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Review

Catalytic Organic Transformations Mediated by Actinide Complexes

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Abstract: This review article presents the development of organoactinides and actinide coordination complexes as catalysts for homogeneous organic transformations. This chapter introduces the basic principles of actinide catalysis and deals with the historic development of actinide complexes in catalytic processes. The application of organoactinides in homogeneous catalysis is exemplified in the hydroelementation reactions, such as the hydroamination, hydrosilylation, hydroalkoxylation and hydrothiolation of alkynes. Additionally, the use of actinide coordination complexes for the catalytic polymerization of α-olefins and the ring opening polymerization of cyclic esters is presented. The last part of this review article highlights novel catalytic transformations mediated by actinide compounds and gives an outlook to the further potential of this field.

Keywords: organoactinides; actinide coordination complexes; homogeneous catalysis; hydroelementations; polymerization of olefins; ROP; activation of heterocumulenes

1. Introduction

The beginning of modern organoactinide chemistry is often attributed to the synthesis of uranocene, $[(\eta^8\text{-}C_8H_8)_2U]$ in 1968, as the analogous compound to ferrocene and other transition metal metallocenes [1,2]. Since then, the organometallic and coordination chemistry of the early actinide elements thorium and uranium has reached a high level of sophistication, including the synthesis and

application of these compounds in stoichiometric and catalytic organic transformations [3–14]. Owing to the large ionic radii of the actinides and the presence of 5f orbitals, actinide coordination complexes often exhibit different catalytic activities, as well as complementary reactivities to their early and late transition metal analogues. This in turn leads to different chemo- and regio-selectivities, thus expanding the scope of accessible products obtained in catalytic organic processes [3]. The extraordinary catalytic reactivity of organoactinides was first exemplified in the homogeneous polymerization of butadiene, mediated by the organometallic uranium complex [(η^3-allyl)$_3$UCl] in combination with the co-catalyst [(C$_2$H$_5$)AlCl] in 1974. This process gave poly-1,4-butadiene with a higher *cis* content and therefore with superior mechanical properties, than the polymers obtained with transition metal catalysts [15–19]. In general, the reactivity of actinide coordination complexes is influenced by steric and electronic factors. The steric hindrance in actinide complexes has been described by the "packing saturation model", which attributes the stability of the respective coordination complex to the sum of the ligands cone angles. Hence, coordinative "over saturated" complexes display lower stabilities [20–22]. In addition, de Matos introduced the "steric coordination number" for actinide complexes, which implies a pure ionic bonding model, and is based on the ligands cone angles [23]. Furthermore, the reactivity of actinide compounds can be further elucidated by using thermochemical studies, which allow for a prediction of new reaction pathways by taking into account the metal ligand bond disruption enthalpies [24–30]. It has been also shown that due to the high energy orbital impediment to undergo oxidative addition and reductive elimination reactions, catalytic processes mediated by neutral organoactinide complexes proceed via an ordered four-membered transition state (Scheme 1) [31]. In this review, we will briefly present a survey of homogeneous catalytic transformations mediated by organoactinides and actinide coordination complexes.
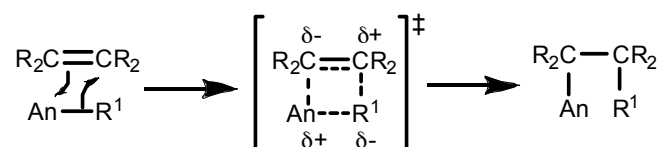
Scheme 1. Operative mechanism in actinide mediated catalytic transformations (R^1: Alkyl, Benzyl, NR$_2$; R$_2$: Alkyl, Aryl, SiMe$_3$).

2. Application of Actinide Complexes in Catalytic Transformations

2.1. Hydroelementation Reactions

2.1.1. Hydroalkoxylation/Cyclization of Alkynyl Alcohols

Hydroalkoxylation reactions present an atom economic route for the preparation of new C–O bond by the addition of an O–H bond across a C–C double, or triple bond [32,33]. Recently, Marks *et al.*, reported the thorium mediated hydroalkoxylation/cyclization of alkynyl alcohol using primary, and secondary alcohols, as well as terminal and internal alkynes as substrates [34]. Kinetic studies revealed a zero order dependence of the reaction rate on substrate and a first order dependence on catalyst. Moreover, the reaction rates with primary alcohols and terminal alkynes was faster, as compared to the rate when using sterically more encumbered substrates, corroborating that the transition state of the

reaction is dominated by steric interactions. The reaction was studied with three different thorium catalysts (Figure 1), among which the constrained geometry catalyst (CGC)Th(NMe₂)₂ **2** exhibited the highest catalytic activity, which was attributed to the more open coordination sphere of complex **2**. All substrate and catalyst combinations reported displayed a high selectivity for the exclusive formation of the *exo*-methylene product (*Markovnikov* selectivity), while internal alkynes afforded alkene products with an E-orientation.
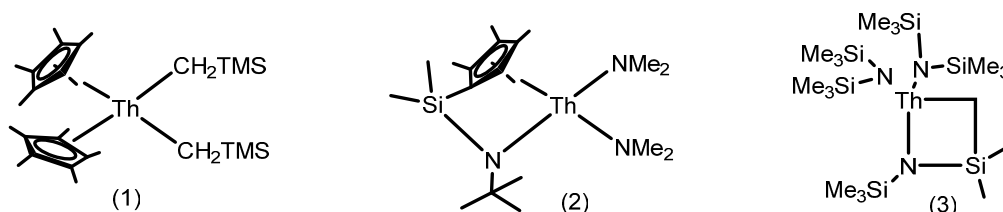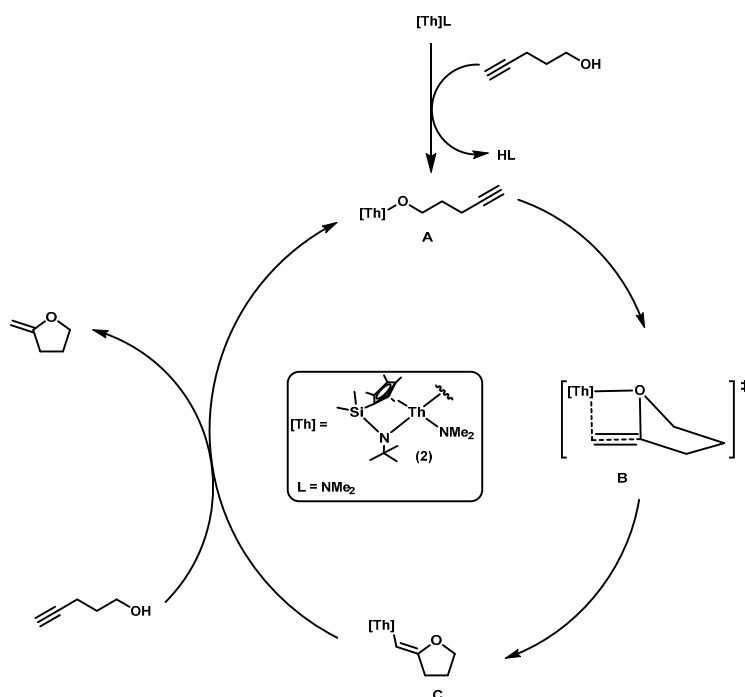
Figure 1. Thorium complexes **1–3** used as pre-catalysts in the hydroalkoxylation/cyclization of alkynyl alcohols.

The mechanism of the reaction (Scheme 2) includes an activation step, which affords the catalytically active Th–OR species **A** after hydrolysis of the benzyl or amide pro-ligands with an incoming alcohol. A subsequent insertion of the alkyne into the Th–OR bond via a four membered transition state leads to the formation of intermediate **C**. The insertion of the alkyne is the thermodynamically most demanding step of the catalytic cycle, hence it presents the rate limiting step of this mechanism. The Th–C bond of intermediate **C** is cleaved rapidly by an incoming substrate, furnishing the product under regeneration of the active catalyst **A** [34].

Scheme 2. Proposed mechanism for the thorium mediated hydroalkoxylation/cyclization of alkynyl alcohols. Adapted with permission from Wobser, S.D.; Marks, T.J. *Organometallics* **2013**, *32*, 2517–2528 [34]. Copyright 2013 American Chemical Society.

2.1.2. Hydrothiolation of Terminal Alkynes

The hydrothiolation of terminal alkynes gives an easy access to vinyl sulfides through the addition of S–H bonds across the C≡C triple bond of an alkyne. While this reaction has been studied with a large variety of early and late transition metal catalysts, achieving selectivity for the formation of the Markovnikov addition product still remains a challenge [35–37]. Additionally, most transition metal catalysts have a limited substrate scope, proceeding with low conversions when using aliphatic thiols [38–44]. Hence, the hydrothiolation of terminal alkynes was studied using the cyclopentadienyl based actinide catalysts **1** and **4** (Figure 2) [45–47].

(4)   (1)

An = U; R = CH$_2$Ph
An = Th; R = CH$_2$TMS

Figure 2. Actinide catalysts **4** and **1** used in the catalytic hydrothiolation of terminal alkynes [45–47].

Bond enthalpy calculations have shown that the insertion of alkynes into An–SR bond is strongly exothermic, allowing for an actinide mediated catalytic hydrothiolation [6,45–47]. The most noticeable aspect of the actinide catalyzed hydrothiolation using the *ansa*-bridged thorium complex **4** as pre-catalyst is the wide substrate scope, which includes aliphatic, benzylic and aromatic thiols, as well as the high selectivity for the formation of the Markovnikov addition product. The Markovnikov selectivity can be mainly attributed to steric interactions, as well as to bond polarity mismatches in the highly ordered four-membered transition state of the reaction (Figure 3). The terminal R-substituent of the alkyne is oriented away from the sterically demanding *ansa*-cyclopentadienyl ligands in the transition state **A**, which leads to the formation of the Markovnikov vinyl sulfide. Furthermore, the larger the electron density on the α-carbon atom to the metal center at the transition state **A**, leads to a better stabilization of the highly electrophilic actinide center [45–47].

Figure 3. Markovnikov (**A**) and anti-Markovnikov (**B**) transition states for the actinide mediated hydrothiolation of alkynes. Adapted with permission from Weiss, C.J.; Marks, T.J. *Dalton Trans.* **2010**, *39*, 6576–6588 [47]. Copyright 2010 Royal Society of Chemistry.

The general mechanism for the hydrothiolation of terminal alkynes mediated by the thorium catalyst **4** is presented in Scheme 3. After an activation step, which leads to the formation of the catalytically active thorium species **A**, the alkyne inserts into the Th–SR bond of **A** to give intermediate **C**, which is the rate limiting step of the catalytic cycle. Subsequent protonolysis with an incoming thiol furnishes the vinyl sulfide product under regeneration of the active catalyst **A**.
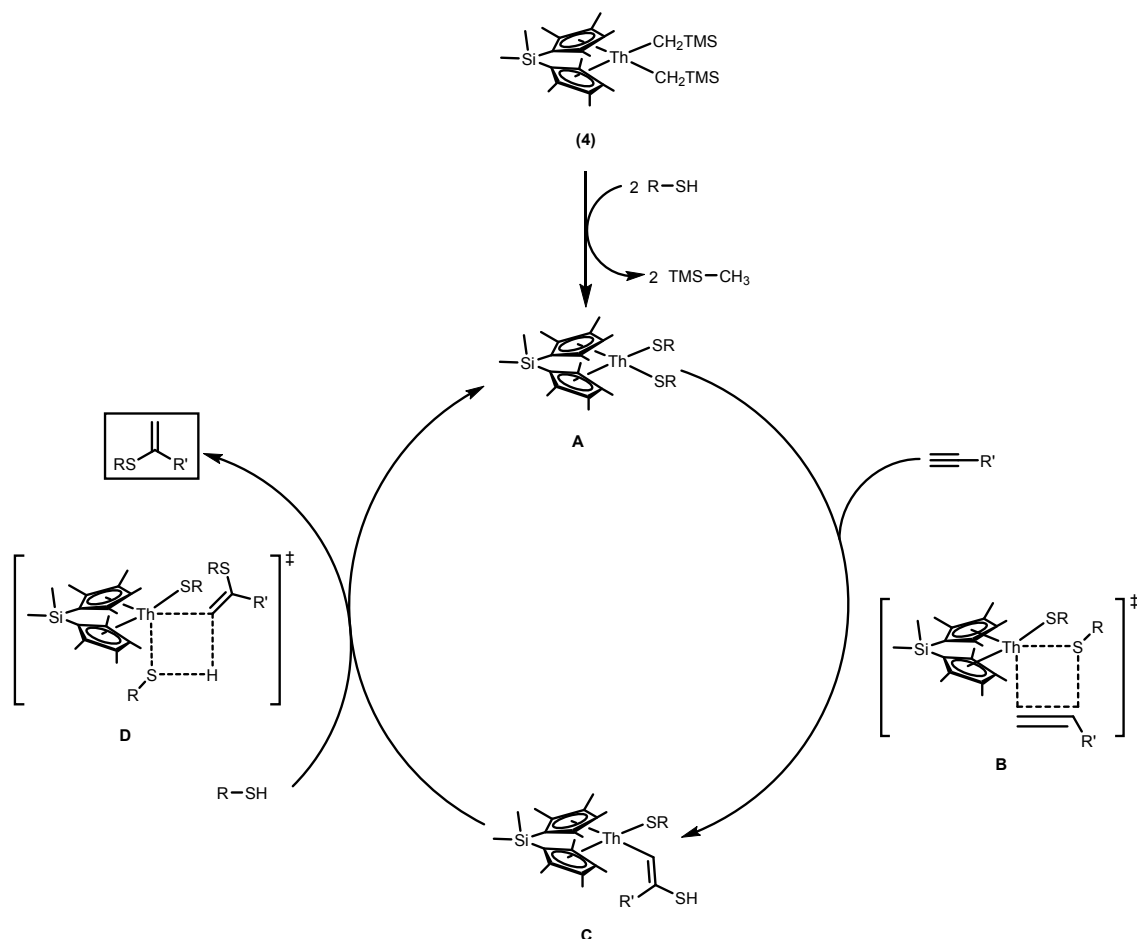
Scheme 3. Proposed mechanism for the thorium mediated hydrothiolation. Adapted with permission from Weiss, C.J.; Wobser, S.D.; Marks, T.J. *J. Am. Chem. Soc.* **2009**, *131*, 2062–2063 [45]. Copyright 2009 American Chemical Society.

2.1.3. Inter- and Intra-Molecular Hydroamination

The intermolecular hydroamination of terminal alkynes with primary aliphatic amines has been explored by Eisen *et al.*, using the Cp*$_2$AnMe$_2$ (An = Th, U; Cp* = C$_5$Me$_5$) complexes **5–6** as catalysts [48,49]. The chemo- and regio-selectivity of the products obtained showed a strong dependence on the nature of the amine and the actinide center, but not on the substituents of the respective alkyne. While the use of Cp*$_2$UMe$_2$ (**5**) lead to the formation of imine products with a *syn*-regiochemistry, the analogous thorium complex Cp*$_2$ThMe$_2$ (**6**) furnished the respective imine products, as well as dimeric and trimeric alkyne oligomers (Scheme 4). Kinetic studies showed a first order dependence of the reaction on the respective actinide pre-catalysts Cp*$_2$AnMe$_2$, a zero order dependence on alkyne concentration, and a reversed first order dependence on amine [48,49].
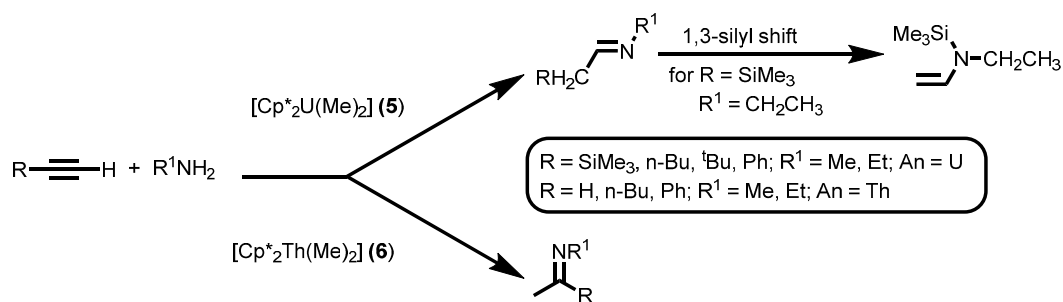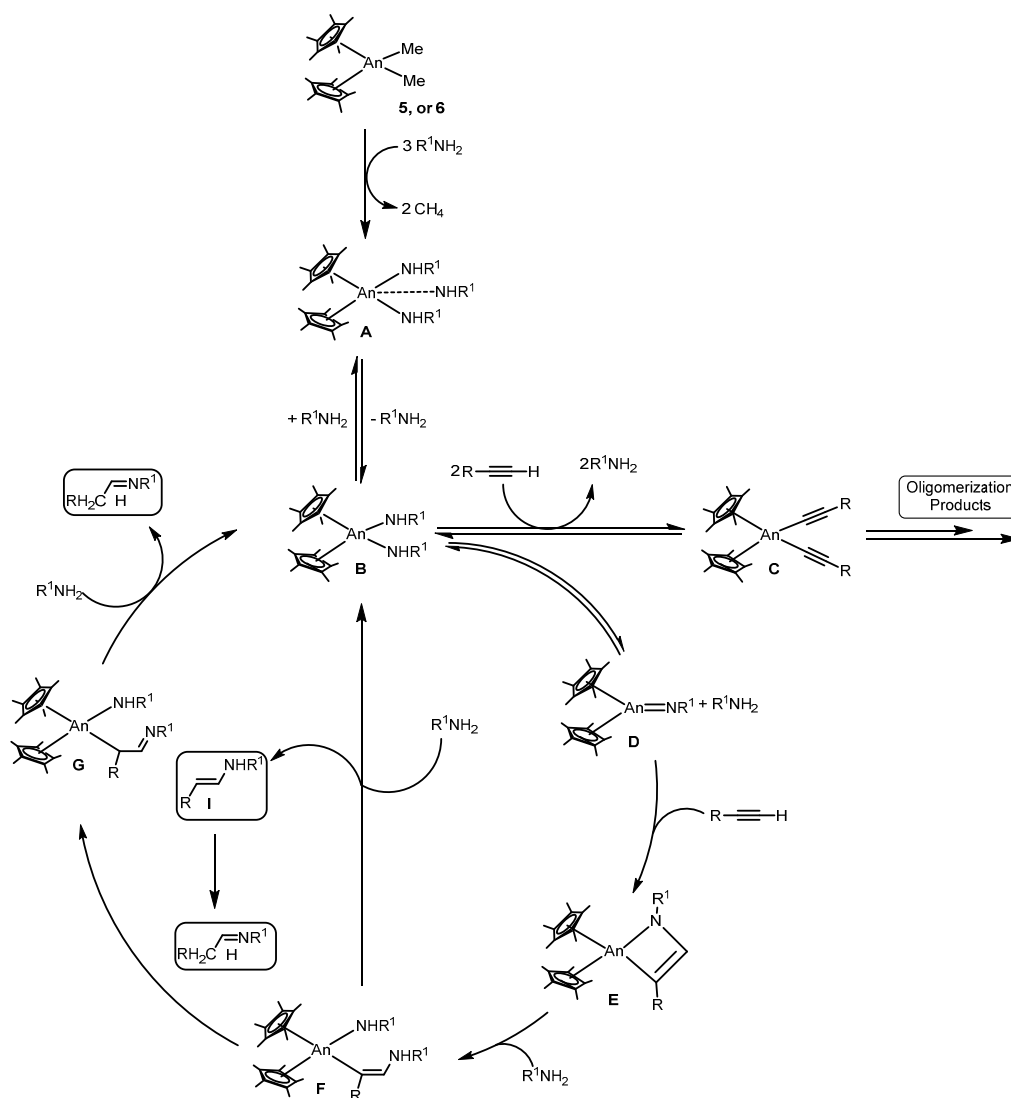
Scheme 4. Chemo- and regio-selectivity of the intermolecular hydroamination mediated by the organoactinide complexes Cp*$_2$AnMe$_2$ (An = U, Th). Adapted with permission from Haskel, A.; Straub, T.; Eisen, M.S. *Organometallics* **1996**, *15*, 3773–3775 [48]. Copyright 1996 American Chemical Society.

The mechanism of the intermolecular hydroamination (Scheme 5) has been shown to go over the formation of an actinide imido species of the type Cp*$_2$An(=NR) (An = Th, U) (**D**), which have been isolated and structurally characterized [49]. The first step of the catalytic cycle is the protonolysis reaction with an incoming amine, furnishing the bis(amido)amine intermediate **A**, as well as two equivalents of methane gas. Intermediate **A** can react via two competitive pathways. In the first case, complex **B** undergoes a σ-bond metathesis with the terminal alkynes, via the bis(acetylide) complex **C**, resulting in the formation of the respective alkyne oligomerization products. The second pathway, which has been shown to be the rate determining step of the catalytic cycle, includes the elimination of one equivalent of amine to generate the actinide imido complex **D**. Intermediate **D** undergoes a rapid bond metathesis with an incoming alkyne (*anti*-insertion) forming the actinide metallacycle **E**, followed by a rapid protonolysis with an incoming amine to furnish the actinide amido intermediate **F**. Complex **F** can now either react with another equivalent of amine, generating an enamine product (**I**) that will rapidly isomerize to the respective imine **H**, under regeneration of the catalytically active complex **B**. In addition, complex **F** can undergo a 1,3-hydride shift furnishing intermediate **G** and a subsequent reaction with an incoming amine to give the imine product **H** under regeneration of the catalytically active species **B** (Scheme 5) [48,49].

In addition to the intermolecular hydroamination of terminal acetylenes, Marks *et al.*, have investigated the intramolecular hydroamination/cyclization of aminoalkenes aminoalkynes, and aminoallenes with the constrained geometry actinide catalysts (CGC)An(NR$_2$)$_2$ (An = Th (**2**); U (**7**)) with various amido ligands [50,51]. The constrained geometry catalysts **2** and **7** display a more open coordination sphere as compared to the respective pentamethyl cyclopentadienyl compounds Cp*$_2$AnR$_2$ (An = U (**5**); Th (**6**)) leading to an increased catalytic activity in the hydroamination/cyclization. Furthermore, Marks and coworkers have shown that the nature of the actinide center influences the rate of the intermolecular hydroamination/cyclization, displaying higher rates for the respective thorium complexes than for their uranium analogues. This was attributed to the more open coordination sphere in (CGC)Th(NR$_2$)$_2$ as compared to the isostructural (CGC)U(NR$_2$)$_2$, due to the larger ionic of thorium as compared to uranium. Investigations with a large variety of R substituents on the amido ligands in (CGC)An(NR$_2$)$_2$ (An = Th or U) catalysts have shown, that the nature of the R substituent does not influence the reaction rate, which was attributed to the rapid protonolysis of the respective amido ligands with an incoming substrate (Scheme 6). Mechanistic studies have led to

proposed mechanism shown in Scheme 6, which displays similar steps to the mechanism of the intermolecular hydroamination/cyclization mediated by organolanthanide complexes. The first step of the mechanism comprises a rapid protonolysis of both amido ligands NR_2 with two equivalents of incoming substrate, generating the active species **A**. Subsequent insertion of the C=C double, or C≡C triple bond into the An–NHR^1 bonds of complex **A** over a four membered transition state (**B**), furnishes intermediate **C**. The intermolecular insertion of the unsaturated C=C, or C≡C bonds into the An–NHR^1 bond of **A** is the rate determining step of the reaction mechanism, followed by a rapid protonolysis with an incoming substrate, which leads to the formation of product **D** under regeneration of the catalytically active species **A**. In comparison to the analogous mechanism using lanthanide (III) complexes as catalysts, the use of CGC(An)$(NR_2)_2$ catalysts, allows for dual simultaneous substrate cyclization, due to the availability of two amido ligands NR_2, whereas lanthanocenes exhibit only one NR_2 ligand, which can be replaced by only one equivalent of substrate [50,51].

Scheme 5. Proposed mechanism for the intermolecular hydroamination of terminal alkynes mediated by the organoactinide complexes **4** and **5**. Adapted with permission from Haskel, A.; Straub, T.; Eisen, M.S. *Organometallics* **1996**, *15*, 3773–3775 [48]. Copyright 1996 American Chemical Society.
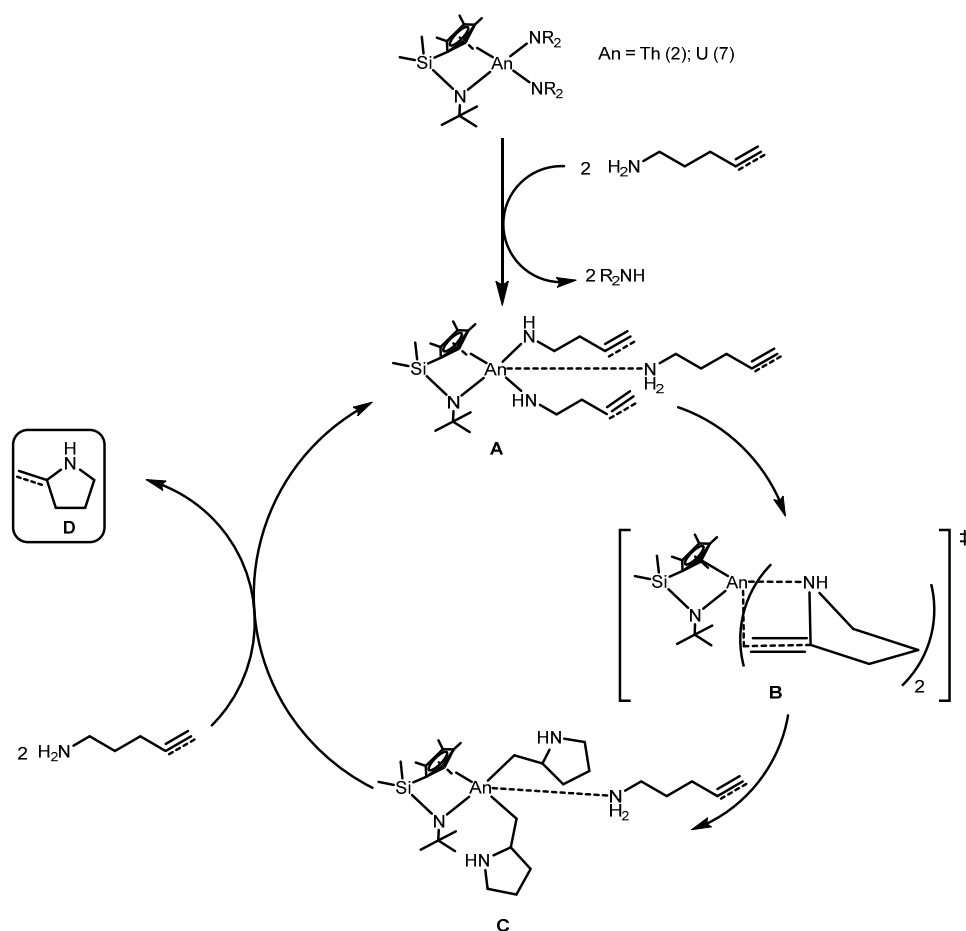
Scheme 6. Intermolecular hydroamination mediated by the constrained geometry actinide complexes **2** and **7**. Stubbert, B.D.; Stern, C.L.; Marks, T.J. *Organometallics* **2003**, *22*, 4836–4838 [50]. Copyright 2003 American Chemical Society.

In order to compare the active mechanism in the inter- and intra-molecular hydroamination reaction, Diaconescu *et al.*, used the ferrocene-diamide supported uranium (IV) complex (fcc)U(CH$_2$Ph)$_2$ **8** (Figure 4) in the intramolecular hydroamination of acetylenes with anilines, as well as in the intermolecular hydroamination/cyclization of aminoalkenes and aminoalkynes [52]. While the intramolecular has been shown to proceed via the imido-mechanism proposed by Eisen *et al.*, (Scheme 5) [48,53,54], an unambiguous result for the intermolecular hydroamination/cyclization with aminoalkenes and aminoalkynes could not be obtained. Furthermore, Leznoff and co-workers have recently applied diamido-ether supported actinide complexes **9** and **10** (Figure 4) for the hydroamination/cyclization of aminoalkenes under mild conditions, displaying high catalytic activities [55].
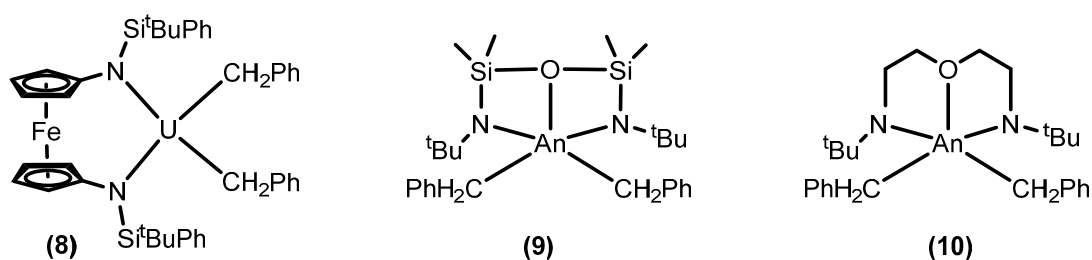

Figure 4. Actinide complexes **8**–**10** used as catalysts for hydroamination reactions [52,55].

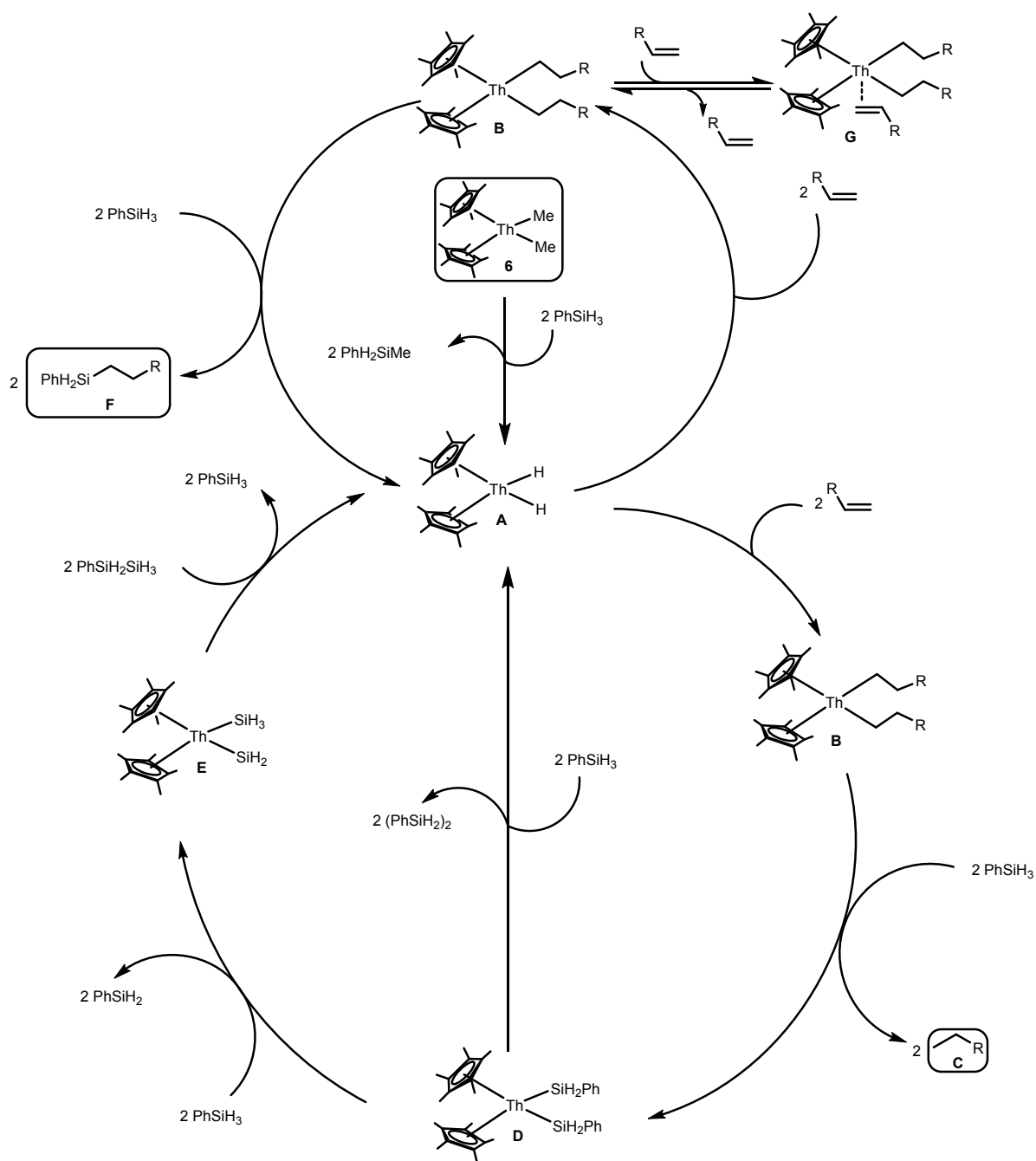2.1.4. Hydrosilylation of Terminal Alkynes

The hydrosilylation of terminal alkynes can proceed to give three different isomeric products (Scheme 7), which comprise the *cis*, and *trans* vinylsilanes, and the geminal vinylsilane, which are obtained due to the 1,2 *syn* and *anti* and the 2,1-insertion modes, respectively. The product distribution obtained has been shown to depend strongly on the nature of the metal catalyst, the substrates and the reaction conditions [56–59].

$$R-\!\!\!\equiv\!\!\!-H + R^1SiH_3 \xrightarrow{\text{[cat.]}}$$

cis   *trans*   *gem*
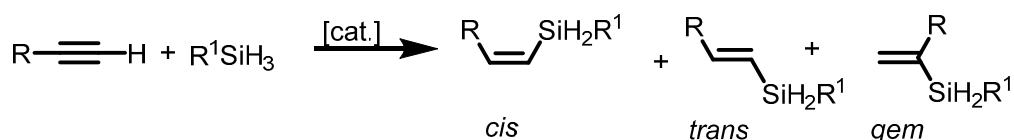
Scheme 7. Possible products in the catalytic hydrosilylation of terminal alkynes. Adapted with permission from Dash, A.K.; Wang, J.Q.; Eisen, M.S. *Organometallics* **1999**, *18*, 4724–4741 [60]. Copyright 1999 American Chemical Society.

Several actinide complexes have been explored as catalysts in the hydrosilylation of terminal acetylenes and olefins with PhSiH₃, displaying different chemo- and regio-selectivities in dependence of the actinide center, the ancillary ligands, the substrates used and the reaction conditions. The organoactinide compounds Cp*₂AnMe₂ (An = U (**5**); Th (**6**)) were shown to mediate the hydrosilylation of terminal alkynes with PhSiH₃, leading to a different product distribution in dependence of the reaction temperature [60]. When the reaction was carried out at room temperature, the *trans* vinylsilane **D** (Scheme 8) was obtained as the major product, as well as silylalkynes and the respective alkene as byproducts. At higher temperatures (50–80 °C), the product distribution depends on the respective actinide center in Cp*₂AnMe₂. While the use of Cp*₂ThMe₂ (**6**) as catalyst displayed the same regio- and chemo-selectivity like at room temperature, the isostructural uranium complex Cp*₂UMe₂ (**5**) led to the formation of the *cis* vinylsilane, as well as the double hydrosilylated product in addition to the products observed at room temperature. These observations suggest a competing reaction pathway at higher temperatures that yields the *cis* vinylsilane, as well as the alkene and silylalkyne. The proposed mechanism for the catalytic hydrosilylation of terminal acetylenes mediated by Cp*₂ThMe₂ (**6**) is presented in Scheme 8. The first step of the catalytic cycle comprised the reaction of Cp*₂ThMe₂ (**6**) with two equivalents of acetylene, generating the bis(acetylide) compound **A**, which upon reaction with PhSiH₃ leads to the formation of the silylalkyne and thorium hydride **B**. After reinsertion of the silylalkyne into **B**, the thorium hydride complex **B** is equilibrium with intermediate **F**. In addition the thorium hydride complex **B** undergoes a rapid insertion of an alkyne into the Th–H bond, forming the thorium alkenyl-acetylide complex **C**. A subsequent reaction of **C** with PhSiH₃, which is the rate determining step of the catalytic cycle, regenerates the catalytically active species **A** with formation of the *trans* vinylsilane **D**. However, the thorium alkenyl-acetylide complex **C** can also react with an additional equivalent of alkyne, generating the alkene product **E** and the thorium bis(acetylide) intermediate **A**. The double hydrosilylated product **H**, which is observed at higher temperatures, is obtained by phenysilane insertion into intermediate **F**, regenerating thorium-hydride intermediate **B**. Additionally, intermediate **F** can also react with an equivalent of alkyne at higher temperatures, furnishing the *cis* vinylsilane **G** and intermediate **A** (Scheme 8) [60].

Scheme 8. Proposed mechanism for the hydrosilylation of terminal alkynes, mediated by Cp*$_2$ThMe$_2$ (**6**). Adapted with permission from Dash, A.K.; Wang, J.Q.; Eisen, M.S. *Organometallics* **1999**, *18*, 4724–4741 [60]. Copyright 1999 American Chemical Society.

An improvement in the reaction rate, as well as in the chemo- and regio-selectivity of the reaction was achieved by using the *ansa*-bridged thorium complex **4** as catalyst for the hydrosilylation of terminal alkynes and alkenes with PhSiH$_3$ [61,62]. The increased reaction rate was attributed to the more open coordination sphere in the *ansa*-bridged complex **4**, as compared the Cp*$_2$ThMe$_2$ (**6**). The increased chemo- and regio-selectivity, which is exhibited in the formation of the *trans* vinylsilane, or the 1-silylalkane as major products in the hydrosilylation of terminal alkynes and alkenes, respectively, was attributed to the more hindered equatorial plane in **4**. The disposition of the methyl groups in the ligand backbone forces the incoming substrates to react in a specific regiochemistry, allowing for a fine-tuning of the organoactinide reactivity by modifying the ancillary ligand backbone. While the hydrosilylation of terminal alkynes proceeds with excellent chemo- and regio-selectivity, generating the respective *trans* vinylsilane as the only product, the hydrosilylation of alkenes shows a high regioselectivity toward the formation of 1-silylalkanes. However only a moderate chemoselectivity is achieved in the later case since the respective alkane is obtained in nearly equimolar amounts. The mechanism for the hydrosilylation of alkenes is shown in Scheme 9. The first step of the catalytic cycle comprises the formation of the catalytically active thorium-hydride complex **A** by reaction of the pre-catalyst **6** with PhSiH$_3$ under formation of PhSiH$_2$Me. Intermediate **A** reacts with an incoming alkene to furnish the thorium-alkyl compound **B**. The thorium-alkyl species **B** can now react via three different pathways: the first option includes a reaction with another equivalent of alkene to give the π-alkene complex **G**. In addition, complex **B** can undergo a metathesis reaction with a Si–H moiety, to give the 1-silylalkane product **F** and complex **A**, or a protonolysis reaction with a Si–H

moiety to give intermediate **D** and the respective alkane **C**. Since these two steps have similar energies of activation, both can take place, furnishing an equimolar amount of 1-silylalkane **F** and alkane **D** (Scheme 9) [61,62].

Scheme 9. Proposed mechanism for the thorium mediated hydrosilylation of alkenes Adapted with permission from Dash, A.K.; Gourevich, I.; Wang, J.Q.; Wang, J.; Kapon, M.; Eisen, M.S. *Organometallics* **2001**, *20*, 5084–5104, Copyright 2001 American Chemical Society [61].

In addition, the cationic uranium (IV) complex [(Et$_2$N)$_3$U] [BPh$_4$] (**11**) was explored as a pre-catalyst in the hydrosilylation of terminal acetylenes, displaying a similar chemo- and regio-selective to the organoactinide system Cp*$_2$UMe$_2$ (**5**) [63].

2.2. Coupling Reactions

2.2.1. Coupling of Terminal Acetylenes

The coupling of terminal alkynes to give oligomeric products through actinide mediated C–H activation processes has been extensively investigated by Eisen and co-workers, using the organoactinides Cp*$_2$AnMe$_2$ (**5** and **6**) [53,54,64], as well as the cationic uranium amide [(Et$_2$N)$_3$U] [BPh$_4$] (**11**) [65–67] as pre-catalysts. While the chemo- and regio-selectivity of the oligomerization process depends on the steric encumbrance of the R substituent on the alkyne RCCH, leading to a different regioselectivity for bulky and non-bulky alkynes, the uranium complex **5** and the isostructural thorium compound **6** displays a similar reactivity [53,64]. When the sterically encumbered alkyne *t*BuCCH is used as substrate, the head-to-tail dimer is obtained. However, the use of TMSCCH leads to the formation head-to-tail geminal dimer, and to the head-to-tail-to-head trimer. Similarly, when sterically not encumbered alkynes, such as PhCCH, and *i*PrCCH are applied, a myriad of products is obtained. The high regioselectivity obtained when using *t*BuCCH can be explained by the insertion of the alkyne into the An–C bond (Figure 5), in which the bulky *tert*-butyl group points away from the sterically encumbering pentamethyl cyclopentadienyl ligands.
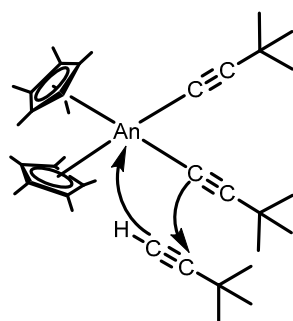
Figure 5. Regioselective insertion of *t*BuCCH into An–C bond. Adapted with permission from Haskel, A.; Straub, T.; Dash, A.K.; Eisen, M.S. *J. Am. Chem. Soc.* **1999**, *121*, 3014–3024 [53]. Copyright 1999 American Chemical Society.

In general, the extent of oligomerization, which describes ratio between the formation of dimers (**E**), or trimers (**D**) *versus* higher oligomers, depends on the difference of the energies of activation $\Delta\Delta G^{\ddagger}$. The difference in the energies of activation $\Delta\Delta G^{\ddagger}$ in turn depends on the size of the metal center, as well as on the steric encumbrance of the R substituents of the alkynes. The mechanism for the actinide mediated oligomerization of alkynes is depicted in Scheme 10. The first step of the mechanism is the formation of the catalytically active actinide bis(acetylide) complex **A** by a protonolysis of Cp*$_2$AnMe$_2$ with two equivalents of alkyne, forming two equivalents of methane. Subsequently, an incoming alkyne inserts into the An–C bond of complex **A** in a 1,2-head-to-tail fashion, the actinide bis(alkenyl) intermediate **B**. Complex **B** can now either undergo a σ-bond metathesis with an incoming alkyne, forming the geminal dimer **E** under regeneration of complex **A**, or an additional 2,1-tail-to-head insertion of an incoming alkyne, furnishing the bis(dienyl) actinide species **C**. A subsequent σ-bond metathesis with an incoming alkyne generates the trimeric product **D** under regeneration of the catalytically active actinide bis(acetylide) complex **A** (Scheme 10) [53,64].
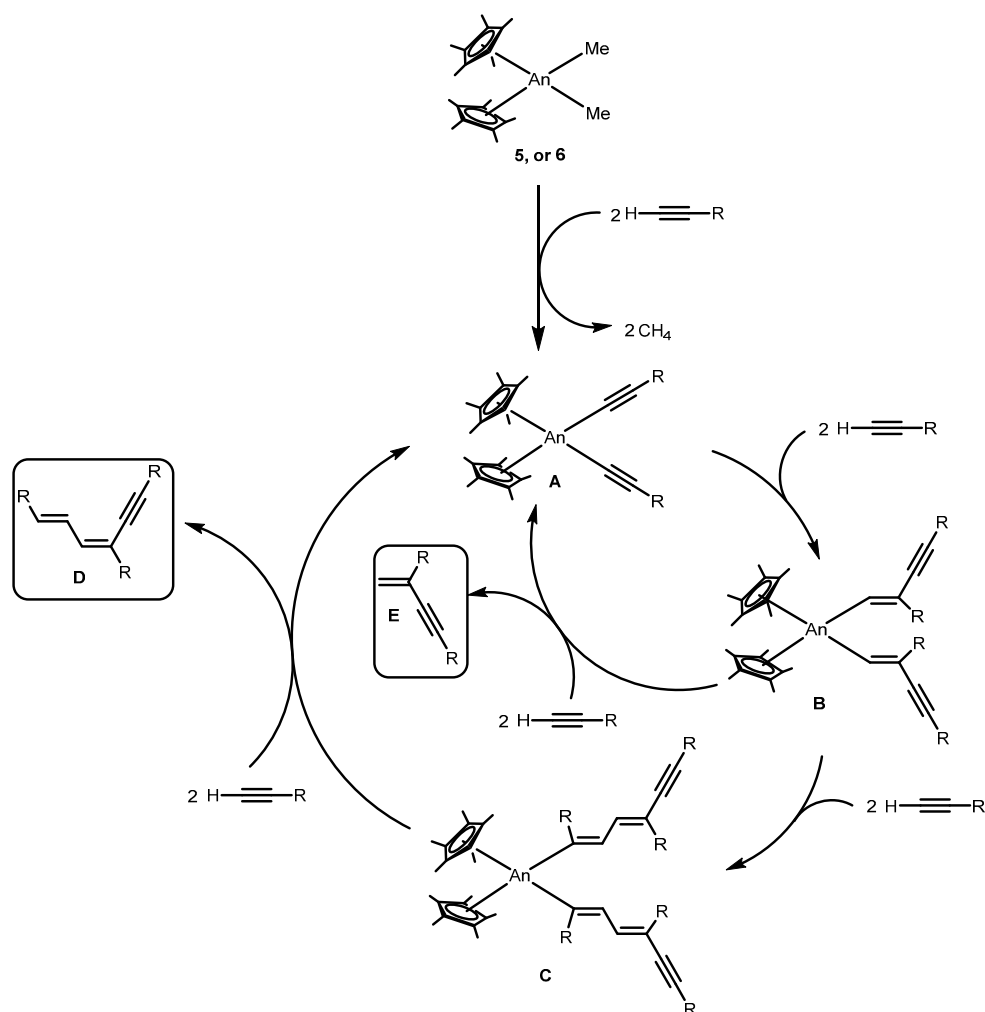
Scheme 10. Proposed mechanism for the actinide mediated oligomerization of terminal alkynes. Adapted with permission from Haskel, A.; Straub, T.; Dash, A.K.; Eisen, M.S. *J. Am. Chem. Soc.* **1999**, *121*, 3014–3024 [53]. Copyright 1999 American Chemical Society.

In order to obtain exclusively short oligomers Eisen *et al.*, developed a methodology, which comprises the addition of external amines to the reaction mixture, leading to a controlled formation of short oligomeric products [54]. The added primary and secondary amines act as chain transfer reagents without being incorporated into the product, and therefore also don't need to be eliminated from the obtained oligomer. The effect of the amine on the chemo- and regio-selectivity of the reaction depends on the nature of the actinide center, and the nature of the alkyne. While the use of $Cp*_2UMe_2$ (**5**) as pre-catalyst lead to the formation of the respective hydroamination product upon addition of an external amine, the use of $Cp*_2ThMe_2$ (**6**) as the pre-catalyst, yields the desired short oligomers. When aromatic alkynes and non-bulky primary amines are used in combination with the organothorium complex **6**, only the *trans* dimer is obtained as product. Per contra, aliphatic alkynes with bulky amines and the pre-catalyst **6** furnished only the geminal dimer, and trimer. The thorium mediated oligomerization of alkynes in addition of an external amine source is presented in Scheme 11. In the first step of the catalytic cycle the catalytically active thorium bis(amido) complex **B** is formed by a protonolysis reaction between $Cp*_2ThMe_2$ (**6**) and two equivalents of amine. The thorium bis(amido) complex **B**, which is in equilibrium with the thorium bis(amido) amine compound **A**, subsequently

reacts with one equivalent of alkyne, generating intermediate **C**. The thorium complex **C** can now undergo a rapid insertion of an incoming alkyne into the Th–σ–carbyl bond, furnishing the thorium-alkynyl-amido intermediate **D**. Complex **D** can now react either in a protonolysis reaction with an incoming amine, forming dimer **E** under regeneration of the catalytically active species **B**, or insert a further equivalent of alkyne into the Th–C bond of **D**, followed by σ-bond protonolysis by an incoming amine to furnish the respective trimer and complex **B** (Scheme 11) [54].
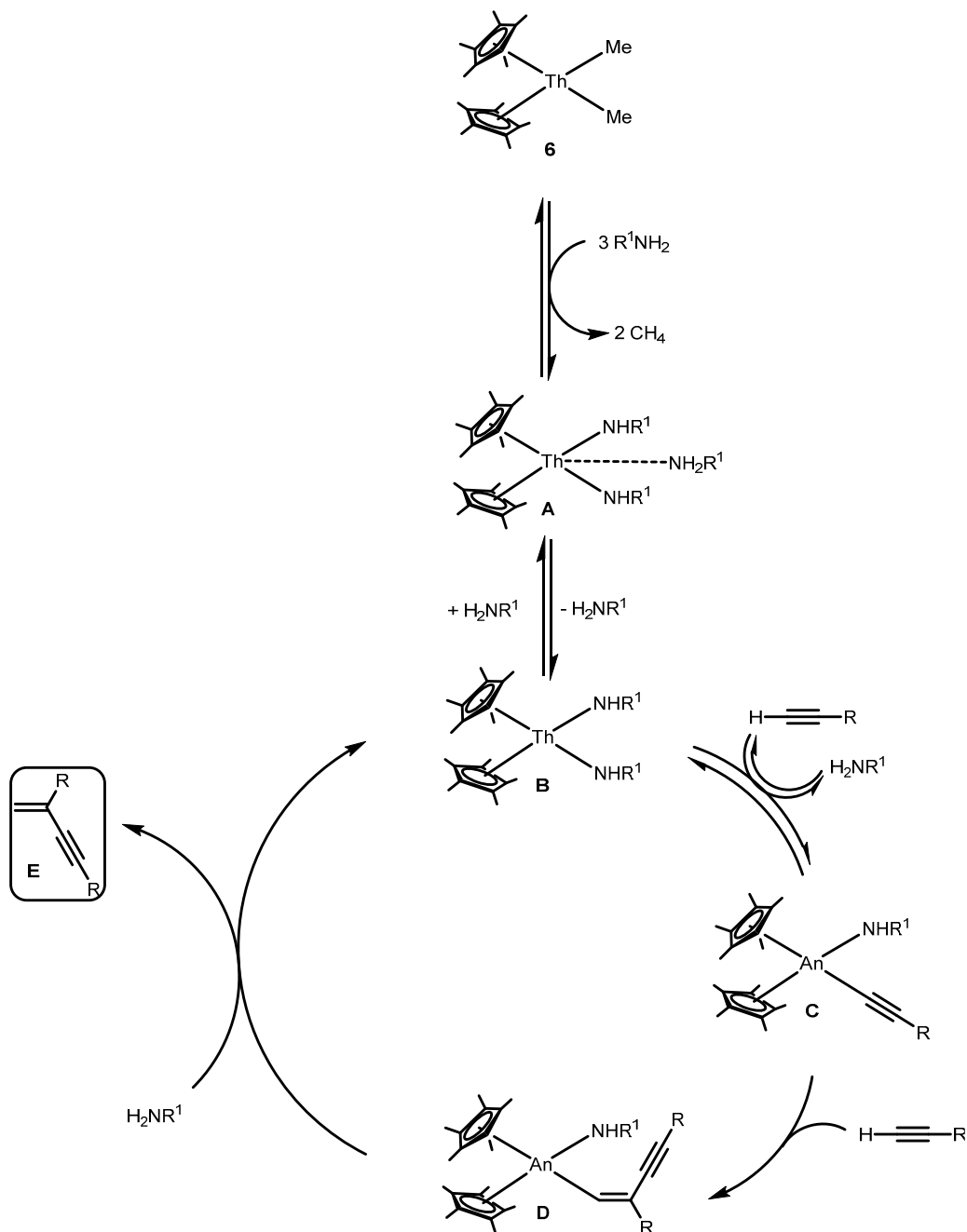
Scheme 11. Proposed mechanism for the thorium mediated dimerization of alkynes using external primary amines. R = Alkyl, Aryl, or SiMe$_3$. The regioselectivity of the alkyne insertion into the Th–C bond is explained in Figure 5 (*vide supra*). Adapted with permission from Haskel, A.; Wang, J.Q.; Straub, T.; Neyroud, T.G.; Eisen, M.S. *J. Am. Chem. Soc.* **1999**, *121*, 3025–3034 [54]. Copyright 1999 American Chemical Society.

In addition to the organoactinides **5** and **6**, the cationic uranium complex [(Et$_2$N)$_3$U] [BPh$_4$] (**11**) was successfully applied in the oligomerization and cross oligomerization of terminal alkynes, leading to the spectroscopic characterization of the first π-alkyne uranium complex as the key intermediate in the catalytic cycle [65–67]. Recently, Meyer *et al.*, investigated the reactivity of a uranium (III) coordination complex toward various terminal acetylenes, which led to the formation of binuclear uranium (IV) species that could be isolated and structurally characterized [68].

An interesting reactivity in the σ-bond metathesis of silylated alkynes was obtained using the oxo-bridged uranium complex [(η^5-(C$_5$Me$_4$)$_2$SiMe$_2$)U(^{n}Bu)(µ-O)]$_2$ (**12**) as pre-catalyst [69]. The product distribution using terminal, or internal acetylenes and catalyst **12** is presented in Scheme 12, and the mechanism of the reaction in Scheme 13. At first, the catalytically active actinide acetylide complex **A** is formed by a protonolysis of complex **12** with TMSCCH, generating two equivalents of butane. The uranium acetylide **A** reacts with an incoming molecule of TMSCCH over the four-membered transition state **B**. This leads to the cleavage of the Si–C bond and the formation of the uranium acetylide species **D** under elimination of the internal alkyne product **C**. Subsequently, complex **D** undergoes a protonolysis reaction with an additional equivalent of TMSCCH, furnishing acetylene (**E**) and regenerating the active catalyst **A** (Scheme 12) [69].

Me$_3$Si——≡——H + R——≡——H $\xrightarrow{\text{[cat. }\mathbf{12}\text{]}}$ Me$_3$Si——≡——SiMe$_3$ + Me$_3$Si——≡——R + H——≡——H

Me$_3$Si——≡——SiMe$_3$ + R——≡——H $\xrightarrow{\text{[cat. }\mathbf{12}\text{]}}$ Me$_3$Si——≡——H + Me$_3$Si——≡——R + H——≡——H
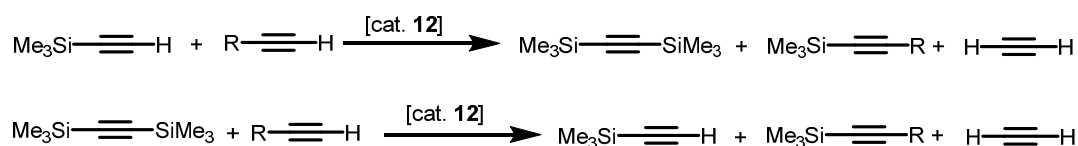
Scheme 12. Product distribution for the cross metathesis of silylated alkynes, mediated by complex **12**. Adapted with permission from Wang, J.; Gurevich, Y.; Botoshansky, M.; Eisen, M.S. *J. Am. Chem. Soc.* **2006**, *128*, 9350–9351 [69]. Copyright 2006 American Chemical Society.

2.2.2. Coupling of Terminal Alkynes and Isonitriles

The coupling of terminal alkynes with isonitriles to furnish α,β-unsaturated aldimines was studied with the organoactinides Cp*$_2$AnMe$_2$ (An = U, Th) **5** and **6**, as well as cationic uranium complex [(Et$_2$N)$_3$U] [BPh$_4$] (**11**). The product distribution depends on the catalyst, and the alkyne to isonitrile ratio [70]. While the cationic uranium complex [(Et$_2$N)$_3$U] [BPh$_4$] (**11**) furnishes selectively the *trans* mono coupling product **D** between one equivalent of alkyne and isonitrile, the organouranium catalyst Cp*$_2$UMe$_2$ (**5**) generates the double insertion product of two equivalents of isonitrile and one equivalent of alkyne besides the mono coupling product **D** (Scheme 14). When the isostructural Cp*$_2$ThMe$_2$ (**6**) is used as pre-catalyst, product **D** is obtained, as well as the double insertion product between two equivalents of alkyne and one equivalent of isonitrile. The different product distributions of Cp*$_2$AnMe$_2$ and [(Et$_2$N)$_3$U] [BPh$_4$] indicate different operative mechanisms for neutral and cationic actinide complexes in this catalytic transformation. The proposed mechanism using Cp*$_2$AnMe$_2$ (An = Th, U) as pre-catalyst is depicted in Scheme 14. The catalytically active actinide bis(acetylide) species **A** is formed by a protonolysis reaction of Cp*$_2$AnMe$_2$ with two equivalents of terminal alkyne, generating two equivalents of methane. A subsequent 1,1-insertion of isonitrile into the An–C bond of **A**, which is the rate determining step of the catalytic cycle, generates the iminoacyl intermediate **B**.

Due to the steric hindrance of the pentamethylcyclopentadienyl ligands, the R group of the isonitrile displays a *syn* regiochemistry to the alkyne in the insertion process. Protonolysis of compound **B** with an incoming alkyne leads to the formation of the *cis* mono insertion product **C**, which isomerizes to yield the more stable *trans* product **D**, under regeneration of the active catalyst **A**. Under alkyne starvation conditions, however, the last protonolysis step is slow, hence the iminoacyl complex **B** can undergo an additional 1,1-insertion with a second isonitrile equivalent, furnishing intermediate **E**. A subsequent protonolysis with an additional equivalent of alkyne yields the double insertion product **F**, which isomerizes to the more stable E,E-isomer, under regeneration of the active catalyst **A**. When an excess of alkyne is used the catalytically active species **A** can insert the triple bond of product **D** into the Th–C bond, generating intermediate **G**, followed by a rapid protonolysis step to furnish product **H** under regeneration of the catalytically active thorium bis(acetylide) species (Scheme 14) [70].
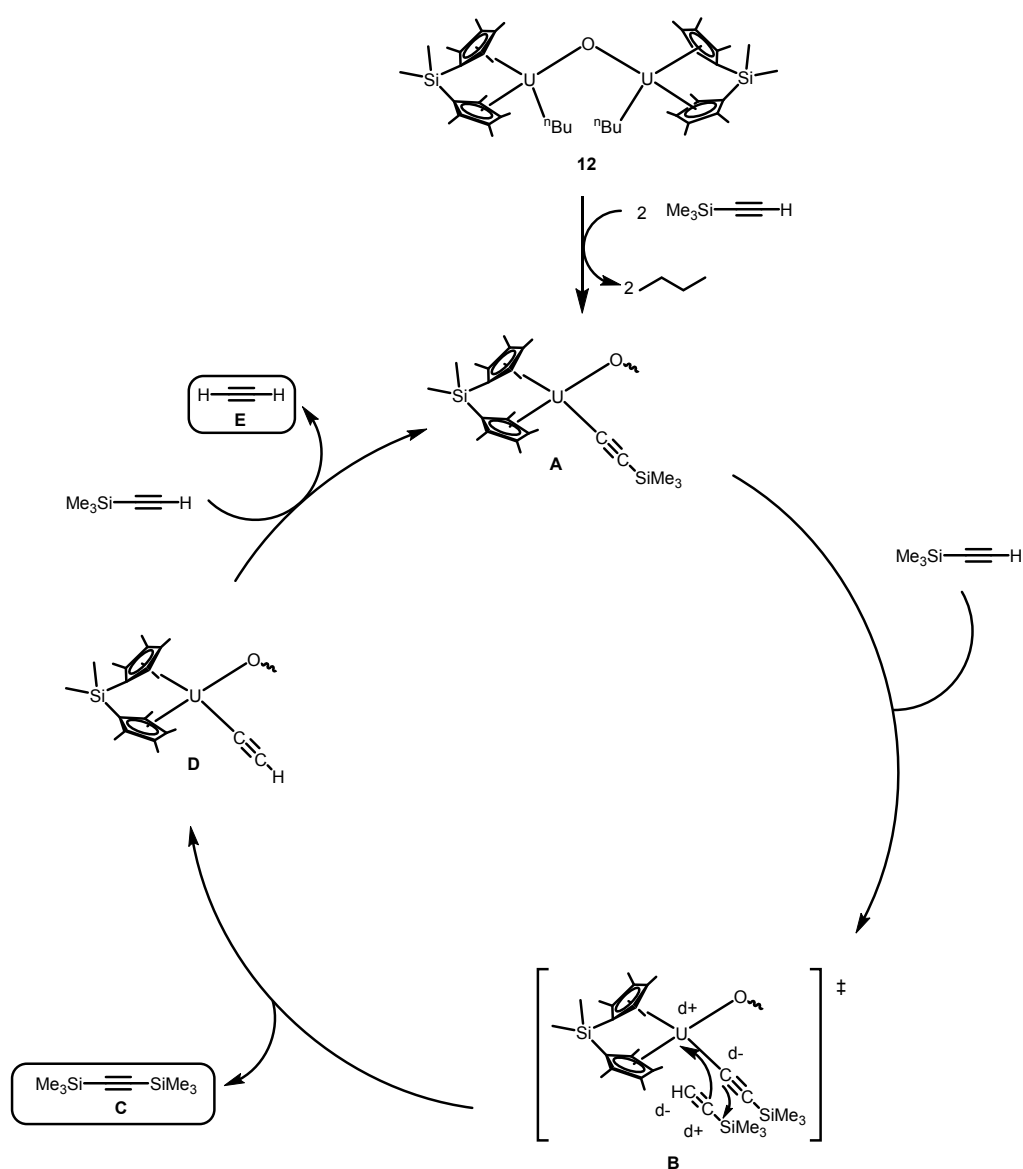
Scheme 13. Proposed mechanism for the cross metathesis of silylated alkynes mediated by complex **12**. A symmetric half of complex **12** has been omitted for clarity. Adapted with permission from Wang, J.; Gurevich, Y.; Botoshansky, M.; Eisen, M.S. *J. Am. Chem. Soc.* **2006**, *128*, 9350–9351 [69]. Copyright 2006 American Chemical Society.
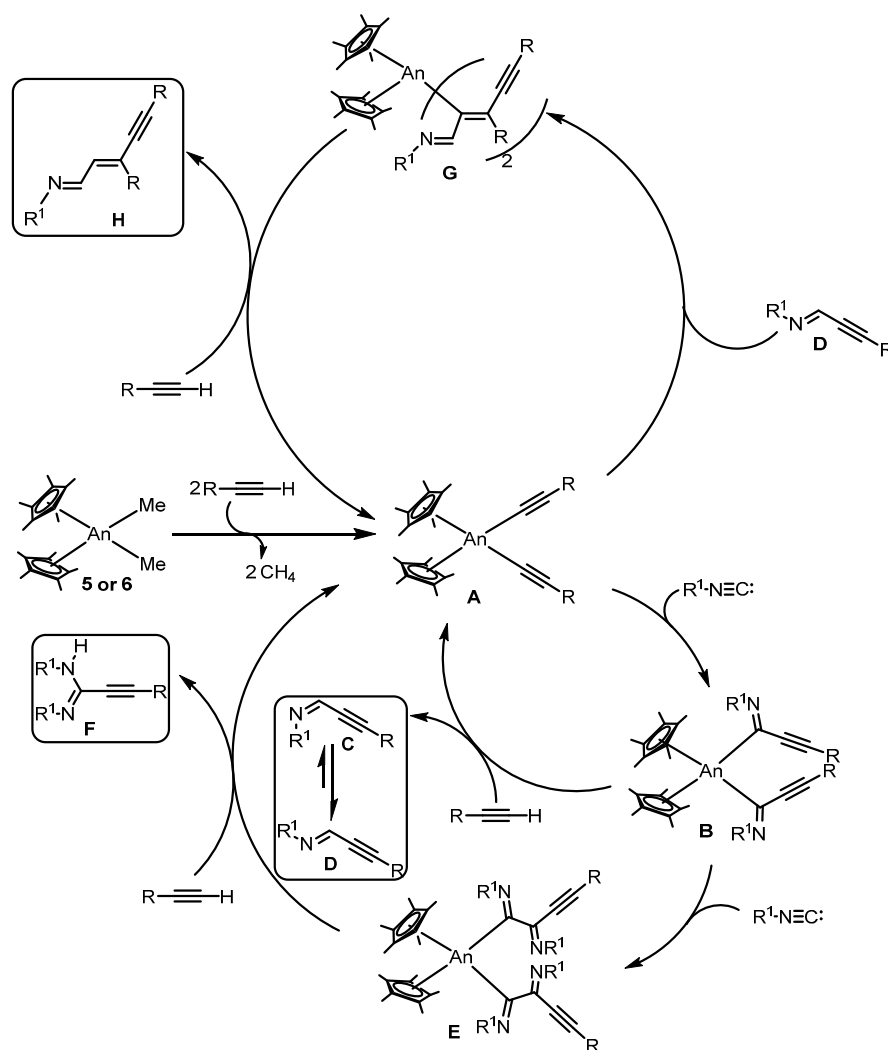
Scheme 14. Proposed mechanisms for the coupling of terminal acetylenes with isonitriles mediated by the organoactinide complexes Cp*$_2$AnMe$_2$ **5** and **6**. Adapted with permission from Barnea, E.; Andrea, T.; Berthet, J.-C.; Ephritikhine, M.; Eisen, M.S. *Organometallics* **2008**, *27*, 3103–3112 [70]. Copyright 2004 American Chemical Society.

In contrary, the use of [(Et$_2$N)$_3$U] [BPh$_4$] (**11**) as pre-catalyst, leads to the selective formation of the mono insertion product **D**, as well as traces of alkyne oligomerization products [70]. Additionally, the product distribution does not depend on the steric encumbrance of the alkyne substituents, suggesting a coordinative more open active catalyst, in which the ligand does not interfere with the approach of the respective substrate. The mechanism for the catalytic coupling terminal acetylenes with isonitriles mediated by complex **11** is presented in Scheme 15. The first step is a rapid equilibrium, leading to the formation of the uranium-acetylide complex **A** by reversible elimination of Et$_2$NH from [(Et$_2$N)$_3$U] [BPh$_4$] (**11**). A subsequent 1,1-insertion of an incoming isonitrile into the U–C bond of **A**, which is the rate determining step of the catalytic cycle, furnishes intermediate **B**. Intermediate **B** can undergo a rapid protonolysis either with an incoming alkyne, or with Et$_2$NH. Due to the stronger basicity of Et$_2$NH as compared to terminal acetylenes, a protonolysis of complex **B** is faster with an additional equivalent of amine, leading to the formation of a stronger M–N bond. Hence, the protonolysis step with Et$_2$NH yields the mono insertion product **D** under regeneration of the

pre-catalyst [(Et₂N)₃U] [BPh₄] (**11**). In addition, the rapid protonolysis by Et₂NH prevents a further insertion of isonitrile into intermediate **B**, avoiding the formation of double insertion products [70].
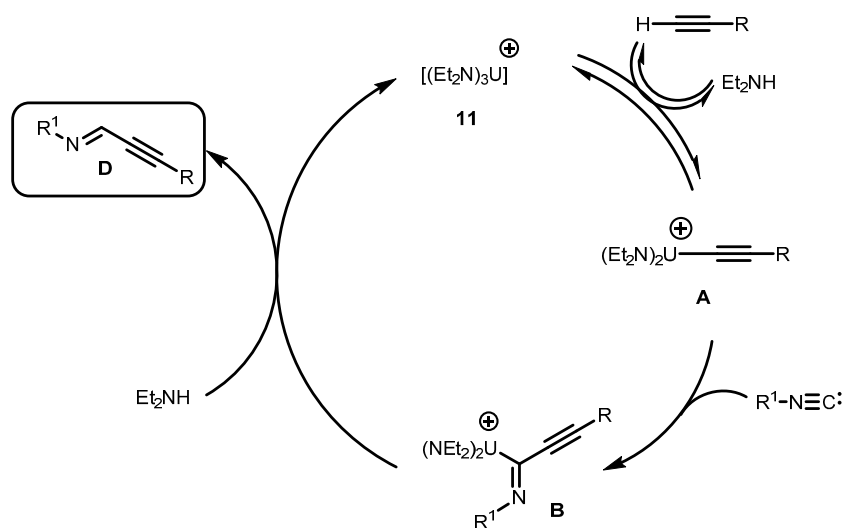
Scheme 15. Proposed mechanism for the coupling of isonitriles and terminal acetylenes mediated by the cationic uranium complex [(Et₂N)₃U] [BPh₄] (**11**). Adapted with permission from Barnea, E.; Andrea, T.; Berthet, J.-C.; Ephritikhine, M.; Eisen, M.S. *Organometallics* **2008**, *27*, 3103–3112 [70]. Copyright 2004 American Chemical Society.

2.2.3. Coupling of Aldehydes: Tishchenko Reaction

Despite the wide application organoactinides have found in various catalytic processes (*vide supra*), transformations involving oxygen containing molecules have been usually been excluded. This can be mainly attributed to the high oxophilicity of the early actinide elements thorium and uranium, which results in a decreased catalytic activity due to the formation of thermodynamically stable An=O (An = actinides) species, which are catalytically inactive [71]. Marks *et al.*, showed, that the replacement of one of the methyl ligands in Cp*₂ThMe₂ by an alkoxo ligand (OR) leads to decrease in the activity by a factor of 4000 in the hydrogenolysis reaction [71]. Eisen *et al.*, broke the myth of catalytically inactive actinide oxo species by developing a methodology based on a nearly thermoneutral reaction, which comprises the reaction of an An–O species with an oxygen containing molecule. Hence, a new An–O bond with similar bond energy is formed, and the reaction is governed by entropy. This methodology has been applied in the catalytic Tishchenko reaction, which comprises the dimerization of two equivalents of aldehyde to furnish the respective ester [72,73]. Thus, the Tishchenko reaction presents an atom economic route for the preparation of esters. Eisen and co-workers have used the thorium catalysts Cp*₂ThMe₂ (**6**), Th(NMeEt)₄ (**13**), and the *ansa*-bridged complex Me₂Si(C₅Me₄)Th(*n*-Bu)₂ (**4**) as pre-catalyst for the dimerization of a variety of aromatic aldehydes. The catalytic activity was shown to increase in the order Cp*₂ThMe₂ (**6**) < Th(NMeEt)₄ (**13**) < Me₂Si(C₅Me₄)Th(*n*-Bu)₂ (**4**), corroborating an increased catalytic activity with a more open coordination sphere of the respective actinide complex [73]. Additionally, the nature of the substituents on the aromatic ring of the respective aldehyde have been shown to influence the reaction rate, displaying higher rates for electron withdrawing substituents on the aromatic ring. While the

Tishchenko reaction with various aromatic aldehydes yielded the respective esters in moderate to high yields, the use of two different aldehydes to give the asymmetrically substituted ester did not prove successful. The mechanism for the thorium mediated dimerization of aldehydes is presented in Scheme 16. In the first step two equivalents of aldehyde insert into Th–C bond of complex **6** forming intermediate **A**, followed by an insertion of two further equivalents of aldehyde into the Th–O bond of **A**, furnishing the thorium-alkoxo species **B**. A hydride transfer over a six membered transition state (**C**), leads to the formation of two equivalents of the α-substituted ester **D**, and the catalytically active thorium alkoxo complex **E**. A subsequent insertion of two equivalents of aldehydes into the Th–O bond of **E** (only one active site of the catalyst is shown for clarity), furnishes the thorium alkoxo intermediate **F**, which can undergo a hydride transfer with an incoming aldehyde, furnishing the ester **H** under regeneration of the active catalyst **E** [72,73].

In addition, Eisen *et al.*, have applied the mixed bis(pentamethyl(cyclopentadienyl)) thorium mono(imidazolin-2-iminato) complex Cp*$_2$Th(Im^{Dipp}N)(Me) (**14**) (Figure 6) (Dipp = di-*iso*-propylphenyl) as pre-catalyst in the dimerization of aromatic, heteroaromatic, cyclic and branched aliphatic aldehydes [74]. Owing to the ability of the imidazolin-2-iminato ligand to donate further electron density to the thorium center, the oxophilicity of complex **14** is slightly decreased, leading to an enhanced catalytic activity with oxygen containing molecules. While Cp*$_2$ThMe$_2$ (**6**) exhibits two catalytically active methyl groups, Cp*$_2$Th(Im^{Dipp}N)(Me) (**14**) has only one labile ligand, allowing for an evaluation of the catalytic activity per active site, which was higher for the mixed ligand thorium complex Cp*$_2$Th(Im^{Dipp}N)(Me) (**14**) than for the structurally similar Cp*$_2$ThMe$_2$ (**6**) [74].
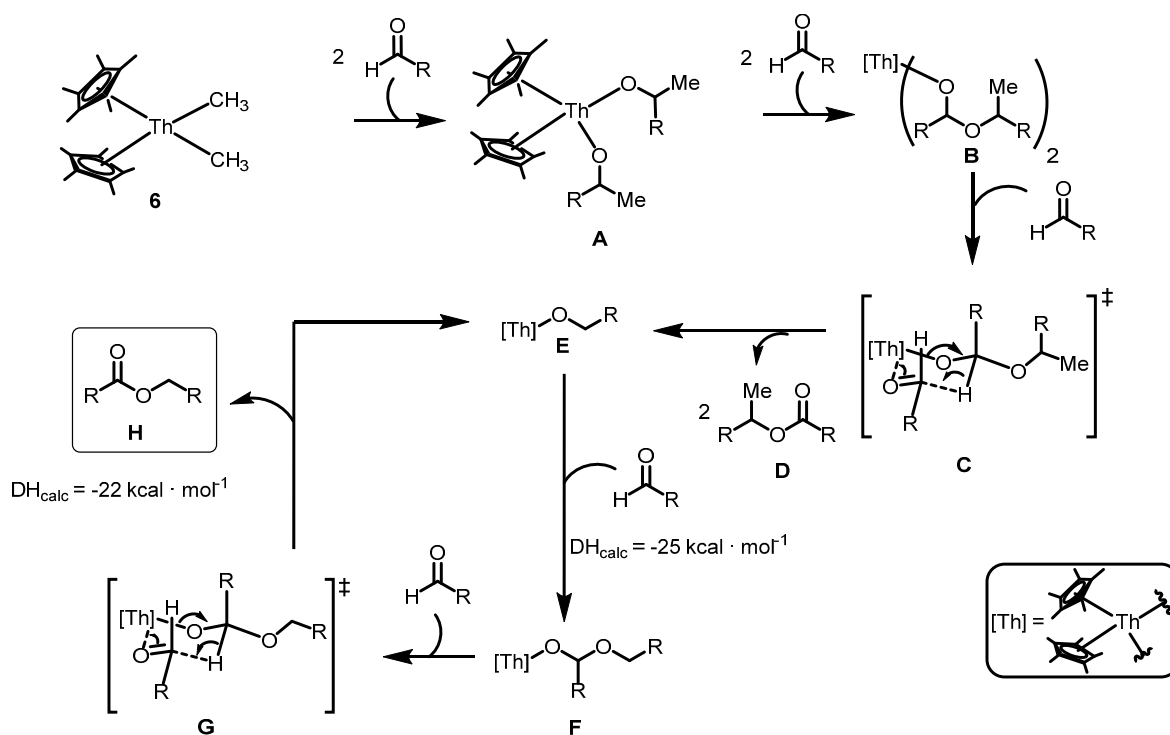
Scheme 16. Proposed mechanism for the catalytic dimerization of aldehydes mediated by Cp*$_2$ThMe$_2$ (**6**). Adapted with permission from Andrea, T.; Barnea, B.; Eisen, M.S. *J. Am. Chem. Soc.* **2008**, *130*, 2454–2455 [72]. Copyright 2008 American Chemical Society.
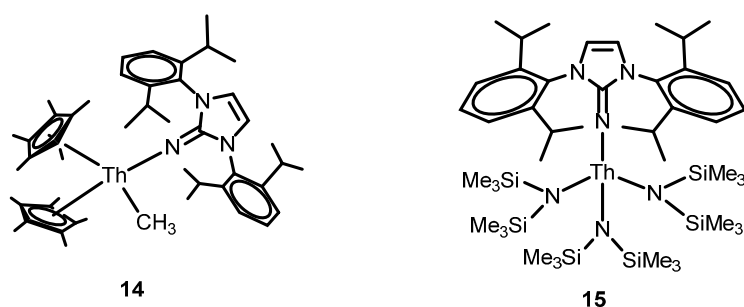
Figure 6. Imidazolin-2-iminato thorium complexes **14** and **15** applied as pre-catalysts for the Tishchenko reaction [74,75].

The Tishchenko reaction was rendered selective toward the formation of asymmetrically substituted esters (Scheme 17) by applying the mono(imidazolin-2-iminato) thorium complex $(Im^{Dipp}N)Th(N(SiMe_3)_2)_3$ (**15**) and an excess of aromatic aldehyde (RCHO/ArCHO 50/200) [75]. While the mechanism using complex **15**, follows the cycle described in Scheme 16, the selectivity toward the formation of the asymmetrically substituted ester could be ascribed to the large difference between the reactions rates for the dimerization of aliphatic aldehydes, as compared to their aromatic counterparts. Hence, the thorium alkoxo species **A** (Scheme 17) will react preferentially with an aliphatic aldehyde, forming a thorium alkoxo intermediate (**B**), which will transfer a hydride to an incoming aromatic aldehyde over the six membered transition state **C**, since aromatic aldehydes are better hydride acceptors than their aliphatic counterparts. Thus, the asymmetrically substitutes ester **D** is obtained, under regeneration of the catalytically active thorium alkoxo species **A** (Scheme 17) [75].
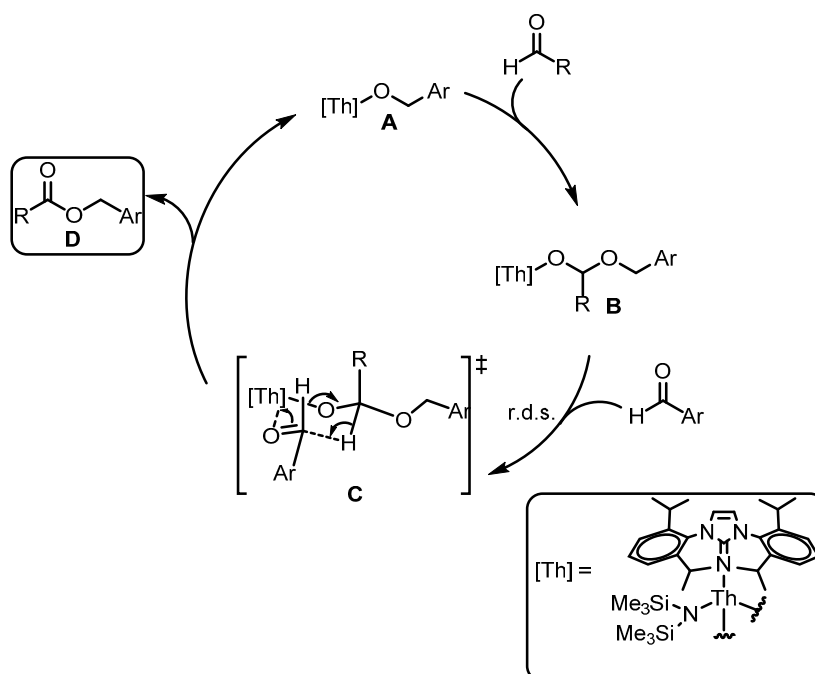
Scheme 17. Mechanism for the crossed Tishchenko reaction mediated by $(Im^{Dipp}N)Th(N(SiMe_3)_2)_3$ (**15**). Adapted with permission from Karmel, I.S.R.; Fridman, N.; Tamm, M.; Eisen, M.S. *J. Am. Chem. Soc.* **2014**, *136*, 17180–17192 [75]. Copyright 2014 American Chemical Society.

2.2.4. Dehydrocoupling of Amines with Silanes

Dehydrocoupling reactions of amines with silanes to form silazanes have gained the interest of the scientific community, since silazanes are important staring materials for the production of silicon nitride materials [76]. Eisen *et al.*, have investigated the use of the cationic uranium amide [(Et$_2$N)$_3$U] [BPh$_4$] (**11**) as pre-catalyst for the catalytic coupling of primary and secondary amines with PhSiH$_3$, furnishing aminosilanes with the general formula PhSiH$_{3-n}$(NHR)$_n$ (n = 1–3) [77]. The yield of the reaction and product distribution depends on the experimental conditions, as well as on the amine, showing higher catalytic activities for the coupling of PhSiH$_3$ with primary amines than with secondary amines. In addition, the steric hindrance of the R substituent of the respective amine exhibited an influence on the product obtained. While small substituents, such as *n*-propyl furnished a mixture of PhSiH(NH^{n}Pr)$_2$ and PhSi(NH^{n}Pr)$_3$, the sterically demanding *tert*-butyl amine, afforded exclusively PhSiH$_2$NH^{t}Bu as product. A plausible mechanism for this reaction is presented in Scheme 18. In the first step, the catalytically active species **A** is formed by a transamination reaction of [(Et$_2$N)$_3$U] [BPh$_4$] (**11**) with an excess of incoming amine RNH$_2$. Subsequent reaction of **A** with PhSiH$_3$ furnishes the uranium hydride complex **C** and one equivalent of PhSiH$_2$NHR (**B**). The uranium hydride intermediate **C** reacts with one equivalent of incoming amine to give one equivalent of H$_2$, under regeneration of the active catalyst **A** (Scheme 18). Different polyaminosilanes of the formula PhSiH$_{3-n}$(NHR)$_n$ are obtained, when complex **A** reacts with PhSiH$_{4-n}$(NHR)$_{n-1}$, instead of PhSiH$_3$ (Scheme 18) [77].
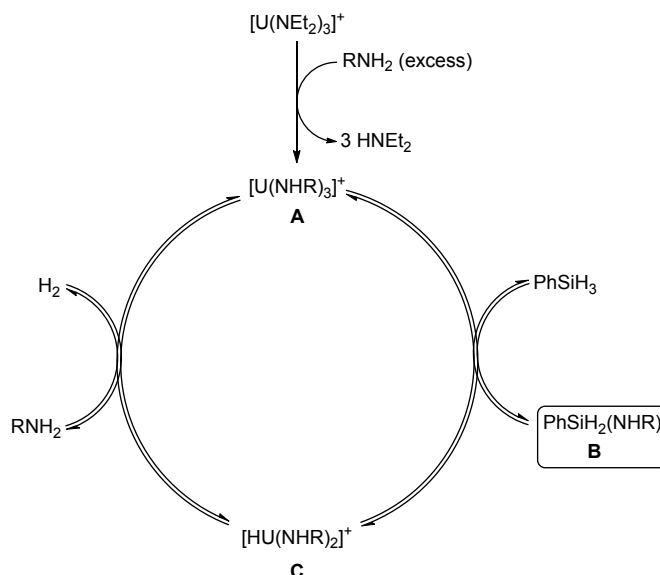
Scheme 18. Mechanism for the dehydrocoupling of amines and silanes, mediated by complex **11**.

2.3. Polymerization Reactions

2.3.1. Polymerization of α-Olefins

The polymerization of α-olefins has been initially studied with the cationic actinide complexes of the type [Cp*$_2$ThMe] [BPh$_4$], and [Cp*$_2$ThMe] [B(C$_6$F$_5$)$_4$], in which a dependence of the catalytic

activity on the nature of the counter-anion was observed [78,79]. Hence, a large variety of counter-anions with different steric and electronic properties has been synthesized, in order to find out the optimal polymerization conditions using organoactinide complexes. Nevertheless, the catalytic activity of cyclopentadienyl based organoactinide complexes in the polymerization of α-olefins remained several orders of magnitude lower, as compared to isostructural group IV metal complexes [80]. An improvement was recently achieved with the use diamido ether uranium (IV) dialkyl complexes **8**, **16**, and **17** (Figure 7), for which catalytic activities up to 560 $g \cdot mol^{-1} \cdot h^{-1} \cdot atm^{-1}$ were obtained in the polymerization of ethylene under ambient conditions [81]. Surprisingly, the addition of co-catalyst, such as MMAO (modified methylalumoxane), Et$_2$AlCl, or B(C$_6$F$_5$)$_3$ led to either a reduced catalytic activity, or to a deactivation of the catalyst.

In addition, the actinide bis(amidinate) complexes **18** and **19** have been explored as pre-catalysts for the polymerization of ethylene with different co-catalysts, such MAO (methylalumoxane), B(C$_6$F$_5$)$_3$ with small amounts of MAO, and TIBA (triisobutyl aluminium), displaying the highest catalytic for the production of high density polyethylene with TIBA as co-catalyst [82]. A series of mechanistic studies, and radical trapping experiments led to the proposed mechanism shown in Scheme 19. In the first step, the alkylation of pre-catalyst **18** with TIBA furnishes the bis(alkyl) compound **A**. A subsequent reduction of **A** to the uranium (III) intermediate **B**, leads to the formation of an isobutyl radical, which was confirmed by trapping experiments with C$_{60}$. Intermediate **B** is oxidized back to the U(IV) complex **C** by ethylene. Complex **C** will undergo further radical insertions of ethylene to give compound **D**. A subsequent β-H-elimination of the oligomeric chain radical, furnishes the metal hydride species **E**. The formation of the radical chain was confirmed by C$_{60}$ trapping experiments. The reaction of complex **F** with an additional equivalent of TIBA generates the catalytically active cationic complex **G** [82].
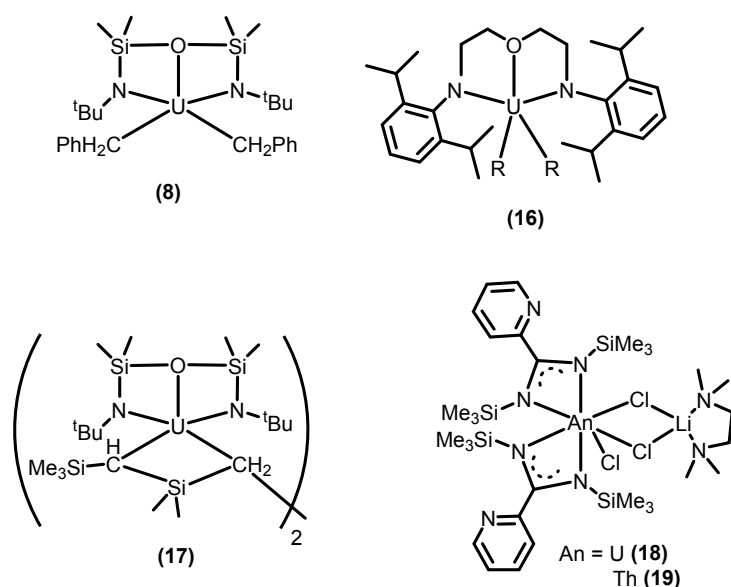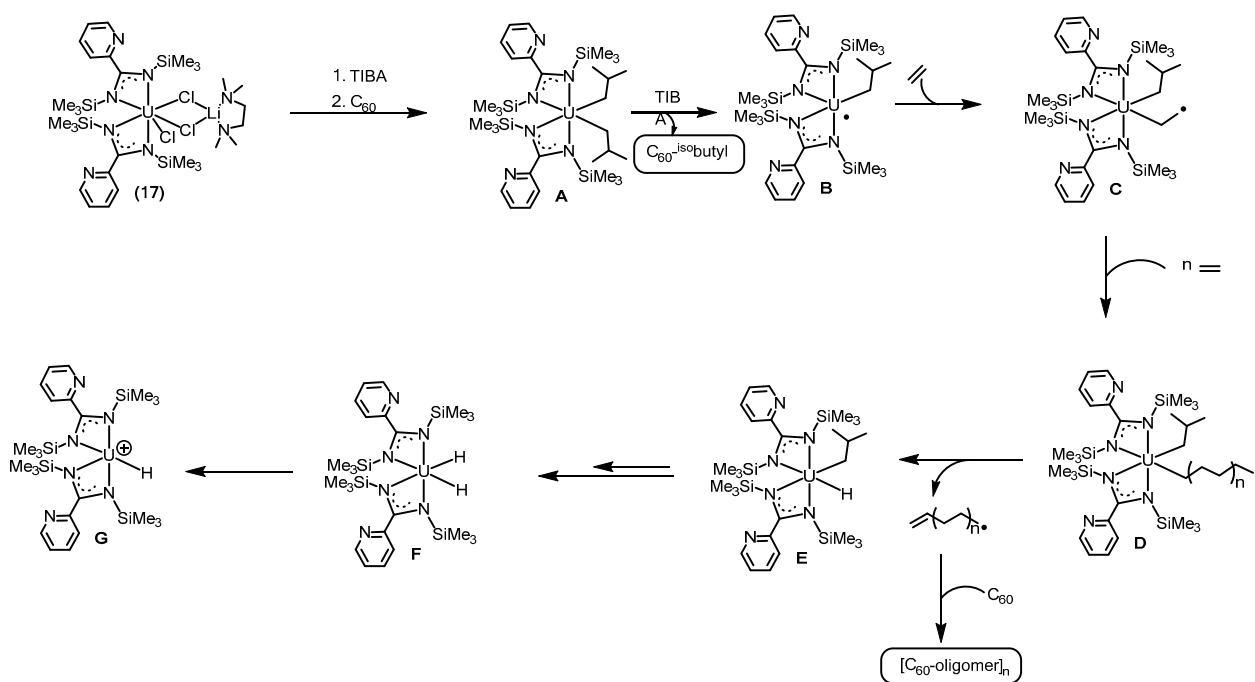

Figure 7. Diamino ether uranium (IV) complexes and bis(amidinate) actinide complexes used as pre-catalysts in the polymerization of ethylene [81,82].
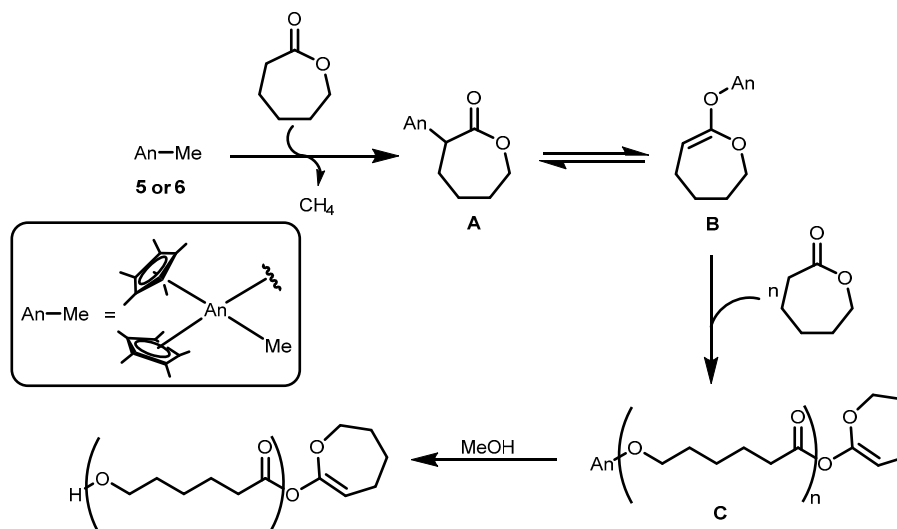
Scheme 19. Proposed mechanism for the polymerization of ethylene mediated by the bis(amidinate) uranium complex **18**. Adapted with permission from Domeshek, E.; Batrice, R.J.; Aharonovich, S.; Tumanskii, B.; Botoshansky, M.; Eisen, M.S. *Dalton Trans.* **2013**, *42*, 9069–9078 [82]. Copyright 2013 Royal Society of Chemistry.

### 2.3.2. Ring Opening Polymerization of Cyclic Esters

Biodegradable polymers such as poly(ε-caprolactone) and polylactide have received growing attention in the course of the past two decades, which can be attributed to the availability of the respective monomers, as well as to the various fields of applications, such environmentally friendly packaging materials [83], microelectronics [84] and adhesives [85]. While main group, transition metal, and lanthanide complexes have been thoroughly studied as pre-catalysts in the ROP (Ring Opening Polymerization) of cyclic esters [86], actinide compounds have only been investigated in the course of the last decade. Ephritikhine *et al.*, carried out a comparative study using a series of tris(amidinate) lanthanide (III) complexes and the isostructural uranium complex for the ROP of ε-caprolactone [87]. While the lanthanide complexes displayed a very high catalytic activity under mild reaction conditions, the uranium analogue was almost completely inactive, which was attributed to the higher oxophilicity of the uranium center [87]. The ROP of ε-caprolactone and L-lactide was rendered catalytic by Eisen *et al.*, using the actinide metallocenes Cp*$_2$AnMe$_2$ (An = U (**5**), Th (**6**)), as well as the cationic uranium complex [(Et$_2$N)$_3$U] [BPh$_4$] (**11**) [88]. The highest catalytic activity was displayed by the cationic complex **11**, due to the more open coordination sphere as compared to **5** and **6**. In addition, Cp*$_2$ThMe$_2$ (**6**) was found to be more active than Cp*$_2$UMe$_2$ (**5**), which was attributed to the higher oxophilicity of uranium as compared to thorium. The polymers obtained displayed high molecular weights and narrow molecular weight distributions, indicative of a living polymerization process. The coordination-insertion mechanism for the ROP of ε-caprolactone mediated by the organoactinides Cp*$_2$AnMe$_2$ is presented in Scheme 20. The first step of the mechanism includes the abstraction of the α-hydrogen of the monomer, furnishing the actinide enolate **B** and two equivalents of

methane. Subsequent insertion of further ε-caprolactone monomers into the An–O bond of **B** gives the open chain intermediate **C**, which upon addition of methanol gives the respective polymer **D** [88]. Similarly, the mixed ligand thorium metallocene Cp*$_2$Th(Im^{Dipp}N)(Me) (**14**) also operates via a coordination insertion mechanism, with one active methyl group per catalyst molecule [74].

Scheme 20. Proposed mechanism for the ROP (Ring Opening Polymerization) of ε-caprolactone, mediated by the organoactinide complexes Cp*$_2$AnMe$_2$ (**5** and **6**). Adapted with permission from Barnea, E.; Moradove, D.; Berthet, J.-C.; Ephritikhine, M.; Eisen, M.S. *Organometallics* **2006**, *25*, 320–322 [88]. Copyright 2006 American Chemical Society.

In addition, several bis(amidinate) actinide compounds have been investigated as pre-catalysts in the ROP of ε-caprolactone. The thorium bis(pyridylamidinate) **19** has been found to promote the cyclooligomerization of ε-caprolactone, in which complex **19** reacts via the amidine moiety (Scheme 21) [89]. The oligomerization reaction mediated by complex **19** furnished two different oligomer fractions: the first fraction contains cyclic pentamers, whereas the second fraction is composed of cyclic undecamers to tridecamers, indicating that two active sites are operative, while the respective fractions are obtained by a similar mechanism. The mechanism for the cyclooligomerization of ε-caprolactone mediated by complex **19** is depicted in Scheme 21. The first step of the mechanism includes the coordination of ε-caprolactone to the thorium center, followed by a displacement of μ-chloro ligand by a molecule of ε-caprolactone, furnishing intermediate **A**. A subsequent nucleophilic attack of an amidinate ligand on the carbonyl moiety of the coordinate ε-caprolactone over a six-membered transition state (**B** and **C**) yields the thorium compound **D**. Intermediate **D** is in an equilibrium with complex **E**, which is further stabilized by an additional coordination of the pyridyl moiety to the thorium center. Insertion of further ε-caprolactone yield complex **F** and additional monomer insertions into the Th–O bond of **F**, gives complex **I** after re-coordination of the cyclic oligomer **G**. Intermediate **I** can react with ε-caprolactone, regenerating the catalytically active species **A**. However, if complex **F** reacts via the second amidinate ligand, then both amidinate moieties are independently active, furnishing the thorium intermediate **H**. Complex **H** can either eliminate the cyclic oligomer **G** under regeneration of complex **F**, or eliminate both cyclic oligomers from both active cites, generating complex **I** [89].
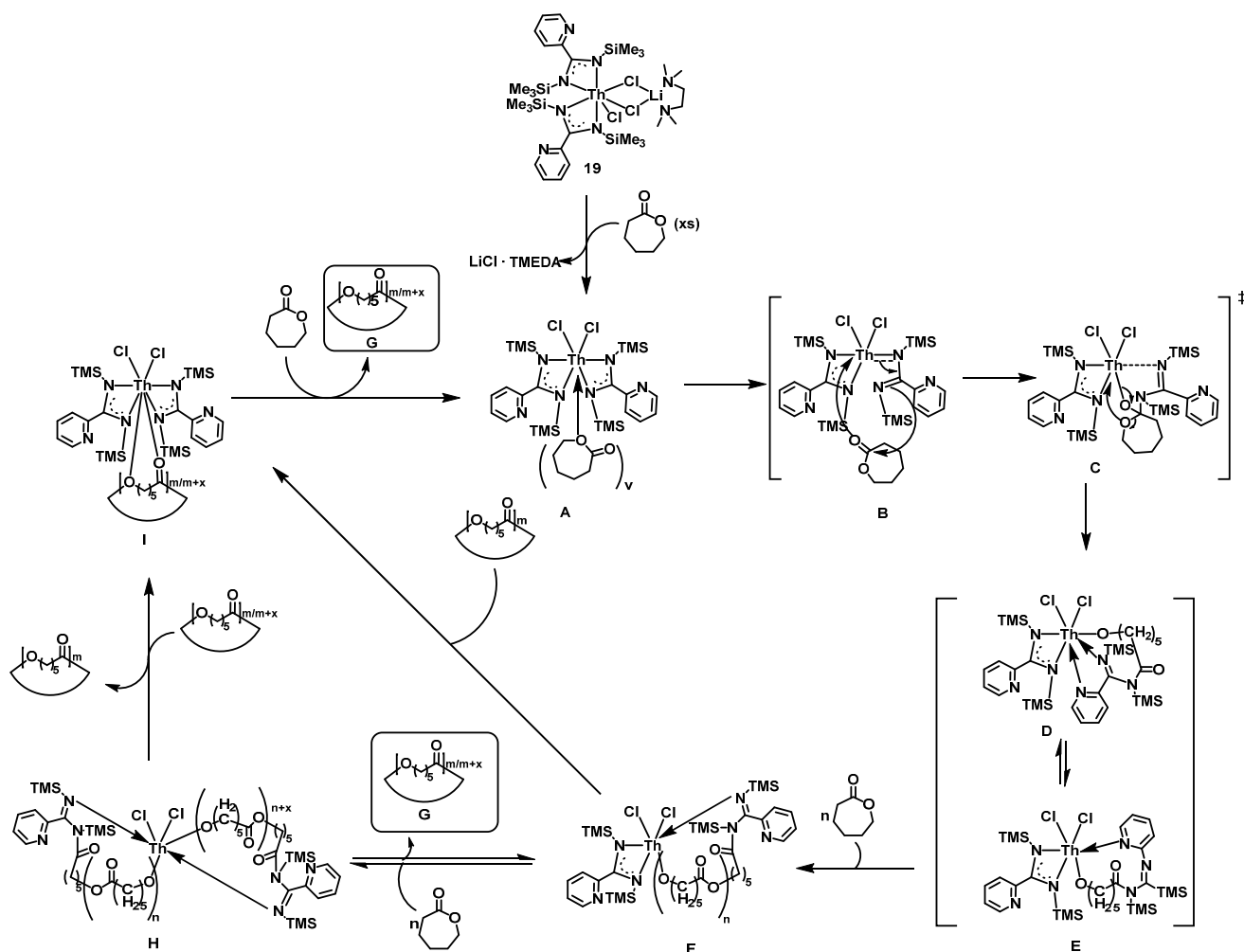
Scheme 21. Mechanism for the thorium mediated cyclooligomerization of ε-caprolactone. Adapted with permission from Rabinovich, E.; Aharonovich, S.; Botoshansky, M.; Eisen, M.S. *Dalton Trans.* **2010**, *39*, 6667–6676 [89]. Copyright 2010 Royal Society of Chemistry.

The actinide bis(amidinate) systems (Figure 8) with functionalized side arms on the amidinate ligand have shown to promote the ROP of ε-caprolactone, furnishing linear polymers with narrow molecular weight distributions [90,91]. A systematic study of a series of bis(amidinate) thorium and uranium complex (**21–25**) with a dimethylamine side arms has shown an increase in the catalytic activity in the order **23** > **24** > **25** > **21** > **22** [91]. Hence, the thorium complexes **23–25** are more active than their uranium analogues **21–22**, and complexes with a phenyl at the *ipso*-position (**21**, **23–24**) are more active than the analogous compounds with a pyridyl moiety at the *ipso*-position (**22** and **25**). Furthermore, complexes **21** and **23** with a shorter carbon linker chain (*n* = 2) display a higher catalytic activity than their analogues **23**, **24–25** with a longer linker chain (*n* = 3), suggesting an increase of the catalytic activity with increasing electron density of the metal center.
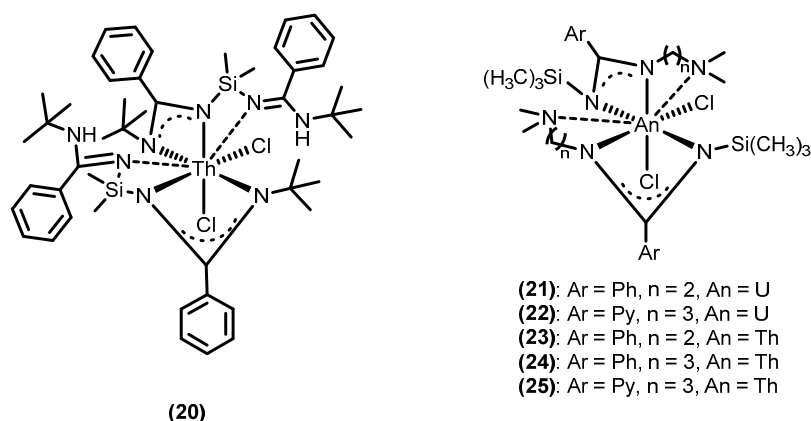
(21): Ar = Ph, n = 2, An = U
(22): Ar = Py, n = 3, An = U
(23): Ar = Ph, n = 2, An = Th
(24): Ar = Ph, n = 3, An = Th
(25): Ar = Py, n = 3, An = Th

(20)

**Figure 8.** Actinide bis(amidinate) complexes **20–25** applied in the ROP of ε-caprolactone [90,91].

The mechanism for the ROP of ε-caprolactone mediated by the actinide bis(amidinate) complexes **20–25** is presented in Scheme 22. The respective actinide complex acts as a Lewis acid; hence none of the ligands is displaced by an ε-caprolactone monomer. Instead the monomer is activated by the Lewis acidic actinide center, generating the actinide alkoxo-caprolate intermediate **A**. A subsequent nucleophilic attack of an incoming monomer on complex **A**, gives the open chain intermediate **B**, which is the rate determining step of the reaction. Further insertion of ε-caprolactone units into the An–O bond of **B**, furnishes compound **C**, which after the elimination of the polymer (**D**) regenerates the active catalyst **A** [90,91]. Also actinide inclusion complexes have been recently shown to operate via the mechanism depicted in Scheme 22 [92].
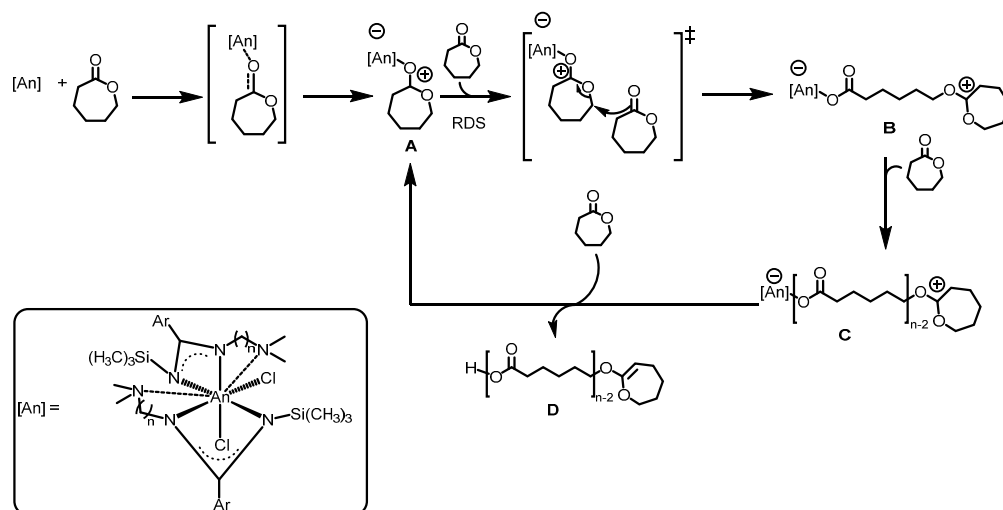
Scheme 22. Mechanism for the Lewis acid catalyzed ROP of ε-caprolactone. Adapted with permission from Karmel, I.S.R.; Elkin, T.; Fridman, N.; Eisen, M.S. *Dalton Trans.* **2014**, *43*, 11376–11387 [90]. Copyright 2014 Royal Society of Chemistry.

Recently, Baker *et al.*, have studied the use of the uranyl complex **26** as pre-catalyst for the cyclooligomerization of various lactones, and the proposed mechanism was further studied using computational methods [93]. While complex **26** mediated the ROP oligomerization of ε-caprolactone and δ-valerolactone to give cyclic oligomers, no catalytic activity was achieved using lactones with smaller ring sizes, such as β-butyrolactone, or γ-butyrolactone. The lack of activity with

β-butyrolactone, and γ-butyrolactone was attributed to the endothermic enthalpy of displacement of a coordinated THF molecule by an incoming monomer. The bimetallic mechanism for the cyclooligomerization of ε-caprolactone mediated by **26** is depicted in Scheme 23. The first step of the mechanism includes the displacement of a coordinated THF molecule by an incoming monomer furnishing intermediate **A**. This step has been calculated to be almost thermoneutral for δ-valerolactone, and ε-caprolactone. The subsequent insertion of the monomer into the U–O bond furnishes the tetrahedral intermediate **B**, which after an intramolecular initiation gives the open chain intermediate **C**. The propagation of the polymerization reaction takes place by the addition of further monomer units, as well as a second catalyst molecule. Thus, two equivalents of catalyst **26** are necessary for the intermolecular propagation, rendering the second part of the mechanism bimetallic (Scheme 23).
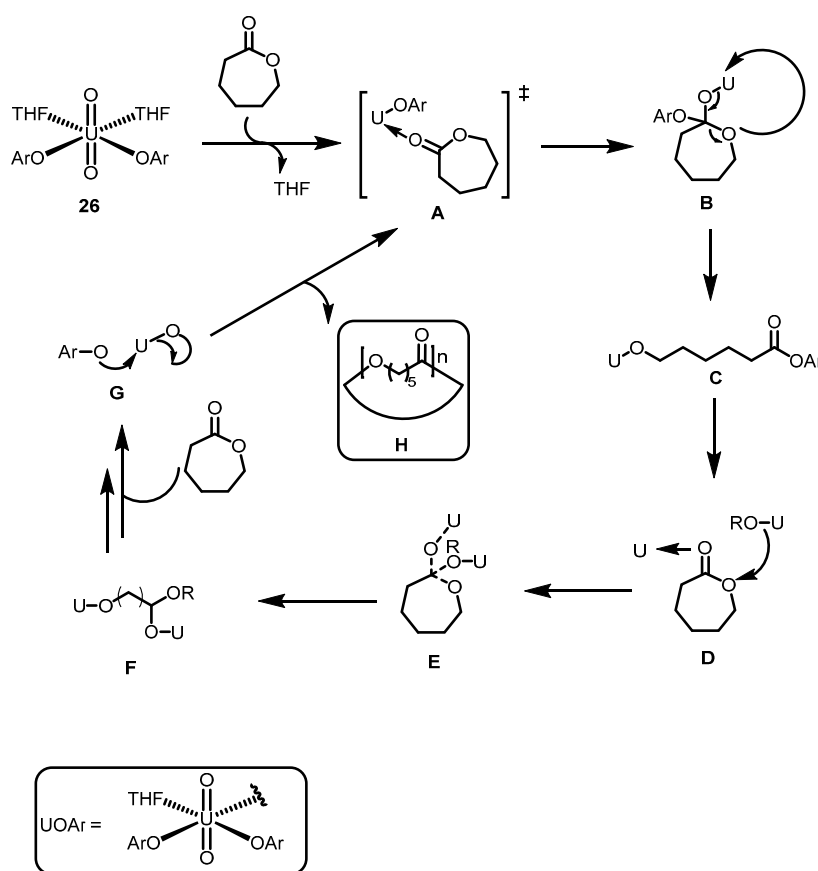
Scheme 23. Mechanism for the cyclooligomerization of ε-caprolactone mediated by the uranyl complex **26**. Adapted with permission from Walshe, A.; Fang, J.; Maron, L.; Baker, R.J. *Inorg. Chem.* **2013**, *52*, 9077–9086 [93]. Copyright 2013 American Chemical Society.

The ROP of *rac*-lactide has been studied with the thorium metallocene complexes **27–29** (Figure 9), furnishing atactic polymers with narrow molecular weight distributions under mild reaction conditions [94,95]. Also the actinide diamido ether compounds have been applied as pre-catalysts for the ROP of *rac*-lactide and L-lactide [96]. The catalytic activity showed a dependence on the actinide center, as well as on the ligand backbone.
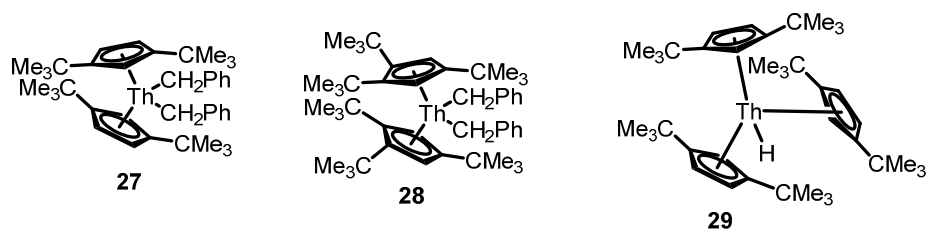
Figure 9. Thorium metallocenes used as pre-catalysts for the ROP of rac-lactide [94,95].

2.4. Further Actinide Mediated Catalytic Transformations

2.4.1. Reduction of Azides and Hydrazines

The catalytic reduction of organic azides to amines requires the transfer of two electrons, which has been achieved by using the high valent U(VI) bis(amido) complex **30** [97]. The catalytic cycle (Scheme 24) consists in the reduction of the U(VI) complex **30** with molecular hydrogen, to furnish the uranium bis(amido) intermediate **A**. Subsequent oxidation of **A** by an incoming organic azide, regenerates the active catalyst **30** under concomitant formation of the primary amine product **B**. Additionally, Cp*$_2$U(=NAd)$_2$ (**30**) has been applied in the catalytic reduction of N,N'-diphenyl hydrazine, generating aniline and azobenzene. Interestingly, this reaction proceeds without the addition of hydrogen, indicating that N,N'-diphenyl hydrazine acts as reducing and oxidizing agent [97].
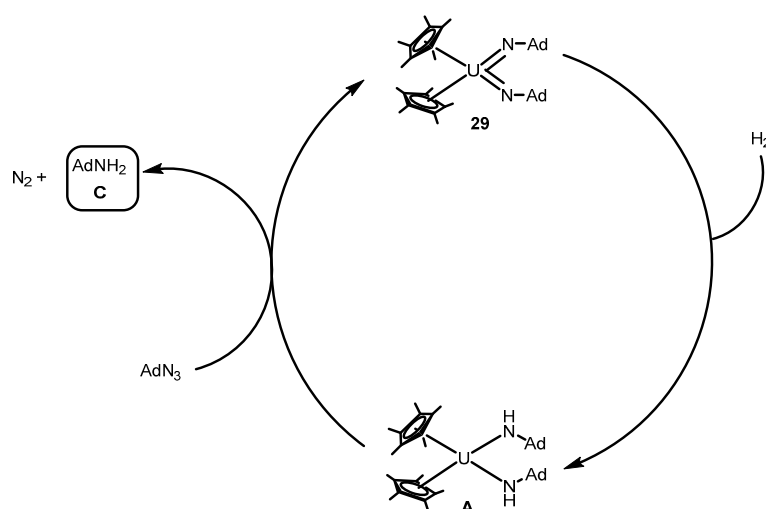

Scheme 24. Catalytic reduction of azides mediated by complex **30**. Ad: Adamantyl. Adapted with permission from Peters, R.G.; Warner, B.P.; Burns, C.J. *J. Am. Chem. Soc.* **1999**, *121*, 5585–5586 [97]. Copyright 1999 American Chemical Society.

2.4.2. ROP of Epoxides

The ring opening polymerization of propylene oxide and cyclohexene oxide using the uranyl compounds [UO$_2$(OAr)$_2$(THF)$_2$] (**26**), [UO$_2$Cl$_2$(THF)$_3$] (**31**), and [UO$_2$Cl$_2$(THF)$_2$]$_2$ (**32**) as pre-catalysts has recently been investigated by Baker *et al.* [98,99]. When using the alkoxo complex **26**, the reaction is expected to be thermodynamically favored, since only U–O bonds are broken, while new U–O bonds with similar bond energies are formed, leading to entropically controlled polymerization. The

polymers obtained using catalysts **26** and **31–32** display narrow molecular weight distributions; however the polymerization process doesn't proceed via a living polymerization mechanism. The proposed bimetallic polymerization mechanism is presented in Scheme 25. The first step of the mechanism is the displacement of a coordinated THF molecule by a molecule of propylene oxide, furnishing intermediate **B**. A subsequent nucleophilic attack on the coordinated propylene oxide monomer represents the rate determining step of the reaction mechanism, giving rise to the open chain intermediate **C**. Further intermolecular nucleophilic attacks on the coordinated monomer via a chain shuttling mechanism generate intermediate **D**. The polymer **E** is obtained after the addition of methanol (Scheme 25) [98,99].
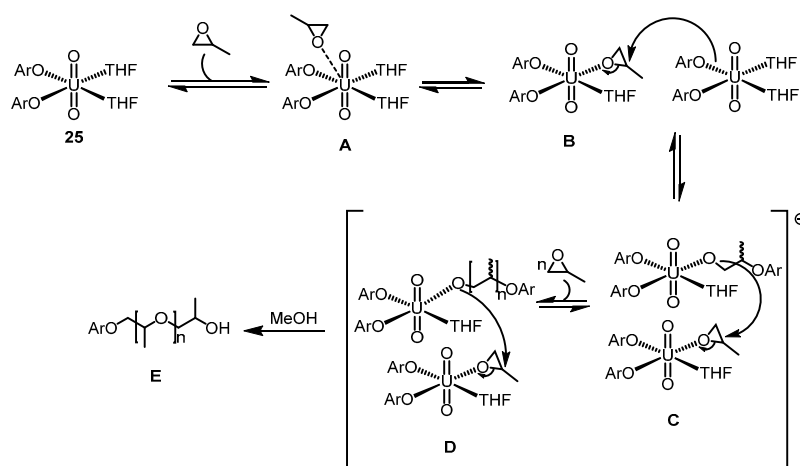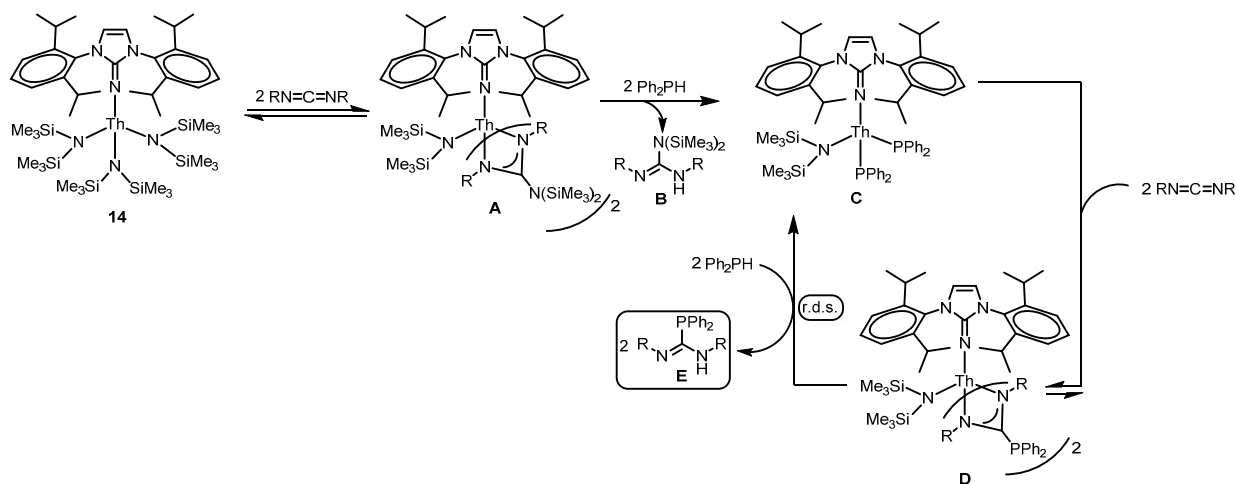

Scheme 25. Proposed mechanism for the ROP of epoxides. Adapted with permission from Baker, R.J.; Walshe, A. *Chem. Commun.* **2012**, *48*, 985–987 [98]. Copyright 2012 Royal Society of Chemistry.

2.4.3. Insertion of Nucleophilic E–H (E = N, P, S) Bonds into Heterocumulenes

The insertion of E–H bonds (E = N, P, S) across heterocumulene systems, such as carbodiimides, isocyanates and isothiocyanates represents and atom-economic route for the generation of a variety of organic synthons, such as guanidines and phosphaguanidines. Therefore this process has been widely studied over the past decade using lanthanide catalysts [100–106]. However, only recently Eisen *et al.*, have reported the application of a thorium catalyst for this type of atom-economic catalytic transformation [107]. The mono(imidazolin-2-iminato) thorium (IV) complex [(Im^{DiPP}N)Th(N(SiMe$_3$)$_2$)$_3$] (**15**) was successfully applied as pre-catalyst for addition of aromatic and aliphatic amines, phosphines and thiols to carbodiimides, isocyanates and isothiocyanates, furnishing the respective addition products in moderate to high yields under mild reaction conditions. Additionally, the thorium complex **15** displayed an unusual high tolerance toward functional groups, and heteroatoms, allowing for a wide scope of products to be accessed. The mechanism for the actinide mediated insertion of phosphines into carbodiimides is presented in Scheme 26. The first step of the reaction mechanism comprises the insertion of two equivalents of carbodiimide into the Th–N$_{amido}$ bonds, furnishing the thorium bis(guanidine) intermediate **A**. Subsequent protonolysis by two equivalents of phosphine leads to the formation of the catalytically active thorium species **C** under generation of two equivalents of guanidine **B**. The insertion of two equivalents of carbodiimide into

the Th–P bond intermediate **C** gives rise to the thorium bis(phosphaguanidine) compound **D**. The rate determining step of the reaction mechanism is the protonolysis reaction of **D** with two equivalents of phosphine, which furnishes the phosphaguanidine product **E** under regeneration of the active catalyst **C** (Scheme 26) [107].

Scheme 26. Proposed mechanism for the actinide mediated insertion of phosphines into carbodiimides [107].

3. Conclusions

The use of organoactinide complexes in catalytic organic transformations has undergone a long journey, since the use of [(η^3-allyl)$_3$UCl] in the homogeneous polymerization of butadiene. The first milestone in organoactinide catalysis was set by the application of bis(pentamethylcyclopentadienyl) actinide complexes for various catalytic organic transformations, giving rise to new reactivities and selectivities. Moreover, the use of actinide catalysts often yields a complementary product distribution as compared to their respective transition metal analogues, allowing for different product classes to be obtained. More recently, the use of novel post-metallocene actinide catalysts has opened a new era for the application of organoactinides and actinide coordination complexes as catalysts in homogeneous organic transformations, allowing for systematic structure–reactivity studies, as well as studies concerning the involvement of f-electrons in the reactivity of the early actinides. Owing to knowledge acquired throughout the past two decades regarding the preparation and reactivity of organoactinide, new catalytic processes involving actinide catalysts can be designed. Furthermore, the unique reactivity patterns, and product distributions observed when using actinide complexes as catalysts, enable the preparation of organic synthons, which are not accessible by traditional transition metal, or organocatalysis. Despite the progress made in the field of actinide catalysis during the last two decades, many new reactivity pathways are yet to be explored using actinide coordination complexes as catalysts.

Author Contributions

This manuscript was prepared through an equal contribution of the authors Isabell S. R. Karmel, Rami J. Batrice and Moris S. Eisen.

Conflicts of Interest

The authors declare no conflict of interest.

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