (**7e**) (2.0%), ^{t}BuCH=CH_2 (**8e**) (12.0%), ^{t}BuCH=C(SiH_2-Ph)Si(H)(Ph)C≡C^{t}Bu (**11e**) (15.5%), Et_2NSiH_2Ph (**9**) (3.2%) and trace amounts of *gem*-H_2C=C(^{t}Bu)C≡C^{t}Bu (**1c**) (0.8%) and ^{t}BuCH=CHSi(H)(Ph)C≡C^{t}Bu (2.2%).

2.5.2.1. Spectroscopic data for ^{t}BuCH=C(SiH_2-Ph)Si(H)(Ph)C≡C^{t}Bu (**11e**).

^{1}H-NMR (200 MHz, benzene-d_6): δ 7.12–7.68 (m, 10 H, Ph), 7.34 (s, 1 H, C*H*-based on 2D C–H correlation to the signal at 176.6 ppm), 5.27 (s, 1 H, PhSi*H*), 5.1 (s, 2 H, PhSiH_2), 1.09 (s, 9 H, C(CH_3)$_3$), 1.02 (s, 9 H, C(CH_3)$_3$). ^{13}C-NMR (50 MHz, benzene-d_6): δ 176.6 (s, H*C*^{t}Bu), 137.2, 133.1, 131.6 (*C*–H–Ph), 132.6 (s, *ipso C–Si*), 77.1 (C≡C), 42.4 (s, *C*Me$_3$), 30.8 (s, C(*C*H$_3$)$_3$), 30.4 (s, C(*C*H$_3$)$_3$). The quaternary carbons for the ^{t}Bu and acetylide moieties were not detected due to large relaxation times. ^{29}Si-NMR (79.5 MHz, benzene-d_6): δ 21.4 (d, $J = 210$ Hz, Ph*Si*H), 4.0 (t, $J = 205$ Hz, Ph*Si*H_2). GC–MS data: m/z 376 [M^+], 375 [$M^+ - H$], 361 [M^+

Table 1
Product distribution of the $[(Et_2N)_3U][BPh_4]$ catalyzed oligomerization of terminal alkynes (RCCH)[a]

R in RCCH	*gem*-H_2C=C(R)CCR (**1**) (%)	*cis*-H_2C=C(R)CCR (**3**) (%)	Trimer (**4**) (%)
Me (**a**)	94	–	–
^{n}Bu (**b**)	94	–	–
^{i}Pr (**c**)	75	–	–
TMS (**d**) [b]	43	16	33
^{t}Bu (**e**)	74	25	–
Me (**f**) [c]	92	–	8
Ph (**g**)	32	–	58

[a] The reaction was carried out in toluene-d_8 at 110°C.
[b] The *trans*-H(TMS)C=CHCCTMS (**2d**; 7%) was also observed.
[c] The alkyne in this entry is MeCCD.

$-CH_3]$, 333 $[M^+ - C_3H_7]$, 319 $[M^+ - {}^t$Bu, 100%), 187 $[{}^t$BuC≡CSiHPh$^+]$, 159 $[{}^t$BuC≡CSiH_2Ph$^+ - C_2H_5]$, 145 $[{}^t$BuC≡CSiH_2Ph$^+ - C_3H_7]$, 131 $[{}^t$BuC≡CSiH_2Ph$^+ - {}^t$Bu], 105 [PhSi$^+$].

(b) According to the general procedure described above, 100% conversion was obtained by the reaction of 0.098 ml of ^{t}BuC≡CH (0.79 mmol) and 0.098 ml of $PhSiH_3$ (0.79 mmol), catalyzed by $[(Et_2N)_3U][BPh_4]$ (0.013 mmol) in benzene-d_6 at 78°C for 6 h, producing *trans*-^{t}BuCH=CHSiH_2Ph (**5e**) (35.8%), *cis*-^{t}BuCH=CHSiH_2Ph (**6e**) (15.8%), ^{t}BuCH=CH_2 (**8e**) (17.4%), ^{t}BuCH=C(SiH_2Ph)Si(H)(Ph)C≡C^{t}Bu (**11e**) (21.7%), Et_2NSiH_2Ph (**9**) (4.2%) and trace amounts of $PhSiH_2$–SiH_2Ph (2.3%), ^{t}BuCH=C(SiH_2Ph)$_2$ (0.9%) and ^{t}BuCH=CHSi(H)(Ph)C≡C^{t}Bu (1.9%).

2.5.3. Hydrosilylation of ^{n}BuC≡CH with $PhSiH_3$ catalyzed by $[(Et_2N)_3U][BPh_4]$

According to the general procedure described above, 100% conversion was obtained by the reaction of 0.117 ml of ^{n}BuC≡CH (1.0 mmol) and 0.118 ml of $PhSiH_3$ (0.96 mmol), catalyzed by $[(Et_2N)_3U][BPh_4]$ (0.013 mmol) in benzene-d_6, at 78°C for 6 h, producing *trans*-^{n}BuCH=CHSiH_2Ph (**5b**) (25.7%), *cis*-^{n}BuCH=CHSiH_2Ph (**6b**) (16.9%) ^{n}BuC≡CSiH_2Ph (**7b**) (19.3%), ^{n}BuCH=CH_2 (**8b**) (26.9%), *gem*-H_2C=C(^{n}Bu)C≡C^{n}Bu (**1b**) (5.0%) Et_2NSiH_2Ph (**9**) (2.7%), ^{n}BuCH=CH-(SiHPh)$_2$ (2.9%) and trace amounts of *gem*-H_2C=C(^{n}Bu)CH=C(^{n}Bu)C≡C^{n}Bu (0.5%).

2.5.4. Hydrosilylation of (TMS)C≡CH with $PhSiH_3$ catalyzed by $[(Et_2N)_3U][BPh_4]$

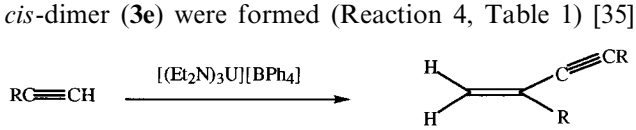
According to the general procedure described above, 100% conversion was obtained by the reaction of 0.118 ml of (TMS)C≡CH (0.834 mmol) and 0.107 ml of $PhSiH_3$ (0.868 mmol), catalyzed by $[(Et_2N)_3U][BPh_4]$ (0.013 mmol) in benzene-d_6, at 78°C for 24 h, producing *trans*-(TMS)CH=CHSiH_2Ph (**5d**) (12.2%), *cis*-(TMS)CH=CHSiH_2Ph (**6d**) (18.5%) (TMS)C≡CSiH_2Ph (**7d**) (21.3%), (TMS)CH=CH_2 (**8d**) (10.6%), Et_2NSiH_2Ph (**9**) (2.6%) and the oligomerization products, *gem*-H_2C=C(TMS)C≡C(TMS) (**1d**) (11.4%) *trans*-H(TMS)-C=CHC≡C(TMS) (4.3%), *cis*-H(TMS)C=CHC≡C(TMS) (1.1%) and *trans*-(TMS)CH=CH–CH=C(TMS)C≡C(TMS) (12.2%), *gem*-H_2C=C(TMS)CH=C(TMS)C≡C(TMS) (5.7%). No reaction was observed at r.t. For the latter compounds, the stereochemistry was assigned by comparison of their GC–MS retention times to pure compounds [14a].

3. Results and discussion

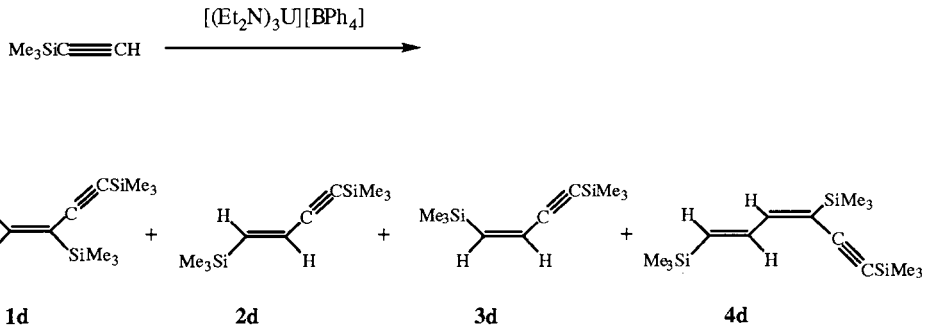
The products from the reactions of the terminal alkynes RC≡CH are noted by **a**, **b**, **c**, **d**, **e** and **g** corresponding to R = Me, ^{n}Bu, ^{i}Pr, TMS, ^{t}Bu and Ph, respectively.

3.1. Catalytic dimerization of alkynes

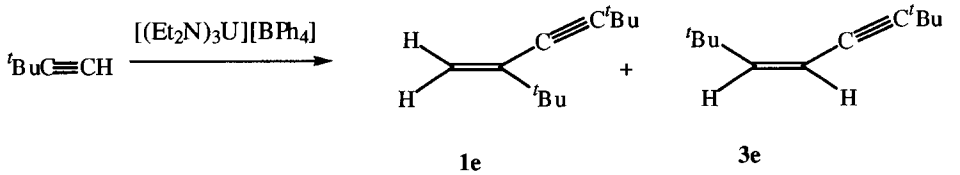
Reaction of $[(Et_2N)_3U][BPh_4]$ [34] with an excess of terminal alkyne RC≡CH (R = Me, ^{n}Bu, ^{i}Pr; toluene-d_8, alkyne/$[(Et_2N)_3U][BPh_4]$ ratio 50: 1) resulted in the chemo- and regio-selective catalytic formation of the head-to-tail *gem*-dimers (**1a–c**) with no formation of the *trans* isomers or major oligomers (Reaction 2). For PhC≡CH, the reaction was less chemoselective allowing the formation of trimers (*geminal* dimer (**1g**): trimers ratio = 32:58). For TMSC≡CH, besides the formation of the *geminal* head-to-tail dimer (**1d**), the *trans*-head-to-head dimer (**2d**), and the regioselective head-to-tail-to-head-trimer (*E*,*E*)-1,4,6-tris(trimethylsilyl)-1-3-hexadien-5-yne (**4d**), the unexpected head-to-head *cis* dimer (**3d**) was also formed (Reaction 3) [35]. Likewise, for ^{t}BuC≡CH, the *geminal* dimer (**1e**) and the unexpected *cis*-dimer (**3e**) were formed (Reaction 4, Table 1) [35].



R = Me (**1a**)
R = ^{n}Bu (**1b**)
R = ^{i}Pr (**1c**) (2)



(3)



(4)

Mechanistically, the presence of relatively low-lying empty σ-bonding orbitals, the relatively polar metal–ligand bonds, and the absence of energetically accessible metal oxidation states for oxidative addition/reductive elimination processes, [36] would implicate a 'four-center' heterolytic transition state in the metal–carbon bond cleavage. Thus, the reaction of the metal acetylide with another terminal alkyne will be in a *syn* mode, and the σ-bond metathesis step of the alkenyl complex with the terminal alkyne hydrogen (replacement of the metal center by a hydrogen of the terminal alkyne) will produce the *trans* product. Hence, the formation of dimers **3d** and **3e** argues for an isomerization pathway before the products are released from the metal center.

It is important to point out that in the oligomerization of terminal alkynes promoted by the cationic complexes $[Cp^*_2AnMe][B(C_6F_5)_4]$ (An = Th, U), only the *geminal* dimer was formed with no trace formation of either *cis* or *trans* dimers [14b]. In addition, in the oligomerization reaction promoted by $Cp^*_2AnMe_2$, the *cis*-dimer was not observed [14a].

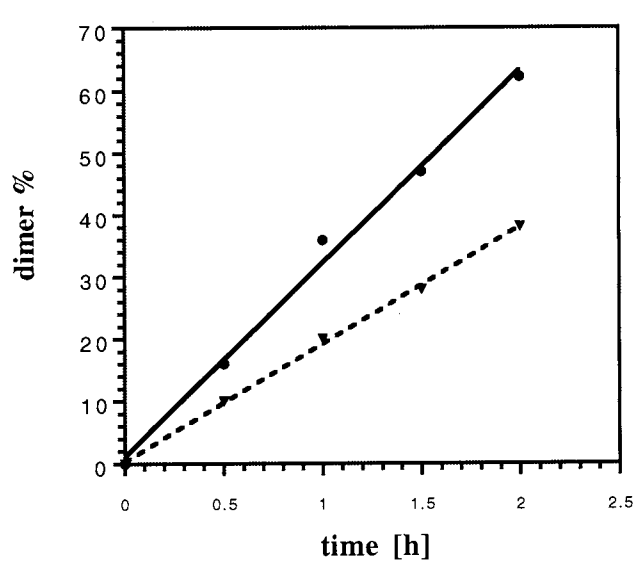
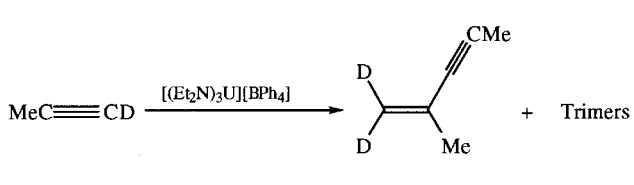


Fig. 1. Rate of catylic dimerization of ^{n}BuC≡CH by $[(Et_2N)_3U][BPh_4]$. (—) without the addition of external diethylamine; (- - -) with addition of an excess of diethyl amine.

In the reaction of $[(Et_2N)_3U][BPh_4]$ with terminal alkynes, one equivalent of the Et_2NH amine was released to the solution, as observed in the NMR, forming presumably the bisamido acetylide cationic complex $[(Et_2N)_2U–C{\equiv}CR][BPh_4]$. This is a slow equilibrium process and the addition of different equimolar amounts of Et_2NH to the reaction mixture led to a lowering of the reaction rate linearly (Fig. 1).

Considering that in the reactions of alkynes the amount of the free amine formed is stoichiometric with that of the catalyst, it seems plausible that the free terminal alkyne is the major protonolytic agent releasing the dimer from the metal–alkenyl complex. To corroborate this protonolytic hypothesis, a novel strategy was implemented to increase the chemoselectivity towards a *trimer*. This was accomplished by providing a kinetic delay for the presumed fast protonolysis by the alkyne, to allow trimer formation, through replacement of the terminal hydrogen at the alkyne with deuterium (Reaction 5). This strategy indeed enabled us to influence the chemoselectivity of the oligomerization allowing the formation of the deuterated *geminal* dimer (**1f**) and some deuterated trimer formation (measured by GC–MS) [37].



(5)

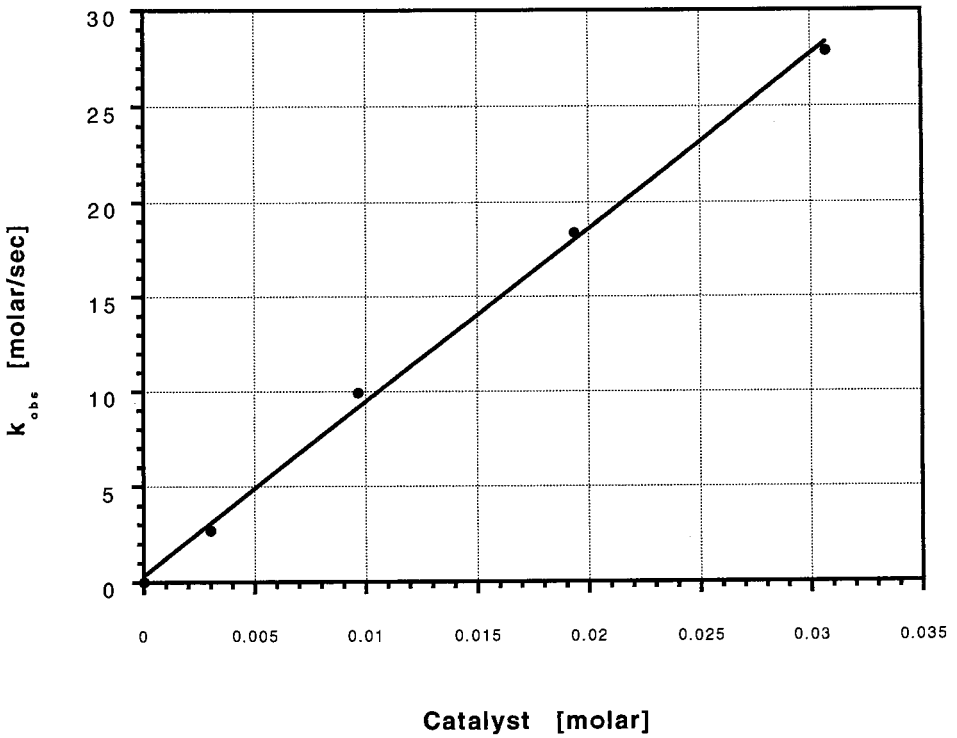


Fig. 2. Determination of the reaction order in $[(E_2N)_3U][BPh_4]$ concentration for the dimerization of ^{n}BuC≡CH in benzene-d_6 at 25°C.

Kinetic measurements on the oligomerization reaction of ^{n}BuC≡CH were studied by in situ ^{1}H-NMR spectroscopy. The reaction of an excess of ^{n}BuC≡CH was controlled with constant catalyst concentration until the complete consumption of the substrate. The disappearance of the C≡CH ^{1}H resonance ($\delta = 2.28$) was normalized. The turnover frequency of the reaction was calculated from the slope of the kinetic plots of substrate to catalyst ratio vs. time. When the initial concentration of the terminal alkyne is held constant and the concentration of the catalytic precursor is varied over a ca. fourfold concentration range (9.7–35 mM), a plot of reaction rate versus precatalyst concentration indicates that the reaction is first-order dependent in precatalyst, in analogy with the oligomerization of terminal alkynes promoted by $Cp^*_2AnMe_2$ (Fig. 2) [14]. When the concentration of the catalyst is maintained at a constant and the concentration of the alkyne is varied over a 10-fold concentration range (0.052–5.92 M) (Fig. 3), a plot of the reaction rate versus alkyne concentration shows a two domain behavior. At low concentrations, an inverse proportionality is observed, indicating that the reaction is in an inverse first order, and at higher concentrations, the reaction exhibits a zero order in alkyne. An inverse proportionality in catalytic systems is consistent with an equilibrium before the rate-determining step. The change from an inverse rate to a zero rate is compatible with two equilibrium processes. One of those is routing the complex out of the catalytic cycle (inverse order), whereas the second process, only at higher concentrations, is the rate-limiting step toward the dimer formation.

The derived activation parameters for the dimerization of ^{n}BuC≡CH (Fig. 4) are characterized by a rather small enthalpy of activation ($\Delta H^\dagger = 15.6(3)$ kcal mol^{-1}) and a negative entropy of activation ($\Delta S^\dagger = -11.4(6)$ eu). This $\Delta S^\dagger$ parameter suggests an ordered transition state with considerable bond-making to compensate for bond breaking. Interestingly, the oligomerization of TMSC≡CH by $Cp^*_2AnMe_2$, which proceeds via a four-centered-transition state, exhibits rather similar enthalpy of activation ($\Delta H^\dagger = 11.1(3)$ kcal mol^{-1}) although a larger negative entropy of activation ($\Delta S^\dagger = -45(5)$ eu) [14].

A possible mechanism for the dimerization of ^{n}BuC≡CH is proposed in Scheme 2. The mechanism consists of a sequence of well-established elementary reactions such as terminal alkyne insertion into a metal–carbon σ-bond and σ-bond metathesis [12]. The initial step in the catalytic cycle is the alkyne C–H activation by the cationic uranium amide complex and the formation of the bisamido carbyl complex $[(Et_2N)_2U–C≡C^nBu][BPh_4]$ (**A**) together with Et_2NH (step 1) [38]. Complex **A** may either be in equilibrium with an alkyne forming the π-alkyne acetylide uranium complex **B**, which drives the active species out of the catalytic cycle (inverse rate dependence), or undergo with an alkyne a head-to-tail insertion into the uranium–carbon σ-bond, yielding the substituted uranium alkenyl complex **C** (step 2) [39]. This complex undergoes a σ-bond metathesis with an additional alkyne

(step 3) leading to the corresponding dimer and regenerating the active carbyl complex **A** [40].

Complex **B** (for R = ^{t}Bu) has been trapped and its structure determined spectroscopically. The ^{1}H- and ^{13}C-NMR spectra of complex **B** show sharp lines as found for other actinide (IV) type of complexes. The ^{1}H-NMR spectrum exhibits one acetylide signal (≡C–H) at $\delta = -2.14$ which was found to correlate in the DEPT and in the 2D C–H correlation experiments to a carbon at $\delta = -19.85$, exhibiting a coupling constant of $^1J = 250$ Hz. In addition, two ^{t}Bu group signals were found in either the ^{1}H-, ^{13}C-NMR, DEPT or C–H correlation spectra. These results clearly indicate that free alkyne must be coordinated to the metal center. A confirmation of the formation of an alkyne η^2-complex, as compared to an acetylide complex or to a free alkyne

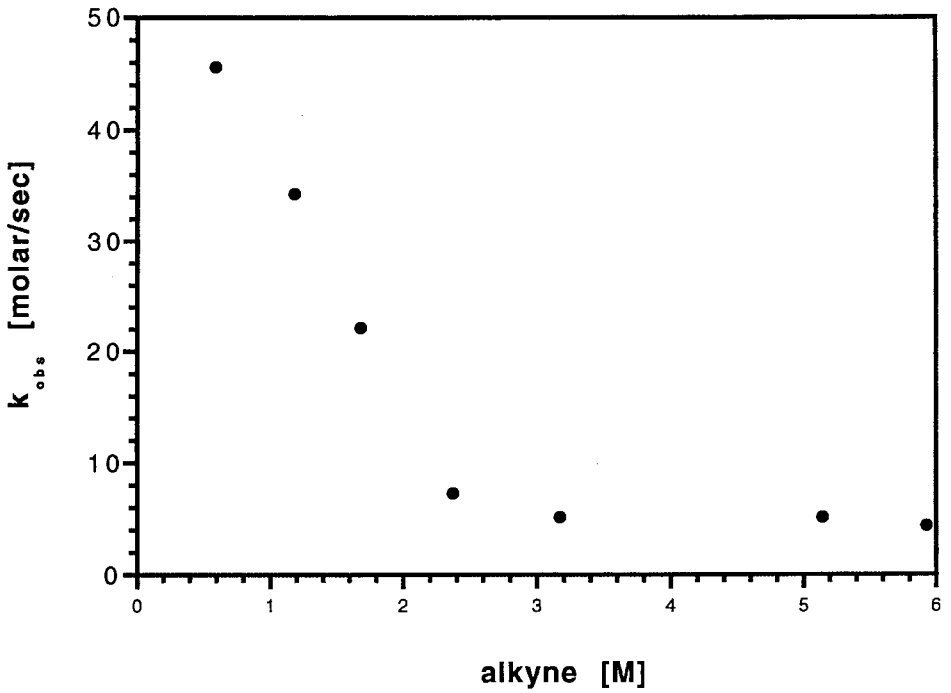


Fig. 3. Determination of the reaction order in alkyne concentration for the dimerization of ^{n}BuC≡CH mediated by $[(Et_2N)_3U][BPh_4]$ as the precatalyst in benzene-d_6 at 25°C.

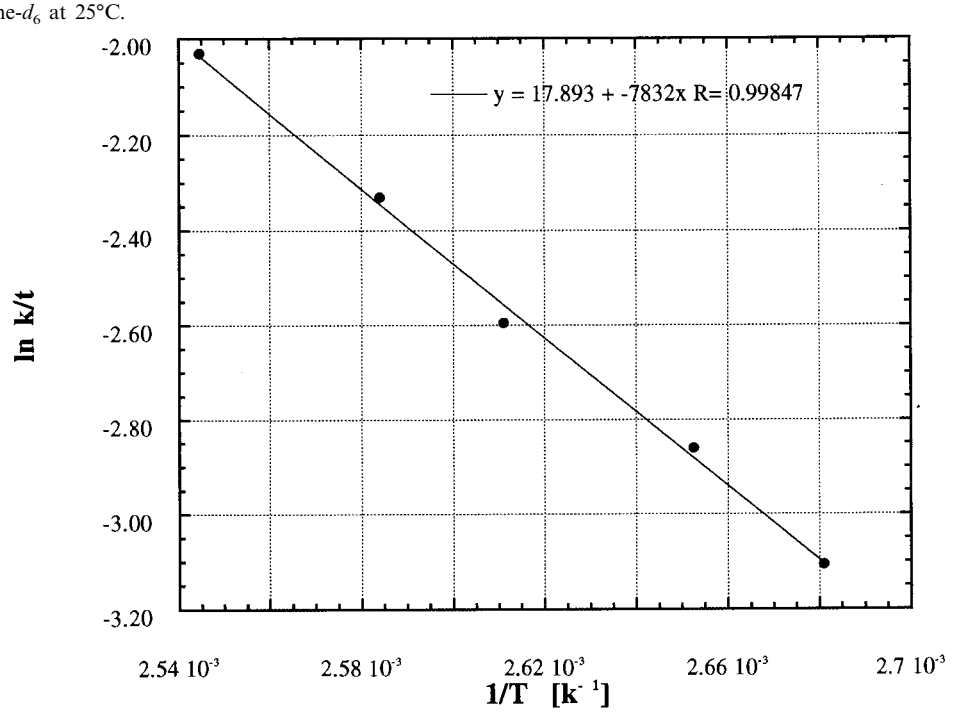
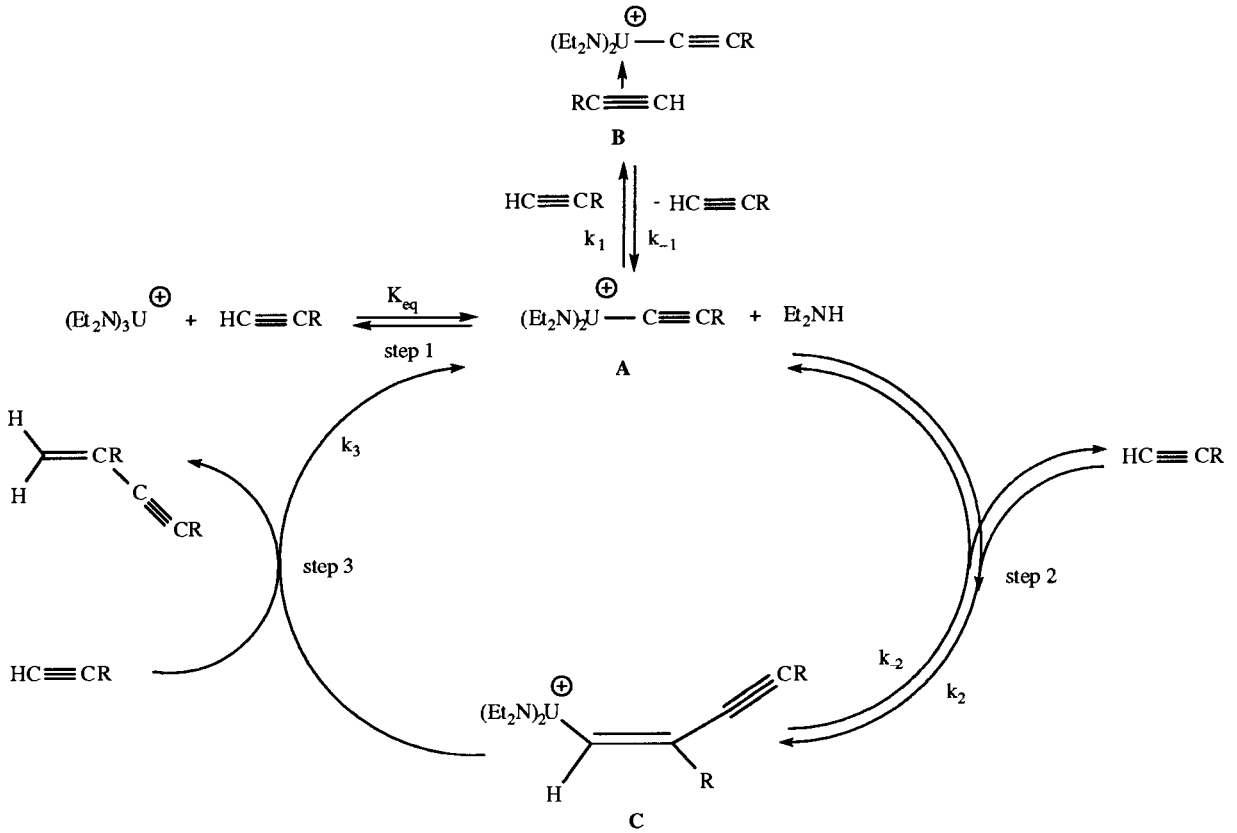


Fig. 4. Erying plot for the dimerization of ^{n}BuC≡CH using $[(E_2N)_3U][BPh_4]$ as the precatalyst in toluene-d_8. This line represents the least-squares fit to the data points.



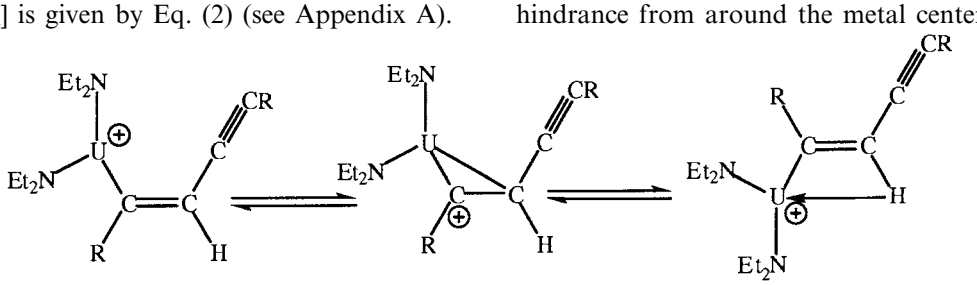
Scheme 2. Plausible mechanism for the dimerization of terminal alkynes promoted by $[(Et_2N)_3U][BPh_4]$.

has been acquired by FT-IR spectroscopy. The C≡C stretching of the free alkyne (2108 cm^{-1}) disappears giving rise to two signals at low frequencies, as expected for η^2-transition metal complexes, one at 2032 cm^{-1} similar to acetylide lanthanides, and the second one at 2059 cm^{-1} [12]. The turnover-limiting step for the catalytic dimerization was found to be the insertion of the alkyne into the uranium–carbyl complex **A** (step 2). This result implies 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 are faster than the insertion of the alkyne into complex **A**. In addition, this result also suggests that trimers are only expected if a kinetic delay in the protonolysis is induced corroborating our observations.

Thus, the derived rate law for the oligomerization of terminal alkynes promoted by the cationic complex $[(Et_2N)_3U][BPh_4]$ is given by Eq. (2) (see Appendix A).

$$v = \frac{k_{-1}k_2[\text{cat}]}{k_1 + k_2 - \dfrac{k_2 k_{-2}}{k_3[\text{alkyne}]}} \tag{2}$$

For sterically demanding alkyne substituents (TMS, ^{t}Bu), it seems essential that the protonolysis step rate is lower than that of the isomerization of the metalla–alkenyl complex **C′**, allowing the formation of the unexpected *cis*-dimer. This process takes place probably through a metalla-cyclopropyl cation, alike the 'envelope isomerization' mechanism (Reaction 6) [41]. The preference towards the *cis*-isomer is possibly due to the β-hydrogen interaction (agostic interaction) to the metal center. In addition, if a metal–acetylide complex is formed for **C′**, the bulkier alkynes will promote the isomerization process (Reaction 6) to remove the steric hindrance from around the metal center.



(6)

3.2. Catalytic hydrosilylation reactions of alkynes

3.2.1. Reaction scope at room temperature

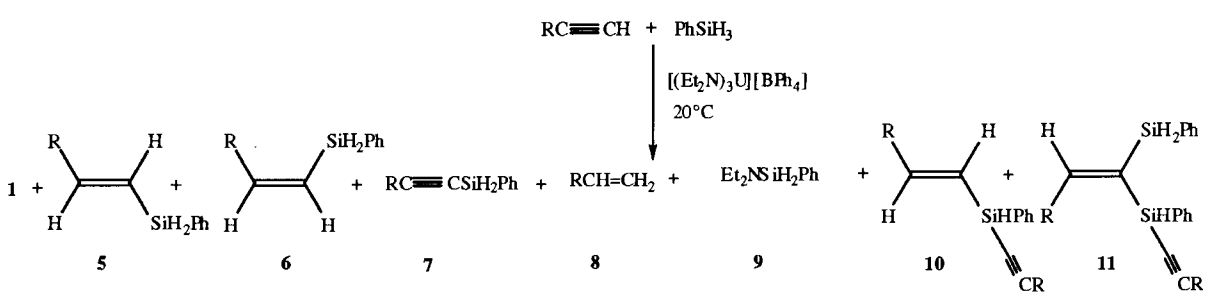
The hydrosilylation reaction of terminal alkynes promoted by $Cp^*_2AnMe_2$ (An = Th, U) have been thoroughly investigated, showing that the mechanism proceeds by the intermediacy of the corresponding hydride complex (Chalk–Harrod mechanism) [22g,26]. A conceptual question regards the possibility to form a similar cationic hydride complex, as an intermediate, in the catalytic hydrosilylation of terminal alkynes promoted by $[(Et_2N)_3U][BPh_4]$. The r.t. reaction in benzene of $[(Et_2N)_3U][BPh_4]$ with an excess of terminal alkynes RC≡CH (R = ^{i}Pr, ^{t}Bu) and $PhSiH_3$ resulted in the catalytic formation of a myriad of products showing the large reactivity of this complex. The products observed to account for 100% conversion with respect to the alkyne were: the *geminal* dimer **1** *trans*-vinylsilane RCH=CHSiH_2Ph (R = ^{i}Pr (**5c**), ^{t}Bu (**5e**)), *cis*-vinylsilane RCH=CHSiH_2Ph (R = ^{i}Pr (**6c**), ^{t}Bu (**6e**)), the dehydrogenative silylalkyne RC≡CSiH_2Ph (R = ^{i}Pr (**7c**), ^{t}Bu (**7e**)), the corresponding alkenes RCH=CH_2 (R = ^{i}Pr (**8c**), ^{t}Bu (**8e**)) and the aminosilane Et_2NSiH_2Ph (**9**). For the bulky *t*-butylacetylene, the tertiary silanes *trans*-^{t}BuCH=CHSi(HPh)(C≡C^{t}Bu) (**10e**), ^{t}BuCH=C(SiH_2Ph)-Si(HPh)(C≡C^{t}Bu) (**11e**), were also observed (Reaction 7, Table 2). Formation of the tertiary silanes **10e** and **11e** can be accounted for by the metathesis reactions of the *trans*-alkenylsilane (**5e**) and the double hydrosilylated compound **12e** [22g] with the metal acetylide complex **A**, respectively, as shown in Reactions 8 and 9.

Interestingly, no hydrosilylation or dehydrogenative coupling products were obtained from TMSC≡CH and $PhSiH_3$ under similar reaction conditions at r.t. In addition, none of the oligomerization dimers or trimers of (TMS)C≡CH were observed [14].

3.2.2. Reaction scope at high temperature

At high temperature (65–78°C), the chemoselectivity and regioselectivity of the products formed in the cationic organouranium-catalyzed hydrosilylation of terminal alkynes with $PhSiH_3$ were found to be different from those obtained at r.t. The reactions were sensitive to the nature of the substituent on the alkyne and to the polarity of the solvent.

The hydrosilylation of RC≡CH (R = ^{n}Bu, ^{i}Pr, ^{t}Bu) with $PhSiH_3$ catalyzed by $[(Et_2N)_3U][BPh_4]$ at high temperature (reflux of the solvent, 65–78°C), produced, in addition to the hydrosilylation products at r.t. (Reaction 7), the corresponding double hydrosilylated compounds: RCH=C(SiH_2Ph)$_2$ (R = ^{n}Bu (**12b**), ^{i}Pr (**12c**), ^{t}Bu (**12e**)), and trimers. Only for ^{t}BuC≡CH, trace amounts of the dehydrogenative coupling of the silane PhH_2Si–SiH_2Ph (**13**) [42] were observed. Since the same myriad of products was obtained from the hydrosilylation of terminal alkynes promoted by $Cp^*_2AnMe_2$ (An = Th, U) [22q], it seems plausible that the same type of mechanism is operative here.



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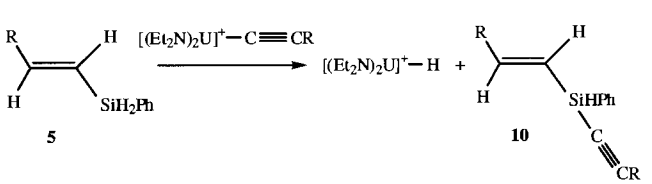

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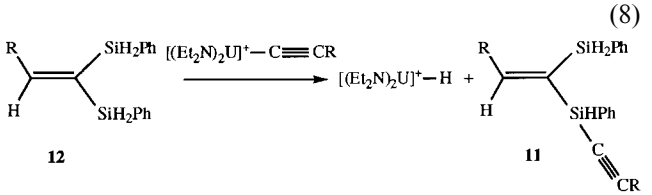


(9)

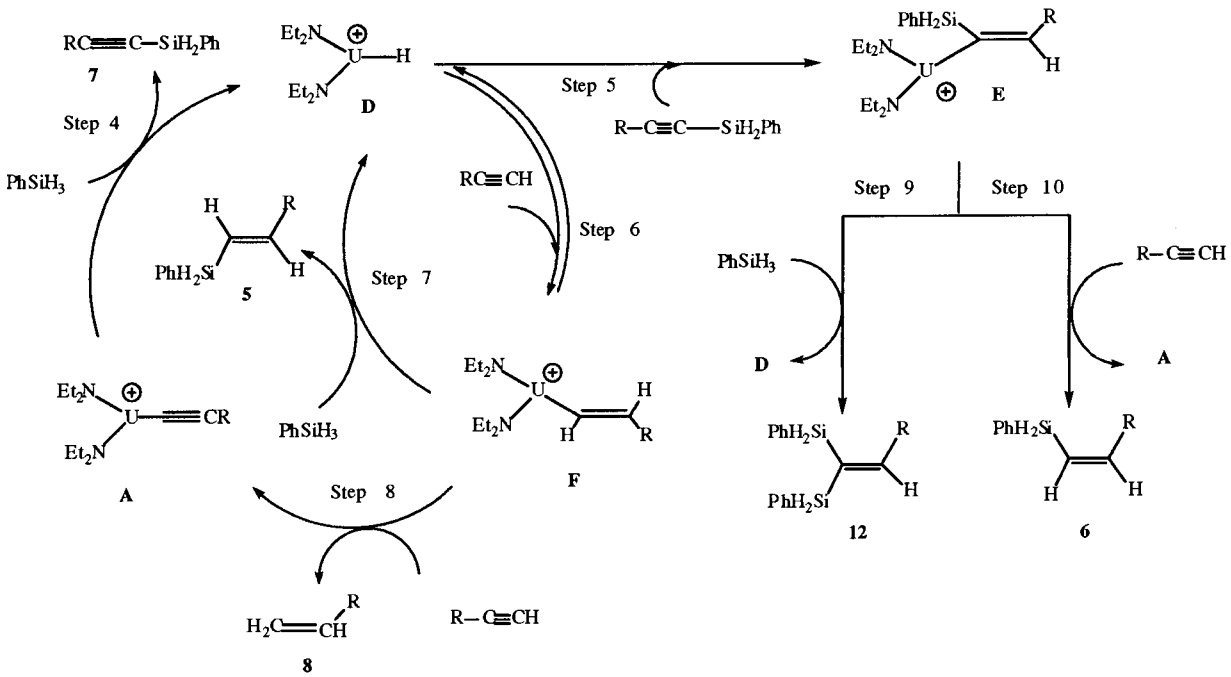
The formation of an active uranium hydride complex **D** is conceivable either by the reaction of the starting cationic complex with a silane molecule, giving the corresponding aminosilane compound **9** [43], or/and by the reaction of the acetylide complex **A** with silane, producing the corresponding silaalkyne **7** as described in Reactions 10 and 11, respectively. The proposed mechanism that takes into account the formation of all the products is described in Scheme 3.

This mechanism consists of a sequence of well-established elementary reactions, such as insertion of a terminal alkyne into a metal–hydride σ-bond, σ-bond

Table 2
Product distribution of the $[(Et_2N)_3U][BPh_4]$ catalyzed hydrosilylation of terminal alkynes (RC≡CH) with $PhSiH_3$ [a]

R in RC≡CH	Temperature (°C)	*trans*-RCH=CHSiH$_2$Ph (**5**) (%)	*cis*-RCH=CHSiH$_2$Ph (**6**) (%)	RCCSiH$_2$Ph (**7**) (%)	RCH=CH$_2$ (**8**) (%)	*gem*-H$_2$C=C(R)C≡CR (**1**) (%)
^{n}Bu (**b**) [b]	78	26	17	19	26	5
^{i}Pr (**c**)	20	28	10	22	28	10
^{i}Pr (**c**) [c]	78	21	17	26	21	8
^{i}Pr (**c**) [d]	65	16	4	30	31	16
TMS (**d**) [e]	78	12	19	21	11	11
^{t}Bu (**e**) [f]	20	54	11	2	12	1
^{t}Bu (**e**) [g]	78	36	16	–	17	–

[a] The reaction was carried out in benzene-d_6 unless otherwise mentioned. Small amount of **9** (ca 2%) was formed in each reaction.
[b] Trace amounts of **12b** (3%) and *gem*-trimer (1%) were also observed.
[c] Traces of trimer **4c**, **10c** and **12c** were also detected from GC/MS spectroscopy.
[d] The reaction was carried out in THF-d_8.
[e] No reaction was observed at r.t. Alkyne dimers (5%) and trimers (18%) were observed.
[f] The compound **11e** (16%) and traces of **10e** (2%) were also observed.
[g] The compound **11e** (22%) and traces of **12e** (1%) and **10e** (2%) were also observed.



Scheme 3. Plausible mechanism for the room and high temperature hydrosilylation of terminal alkynes promoted by $[(Et_2N)_3U][BPh_4]$. The transformation of the starting complex into the acetylide complex $[(Et_2N)_2U–C{\equiv}CR][BPh_4]$ (**A**) was described in Scheme 2, and is omitted here for clarity.

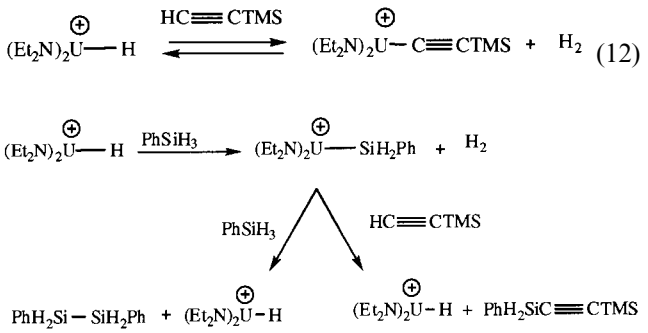
$$[(Et_2N)_3U]^+ \xrightarrow{PhSiH_3} [(Et_2N)_2U]^+-H \;(\mathbf{D}) \;+\; PhSiH_2NEt_2 \;(\mathbf{9}) \qquad (10)$$

$$[(Et_2N)_2U]^+-C{\equiv}CR \;(\mathbf{A}) \xrightarrow{PhSiH_3} [(Et_2N)_2U]^+-H \;(\mathbf{D}) \;+\; RC{\equiv}CSiH_2Ph \;(\mathbf{7}) \qquad (11)$$

metathesis by a silane, and protonolysis by an acidic alkyne hydrogen. The precatalyst $[(Et_2N)_3U][BPh_4]$ in the presence of alkyne is converted to the acetylide complex **A** removing one of the amido ligands (Scheme 2). Complex **A** reacts with $PhSiH_3$ to give the silylalkyne **7** and the actinide hydride **D** (step 4) (a competitive pathway is the formation of the aminosilane **9**). The hydride complex **D** may reinsert the silaalkyne in a

very regiospecific manner, as already observed in the thorium and uranium catalyzed hydrosilylation of alkynes, forming complex **E** (step 5) [36]. Complex **D** will also react rapidly with the alkyne to produce the alkenyl uranium complex **F** (step 6), which is presumably in rapid equilibrium with complex **D**. For example, in the hydrogenation of alkenes by the metallocene thorium bis(hydride) complex, this insertion step was found to be reversible [12]. Complex **F** will react with $PhSiH_3$, producing back the organouranium hydride complex **D** and the *trans*-hydrosilylated product **5** (step 7). Under the catalytic conditions, complex **F** may also react with a second alkyne giving the alkene **8** and the acetylide complex **A** (step 8). Complex **E** may react with a silane (step 9) yielding complex **D** and the double hydrosilylation product **12** or with an alkyne (step 10) yielding complex **A** and the *cis*-isomer **6.** Formation of compounds **9**, **10** and **11** has been explained by the reactions described in Reactions 10, 8 and 9, respectively.

This mechanistic scenario takes into account the higher yields observed for the alkene compound **8** as compared with those obtained for the silylalkyne **7**. For TMSC≡CH and ^{i}PrC≡CH, at high temperature, the amount of the hydrosilylated products is larger than that of the alkenes, indicating that an optional competing equilibrium route should be operative. This would involve the transformation of the hydride **D** back into the acetylide complex **A** by reaction with the alkyne (Reaction 12) allowing the production of more silylalkyne without producing the alkene. The hydride **D** could alternatively react with $PhSiH_3$ to give the silylorganometallic compound $[(Et_2N)_2USiH_2Ph][BPh_4]$ (Reaction 13) which would further react with $PhSiH_3$ or RC≡CH to give back the hydride **D** and $PhH_2Si–SiH_2$-Ph or $PhH_2SiC{\equiv}CR$, respectively.



It is noteworthy that only for the hydrosilylation reaction of ^{t}BuC≡CH at high temperature (78°C), a small amount of the dehydrogenative coupling of phenylsilane was observed. This result argues for the formation of a compound with an uranium silicon bond although not as a major operative intermediate. The compound $[(Et_2N)_2USiH_2Ph][BPh_4]$ can be formed instead of the hydride complex **D** either from steps 4, 7 or 9 in the catalytic cycle (Scheme 3). In these steps, the silane is acting as the protonolytic source.

4. Conclusions

These results demonstrated that cationic actinide complexes are active catalysts for the dimerization of terminal alkynes by a mechanism that consists of insertion and σ-bond metathesis reactions. A delicate balance between alkyne insertion and alkyne C–H σ-bond metathesis determines the dimer: trimer oligomer ratio and the *geminal*:*cis*:*trans* isomer ratio. The trapped π-alkyne acetylide complex is, to the best of our knowledge, the first characterized actinide π-alkyne complex. Cationic uranium complexes were also found to be very efficient for the catalytic hydrosilylation of terminal alkynes. All these reactions likely involve uranium acetylide and uranium hydride species as active intermediates. Further studies are presently under investigation.

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Appendix A. Derivation of the kinetic rate equation based on the mechanism as presented in Scheme 2

$$\partial P/\partial t = k_3[\mathbf{C}][\mathrm{RC{\equiv}CH}] \quad \text{(A1)}$$

steady state approximation on [**C**]

$$\partial C/\partial t \approx 0 \approx -k_3[\mathbf{C}][\mathrm{RC{\equiv}CH}] - k_{-2}[\mathbf{C}] + k_2[\mathbf{A}][\mathrm{RC{\equiv}CH}] \quad \text{(A2)}$$

$$[\mathbf{C}] = k_2[\mathbf{A}][\mathrm{RC{\equiv}CH}]/k_3[\mathrm{RC{\equiv}CH}] + k_{-2} \quad \text{(A3)}$$

$$[\mathbf{C}] = k_2[\mathbf{A}]/k_3 \Rightarrow k_3[\mathrm{RC{\equiv}CH}] \gg k_{-2} \quad \text{(A4)}$$

This assumption is made since no scrambling of alkynes have been observed even at low alkyne concentrations when the reaction is the fastest.

$$\partial P/\partial t = k_2[\mathbf{A}][\mathrm{RC{\equiv}CH}] \quad \text{(A5)}$$

steady state approximation on [**A**]

$$\partial A/\partial t \approx 0 \approx -k_1[\mathbf{A}][\mathrm{RC{\equiv}CH}] - k_2[\mathbf{A}][\mathrm{RC{\equiv}CH}] + k_{-1}[\mathbf{B}] + k_{-2}[\mathbf{C}] \quad \text{(A6)}$$

$$\partial A/\partial t \approx 0 \approx -k_1[\mathbf{A}][\mathrm{RC{\equiv}CH}] - k_2[\mathbf{A}][\mathrm{RC{\equiv}CH}] + k_{-1}[\mathbf{B}] + k_{-2}k_2[\mathbf{A}][\mathrm{RC{\equiv}CH}]/k_3[\mathrm{RC{\equiv}CH}] + k_{-2}$$

$$k_{-1}[\mathbf{B}] = [\mathbf{A}][\mathrm{RC{\equiv}CH}]\{k_1 + k_2 - k_2k_{-2}/k_3[\mathrm{RC{\equiv}CH}] + k_{-2}\} \quad \text{(A7)}$$

$$[\mathbf{A}] = \frac{k_{-1}[\mathbf{B}]}{[\mathrm{RC{\equiv}CH}]} \frac{1}{\{k_1 + k_2 - k_2k_{-2}/k_3[\mathrm{RC{\equiv}CH}] + k_{-2}\}} \quad \text{(A8)}$$

Substituting for [**A**] in Eq. (A5)

$$\frac{\partial P}{\partial t} = \frac{k_{-1}k_2[\mathbf{B}]}{\{k_1 + k_2 - k_2k_{-2}/k_3[\mathrm{RC{\equiv}CH}] + k_{-2}\}} \quad \text{(A9)}$$

as before $k_3[\mathrm{RC{\equiv}CH}] \gg k_{-2}$

$$\frac{\partial P}{\partial t} = \frac{k_{-1}k_2[\mathbf{B}]}{k_1 + k_2 - k_2k_{-2}/k_3[\mathrm{RC{\equiv}CH}]} \quad \text{(A10)}$$

Thus the derived rate law for the oligomerization of terminal alkynes promoted by cationic $[(Et_2N)_3U]^+[BPh_4]^-$ is given by Eq. (A11)

$$v = \frac{k_{-1}k_2[\mathrm{cat}]}{k_1 + k_2 - \dfrac{k_2k_{-2}}{k_3[\mathrm{alkyne}]}} \quad \text{(A11)}$$

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[38] Theoretically it is possible that the terminal alkynes replace all the amido groups at the metal center, although at the reaction conditions we have found only one equivalent of free amine. Interestingly, the transammination reaction of $[(Et_2N)_3U][BPh_4]$ with $^iPrNH_2$ replace all the three ethylamine groups.
[39] In the proposed catalytic cycle, an intermediate (reactive isomer of **B** could also appear between **A** and **C**, which is at a steady state, before the insertion of the second alkyne.
[40] No Ellington oxidizing coupling products (RC≡C–C≡CR, or $RC{\equiv}C{-}NEt_2$) were observed.
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