Recent advances in organothorium and organouranium catalysis

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In this *critical review* we summarize the latest results obtained during the last decade concerning the catalytic activities of organoactinide complexes. We begin with a brief summary of the synthesis and characterization of uranium and thorium complexes that later will be used as catalysts for demanding chemical transformations. Hydroamination, hydrosilylation of terminal alkynes, coupling of terminal alkynes with isonitriles, catalytic reduction of azides and hydrazines, ring opening polymerization of cyclic esters and polymerization of α-olefins are covered in this review (118 references). The topics covered in this review regarding organoactinide chemistry will be of interest to inorganic, organic and organometallic chemists, material and catalytic scientists due to its unique mode of activation as compared to late transition-metals. In addition, the field of organoactinide complexes in catalysis is steadily growing, because of the complementary reactivity of organoactinides as compared to other early or late transition complexes, in demanding chemical transformations.

1 Introduction

During the last decade the chemistry of electrophilic d^0/f^n actinides has been flourishing and reaching high levels of sophistication. The unique rich and complex feature of organoactinides prompted us to develop this field towards catalysis and demanding chemical transformations. Actinides have a very sizeable ionic radii, which give rise to large formal coordination numbers and unusual coordination geometries. The presence of the 5f valence orbitals is another characteristic of actinides that differs from d-block elements. The presence of these two features in organoactinides induce distinctive chemistry. The actinides may exhibit parallel reactivities, as compared to early and late transition metal complexes for similar organic processes, but mostly they differ in their catalytic activities. In many instances the regio- and chemo-selectivities displayed by organoactinides are complementary to those observed for other transition-metal complexes.

Many review articles[1–5] dealing mostly with the synthesis of new actinide complexes confirm the broad and rapidly expanding scope of this field. Recently, two comprehensive reviews which cover catalytic processes of neutral and cationic organoactinides have been disclosed.[6]

In this review we present a brief and selective survey of the recent developments in homogeneous catalysis of the organoactinide complexes. We will focus on recent discoveries related to the reactivity of organoactinide complexes as catalysts for demanding organic transformations. In the beginning of this review, the synthesis of the organoactinide catalysts will be presented, followed by a survey of organic transformations catalyzed by these complexes.

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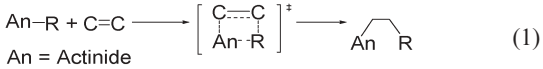
Moris S. Eisen immigrated to Israel in 1977 from Colombia. He received his PhD from the Hebrew University in Jerusalem under the supervision of Prof. Jochanan Blum. In 1990 as a Weizmann Postdoctoral Fellow, he joined Prof. Tobin J. Marks' group at Northwestern University. In 1993 he was awarded the State of Israel Alon Fellowship and joined the Department of Chemistry at the Technion –Israel Institute of Technology (Since 2007, Schulich Faculty of Chemistry). Since 2003 he is a full Professor and serving from 2004 as the Head of the Institute of Catalysis Science and Technology at the Technion. He is incumbent of the Samuel O. Friedlander Academic Chair in Chemistry.

Neutral organoactinide complexes have been proved to go through a mechanism which includes a four-center transition state (eqn (1)). Oxidative addition and reductive elimination mechanisms are not expected due to the high energy of the orbitals. Such a transition state allows the prediction of new actinide reactivities if the negative entropies of activation is taken into account.[7]

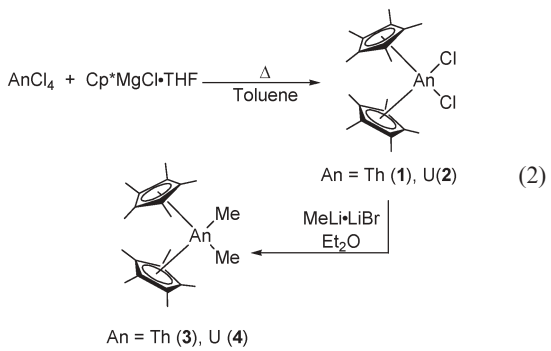


(1)

2 Synthesis of organoactinide catalysts

Synthesis of bis(cyclopentadienyl) actinide complexes ($Cp^*_2AnR_2$)

In this section we focus on the synthesis of $Cp^*_2AnMe_2$ complexes (An = Th (**3**), U (**4**), Cp* = C_5Me_5). The pentamethylcyclopendadienyl (Cp*) is well known for its thermal stability, solubility and crystallinity, hence it is widely used as an ancillary ligand in organoactinide synthesis. In 1981, Fagan *et al.* reported the synthesis of complex **4** (eqn (2)) by starting from the uranium tetrachloride salt and reacting it with two equivalents of the Grignard reagent Cp*MgCl to obtain the corresponding dichloro complex $Cp^*_2UCl_2$, followed by methylation with 2 equivalents of MeLi to obtain the dimethyl complex **4** (eqn (2)).[8]



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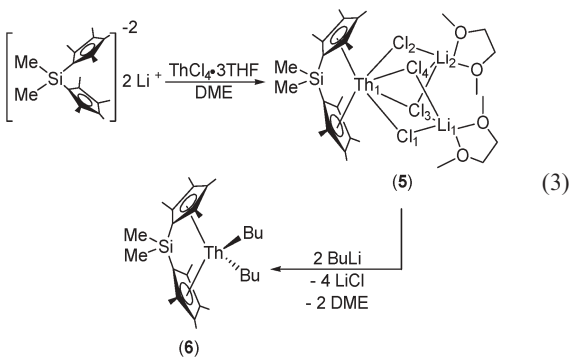
The crystal structure of thorium and uranium dichloride complexes **1** and **2** and other halogenated adducts were reported by Spirlet *et al*. in 1992–1993,[9–12] while the crystal structure of **4** was reported twelve years later.[13]

The chloride and methyl groups in **1–4** can be easily replaced by other functional groups such as alkyls,[14–16] hydrides,[17] amides,[8,16] imides,[18,19] ketenes,[20] thiolates,[21] phosphides[22,23] and phosphinidenes.[24]

Synthesis of *ansa*-organoactinide complexes ($Me_2SiCp''_2AnR_2$)

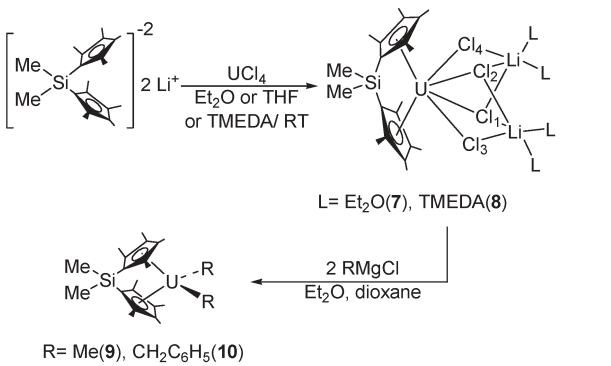
The π ancillary ligand has a major effect on the stoichiometric and catalytic properties of organo-f-complexes.[25–28] In order to ease the accessibility to the equatorial girdle where the σ-ligation is disposed, the two Cp ligands where drawn close by using a bridging ligation, such as $SiMe_2$, to obtain the corresponding complex ($Me_2SiCp''_2AnR_2$). The effect of opening the coordination sphere in organolanthanides allowed an increase of 10–100 fold in rates for the olefin insertion into the M–R bond.[29–32] In organoactinides this modification was shown to cause an increase of 10^3 fold in their catalytic activity for the hydrogenation of 1-hexene.[31,33] The complete synthesis of the complexes $Me_2SiCp''_2ThCl_2$ (**5**) and $Me_2SiCp''_2Th''Bu_2$ (**6**) is presented in eqn (3). The complex $Me_2SiCp''_2ThCl_2$ was isolated in 82% yield with the lithium chloride salt as an adduct. The single-crystal X-ray diffraction revealed a typical bent metallocene complex.

The ring-centroid–Th–centroid angle in complex **5** (113.3°), is smaller as compared to the unhindered bis(pentamethylcyclopentadienyl) thorium complex **3** (130–138°),[34] and slightly smaller than the angle determined for the bridged complex $[Me_2SiCp''_2Th(CH_2Si(CH_3)_3)_2]$ (118.4°).[33] The thorium–carbon (carbon = Cp″ ring carbons) bond lengths are not equidistant having the shorter distance between the metal and the first carbon adjacent to the silicon bridge. The reason for that is the strain generated by the Me_2Si-bridge as reported for other *ansa* type of complexes.[35] The X-ray analysis of complex **5** showed that two of the thorium–chloride bonds are shorter than the other two: Th(1)–Cl(1) 2.770(2), Th(1)–Cl(2) 2.661(2), Th(1)–Cl(3) 2.950(2), Th(1)–Cl(4) 2.918(2) Å. The longer Th–Cl distances are those corresponding to the chlorine atoms disposed in the three-fold bridging positions and coordinated to both lithium atoms. Each of the remaining two chlorine atoms (Cl(1) and Cl(2)) are coordinated only to one lithium atom. All the Th–Cl distances are longer than those observed for terminal Th–Cl distances (Th–Cl 2.60 Å for $Cp^*_2ThCl_2$ or 2.65 Å for $Cp^*_2Th(Cl)Me$). *Ansa*-Chelating bis(cyclopentadienyl) complexes of uranium (**7–11**, eqn (4)) were prepared and reported by Schnabel *et al*.[36]



(3)

These uranium complexes were obtained as dark-red air- and moisture-sensitive materials. The complexes are soluble in aromatic solvents, but insoluble in hexane. In solution these complexes have shown no dynamic behavior. The molecular structure of complex **7** exposed a normal bent metallocene with an angle of 114.1° for the ring-centroid–metal–ring centroid. This angle is smaller as compared to the non-bridge uranium complexes (133–138°).[8,37–40] The uranium atom is bonded to four bridging chloride ligands for which two bonds are much longer than the other two: U–Cl(1) 2.885(3), U–Cl(2) 2.853(3), U–Cl(3) 2.760(3), U–Cl(4) 2.746(3) Å. Here also, two chlorine atoms (Cl(1) and Cl(2)) are disposed in three-fold bridging positions and coordinate to both lithium atoms. The remaining two chlorines (Cl(3) and Cl(4)) are coordinated to one lithium atom.



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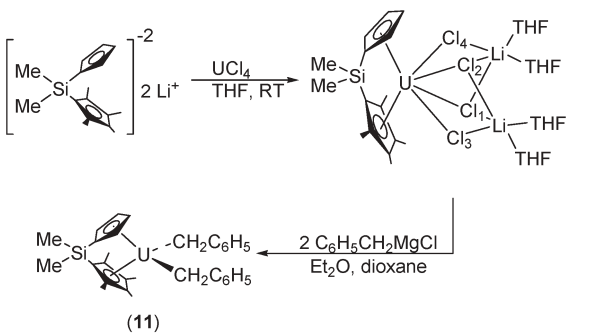
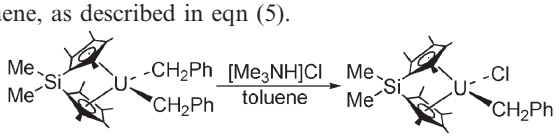


For the preparation of the dialkyl complexes the corresponding chloride–TMEDA complex (**8**) was used as a precursor. The alkylation of the halo-precursors with the suitable Grignard reagents produced the corresponding alkyl complexes, when a large excess of dioxane as solvent was used. Interestingly, the stability of complex **10** is much larger as compared to the corresponding relatively unstable dimethyl thorium complex.[33] The dimethyl complex of the mixed cyclopentadienyl precursor (**11**) was not formed, instead, precipitation of insoluble material and evolution of gas were observed. As opposed to that, with bulky alkyls substituents, such as benzyl, the corresponding complexes **10** and **11** were obtained in high yields.[36] The mixed benzyl–chloride complex was obtained by protonation of the dibenzyl complex **10** with a stoichiometric amount of the protonating salt $[Me_3NH]Cl$ in toluene, as described in eqn (5).

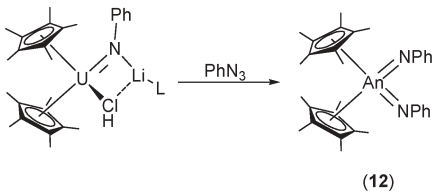


(5)

Synthesis of high-valent organouranium complexes

The reactivity of organoactinide(IV) alkyl, amido or imido complexes towards unsaturated organic substrates, such as olefin, alkynes and nitriles, follows normally a four-center transition state (*vide supra*). This reactivity is exhibited by these complexes, due to the high-energy orbital impediment, to undergo oxidative addition and reductive elimination. Consequently, the synthesis, characterization, and reactivity studies of high-valent organouranium complexes are highly important. The ability to transform U(IV) to U(VI) and *vice versa* can originate complementary modes of activation and induce unique and novel reactivities.

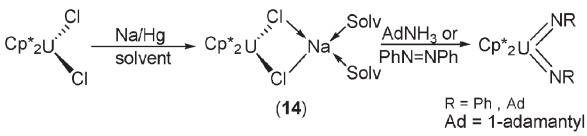
The first high-valent organouranium(VI) bis imido complex (**12**) was prepared by Arney *et al.* by oxidation of the lithium salt of an organoimido uranium chloride complex with phenyl azide (eqn (6)).[41]



(6)

Other bis(imido) organouranium(VI) complexes were prepared as described in Scheme 1. These reactions involve the oxidation of uranium(IV) bis alkyl or uranium(IV) imido complexes with the two-electron atom transfer reagents.[34]

Warner *et al.* reported an elegant and simple procedure for generation of high-valent bis(imido) organouranium(VI) complexes by direct reduction of diazenes or azides (eqn (7)).[42]

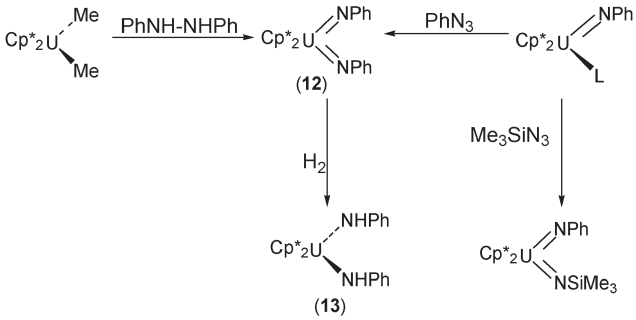


(7)

Reactivity of the cationic complex $[(Et_2N)_3U][BPh_4]$

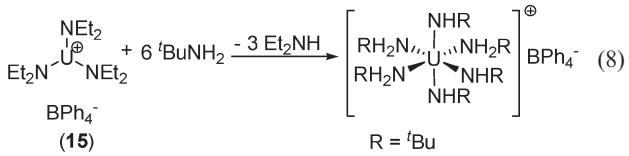
The synthesis of the cationic complex $[(Et_2N)_3U]^+[BPh_4]^-$ (**15**) was described by Berthet *et al.*[43] In order to tailor the possibilities of such cationic complexes, stoichiometric reactions with amines were studied. Under mild conditions, at room temperature in benzene the amido ligands of $[(Et_2N)_3U][BPh_4]$ were straightforwardly activated. The Et_2NH was proved to be labile; the cationic complex reacted with *n*-propylamine, after quenching with water only *n*-propylamine was detected without traces of Et_2NH.[44] NMR spectra has indicated that complexes of the type $[(R_2N)_3U][BPh_4]$ normally adopt a zwitterionic structure in non-coordinating solvents, with two phenyl groups of BPh_4 coordinated to the metal center.[45]

Similar reaction of $[(Et_2N)_3U][BPh_4]$ with *tert*-butylamine allowed the formation of complex $[(^tBuNH_2)_3(^tBuNH)_3U][BPh_4]$ (eqn (8)).[46] The X-ray diffraction of the product



Scheme 1 Alternative synthetic pathways for the preparation of high-valent organouranium imido complexes and their reactivity with hydrogen.

revealed an uranium atom in a slightly distorted octahedral environment with the three amido and three amine ligands arranged in a *mer* geometry. The U–N(amido) bond lengths average 2.20(2) Å were similar to those determined in the distorted facial octahedral cation $[(Et_2N)_3(THF)_3U]^+$ (mean value of 2.18(1) Å).[45] The complex $[(^tBuNH_2)_3(^tBuNH)_3U][BPh_4]$ is a unique uranium(IV) complex with primary amine ligands that were crystallographically characterized.[47] The mean U–N(amino) bond distance of 2.67(3) Å can be compared with the average U–N bond length of 2.79(2) Å in $UCl_4(Me_2NCH_2CH_2NMe_2)_2$.[47] The shorter U–N(amido) bond length (U–N 2.185(7) Å) and the longer U–N(amine) bond (U–N 2.705(8) Å) were found to be in *trans* positions. The small octahedral distortion was manifested by the different angles between the amine–amido, amine–amine and amido–amido groups.

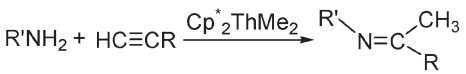


(8)

3 Intermolecular hydroamination of terminal alkynes

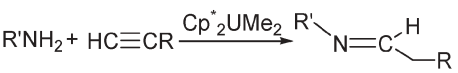
Molecules with nitrogen atoms are well known in pharmaceutical, agricultural and environmental disciplines. The synthesis of nitrogen-containing molecules is extensively studied.[48] The hydroamination of alkenes and alkynes is completely clean (without by-products), economically efficient, thermodynamically favorable, but entropically disfavored. Therefore, the hydroamination of olefins and alkynes was described as the most attractive and easy way for this purpose and was declared a decade ago as one of the 10 most important challenges in catalysis.[49]

The organoactinide complexes $Cp^*_2AnR_2$ (An = Th, U; R = Me, NHR; R = alkyl) were found to be excellent precatalysts for the intermolecular hydroamination of terminal aliphatic and aromatic alkynes in the presence of primary aliphatic amines to yield the corresponding imido compounds.[50,51] The reactivity exhibited for the thorium complexes was different, depending on the alkynes, as compared to organouranium complexes (eqn (9) and (10)).



R = H; R' = Et
R = ^{n}Bu; R' = Me, Et
R = Ph; R' = Et
R = ^{i}Pr; R' = Ph

(9)

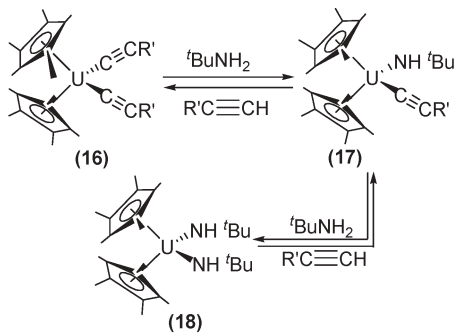


R = TMS, ^{t}Bu; R' = Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu, ^{i}Bu
R = ^{n}Bu; R' = Me, Et, ^{n}Pr, ^{i}Pr, ^{i}Bu
R = Ph; R' = Me, Et
R = ^{i}Bu; R' = Et
R = C_5H_{11}; R' = Et

(10)

The intermolecular hydroamination catalyzed by the thorium catalyst (eqn (9)) yielded the methyl alkyl-substituted imines in moderate yields with the concomitant formation of the alkyne *gem*dimer. With the uranium catalyst (eqn (10)) the reaction exhibited large regio- and chemo-selectivity towards one type of imine in which amine and alkyne substituents are disposed, almost always, in *E*-regiochemistry. When the alkyne reactions catalyzed by the uranium complexes were performed with bulky $^tBuNH_2$ as the primary amine, no hydroamination products were obtained. The products observed were only selective *gem* dimers corresponding to the starting alkyne. This result indicates that with $^tBuNH_2$ the proposed active species responsible for the intermolecular hydroamination was not obtained. Using this bulky amine, the observed organouranium complexes in solutions were the corresponding uranium bis(acetylide) (**16**) and the uranium bis(amido) (**18**) complexes. These two compounds were found to be in rapid equilibrium to the monoamido acetylide complex (**17**),which is responsible for the oligomerization of alkynes in the presence of amines (eqn (11)).

The rates for hydroamination with participation of various amines were compared, the bulkier were the amines, the lower was the turnover frequency. Also, hydroamination rates for a particular amine ($MeNH_2$), using various alkynes, showed similar turnover frequencies. This lack of changes in alkyne suggested that there is no major steric effect on the hydroamination process.

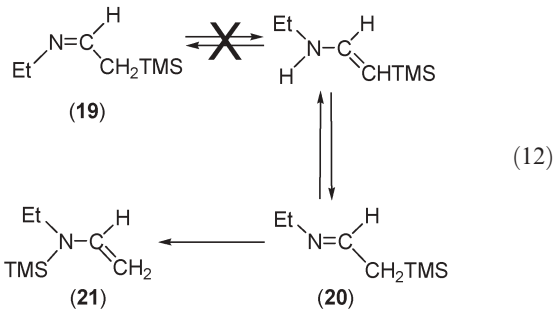


(11)

The intermolecular hydroamination catalyzed by the analogous organothorium complex $Cp^*_2ThMe_2$ exhibited similar reactivities with $Me_3SiC{\equiv}CH$ and $MeNH_2$ or $EtNH_2$ as with the uranium complex (eqn (10)). However, in the intermolecular hydroamination with ^{n}BuC≡CH or PhC≡CH, and $MeNH_2$ or $EtNH_2$, a radical change in the regioselectivity was obtained, generating the unexpected imines (eqn (9)). For all the organoactinides no hydroamination products were formed when either internal alkynes or secondary amines were used. However, with secondary amines the chemoselective alkyne dimers and, in some cases, trimers were obtained. Hence it seems that secondary amines are able to control the oligomerization of terminal alkynes towards a specific dimer.

The catalytic hydroamination of ^{n}BuC≡CH or $Me_3SiC{\equiv}CH$ with $EtNH_2$ and either the organothorium complex **1** or the bisamido complex, gave identical results (yields, stereochemistry of the products, rate and kinetic curves), Therefore, both complexes were routed through a mutual active species, parallel to the observed behavior of the different uranium complexes. It should be mentioned that when the mixture of imines **19** and **20** was obtained, **20** was found to undergo a

non-catalyzed Brook silyl rearrangement to form the corresponding enamine **21** (eqn (12)).[52] The rearrangement followed a first-order kinetic dependence on the imine **20** towards product **21**, leaving the concentration of **19** unaffected.

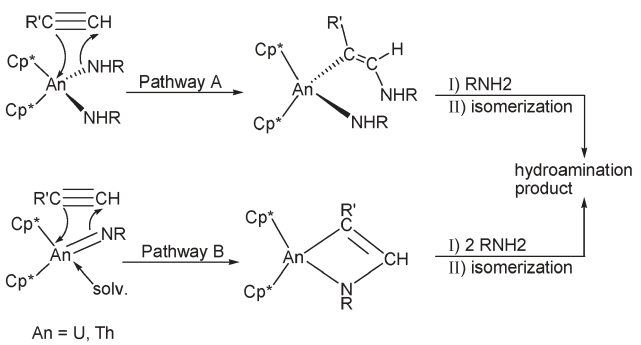


(12)

Kinetic and mechanistic studies of the intermolecular hydroamination

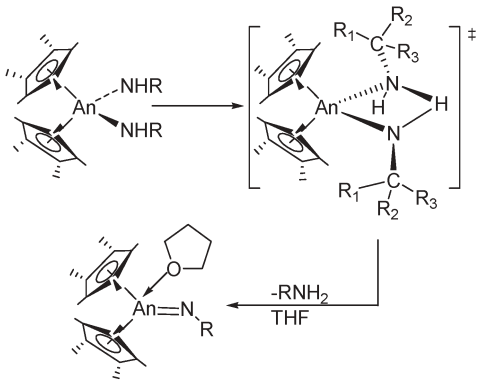
The formation of oligomers observed in the hydroamination reactions catalyzed by thorium complexes indicated that two different complexes were active in solution, plausibly interconverting and caused the occurrence of two parallel processes. The discrimination between the two most probable mechanistic pathways in order to find the key organometallic intermediate, which is responsible for the hydroamination process, was performed by kinetic and thermodynamic studies (Scheme 2). The first route regarded the insertion of an alkyne into a metal–amido bond, as found in lanthanide chemistry.[32,53–55] The second route proposed the insertion of an alkyne into a metal–imido (M=N) bond, as observed for early transition-metal complexes.[56,57] Kinetic measurements on the hydroamination of $Me_3SiC{\equiv}CH$ with $EtNH_2$ were conducted by monitoring the reaction *via* ^{1}H NMR. The results revealed that the reaction has an inverse first-order dependence in amine, first-order dependence in precatalyst and zero-order dependence in alkyne concentration, as presented in the general rate law for the hydroamination of terminal alkynes promoted by organoactinides (eqn (13)). The derived $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ parameter values from a thermal Eyring analysis (in the range 60–120 °C, error values are in parenthesis) were 11.7(3) kcal mol^{-1} and −-44.5(8) cal K^{-1} mol^{-1}, respectively.

$$v = k[\mathrm{An}][\mathrm{amine}]^{-1}[\mathrm{alkyne}]^{0} \qquad (13)$$



Scheme 2 Possible pathways for the hydroamination of terminal alkynes mediated by organoactinide complexes. For thorium the approach of some alkynes was inverted before insertion

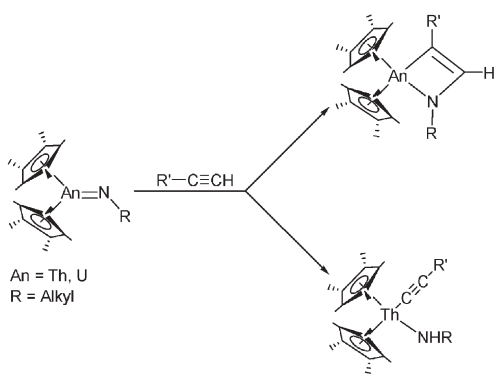
Since the stereochemical approach of either alkyne or amine to the organometallic moiety is expected to follow a side approach, the lack of alkyne effect on the kinetic hydroamination rate suggested that pathway A (Scheme 2) was not a major operative route. The zero kinetic order with respect to alkyne predicted for pathway B (Scheme 2) is consistent with the high coordinative unsaturation of the imido complexes and allows fast insertion of different alkynes with indistinguishable rates. This pathway can also support the lack of reactivity with bulky ^{t}BuNH$_2$; the steric hindrance mediated by bulky amine groups slowed down the formation of the corresponding imido complexes due to the encumbered transition state (eqn (14)).



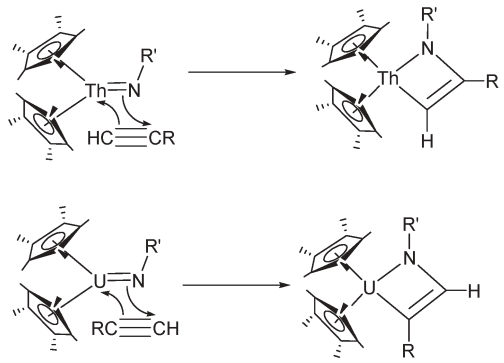
(14)

The different mode of activation for the different organoactinides is very unusual. For both organoactinide–imido complexes, a selective metathesis with the alkyne π-bond was operative (hydroamination products), whereas for the thorium complex a competing protonolysis reaction also occurs. This competing reaction was responsible for selective dimerization of terminal alkynes (Scheme 3). The product distinction between the two organoactinide catalysts in the hydroamination reaction is a result of a contrasting stereochemistry in the metathesis of the alkyne toward the imido complex (Scheme 4). It seems plausible that the regiochemistry of the intermolecular hydroamination was driven by organometallic differences in their imido- configurations, rather than by difference in their thermodynamic characteristics (plausible two f electrons in the uranium complex).

Scheme 5 presents a plausible mechanism for the intermolecular hydroamination of terminal alkynes promoted by the organothorium complex **3**. The first step in the catalytic



Scheme 3 Activation of terminal alkynes mediated by organoactinide–imido complex.



Scheme 4 Different activation modes for thorium and uranium imido complexes.

cycle involves the N–H σ-bond activation of the primary amine by the organothorium complex (**3**) which yields yielding the bisamido–amine complex $Cp^*_2Th(NHR')_2(H_2NR')$ (**22**) and methane (step 1). Complex **22** was found to be in rapid equilibrium with the corresponding bis(amido) complex **23** (step 2).[58,59] An additional starting point involved a similar C–H activation of an alkyne with complex **3**, yielding methane and the bis(acetylide) complex **24** (step 3). The complex may react rapidly with an equivalent amount of present amine (step 5), yielding complex **25**. Complex **25** may follow two competitive equilibrium pathways. The σ-bond metathesis with a terminal alkyne which induced the production of selective dimers (step 12), or/and the metathesis reaction with an amine giving the bis-amido complex **23**. If an amine molecule is eliminated from complex **23**, the corresponding imido complex **26** is obtained and normally this step is the rate determining step (step 7). The imido complex may follow a rapid σ-bond metathesis with an incoming alkyne, yielding metallacycle **27** (step 8). Rapid protonolytic ring opening of complex **27** by an amine yielded the actinide–enamine amido complex **28** (step 9), which, in its turn, isomerized quickly into the actinide–alkyl(imine) amido **29** by intramolecular 1,3-sigmatropic hydrogen shift (step 10). Upon a subsequent protonolysis by an additional amine, complex **29** produced the imine and regenerated the bis(amido) complex **23** (step 11). It is also plausible that the last protonolysis may be conducted with an alkyne, although this pathway was studied using deuterium labeled compounds and was found to be not a major operative pathway.

The larger amount of the *E* imine isomer, as compared to that of the *Z* isomer, can be illustrated by simple steric hindrance of the amine substituents and ene-amine group, as described in Scheme 6.

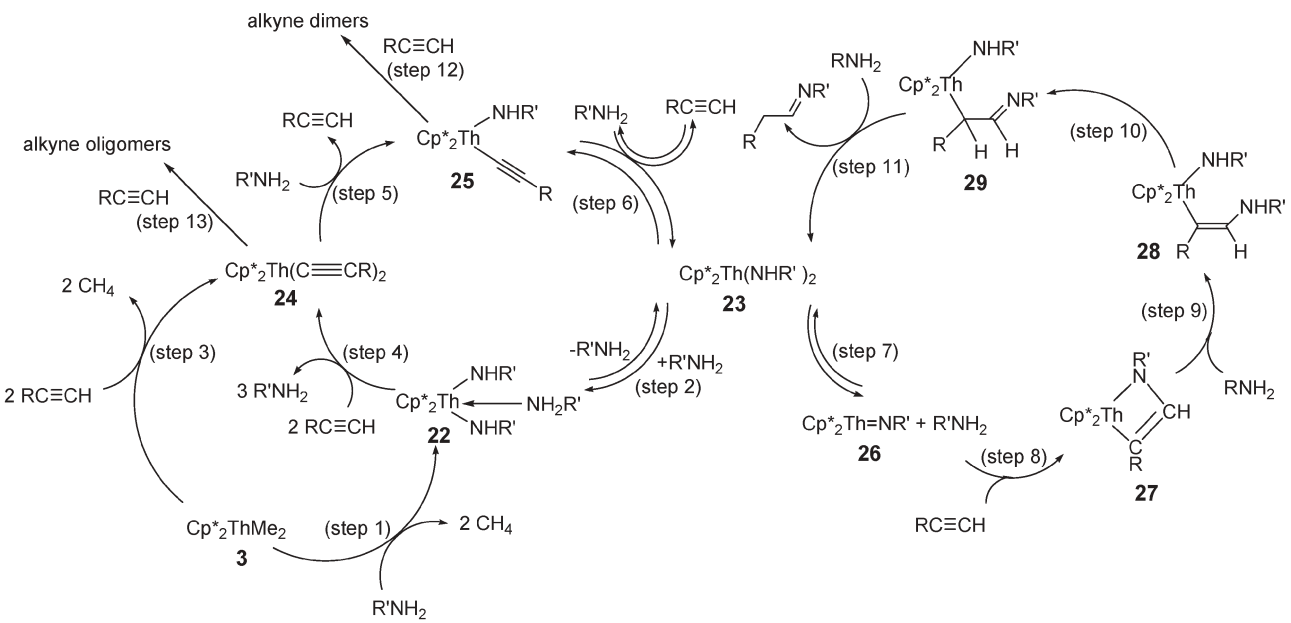
4 Intramolecular hydroamination/cyclization of aminoalkenes and aminoalkynes

Hydroamination is known as atom-economic transformation for introducing R_2NH moiety across a C–C double or triple bond. This field is widely studied with different organometallic compounds, including late transition-metals,[60–65] early transition-metals[66–71] and lanthanides.[72–77]

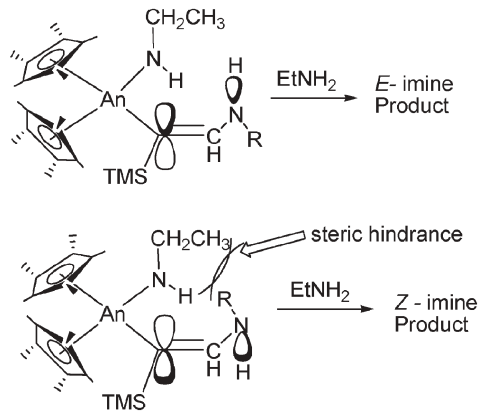
Recently a new type of organoactinide complexes, containing constrained geometry ligand, were prepared by reacting the appropriate neutral ligand and the corresponding homoleptic aminoactinide (Scheme 7).[78] High yields were achieved by controlling the dialkylamine concentration and removal of the concomitant by-products.[78,79]

The comparison between the crystal structure of these actinide complexes and the structures of their isolobal lanthanides revealed that the Cp (centroid)–metal–nitrogen angles follow the order Th > U > Sm > Yb.

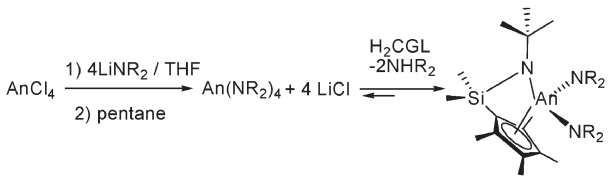
Kinetic studies on intramolecular hydroamination/cyclization reaction shows first-order dependence on the precatalyst and zero-order dependence on the substrate, making the kinetic rate law:



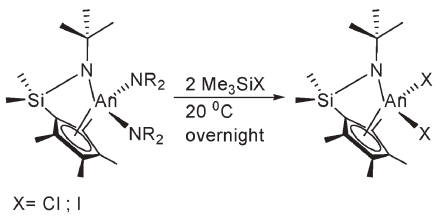
Scheme 5 Plausible mechanism for the intermolecular hydroamination of terminal alkynes catalyzed by $Cp^*_2ThMe_2$.



Scheme 6 Illustration of the steric hindrance which prevents the formation of the *Z*-imine.



An = Th; NR_2 : NMe_2 = 33.1% ; NEtMe = 20.7% ; NEt_2 = 22.1%
An = U ; NR_2 : NMe_2 = 57.9% ; NEtMe = 77.1% ; NEt_2 = 26.0%



X= Cl ; I

Scheme 7 Synthesis of constrained geometry organoactinide complexes (H_2CGL = neutral constrained geometry ligand).

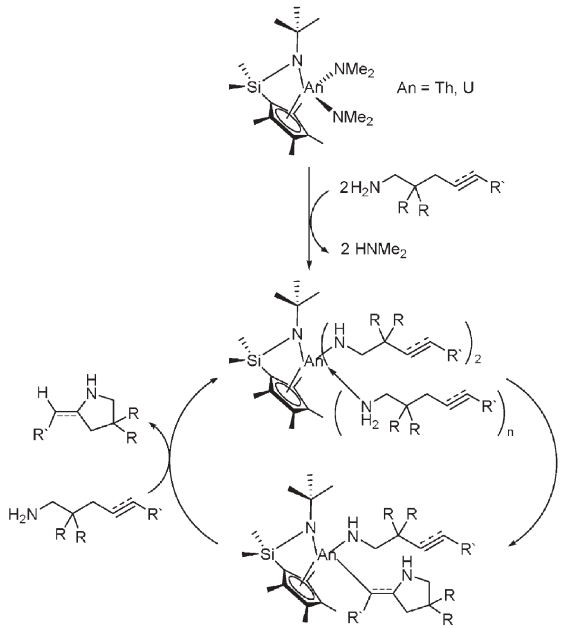
$$v = k_{obs}[\text{precatalyst}]^1[\text{substrate}]^0.^{80}$$

This result indicates that the protonolysis of the amido-complex by the substrate is rapid, and the rate determining step includes the insertion of the olefin into the An–NHR bond. As for aminoalkenes, it was found that the reaction is faster with organoactinides containing larger ionic radius, while the opposite is true for aminoalkynes. However, both constrained complexes (Th and U) were found to react faster with aminoalkenes and aminoalkynes than the corresponding metallocenes. A plausible mechanism is presented in Scheme 8.[80]

5 Catalytic hydrosilylation of terminal alkynes

Catalytic hydrosilylation of terminal alkynes promoted by neutral organoactinide complexes

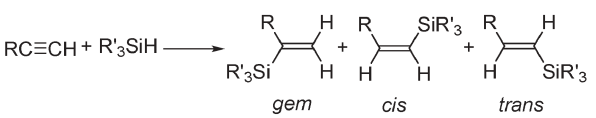
The catalytic insertion of Si–H bond into C–C multiple bond is considered as one of the most important reactions in organosilicon chemistry. The hydrosilylation reaction is used in industrial production of organosilicon compounds



Scheme 8 Proposed mechanism for the organoactinide-catalyzed intramolecular hydroamination/cyclization of terminal and disubstituted aminoalkenes, aminoalkynes, aminoallenes and aminodienes.

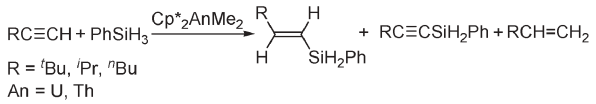
(adhesives, binders and coupling agents) and in research laboratories as an efficient route for the syntheses of a variety of organosilicon compounds, silicon-based polymers and new type of dendrimeric materials. The versatile and rich chemistry of vinylsilanes have attracted considerable attention in recent years as they are considered to be important building blocks in organic synthesis.[81,82]

The syntheses of vinylsilanes has been extensively studied, being one of the most convenient and straightforward methods for hydrosilylation of alkynes.[83–85] In general, hydrosilylation of terminal alkynes produces 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 eqn (15). The distribution of the products is found to be varying considerably with the nature of the catalyst, substrates and the specific reaction conditions.



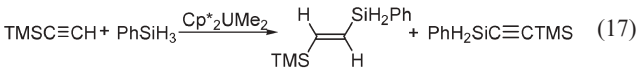
(15)

At room temperature, the reaction of $Cp^*_2AnMe_2$ (An = Th, U) with an excess of terminal alkynes RC≡CH (R = ^{t}Bu, ^{i}Pr, ^{n}Bu) and $PhSiH_3$ resulted in catalytic formation of the corresponding *trans*-vinylsilanes $RCH{=}CHSiH_2Ph$, the dehydrogenative silylalkyne coupling product, $RC{\equiv}CSiH_2Ph$, and the corresponding alkenes $RCH{=}CH_2$ (R = ^{t}Bu, ^{i}Pr, ^{n}Bu) (eqn (16)).[86] The *trans*-vinylsilane was obtained exclusively and independently on the metal center. With bulky substituted alkynes the product distribution was similar when using any of the two organoactinide complexes. However, the products distribution varied when less hindered alkynes were used.



(16)

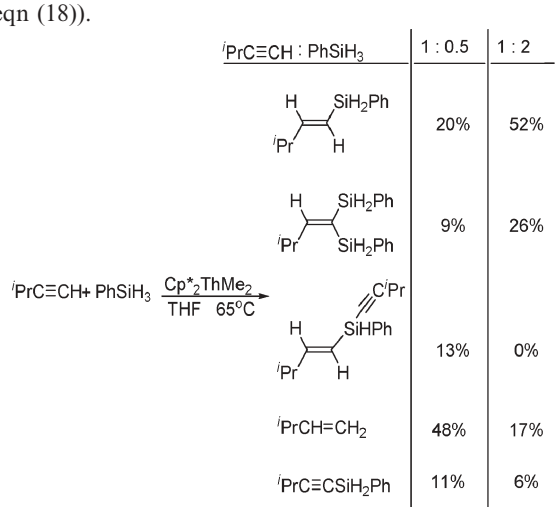
For TMSC≡CH a different chemistry was found. The reaction of $Cp^*_2UMe_2$ with TMSC≡CH (TMS = Me_3Si) and $PhSiH_3$ produced the *trans* TMSCH=CHSiH$_2$Ph and the silylalkyne TMSC≡CSiH$_2$Ph respectively, whereas for the analogous $Cp^*_2ThMe_2$ no hydrosilylation or dehydrogenative coupling products were observed (eqn (17)).



(17)

Interestingly, the chemoselectivity and the regioselectivity of the vinylsilanes formed in the organoactinide-catalyzed hydrosilylation of terminal alkynes with $PhSiH_3$ at high temperature (65–78 °C) were found to be diverse, as compared to the hydrosilylation results obtained at room temperature. With $Cp^*_2UMe_2$ the corresponding *cis*-hydrosilylated compounds, *cis*-RCH=CHSiH$_2$Ph and small amount of the double hydrosilylation products RCH=C(SiH$_2$Ph)$_2$ (R = ^{t}Bu, ^{i}Pr, ^{n}Bu) were achieved in addition to the products obtained at room temperature (eqn (16)).[86] However, the $Cp^*_2ThMe_2$ afforded only *trans*-vinylsilane. In the hydrosilylation reaction of TMSC≡CH with $PhSiH_3$ catalyzed by $Cp^*_2UMe_2$, besides the *trans*-vinylsilane and the silylalkyne products, which were also obtained at room temperature (eqn (17)), the *cis*-vinylsilane and the olefin TMSCH=CH$_2$ were also observed. As for $Cp^*_2ThMe_2$, the same products as in the hydrosilylation reaction promoted by $Cp^*_2UMe_2$ were formed besides the production of *cis*-vinylsilane, in contrast to room temperature reaction, where no products were found.

The effect of $PhSiH_3$ on formation of the different products was found to be highly dependent on the silane concentration (eqn (18)).



(18)

The replacement of a hydrogen atom on $PhSiH_3$ by either an alkyl or a phenyl group generated a delay in the hydrosilylation rate reaction, as compared to the rate obtained with phenylsilane. The selectivity was appreciably diverse in comparison to that observed in the reaction with $PhSiH_3$ as hydrosilylating agent.[86]

Kinetic studies on the hydrosilylation of ^{i}PrC≡CH with $PhSiH_3$ catalyzed by $Cp^*_2ThMe_2$

Kinetic study of the hydrosilylation of ^{i}PrC≡CH with $PhSiH_3$ catalyzed by $Cp^*_2ThMe_2$ shows a first-order dependence in alkyne, silane and catalyst. The empirical rate law expression for the $Cp^*_2ThMe_2$ catalyzed hydrosilylation of ^{i}PrC≡CH with $PhSiH_3$ is given in eqn (19).

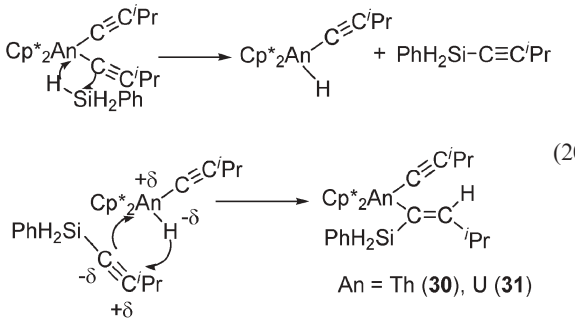
$$v = k[^i\text{PrC}{\equiv}\text{CH}][\text{PhSiH}_3][\text{Cp}^*_2\text{ThMe}_2] \quad (19)$$

The derived activation parameters from the Eyring analysis, E_a, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values were found to be 6.9(3) kcal mol^{-1}, 6.3(3) kcal mol^{-1} and 51.1(5) cal K^{-1} mol^{-1}, respectively.

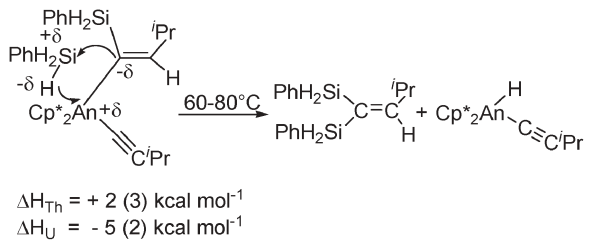
The reaction of $Cp^*_2An(C{\equiv}C^iPr)_2$ (An = Th, U) complexes with $PhSiH_3$ gave complexes **30** and **31** quantitatively. These complexes were formed by σ-bond metathesis with the silane forming the corresponding actinide hydrides and the silylalkyne, which rapidly reinsert with the right stereochemistry to produce products **30** or **31** (eqn (20)).

The obtained regioselective mode of insertion for PhSiH$_2$C≡C^{i}Pr approaching the actinide hydride complex is electronically favored, as expected for polarization of organoactinides and the π* orbital of the alkyne.[87]

In addition, since the insertion followed a four-center transition state mechanism, *cis*-stereochemistry was expected, as corroborated by H_2O poisoning experiment and high temperature reactions with alkyne or silane. The same regioselective insertion of TMSC≡CH to an organothorium alkenyl complex was observed in organoactinide-catalyzed oligomerization of alkynes.[88,89]

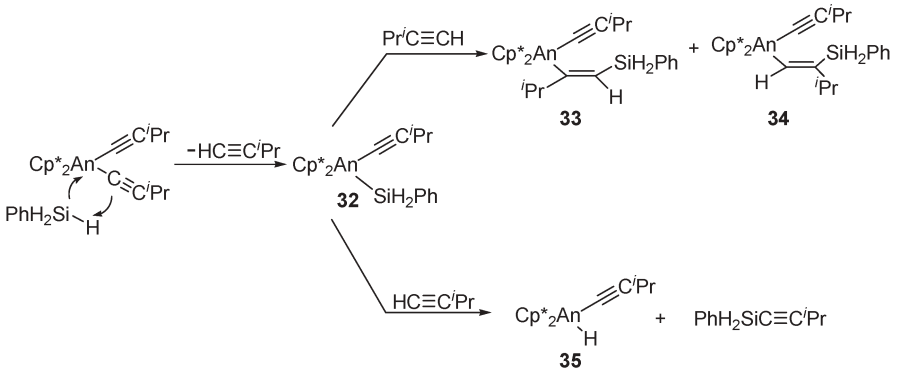


(20)



(21)

The reactions of complexes **30** or **31**, yielding the double hydrosilylated product (eqn (21)), were proposed to be stereoselectively favored, due to the assumed polarization of $PhSiH_3$ towards the metal center. This reaction is thermodynamically more favored as compared to protonolysis by the silane which produced complex **32** (Scheme 9) and the



Scheme 9 Expected intermediates in the stoichiometric hydrosilylation of terminal alkynes.

cis-hydrosilylated product (ΔH(Th) = +15(4) kcal mol^{-1}; ΔH(U) = −3(2) kcal mol^{-1}.

The most remarkable observation is concerning the reaction products of complexes **30** or **31** with an alkyne at either low or high temperature. At elevated temperatures the expected *cis*-hydrosilylated product was obtained, but at low temperatures an unexpected *trans*-isomer was achieved. These results were explained through an operative competitive mechanism taking into account an equilibrium process which gives the different hydrosilylation products at different temperatures.

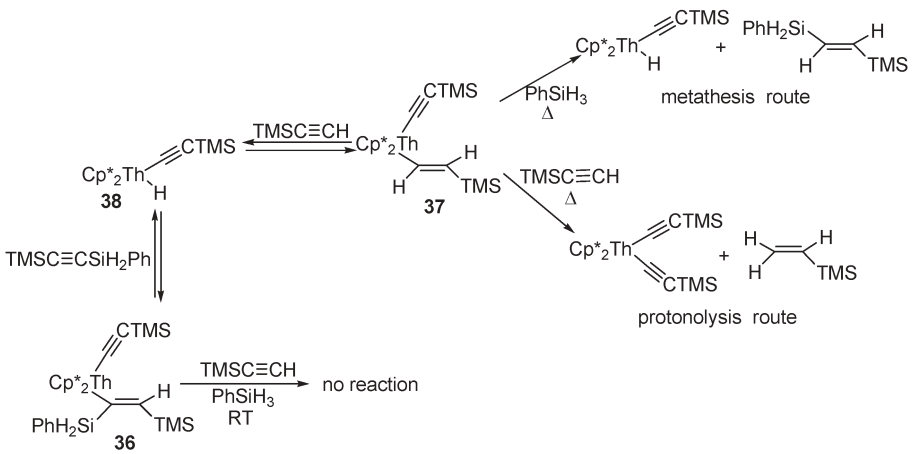
Hence, theoretically, formulation of an organoactinide–silane intermediate **32** as described in Scheme 9 was shown to be not operative due to the following arguments: (1) the quenching experiments with water gave exclusively *cis*-vinylsilane. (2) Under stoichiometric conditions the addition of silane did not induce protonolysis of the acetylide–alkenylsilane complex (**30** or **31**), arguing how difficult should be the production of complex **32**. (3) No geminal hydrosilylated products were obtained (the case in which the complex **34** is an intermediate). (4) No *cis*-hydrosilylated products can be obtained from complex **32** at low temperatures, and (5) no *cis*-double hydrosilylated products were observed at low temperatures (if σ-bond metathesis occurred from complex **33** or **34**).[86]

Regarding the alkynes, TMSC≡CH exhibited a total lack in reactivity with $PhSiH_3$ in presence of $Cp^*_2ThMe_2$ at room temperature. However, at high temperature the *trans*-vinylsilane, silylalkyne and alkene were obtained. This type of reactivity was explained, in general, as the result of a kinetic effect, suggesting also an equilibrium between the organometallic complexes **36** and **37** (Scheme 10). Complex **37** was obtained by insertion of the alkyne into a hydride complex. Complex **37** is able to react with another alkyne, yielding an alkene and a bis(acetylide) complex (protonolysis route) or react with silane, producing an organometallic hydride and a *trans*-product (σ-bond metathesis route). The low activity obtained for TMSC≡CH was explained *via* elevated activation energy required to perform both metathesis or protonolysis of complex **37**, as compared with other alkynes.[86]

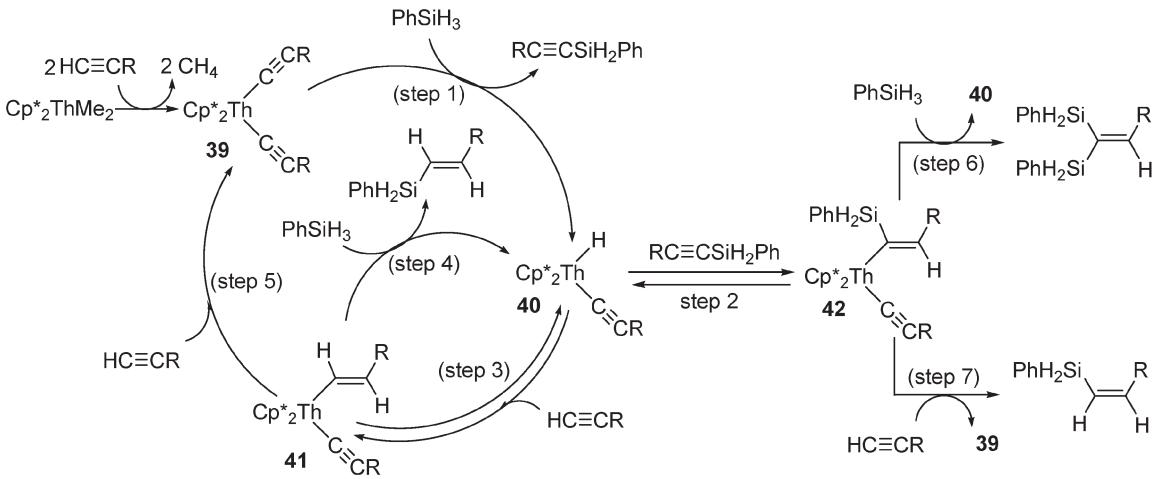
The ratio between the silane and the alkyne were found to govern the kinetics toward the different products. Thus, when the $PhSiH_3$: $^tPrC{\equiv}CH$ ratio was 2 : 1, *trans*- and double-hydrosilylation products were major ones (metathesis route). Increasing the alkyne concentration routed the reaction towards alkene and bis(acetylide) complex (protonolysis route).

A possible mechanism for hydrosilylation of terminal alkynes catalyzed by $Cp^*_2ThMe_2$ was proposed and described in Scheme 11. This mechanism involves simple processes, such as insertion of acetylene into a metal–hydride σ-bond, σ-bond metathesis by silane and protonolysis by an acidic alkyne hydrogen.

The precatalyst $Cp^*_2ThMe_2$ in presence of alkyne was converted to bis(acetylide) complex **39**. Complex **39** reacts with



Scheme 10 σ-Bond metathesis and protonolysis routes for hydrosilylation of TMSC≡CH with $PhSiH_3$ at high temperatures.

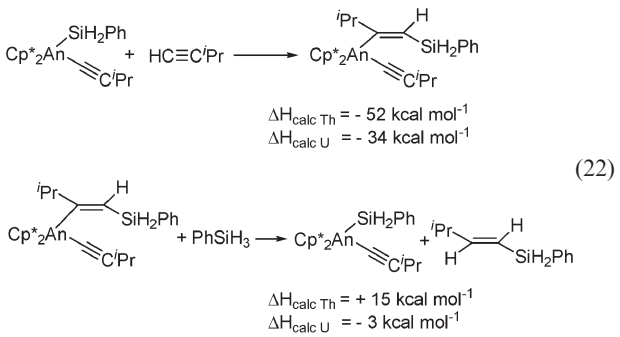


Scheme 11 Plausible mechanism for the hydrosilylation of terminal alkynes with $PhSiH_3$ by $Cp^*_2ThMe_2$.

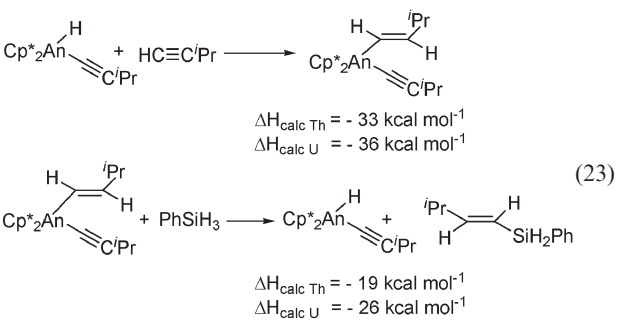
$PhSiH_3$ towards silylalkyne and organoactinide hydride **40** (step 1), which was found to be in equilibrium with intermediate **42** after reinsertion of silylalkyne with preferential stereochemistry (step 2). Complex **42** was found to be the principal complex under silane and alkyne starvation. Complex **40** would react with an alkyne, producing the alkenyl acetylide organothorium complex **41** (step 3), which is, presumably in equilibrium with complex **40** (first order in alkyne). Complex **41** was proposed to react with $PhSiH_3$ as the rate-determining step, regenerating the hydride complex **40** and the *trans*-hydrosilylated product (step 4). Under catalytic conditions, complex **41** can also react with a second alkyne producing the alkene and the bis(acetylide) complex **39** (step 5). A similar insertion of the alkene into complex **40** with the concomitant reaction with an additional alkyne, produced double hydrogenated product, as found for isopropylacetylene. At high temperatures complex **42** may react with silane (step 6), yielding complex **40** and double hydrosilylation product, or with an alkyne (step 7), yielding complex **39** and the *cis*-isomer. Thus, the reaction rate law (eqn (19)) was rationalized with rapid irreversible phenylsilane metathesis with complex **39**, rapid pre-equilibrium, involving the hydride and alkenyl complexes **40** and **41** and slow metathesis by the $PhSiH_3$. For the thorium complex, step 6 was found to be much faster than step 7, since the *cis*-product was obtained only in trace amounts.

The proposed mechanism took into account comparable yields for the alkene and silylalkyne even when the alkyne concentration was in excess (the sum of the silylated products must be equal to the amount of the alkene). In both thorium or uranium complexes the amount of the hydrosilylated product was always similar or larger than that of the alkene, indicating that a competing equilibrium should be operative. This equilibrium is responsible for the transformation of the hydride complex back to the bis(acetylide) complex, allowing the production of the silylalkyne without producing the alkene.

Thermodynamically, it is very interesting to compare the possible mechanistic silane and hydride intermediates towards the possible hydrosilylation *trans*-product as presented in eqn (22) and (23), respectively. The calculated enthalpies of reaction for insertion of an alkyne into an actinide–silane bond (eqn (22)) (ΔH(Th) = −52 kcal mol^{-1}; ΔH(U) = −34 kcal mol^{-1}) or into an actinide hydride bond (eqn (23)) (ΔH(Th) = −33 kcal mol^{-1}; ΔH(U) = −36 kcal mol^{-1}) are expected to be exothermic. However, with thorium the protonolysis by phenylsilane, yielding an An–Si bond and the *trans*-product (eqn (22)), was endothermic (ΔH(Th) = +15 kcal mol^{-1}), while the σ-bond metathesis (eqn (22)) of the thorium alkenyl complex by the silane (ΔH(Th) = −19 kcal mol^{-1}), yielding the corresponding Th–H bond and the *trans*-product, was exothermic. In corresponding uranium complexes the latter processes were calculated to be exothermic, although the σ-bond metathesis route (eqn (23)) is more exothermic (ΔH(U) = −26 kcal mol^{-1}) than the protonolysis route (eqn (22)) (ΔH(U) = −3 kcal mol^{-1}).



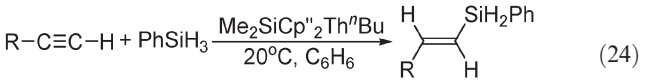
(22)



(23)

Catalytic hydrosilylation of terminal alkynes promoted by $Me_2SiCp''_2Th^nBu_2$

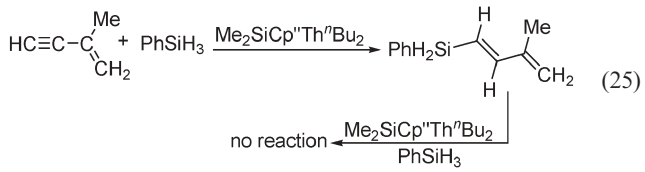
The complex $Me_2SiCp''_2Th^nBu_2$ ($Cp'' = C_5Me_4$) was found to catalyze the reaction between terminal alkynes and $PhSiH_3$ in a fast and regioselective manner, to produce the *trans*-vinylsilane (eqn (24)).[90]



(24)

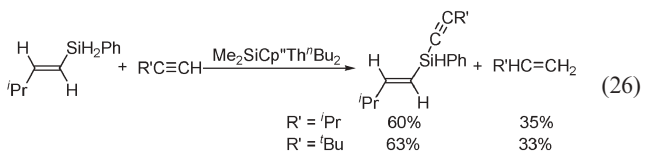
R = ^{t}Bu, ^{i}Pr, ^{n}Bu, Ph, 4-^{t}Bu-Ph

The hydrosilylation of eneyne with $PhSiH_3$ takes place on the triple bond regioselectively to produce the *trans*-diene, the excess of $PhSiH_3$ did not induce any subsequent hydrosilylation (eqn (25))



(25)

However, addition of second equivalent of alkyne to hydrosilylation product allowed the formation of the corresponding alkene and the dehydrogenative coupling of alkyne with *trans*-vinylsilane (eqn (26)).[91–93]



(26)

Kinetic and thermodynamic studies for the hydrosilylation of terminal alkynes with primary silanes promoted by the bridged complex $Me_2SiCp''_2Th^nBu_2$

Kinetic measurements on the hydrosilylation of ^{i}PrC≡CH with $PhSiH_3$ catalyzed by $Me_2SiCp''_2Th^nBu_2$ indicates that the reaction behaved with a first-order dependence in precatalyst and silane, but exhibited an inverse proportionality (inverse first order) in alkyne. The inverse proportionality was consistent with a rapid equilibrium before the turnover limiting-step and routed one of the key organoactinide intermediates out of the catalytic cycle (eqn (27))

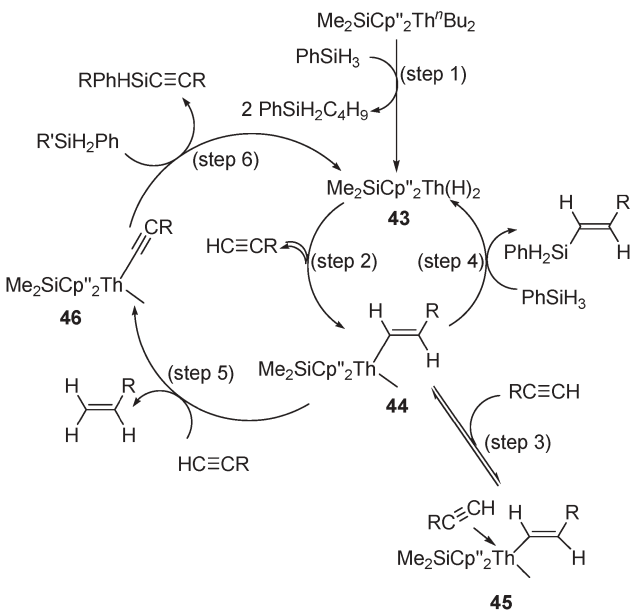
$$v = k[Me_2SiCp''_2Th^nBu_2][\text{silane}][\text{alkyne}]^{-1} \qquad (27)$$

The derived $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ parameter values from thermal Eyring analysis were measured to be 10.07(5) kcal mol^{-1} and $-22.06(5)$ cal K^{-1} mol^{-1}, respectively.[90]

Mechanistically, in hydrosilylation reactions of organo-f-element complexes two Chalk–Harrod mechanisms were proposed as plausible routes, except for inclusion of σ-bond metathesis, instead of the classical oxidative addition–reductive elimination processes. The two mechanisms differ in the reactive intermediates: the hydride (M–H) route and the silane (M–SiR_3) route.[94–104] The use of terminal alkynes, for bridged organoactinides, was an excellent probe to investigate which of the two routes was the major one. Thus, taking into account that the alkyne was expected to insert with the substituent group pointing away from the metal center (as observed in the dimerization) the following mechanistic insights were obtained. If the hydrosilylation reaction goes through an M–SiR_3 intermediate, a *gem*-hydrosilylated vinyl isomer will be formed, whereas through the M–H route only a *trans*-isomer will be obtained (if the insertion stereochemistry is not maintained, the *cis* product will be observed). The exclusive selectivity obtained for $Me_2SiCp''_2Th^nBu_2$ towards the *trans* hydrosilylated isomer argued that the hydride route was acting as the major operative mechanistic pathway.

The hydrosilylation of terminal alkynes with $PhSiH_3$ promoted by the bridged complex $Me_2SiCp''_2Th^nBu_2$ produced the *trans*-hydrosilylated vinylsilane regio- and chemoselectively without any other by-products. The non-appearance of silylalkynes, dehydrogenative silane coupling products or any other geometrical isomer of the vinylsilane strongly indicated that the Th–H pathway was the major operative route in the hydrosilylation reaction. A plausible mechanism for hydrosilylation of terminal alkynes appears in Scheme 12.

The precatalyst $Me_2SiCp''_2Th^nBu_2$ in presence of silane and alkyne was converted into hydride complex **43** (step 1), as observed by stoichiometric formation of *n*-$BuSiH_2Ph$. Rapid insertion of an alkyne into complex **43** allows formation of vinylic complex **44** (step 2). Complex **44** was found to be in rapid equilibrium with the proposed π-complex **45** (step 3), responsible for the inverse order in alkyne. Also, it underwent σ-bond metathesis with $PhSiH_3$ as the rate-determining step (step 4), producing selectively the *trans*-hydrosilylated vinyl product and regenerating complex **43**. Since no geometrical isomers or different products were observed after adding an excess of $PhSiH_3$ to any of the vinylsilanes neither the hydride



Scheme 12 Plausible mechanism for hydrosilylation of terminal alkynes promoted by $Me_2SiCp''_2Th^nBu_2$ (only one catalytic site is shown for clarity)

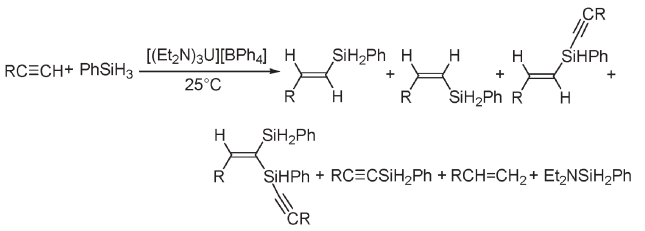
complex **43** nor the alkenyl complex **44** were found to be the resting catalytic state. These results pointed towards complex **45** as the resting state. However, the subsequent addition of a second equivalent of alkyne to the reaction mixture formed the corresponding alkene and the acetylide complex **46**, as obtained in absence of primary silane, (step 5). A σ-bond metathesis of complex **46** with the Si–H bond of the vinylsilane (step 6) formed the dehydrogenative coupling product and regenerated the hydride complex **43**.[35]

The yield of the alkene was found to be lower than that of the silylalkyne product. Therefore, an additional equilibrium reaction was proposed operative and responsible for transformation of complex **43** into the acetylide complex **46**, allowing the formation of the silylalkyne without forming the alkene. Regarding the rates in the hydrosilylation process catalyzed by the bridged complex, larger turnover frequencies were measured as compared to $Cp^*_2YCH_3{\cdot}THF$ or other lanthanide complexes.[105] The yttrium complex was found to induce the hydrosilylation reaction of internal alkynes preferentially towards the *E*-isomer, although in some cases the *Z*-isomer was found in comparable amounts.

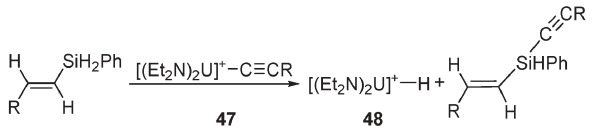
Mechanistically, the active species for the yttrium hydrosilylation of internal alkynes was proposed to be the corresponding hydride.[106] It is well known that the hydrosilylation of alkynes is induced either by radical initiators[107] or by transition metal catalysts.[108] The radical procedure often provides a mixture of *trans*- and *cis*-hydrosilylation products, although the transition metal catalyzed reaction proceeds with high stereoselectivity *via* a *cis*-hydrosilylation pathway, usually producing a mixture of two regioisomers (terminal and internal adducts). Thus, the organoactinide process seems to contain a unique chemical environment, which allows the production of the *trans*-vinylsilane.

Hydrosilylation of terminal alkynes promoted by the cationic complex $[(Et_2N)_3U][BPh_4]$

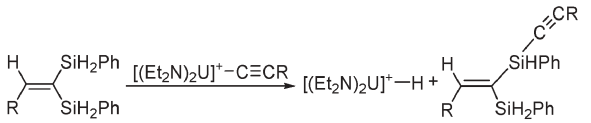
The hydrosilylation reaction pathways of terminal alkynes promoted by neutral organoactinides has been the motivation regarding the possibility to form a similar cationic hydride complex as an intermediate. Hence, the catalytic hydrosilylation of terminal alkynes, promoted by the cationic complex $[(Et_2N)_3U][BPh_4]$ was studied.[109] The reaction of $[(Et_2N)_3U][BPh_4]$ with terminal alkynes RC≡CH (R = ^{i}Pr, ^{t}Bu) and $PhSiH_3$ resulted in catalytic formation of numerous products. The products observed to account for 100% conversion with respect to the alkyne were: *cis*- and *trans*-vinylsilane (RCH=CHSiH_2Ph), dehydrogenative silylalkyne (RC≡CSiH_2Ph), and alkenes (RCH=CH_2; R = ^{i}Pr, ^{t}Bu), in addition to stoichiometric amounts of the corresponding aminosilane Et_2NSiH_2Ph. With bulky ^{t}BuC≡CH, the tertiary silanes *trans*-^{t}BuCH=CHSi(HPh)(C≡C^{t}Bu) and ^{t}BuCH=C(SiH_2Ph)Si(HPh)(C≡C^{t}Bu) were also observed (eqn (28)). Formation of the tertiary silanes can be accounted for by metathesis reactions of the *trans*-alkenylsilane and the double hydrosilylated compound with the metal acetylide complex $[(Et_2N)_2U^+–C{\equiv}CR$ (**47**), respectively, as shown in (eqn (29) and (30)).



(28)

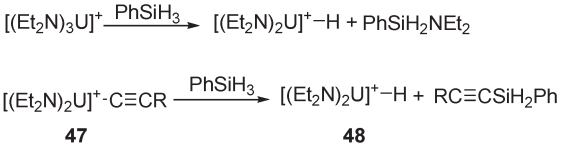


(29)



(30)

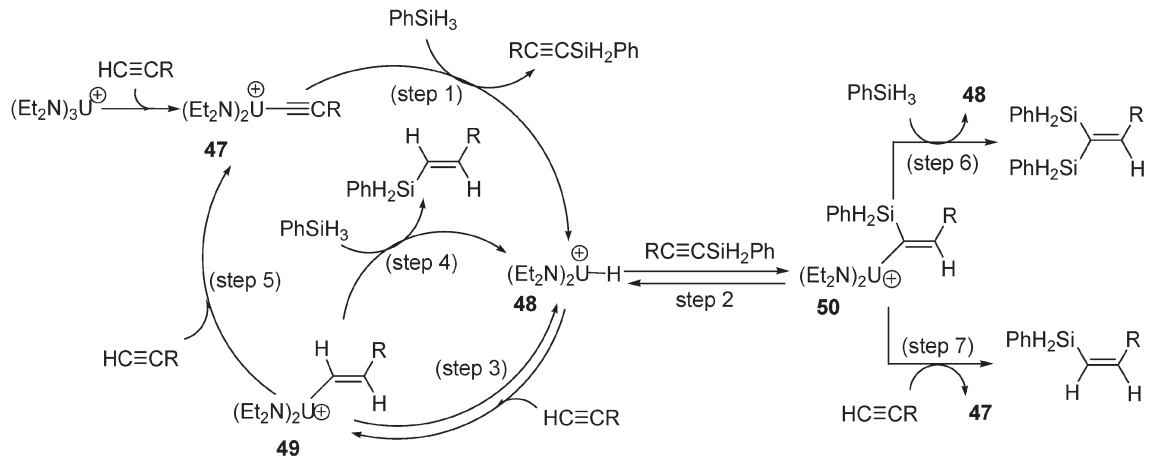
At high temperature (65–78 °C), the chemoselectivity and regioselectivity of the products formed in the cationic organouranium-catalyzed hydrosilylation of terminal alkynes with $PhSiH_3$ were found to be different as compared to those obtained at room temperature. The hydrosilylation of RC≡CH (R = ^{n}Bu, ^{i}Pr, ^{t}Bu) with $PhSiH_3$ catalyzed by $[(Et_2N)_3U][BPh_4]$ produced, in addition to the hydrosilylation products at room temperature (eqn (28)), the corresponding double hydrosilylated compounds: RCH=C($SiH_2Ph)_2$ (R = ^{n}Bu, ^{i}Pr, ^{t}Bu), and small amount of the corresponding geminal dimers and trimers. Based on kinetic and product distributions, the mechanism for this reaction is proposed to be similar to that observed with neutral organoactinides. The formation of an active uranium hydride complex **48** was conceivable either by the reaction of the cationic complex with a silane molecule to give the corresponding aminosilane, or/and by the reaction of the acetylide complex **47** with silane, when the corresponding silaalkyne was produced (eqn (31)).



(31)

Kinetic and mechanistic studies for the hydrosilylation of terminal alkynes with primary silanes promoted by the cationic complex $[(Et_2N)_3U][BPh_4]$

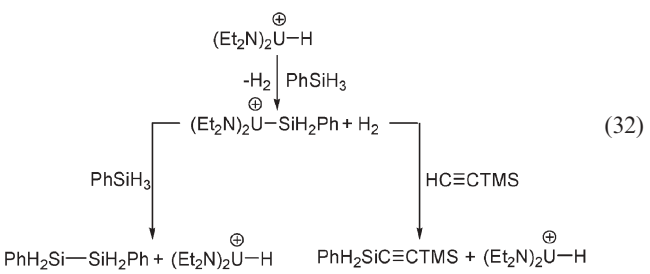
The proposed mechanism, which concerns the formation of all the products, is described in Scheme 13.[109] The precatalyst $[(Et_2N)_3U][BPh_4]$ in the presence of alkyne was converted into the monoacetylide complex **47** and removed one of the amido ligands. Complex **47** was proposed to react with $PhSiH_3$ to give the silylalkyne and the actinide hydride **48** (step 1). The hydride **48** may reinsert the silaalkyne and form complex **50** (step 2), or react with the alkyne to produce the alkenyl uranium complex **49** (step 3). Complex **49** will then probably react with $PhSiH_3$ and produce back the organouranium



Scheme 13 Plausible mechanism for the hydrosilylation of terminal alkynes with $PhSiH_3$ by the cationic complex $(Et_2N)_3U^+$.

hydride complex **48**, as well as the *trans*-hydrosilylated product (step 4). Under the catalytic conditions, complex **49** can also react with a second alkyne and produce the alkene and the acetylide complex **47** (step 5). Complex **50** may react with a silane (step 6), yielding complex **48** and the double hydrosilylation product, or with an alkyne (step 7), yielding complex **47** and the *cis*-hydrosilylation isomer.

This mechanistic scenario took into account the higher yields observed for the alkene compound, as compared with those obtained for the silylalkyne. For TMSC≡CH and ^{i}PrC≡CH at high temperature, the amount of the hydrosilylated products is larger than that of the alkenes. This fact indicates that an optional competing equilibrium route was operative. This would again involve the transformation of the hydride **48** back into the acetylide complex **47**, which allows to produce more silylalkyne without producing the alkene. The hydride **48** could alternatively react with $PhSiH_3$ to give the organometallic silyl compound $[(Et_2N)_2USiH_2Ph][BPh_4]$ (eqn (32)), which would further react with $PhSiH_3$ or RC≡CH to give back the hydride **48** and $PhH_2Si–SiH_2Ph$, or $PhH_2SiC{\equiv}CR$, respectively.



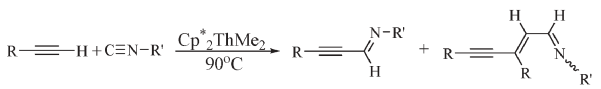
(32)

In hydrosilylation reaction of ^{t}BuC≡CH at high temperature a small amount of dehydrogenative coupling of phenylsilane was observed. This product argued for formation of a compound with an uranium-silicon bond, although not as a major operative intermediate. The compound $[(Et_2N)USiH_2Ph][BPh_4]$ can be theoretically postulated instead of the hydride complex **48** either from steps 1, 4 or 6 in the catalytic cycle (Scheme 13). In these steps the silane would act as the protonolytic source.

6 Catalytic coupling of isonitriles with terminal alkynes

Isonitriles RN≡C: (carbene alike) are known to undergo 1,1-insertion into metal–acetylide bonds of early and late transition metals under stoichiometric conditions.[110–112] The obtained 1-aza-1,3-enyne (α,β-acetylenic aldimines) $R^1C{\equiv}C–CH{=}NR^2$ have attracted great interest as important synthons in organic synthesis since they include three reactive sites: the triple bond, the double bond and the lone pairs on the nitrogen.

Recently organoactinides were also found to be very reactive in the coupling of isonitrile with terminal alkynes.[13] $Cp^*_2AnMe_2$ (An = Th (**3**), U (**4**)) and $[(Et_2N)_3U][BPh_4]$ successfully coupled between the isonitrile and terminal alkyne, a complete conversion was achieved in toluene or benzene at 90–100 °C, while no reaction was observed without catalyst (eqn (33)–(35)).



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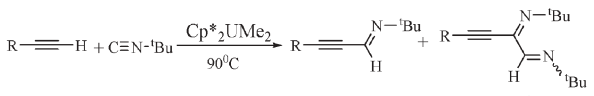
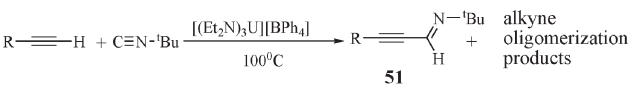


(34)



(35)

Both the catalyst and the alkyne/isonitrile ratio have a great effect on the products. For example, the thorium complex **3** produced compound **51** (eqn (33)) as a major product. The double insertion of alkyne **52** was detected with unhindered

terminal alkynes (*e.g.* ^{i}PrC≡CH). Interestingly, the uranium complex **4** also produced compound **51** but **52** was not observed, instead, a double insertion of isonitrile into alkyne took place (eqn (34)). The percentage of **53** can be raised by increasing the percentage of the isonitrile. The cationic complex produced **51** exclusively and independently on the isonitrile or the alkyne concentration (eqn (35)). Neither **52** nor **53** were detected when cationic complex was used, rather a small amount of oligomers was detected.

NOE NMR studies of the products showed space proximity between the R′ group and the imine hydrogen (vinylic), hence, we deduced that these two groups should be *cis* to each other having the *E* configuration. Interestingly, computational calculations of ΔE_0 for the reaction of ^{t}Bu–N≡C and TMS–C≡CH showed that the reaction to produce the monocoupling *E* product **51** (ΔE_0= −17.6 kcal mol^{-1}) is thermodynamically more preferable as compared to the production of the corresponding *Z* isomer (ΔE_0= −14.5 kcal mol^{-1}).

Kinetic and mechanistic studies of the catalytic coupling between isonitriles and terminal alkynes

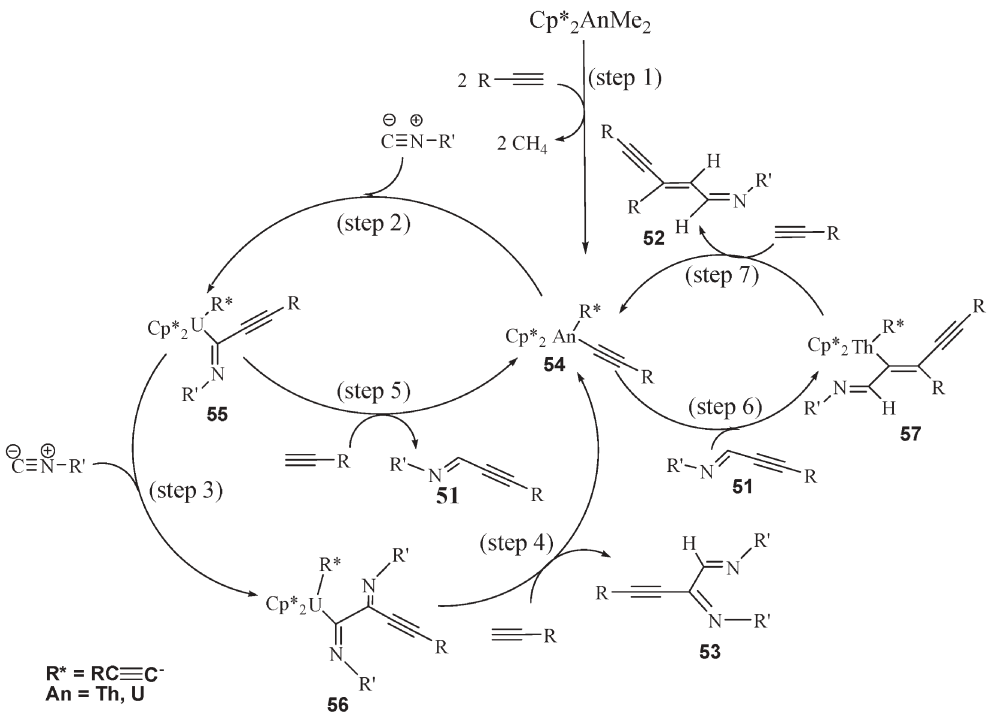
Kinetic studies for coupling of terminal alkynes with isonitriles promoted by $Cp^*_2ThMe_2$ or $[(Et_2N)_3U][BPh]_4$ were performed by monitoring the reaction using ^{1}H NMR. The results indicate that the reaction behaves with first-order dependence in both catalyst and isonitrile and zero-order dependence in alkyne. Thus, the rate law for the coupling of isonitrile with terminal alkynes promoted by $Cp^*_2ThMe_2$ or $[(Et_2N)_3U][BPh]_4$ can be written as presented in eqn (36). The derived $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ parameter values from the thermal Eyring analysis were measured to be 22.32(4) kcal mol^{-1} and −18.6(2) cal K^{-1} mol^{-1} in the case of the thorium complex, and 7.85(4) kcal mol^{-1} and −63.7(2) cal K^{-1} mol^{-1} in the case of the uranium complex.

A plausible mechanism for coupling promoted by the metallocene complexes or the cationic complex is described in Scheme 14.

$$v = k[\text{cat}][\text{isonitrile}][\text{alkyne}]^0 \quad (36)$$

$$\text{cat} = Cp^*_2ThMe_2 \text{ or } [(Et_2N)_3U][BPh_4]$$

The organoactinide complex **3** react with the terminal alkynes to yield the bis(acetylide) complex **54** (step 1). This complex undergoes a 1,1-insertion of the isonitrile into the metal–carbon bond to form the acetylenic imido complex **55** (step 2) as the rate determining step of the coupling reaction. In alkyne starvation conditions this protonolysis step is not as rapid as with near equimolar ratios, permitting complex **55** to undergo an additional 1,1-insertion of a second isonitrile molecule to yield the corresponding intermediate **56** (step 3). The double insertion product **53** is then obtained by the protonolysis with a terminal alkyne (step 4) regenerating the active bis(acetylide) complex **54**. Protonolysis of **55** by another terminal alkyne yields the mono-insertion product **51** and regenerates complex **54** as the active species in the catalytic cycle (step 5). With an excess of non-bulky terminal alkynes, the bis(acetylide) complex **54** can react with the product **51** to yield complex **57** by insertion of the triple bond of **51** into the Th–acetylide bond (step 6). Protonolysis of **57** by another terminal alkyne yields product **52** and the active species **54** (step 7). As for organoactinides, it has been shown that the insertion of an internal triple bond is a high energy process in comparison to terminal alkynes. However, here the formation



Scheme 14 Plausible mechanism for the catalytic coupling of terminal alkynes with isonitrile by $Cp^*_2AnMe_2$.

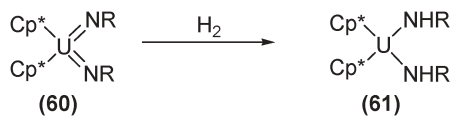
of **52** indicates that even in the presence of a terminal alkyne the insertion of the internal triple bond of **51** was preferred, presumably due to the electronic effects of the imine fragment (^{t}Bu–N=C–), which induces polarization of the internal triple bond.

The cationic complex is believed to be involved in a different mechanism (Scheme 15) because of the existence of Et_2NH molecules that may serve as an additional source of protons as compared to that of the terminal alkynes. Therefore, the Et_2NH will also serve as a protonolytic agent in the last step of the catalytic cycle (Scheme 15, step 3) instead of the alkyne. This alternative fast protonolysis process produces the monoinsertion product **51** and the pre-catalyst $(Et_2N)_3U^+$ concomitantly. Moreover, the fast protonolysis prevents further insertions of isonitriles or alkynes into **59** which explains the absence of the double-insertion product when using $[(Et_2N)_3U][BPh_4]$.

7 Catalytic reduction of azides and hydrazines by high-valent organouranium complexes

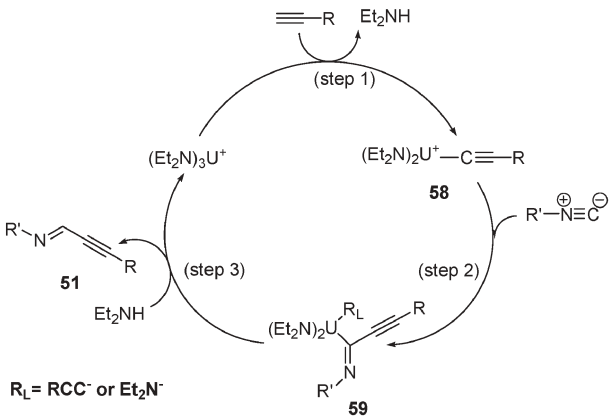
U(IV) metallocene compounds frequently show reactivities comparable to group IV transition-metal and lanthanide metallocenes. Unlike the lanthanides and group IV metals, uranium can access the +6 oxidation state, giving rise to the possibility of two-electron (+4/+6) redox processes.

Exposing the U(VI) complexes $Cp^*_2U(NR)_2$ (R = Ph, Ad = 1-adamantyl) to molecular hydrogen induced the reduced bisamide complex $(Cp^*)_2U(NHR)_2$ (eqn (37)). The rate of hydrogenation for the complex bearing the phenyl substituent was found to be slower than the corresponding adamantyl.[113]

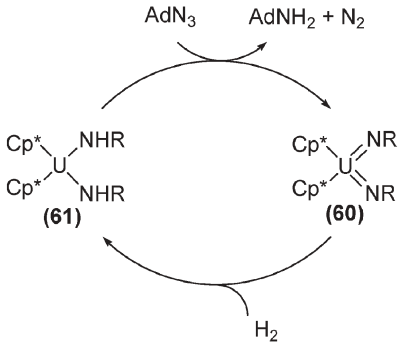


(60) (61) (37)

When AdN_3 (Ad = adamantyl) was added to a solution of $Cp^*_2U(NHR)_2$, the bisimido complex was reformed in addition to free $AdNH_2$. When complex **60** (R = Ad) was reacted with AdN_3 under a dihydrogen atmosphere catalytic hydrogenation of AdN_3 to $AdNH_2$ was observed (Scheme 16).[113]

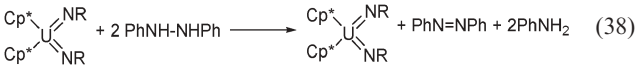


Scheme 15 Plausible mechanism for catalytic coupling of terminal alkynes with isonitrile by $[(Et_2N)_3U][BPh]_4$.



Scheme 16 catalytic reduction of azides by organouranium complex.

N,*N*′-diphenylhydrazine was also used as an oxidant for the conversion of $Cp^*_2UMe_2$ to **60** (R = Ph). The reaction occurs by the protonation of the methyl groups with the release of methane. When $Cp^*_2U(NPh)_2$ was treated with an excess of *N*,*N*′- diphenylhydrazine under starving hydrogen conditions the reaction came to completion, producing aniline and azobenzene in a 2 : 1 ratio (eqn (38)). This disproportionation indicated that the *N*,*N*′-diphenylhydrazine function as both oxidant and reductant. The formation of aniline during this reaction suggested that the U(IV) bis(amide) **61** should be present to reduce the hydrazine, although the only observed uranium species in solution throughout the reaction was $Cp^*_2U(NPh)_2$. This indicates that the oxidation from U(IV) to U(VI) is faster than the subsequent reduction.[113]



(38)

From the thermodynamic point of view, the reaction should be favored by both enthalpy and entropy. The calculated ΔH_f for producing two molecules of aniline and one molecule of azobenzene from two *N*,*N*′-diphenylhydrazine molecules was calculated to be -14.6 kcal mol^{-1}. Entropy considerations also qualitatively favor the formation of the products.

The reaction of $Cp^*_2U(=NPh)_2$ with *N*,*N*′-diphenylhydrazine was postulated to proceed *via* protonation of U(IV) bis(amide) by *N*,*N*′-diphenylhydrazine. Therefore, it was proposed that for the reaction of $Cp^*_2U(=NAd)_2$ with *N*,*N*′-diphenylhydrazine, the initial product would include 1- adamantylamine and azobenzene with the concomitant formation of $Cp^*_2U(=NPh)_2$. However, when the reaction was performed $Cp^*_2U(=NAd)_2$, aniline and azobenzene were the only products observed, indicating that the imido ligands might operate as sites for mediating H-atom transfer. No reaction was observed in the stoichiometric reaction of $Cp^*_2U(=NPh)_2$ with 1-adamantanamine. This result rules out the possibility of U–N bond break in which $Cp^*_2U(=NPh)_2$ is formed and undergoes subsequent rapid reaction with 1-adamantanamine, regenerating $Cp^*_2U(=NAd)_2$.[113] The catalytic two-electron oxidation/reduction processes presented here are a novel type of reactivity for organoactinide complexes. The involvement of U(VI) species strongly argued the necessity of f-orbital participation.

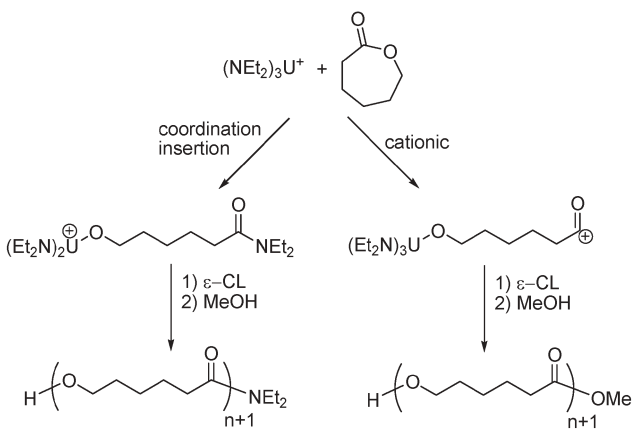
8 Polymerization of ε-caprolactone and L-lactide by organoactinide complexes

Main group metals and lanthanide complexes are known as good catalysts for ring opening polymerization of cyclic esters to form poly-L-lactide (PLLA) and polycaprolactone (PCL). These families of polyesters are highly applicable in everyday life due to their biodegradable and biocompatible properties. However, actinide complexes were excluded from any catalysis that included alkoxy reactants, since it was believed that these reactants will dramatically reduce the catalytic activity, due to the high oxophilic nature of the early actinides. For example, Lin *et al.* proved that the use of alkoxy ligand induces a reduced catalytic activity in the organoactinide-catalyzed hydrogenation of olefins, when compared to alkyl ligands.[114]

Polymerization of ε-caprolactone by organoactinide complexes

The first example of using organoactinides in the polymerization of ε-caprolactone was recently reported by Barnea *et al.*[115] The activity of the three organoactinide complexes ($Cp^*_2ThMe_2$ (**3**), $Cp^*_2UMe_2$ (**4**) and $[(Et_2N)_3U][BPh]_4$ (**15**)) was well studied.

It was found that the cationic complex **15** possessed the highest activity in comparison with complexes **3** and **4**. This result was explained by a higher steric hindrance implied by the Cp* ligand in **3** and **4**. The thorium complex **3** is more active than the uranium complex **4** because of a higher oxophilic nature of the uranium. Increasing the cat/monomer ratio induced an increase in the M_n (number molecular weight) of the obtained polyester. However, very high ratios (1 : 2400) caused a decrease in the reactivity, due to a high viscosity that resulted in the polymerizing solution. In all cases the molecular weight distribution (MWD) was found to be narrow, indicating an unexpected living polymerization. ^{1}H NMR and GC/MS studies revealed that the chain end of the polymer contains a methoxy group, suggesting a cationic mechanism (Scheme 17). However, as evident from the high M_n and low MWD, it is suggested that the cationic end stays close to the metal center since no terminations were observed.



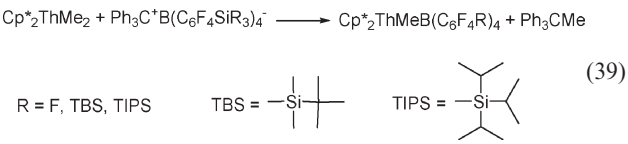
Scheme 17 The cationic and coordination insertion mechanisms for polymerization of ε-caprolactone.

Polymerization of L-lactide by organoactinide complexes

The polymerization of L-lactide (L-LA) was studied with the three organoactinide complexes **3**, **4** and **15**. The cationic complex **15** showed the highest activity at 70 °C in THF. The cationic complex also showed a narrow polydispersity (1.06–1.21), which supports the assumption that the polymerization proceeds in a living fashion at least in the early stages of the reaction.[115] At higher conversions (more than 60%) the reaction gradually slows down due to the viscosity and stickiness of the solution. In contrast to complexes **3** and **4** which produce only CH_4 at room temperature, complex **15** was found to be active for the polymerization of L-LA at room temperature, yielding living polymers with high M_n and low MWD. The initial catalyst to monomer ratio and the GPC results for complexes **3**, **4** and **15** suggest that the polymerization proceeds with only one active site.

9 Polymerization of α-olefins

Since the first report on synthesis of cationic actinide complexes $[Cp^*_2ThMe][BPh_4]$ and $[Cp^*_2ThMe][B(C_6F_5)_4]$ and the study for their polymerization of α-olefins,[116] other highly coordinatively unsaturated organothorium complexes have been prepared (eqn (39)).[117] The reactivity of the newly synthesized organothorium complexes for the polymerization of ethylene follows the order $[Cp^*_2ThMe][B(C_6F_5)_4] > [Cp^*_2ThMe][B(C_6F_4TIPS] > [Cp^*_2ThMe][B(C_6F_4TBS)_4]$, though their activity is an order of magnitude lower than that one observed for analogous zirconium complexes.



(39)

Conclusion

As presented in this review, the structural and catalytic studies on actinide complexes have been growing steadily since the 1950s. However, there is still much more to understand about the catalytic properties of this family of complexes.[118] The ability to tailor a catalytic reaction using these complexes by a rational design of its electronic and steric features remains a challenge. A variety of new unexpected chemical transformations with actinide complexes were recently discovered, such as catalytic reactions which include reactions with alkoxide monomers. We believe that these new transformations will help to design new ligands towards demanding chemical processes and, hopefully, to create similar isolobal complexes that can be used in industrial environments.

The incorporation of these materials will depend on their safety and economic advantage.

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