Oligomerization and Cross-Oligomerization of Terminal Alkynes Catalyzed by Organoactinide Complexes

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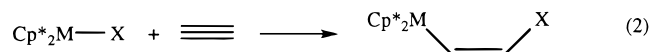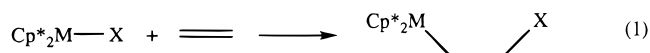
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Abstract: Various organoactinides of the type $Cp*_2An(C{\equiv}CR)_2$ ($Cp* = C_5Me_5$; An = Th, U) have been synthesized from the corresponding $Cp*_2AnMe_2$ complexes by addition of an equimolar amount or an excess of the corresponding terminal alkyne. Attempts to trap the mono(acetylide) complexes $Cp*_2An(C{\equiv}CR)(Me)$ were successful for only the transient species $Cp*_2U(C{\equiv}C(i\text{-}Pr))(Me)$. The bis(acetylide) complexes are active catalysts for the linear oligomerization of terminal alkynes $HC{\equiv}CR$. The regioselectivity and the extent of oligomerization depend strongly on the alkyne substituent R, whereas the catalytic reactivities are similar for both organoactinides. Reaction with *tert*-butylacetylene regioselectively yields the 2,4-disubstituted 1-butene-3-yne dimer, whereas (trimethylsilyl)acetylene is regioselectively trimerized to (*E,E*)-1,4,6-tris(trimethylsilyl)-1,3-hexadiene-5-yne, with small amounts (3−5%) of the corresponding 2,4-disubstituted 1-butene-3-yne dimer. Oligomerization with less bulky alkyl- and aryl-substituted alkynes produces a mixture of oligomers. Cross-oligomerizations reactions induce the formation of specific cross dimers and trimers. Mechanistic studies on the selective trimerization of $HC{\equiv}CSiMe_3$ show that the first step in the catalytic cycle is the $C{\equiv}C$ bond insertion of the terminal alkyne into the actinide−acetylide bond. The kinetic rate law is first order in organoactinide and in alkyne, with $\Delta H^{\ddagger} = 11.1(3)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -45.2(6)$ eu. The turnover-limiting step is the release of the organic oligomer from the alkenyl−actinide complex. The latter key organometallic intermediate has been characterized by spectroscopic and poisoning studies. A plausible mechanistic scenario is proposed for the oligomerization of terminal alkynes.

Introduction

During the past decade the chemistry of electrophilic d^0/f lanthanide and actinide metallocenes has been under intense investigation.[1] Recent progress has made a significant impact in diverse catalytic areas, where the crucial step is an insertion of an olefinic (alkene or alkyne) functionality into a metal−alkyl, metal−hydride, or metal−heteroatom moiety (eqs 1 and 2; $Cp* = \eta^5\text{-}C_5Me_5$; X = alkyl, H, NR_2). For organolanthanides,

$$Cp*_2M{-}X \; + \; {=\!\!=\!\!=} \; \longrightarrow \; Cp*_2M\diagdown\!\diagup^X \qquad (1)$$

$$Cp*_2M{-}X \; + \; {\equiv\!\!\equiv\!\!\equiv} \; \longrightarrow \; Cp*_2M\diagdown\!=\!\diagup^X \qquad (2)$$

such processes include hydrogenation,[2] dimerization,[3] oligomerization/polymerization,[4] hydroamination,[5] hydrosilylation,[2d,6] hydrophosphination,[7] hydroboration,[8] and ring-opening Ziegler polymerization.[9] For organoactinides, C−H activation,[10] hy-

drogenation,[11] hydroamination,[12] hydrosilylation,[13] and selective dimerization[14] comprise such processes. Mechanistically, these

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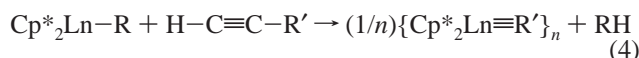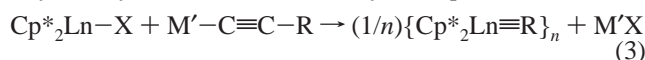
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insertion processes are not in general well-understood and are certainly efficient in very different metal−ligand environments than the more extensive studied analogues of the middle and late transition metals.[15] Hence, the d^0/f metal ions are likely to be in a formal high oxidation state, to be electronically unsuitable for π-back-donation or for forming stable olefin/alkyne complexes, to be affianced in relatively polar metal−ligand bonding with strong affinity for "hard" ligands, and to feature startling M−C/M−H bond disruption enthalpy patterns as compared with those of the late transition elements.[7,16]

Organometallics containing an acetylide moiety have played an important role in the development of organolanthanide chemistry.[17] Comprehensive applicable synthetic routes to this class of compounds have been developed, examples of which include the salt metathesis between lanthanide halides and main group acetylides and the σ-bond metathesis between lanthanide alkyls or hydrides and terminal alkynes (eqs 3 and 4).

$$Cp^*_2Ln-X + M'-C{\equiv}C-R \rightarrow (1/n)\{Cp^*_2Ln{\equiv}R\}_n + M'X \tag{3}$$

$$Cp^*_2Ln-R + H-C{\equiv}C-R' \rightarrow (1/n)\{Cp^*_2Ln{\equiv}R'\}_n + RH \tag{4}$$

The molecular structures of several compounds have been determined by single-crystal X-ray diffraction, and most have been shown to be oligomeric with bridging acetylide ligands.[17,18] Furthermore, significant progress has been made in understanding the principles of alkyne oligomerization/polymerization by group 3−organolanthanide complexes.[4e,19] In contrast to the case of organolanthanides, very little is known about organoactinide−acetylide complexes or organoactinide-catalyzed alkyne oligomerization.[20] In this contribution we report the synthesis and characterization of well-defined acetylide−actinide complexes and their reactivity for the linear oligomerization of terminal alkynes.[21] We present a full discussion of the reaction scope, substrate substituent effect, metal effect, and trapping of the key organometallic intermediate in the catalytic cycle, as well as of the kinetics and mechanism. In a companion contribution,[22] we present a unique principle to selectively tailor the oligomerization of alkynes toward exclusive small oligomers such as dimers and/or trimers comprising scope, metal effect, amine effect, regioselectivity, chemoselectivity, and key intermediates, as well as the kinetics and mechanism for the controlled dimerization of terminal alkynes promoted by these types of organoactinide complexes.

Experimental Section

Materials and Methods. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual-manifold Schlenk line, or interfaced to a high-vacuum (10^{-5} Torr) line, or in a nitrogen-filled Vacuum Atmospheres glovebox with a medium-capacity recirculator (1−2 ppm of O_2). Argon, acetylene, and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Depleted $Th(NO_3)_4$ and $U(NO_3)_4$ were purchased from Cerac Inc. Ether solvents were distilled under argon from sodium benzophenone ketyl. Hydrocarbon solvents (THF-d_8, toluene-d_8, benzene-d_6, cyclohexane-d_{12}) were distilled under nitrogen from Na/K alloy. All solvents for vacuum-line manipulations were stored in vacuo over Na/K alloy in resealable bulbs. Acetylenic compounds (Aldrich) were dried and stored over activated molecular sieves (4 Å), degassed, and freshly vacuum-distilled. Deuterium oxide was purchased from Cambridge Isotopes. $Cp^*_2AnMe_2$ (An = Th, U) were prepared according to published procedures.[23] $Cp^*_2U(C{\equiv}CR)_2$ (R = Ph (**4**), *t*-Bu (**5**)) were prepared according to published procedures.[24] NMR spectra were recorded on Bruker AM 200 and Bruker AM 400 spectrometers. For oligomers of cyclopentylacetylene, 2D NMR spectroscopic techniques such as DEPT, JMOD, COSY, C−H correlation, and HETEROCOSY were used to assign the signals to each of the carbons of the oligomers. When necessary, clean dimers were prepared independently to eliminate any uncertainty regarding the assigned signals. Chemical shifts for ^1H NMR and ^{13}C NMR were referenced to internal solvent resonances and are reported relative to tetramethylsilane. The NMR experiments were conducted in Teflon valve-sealed tubes (J. Young) after vacuum transfer of the liquids in a

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high-vacuum line. GC/MS experiments were conducted in a GC/MS (Finnigan Magnum) spectrometer.

Synthesis of Cp*₂U(Me)(C≡C(*i*-Pr) (1). A 50 mL Schlenk tube was charged in the glovebox with 52 mg (0.0969 mmol) of Cp*₂UMe₂. A 6 mL portion of C₆H₆ was added to the Schlenk tube by vacuum transfer at −78 °C, and then 0.01 mL (0.096 mmol) of isopropylacetylene was vacuum-transferred into the tube. The solution was stirred at room temperature for 4 h, and the reaction was monitored to completion by following the disappearance of the methyl signal of the starting complex. The mono(acetylide) complex **1** was formed together with the bis(acetylide) complex.

^{1}H NMR (C₆D₆): δ 7.26 (s, 30H, Cp*), −14.74 (d, 6H, $^{3}J_{HH}$ = 7.3 Hz, CH(C*H₃*)₂), −37.39 (sept, 1H, $^{3}J_{HH}$ = 7.3 Hz, C*H*(CH₃)₂), −133.27 (s, 3H, C*H₃*). ^{13}C NMR (C₆D₆): δ 169.7 (s, *C*≡CCHMe₂), 154.1 (s, C≡*C*CHMe₂), 119.5 (s, Cp), 44.1 (d, J_{HH} = 122 Hz, *C*H(CH₃)₂), −25.0 (q, $^{1}J_{CH}$ = 125 Hz, (CH₃)₅C₅), −29.5 (q, $^{1}J_{CH}$ = 125 Hz, *C*H₃−U), −45.2 (q, $^{1}J_{CH}$ = 125 Hz, (*C*H₃)₂CH).

Synthesis of Cp*₂Th(C≡C(TMS))₂ (2). A 50 mL Schlenk tube was charged in the glovebox with 50 mg (0.0939 mmol) of Cp*₂ThMe₂. An 8 mL portion of THF was added to the Schlenk tube by vacuum transfer at −78 °C, and then 0.018 mL (0.1938 mmol) of (trimethyl-silyl)acetylene was vacuum-transferred into the tube. The solution was stirred at −78 °C for 4 h, and the reaction was monitored to completion by following the disappearance of the methyl signal of the starting complex. The bis(acetylide) complex **2**, in the absence of an excess of alkyne, slowly decomposed at room temperature.

^{1}H NMR (THF-d_8): δ 2.16 (s, 30H, Cp*), 0.25 (s, 18H, (C*H₃*)₃Si). ^{13}C NMR (THF-d_8): δ 208.3 (Th−*C*≡), 126.2 (Cp), 114.9 (Th−C≡*C*), 11.7 (*C*H₃), 0.6 (Si−(*C*H₃)₃).

Synthesis of Cp*₂Th(C≡CCHMe₂)₂ (3). A 50 mL Schlenk tube was charged in the glovebox with 50 mg (0.0939 mmol) of Cp*₂ThMe₂. An 8 mL portion of THF was added to the Schlenk tube by vacuum transfer at −78 °C, and then 0.02 mL (0.1938 mmol) of isopropyl-acetylene was vacuum-transferred into the tube. The solution was stirred at room temperature for 12 h, and the reaction was monitored to completion by following the disappearance of the methyl signal of the starting complex. The solution and small excess of the isopropylacety-lene were removed by vacuum distillation to yield a yellow powder. Recrystallization of the complex from toluene−hexane at −50 °C yielded 50.8 mg (85%) of white microcrystalline Cp*₂Th(C≡CCHMe₂)₂.

^{1}H NMR (THF−d_8): δ 2.51 (sept, 2H, ^{3}J = 6.8 Hz, C*H*(CH₃)₂), 2.21 (s, 30H, Cp*), 1.15 (d, 12H, ^{3}J = 6.8 Hz, CH(C*H₃*)₂). ^{13}C NMR (THF-d_8): δ 174.8 (Th−*C*≡C), 125.2 (Cp), 116.1 (Th−C≡*C*), 23.9 (q, $^{1}J_{CH}$ = 125 Hz, (CH₃)₂*C*H), 21.6 (d, $^{1}J_{CH}$ = 125 Hz, (CH₃)₂*C*H), 11.7 (q, $^{1}J_{CH}$ = 126 Hz, (CH₃)₅C₅)). Anal. Calcd for C₃₀H₄₄Th: C, 56.59; H, 6.97. Found: C, 56.21; H, 6.68. Mp (dec) = 92 °C.

Synthesis of Cp*₂U(C≡C(*i*-Pr)₂ (6). A 50 mL Schlenk tube was charged in the glovebox with 52 mg (0.0969 mmol) of Cp*₂UMe₂. A 6 mL portion of C₆H₆ was added to the Schlenk tube by vacuum transfer at −78 °C, and then 0.02 mL (0.0192 mmol) of isopropylacetylene was vacuum-transferred into the tube. The solution was stirred at room temperature for 4 h, and the reaction was monitored to completion by following the disappearance of the methyl signal of the starting complex.

^{1}H NMR (C₆D₆): δ 9.49 (s, 30H, Cp*), −15.87 (d, 12H, $^{3}J_{HH}$ = 4.5 Hz, CH(C*H₃*)₂), −38.03 (sept, 2H, $^{3}J_{HH}$ = 4.5 Hz, C*H*(CH₃)₂). ^{13}C NMR (C₆D₆): δ 169.0 (s, *C*≡CCHMe₂), 154.0 (s, C≡*C*CHMe₂), 119.1 (s, Cp), 39.7 (d, $^{1}J_{CH}$ = 122 Hz, *C*H(CH₃)₂), 19.42 (q, $^{1}J_{CH}$ = 125 Hz, (CH₃)₅C₅), −44.0 (q, $^{1}J_{CH}$ = 125 Hz, (*C*H₃)₂CH). Mp = 85 °C. Elemental analysis was not possible due to the formation of uranium carbide even in the presence of V₂O₅.

Catalytic Oligomerization of HC≡CR by Cp*₂AnMe₂ (An = Th, U). (a) General Procedure. In a typical procedure, alkynes were added to an NMR tube containing ≈5 mg (0.01 mmol) of the catalyst in ca. 0.5 mL of solvent (THF-d_8 where not stated otherwise) by vacuum transfer in a high-vacuum line. The sealed tube was heated in an oil bath (oil temperature 80 °C). For the thorium complex, the formation of the metal bis(acetylide) complexes was indicated by a change in color of the reaction mixture, from transparent to pale yellow. For the corresponding uranium complex, the color of the reaction mixture changed from orange to a red-brown during the formation of the bis-(acetylide) complexes. After 100% conversion of the alkyne (detected by the disappearance of the acetylenic hydrogen of the alkyne by ^{1}H NMR spectroscopy), the organic products were vacuum-transferred to another NMR tube and identified by ^{1}H and ^{13}C NMR spectroscopy and GC/MS.

(b) Oligomerization of *tert*-Butylacetylene by Cp*₂UMe₂. (1) A 50% conversion of 0.5 mL (3.3 mmol) of *tert*-butylacetylene in THF-d_8 was achieved after 80 h, producing the head-to-tail dimer **7** (98%) and the head-to-head dimer **8** (2%) (determined by ^{1}H NMR spectros-copy). After vacuum transfer of the compounds, the NMR and GC/MS spectra were recorded.

^{1}H NMR data for **7** (benzene-d_6, 293 K): δ 5.38 (d, 1H, $^{3}J_{HH}$ = 1.6 Hz), 5.12 (d, 1H, $^{3}J_{HH}$ = 1.6 Hz), 1.20 (s, 9H), 1.17 (s, 9H). ^{1}H NMR data for **8** (THF-d_8, 293 K): δ 5.55 (d, 1H, $^{3}J_{HH}$ = 11.9 Hz), 5.18 (d, 1H, $^{3}J_{HH}$ = 11.9 Hz) 1.15 (s, 9H), 1.00 (s, 9H). GC/MS data: *m/z* 164 (M⁺), 149 (M⁺ − CH₃, 100%), 133 (M⁺ − CH₃ − CH₄), 121 (M⁺ − CH₃ − CH₂ − CH₂), 107 (M⁺ − *t*-Bu), 77 (M⁺ − *t*-Bu − 2CH₃).

(2) A 0.5 mL (3.3 mmol) portion of *tert*-butylacetylene was 100% converted into dimers in benzene-d_6 after 183 h, yielding **7** (95%) and **8** (5). During the reaction, the uranium bis(acetylide) complex was detected showing a small shift of the signals as compared to the bis-(acetylide) complex reported in the literature, due to the difference in solvent. ^{1}H NMR data (benzene-d_6, 293 K): δ 6.7 (s, 30H, br, $\nu_{1/2}$ = 20 Hz, Cp*), −1.45 (s, 18H, br, $\nu_{1/2}$ = 35 Hz, *t*-Bu).

(c) Oligomerization of *tert*-Butylacetylene by Cp*₂ThMe₂. According to the general procedure, 100% conversion was achieved by reacting 0.1 mL (0.81 mmol) of *tert*-butylacetylene in THF-d_8 after 48 h, producing the head-to-tail dimer **7** (99.95%) and the head-to-head dimer **8** (0.05%) (**7** was determined by ^{1}H NMR spectroscopy, whereas compound **8** was only observed by GC/MS).

(d) Oligomerization of (Trimethylsilyl)acetylene by Cp*₂UMe₂. (1) In a procedure similar to that described above, 0.5 mL (3.5 mmol) of (trimethylsilyl)acetylene in THF-d_8 was 100% converted after 35 h, yielding exclusively dimer **9** (5%) and trimer **10** (95%). The latter was purified as a colorless liquid by vacuum distillation at 368 K and 4.5 × 10⁻⁴ bar.

^{1}H NMR data for **9** (THF-d_8, 293 K): δ 6.20 (d, 1H, $^{2}J_{HH}$ = 3.9 Hz), 5.98 (d, 1H, $^{2}J_{HH}$ = 3.9 Hz), 0.37 (s, 18 H). GC/MS data: *m/z* 196 (M⁺), 181 (M⁺ − CH₃, 100%), 155 (M⁺ − SiCH), 125 (M⁺ − SiCH − 2CH₃), 97 (C≡CSiMe₃), 73 (SiMe₃). ^{1}H NMR data for **10** (THF-d_8, 293 K): δ 7.60 (dd, 1H, $^{3}J_{HH}$ = 14.1 Hz, 11.5 Hz), 7.11 (dd, 1H, $^{3}J_{HH}$ = 11.5 Hz; $^{4}J_{HH}$ = 1.0 Hz), 6.12 (dd, 1H, $^{3}J_{HH}$ = 14.1 Hz; $^{4}J_{HH}$ = 1.0 Hz), 0.44 (s, 9H, SiMe₃), 0.13 (18H, SiMe₃). ^{13}C NMR data (THF-d_8, 293 K): δ 147.2 (d, CH, J_{CH} = 158 Hz), 144.0 (d, CH, J_{CH} = 154 Hz), 137.3 (d, CH, J_{CH} = 137 Hz), 130.6 (s, C), 107.9 (s, C), 104.8 (s, C), 2.5 (q, CH₃, J_{CH} = 120 Hz), −2.5 (q, CH₃, J_{CH} = 120 Hz). GC/MS data: *m/z* 294 (M⁺), 279 (M⁺ − CH₃), 264 (M⁺ − 2CH₃), 249 (M⁺ − 3CH₃), 221 (M⁺ − SiMe₃), 206 (M⁺ − SiMe₃ − CH₃), 191 (M⁺ − SiMe₃ − 2CH₃), 176 (M⁺ − SiMe₃ − 3CH₃), 163 (M⁺ − SiMe₃ − 3CH₃ − CH), 145 (M⁺ − SiMe₃ − SiMe₃ − 3CH), 132 (M⁺ − SiMe₃ − SiMe₃ − CH₃), 97 (C≡CSiMe₃), 73 (SiMe₃).

(2) In cyclohexane-d_{12}, dimer **9** (4%) and trimer **10** (96%) were obtained when 0.1 mL (0.7 mmol) of (trimethylsilyl)acetylene was oligomerized to 100% conversion after 12 h.

(e) Oligomerization of (Trimethylsilyl)acetylene by Cp*₂ThMe₂. As described above, 0.1 mL (0.71 mmol) (trimethylsilyl)acetylene was 100% converted after 10 h in THF-d_8, yielding dimer **9** (12%) and trimer **10** (88%). In C₆D₆, **9** (10%) and **10** (90%) were obtained in 100% conversion, after 11 h.

(f) Oligomerization of 1-Hexyne by Cp*₂UMe₂. According to the general procedure described above, 0.5 mL (3.6 mmol) of 1-hexyne was oligomerized (100% conversion after 70 h) to a mixture of trimers (18%), tetramers (11%), pentamers (31%), and hexamers (40%), and their ratio was determined by GC/MS.

GC/MS data: trimer *m/z* 246 (M⁺), 231 (M⁺ − CH₃), 216 (M⁺ − CH₃ − CH₂), 202 (M⁺ − CH₃ − CH₂ − CH₂), 188 (M⁺ − CH₃ − CH₂ − CH₂ − CH₂; 100%); tetramer *m/z* 328 (M⁺), 313 (M⁺ − CH₃), 299 (M⁺ − CH₃ − CH₂), 285 (M⁺ − CH₃ − CH₂ − CH₂), 271 (M⁺ − CH₃ − CH₂ − CH₂ − CH₂, 100%); pentamer *m/z* 410 (M⁺), 381 (M⁺ − CH₂CH₃), 367 (M⁺ − CH₂CH₃ − CH₂), 353 (M⁺ − CH₂CH₃ − CH₂ − CH₂; 100%); hexamer *m/z* 490 (M⁺), 433 (M⁺ − CH₂ − CH₂ − CH₂ − CH₃; 100%).

(g) Oligomerization of 1-Hexyne by Cp*$_2$ThMe$_2$. As described above, 0.1 mL (0.81 mmol) of 1-hexyne was oligomerized (100% conversion after 16 h) to a mixture of dimers (39%), trimers (35%), tetramers (13%), and pentamers (13%), and their ratio was determined by GC/MS as above.

GC/MS data: dimer m/z 164 (M$^+$), 149 (M$^+$ − CH$_3$), 135 (M$^+$ − CH$_3$ − CH$_2$), 121 (M$^+$ − CH$_3$ − CH$_2$ − CH$_2$), 107 (M$^+$ − CH$_3$ − CH$_2$ − CH$_2$ − CH$_2$), 93 (M$^+$ − CH$_3$ − CH$_2$ − CH$_2$ − CH$_2$ − CH$_2$, 100%).

(h) Oligomerization of Phenylacetylene by Cp*$_2$UMe$_2$. (1) In a similar manner, 0.1 mL (0.91 mmol) of phenylacetylene was oligomerized (100% conversion after 15 h) to a mixture of dimers (30%), trimers (50%), and tetramers (20%) and their ratio was determined by GC/MS.

GC/MS data: dimer m/z 204 (M$^+$), 102 (M$^+$ − PhC≡CH; 100%); trimer m/z 306 (M$^+$; 100%), 292 (M$^+$ − CH$_2$), 228(M$^+$ − CH$_2$ − C$_6$H$_6$), 215 (M$^+$ − CH$_2$ − C$_7$H$_7$); tetramer m/z 408 (M$^+$; 100%), 331 (M$^+$ − C$_6$H$_5$), 317 (M$^+$ − C$_7$H$_5$), 239 (M$^+$ − C$_7$H$_5$ − C$_6$H$_6$).

(2) During the reaction described in the previous paragraph (section h1), the metal bis(acetylide) complex Cp*$_2$U(C≡CPh)$_2$ was detected.

^{1}H NMR data (THF-d_8, 293 K): δ 21.71 (d, 2H, $^3J_{HH}$ = 7.7 Hz, o-H), 13.14 (t, 1H, $^3J_{HH}$ = 7.7 Hz, p-H), 12.34 (t, 2H, $^3J_{HH}$ = 7.7 Hz, m-H), 3.02 (s, 30H, Cp*).

(i) Oligomerization of Phenylacetylene by Cp*$_2$ThMe$_2$. As described above, 0.1 mL (0.91 mmol) of phenylacetylene was oligomerized (100% conversion after 15 h) to a mixture of dimers (28%), trimers (57%), and tetramers (15%), and their ratio was determined by GC/MS.

(j) Oligomerization of Cyclopentylacetylene by Cp*$_2$UMe$_2$. A 0.4 mL (3.8 mmol) quantity of ethynylcyclopentane in 0.3 mL of THF was 100% oligomerized in 42 h, yielding a mixture of the geminal dimer (17%) and the trans dimer (11%), which were vacuum-transferred from the reaction mixture, and to a mixture of trimers (47%), tetramers (15%), and pentamers (10%). For the clean formation of the geminal dimer, see ref 22.

Analytical data for the geminal dimer C$_5$H$_9$C≡C(C$_5$H$_9$)C=CH$_2$ are as follows. ^{1}H NMR data (C$_6$D$_6$, 293 K): δ 5.17 (d, 1H, ^2J = 1.95 Hz, HHC=C), 5.06 (d, 1H, ^2J = 1.95 Hz, HHC=C), 1.9−1.3 (m, 18H, C$_5$H$_9$). ^{13}C NMR data (C$_6$D$_6$, 293 K): δ 136.9 (s, CH$_2$=C, J_{CH} = 156.1 Hz), 117.7 (t, CH$_2$=C, J_{CH} = 159.0 Hz), 94.9 (s, C=CC≡), 77.7 (s, ≡CC$_5$H$_9$), 47.6 (d, C=CCHC$_4$H$_8$, J_{CH} = 126.3 Hz), 41.3 (d, ≡CCHC$_4$H$_8$, J_{CH} = 142 Hz), 33.4 (t, =CCHC$_2$H$_4$−C$_2$H$_4$, J_{CH} = 126.4 Hz), 31.2 (t, ≡CCHC$_2$H$_4$C$_2$H$_4$, J_{CH} = 134.9 Hz), 25.9 (t, =CCHC$_2$H$_4$C$_2$H$_4$, J_{CH} = 132.0 Hz), 25.1 (t, ≡CCHC$_2$H$_4$C$_2$H$_4$, J_{CH} = 129.2 Hz).

Analytical data for the trans dimer C$_5$H$_9$C≡CCH=CH(C$_5$H$_9$) are as follows. ^{1}H NMR data (C$_6$D$_6$, 293 K): δ 5.54 (dd, 1H, C$_5$H$_9$$H$C=CH, ^3J = 6.84 Hz, ^3J = 10.74 Hz), 5.38 (d, 1H, =CHC≡C, ^3J = 10.74 Hz), 3.1 (m, 2H, CHC$_4$H$_8$), 1.9−1.3 (m, 16H, CHC$_4$H$_8$). ^{13}C NMR data (C$_6$D$_6$, 293 K): δ 147.0 (d, C$_5$H$_9$$C$H=CH, J_{CH} = 156.1 Hz), 108.8 (d, =CHC≡C, J_{CH} = 163.2 Hz), 98.4 (s, C=CC$_5$H$_9$), 80.1 (s, =CCC$_5$H$_9$), 51.8 (d, C=CCHC$_4$H$_8$, J_{CH} = 127.7 Hz), 41.3 (d, ≡CCHC$_4$H$_8$, J_{CH} = 142 Hz), 34.3 (t, =CCHC$_2$H$_4$C$_2$H$_4$, J_{CH} = 134.9 Hz), 32.3 (t, ≡CCHC$_2$H$_4$C$_2$H$_4$, J_{CH} = 127.0 Hz), 29.9 (t, =CCHC_2H$_4$C$_2$H$_4$, J_{CH} = 130.6 Hz), 25.8 (t, ≡CCHC_2H$_4$C$_2$H$_4$, J_{CH} = 132.0 Hz).

GC/MS data: dimer m/z 188 (M$^+$), 173 (M$^+$ − CH$_3$), 160 (M$^+$ − C$_2$H$_4$), 145 (M$^+$ − C$_3$H$_7$), 131 (M$^+$ − C$_4$H$_9$), 119 (M$^+$ − C$_5$H$_9$), 105 (M$^+$ − CH$_2$ − C$_5$H$_9$), 91 (M$^+$ − C$_2$H$_4$ − C$_5$H$_9$; 100%); trimer m/z 282 (M$^+$), 267 (M$^+$ − CH$_3$), 253 (M$^+$ − CH$_2$ − CH$_3$), 239 (M$^+$ − CH$_2$ − CH$_2$ − CH$_3$), 225 (M$^+$ − CH$_2$ − CH$_2$ − CH$_2$ − CH$_3$), 213 ((M$^+$ − C$_2$H$_9$; 100%), 199 (M$^+$ − CH$_2$ − C$_5$H$_9$), 185 (M$^+$ − CH$_2$ − CH$_2$ − C$_5$H$_9$), 171 (M$^+$ − CH$_2$ − CH$_2$ − CH$_2$ − C$_5$H$_9$), 157 (M$^+$ − CH$_2$ − CH$_2$ − CH$_2$ − C$_5$H$_9$), 131 (M$^+$ − CH$_2$ − C$_5$H$_8$ − C$_5$H$_9$); tetramers m/z 376 (M$^+$), 307 (M$^+$ − C$_5$H$_9$; 100%), 265 (M$^+$ − CH$_2$ − CH$_2$ − CH$_2$ − C$_5$H$_9$), 239 (M$^+$ − C$_5$H$_8$ − C$_5$H$_9$), 225 (M$^+$ − CH$_2$ − C$_5$H$_8$ − C$_5$H$_9$), 211 (M$^+$ − CH$_2$ − CH$_2$ − C$_5$H$_8$ − C$_5$H$_9$), 170 (M$^+$ − C$_5$H$_9$ − C$_5$H$_8$ − C$_5$H$_9$), 95 (CH$_2$=C(C$_5$H$_9$)).

(k) Oligomerization of Cyclopentylacetylene by Cp*$_2$ThMe$_2$. In a similar manner, 0.04 mL (0.3 mmol) of cyclopentylacetylene was oligomerized (100% conversion after 45 h) to a mixture of dimers

(13%), trimers (57%), and tetramers (30%). The catalyst solution color changed from faint yellow to red after 3 h of heating.

(l) Oligomerization of 3-Methyl-1-butyne by Cp*$_2$UMe$_2$. A 0.3 mL (3.0 mmol) quantity of 3-methyl-1-butyne, in 0.25 mL of THF, was 100% oligomerized in 20 h, yielding a mixture of trimers (35%), tetramers (60%), pentamers (4%), and hexamers (1%). Their ratio was determined by GC/MS.

GC/MS data: trimer m/z 204 (M$^+$), 189 (M$^+$ − CH$_3$), 175 (M$^+$ − CH$_2$ − CH$_3$), 161 (M$^+$ − CH(CH$_3$)$_2$; 100%), 147 (M$^+$ − CH$_2$ − CH(CH$_3$)$_2$), 133 (M$^+$ − CH$_2$ − CH$_2$ − CH(CH$_3$)$_2$); tetramer m/z 272 (M$^+$), 257 (M$^+$ − CH$_3$), 229 (M$^+$ − CH(CH$_3$)$_2$), 173 (M$^+$ − C$_2$H$_4$ − CH(CH$_3$)$_2$), 145 (M$^+$ − C$_3$H$_6$ − CH(CH$_3$)$_2$; 100%); pentamer m/z 340 (M$^+$), 325 (M$^+$ − CH$_3$), 297 (M$^+$ − CH(CH$_3$)$_2$; 100%), 269 (M$^+$ − C$_2$H$_4$ − CH(CH$_3$)$_2$), 255 (M$^+$ − C$_3$H$_6$ − CH(CH$_3$)$_2$); hexamer m/z 408 (M$^+$), 365 (M$^+$ − CH(CH$_3$)$_2$), 323 (M$^+$ − C$_3$H$_6$ − CH(CH$_3$)$_2$), 295 (M$^+$ − C$_2$H$_4$ − C$_3$H$_6$ − CH(CH$_3$)$_2$), 281 (M$^+$ − C$_3$H$_6$ − C$_3$H$_6$ − CH(CH$_3$)$_2$), 253 (M$^+$ − C$_2$H$_4$ − C$_3$H$_6$ − C$_3$H$_6$ − CH(CH$_3$)$_2$), 227 (M$^+$ − C$_2$H$_2$ − C$_2$H$_4$ − C$_3$H$_6$ − C$_3$H$_6$ − CH(CH$_3$)$_2$; 100%).

(m) Oligomerization of 3-Methyl-1-butyne by Cp*$_2$ThMe$_2$. In a similar manner, 0.08 mL (0.76 mmol) of 3-methyl-1-butyne in 0.3 mL of benzene was oligomerized (100% conversion after 22 h) to a mixture of dimers (1%), trimers (6%), tetramers (2%), pentamers (72%), hexamers (9%), and heptamers (10%). Their ratio was determined by GC/MS.

GC/MS data: heptamer m/z 476 (M$^+$), 433 (M$^+$ − CH(CH$_3$)$_2$), 390 (M$^+$ − 2CH(CH$_3$)$_2$), 347 (M$^+$ − 3CH(CH$_3$)$_2$), 305 (M$^+$ − C$_3$H$_6$ − 3CH(CH$_3$)$_2$).

(n) Oligomerization of 4-*tert*-Butylphenylacetylene by Cp*$_2$UMe$_2$. A 0.3 mL (0.18 mmol) quantity of 4-*tert*-butylphenylacetylene in 0.25 mL of THF was 50% oligomerized after 120 h, yielding exclusively the trans head-to-head dimer.

^{1}H NMR (400 MHz, C$_6$D$_6$): δ 8.00 (d, 2H, $^3J_{HH}$ = 7.81 Hz, o-CHC≡C), 7.50 (d, 2H, $^3J_{HH}$ = 7.81 Hz, o-CHC=C), 7.35 (d, 2H, $^3J_{HH}$ = 7.81 Hz, m-CHC≡C), 7.18 (d, 2H, $^3J_{HH}$ = 7.81 Hz, m-CHC=C), 6.54 (d, 1H, $^3J_{HH}$ = 11.72 Hz, ArCH=CH), 5.87 (d, 1H, $^3J_{HH}$ = 11.72 Hz, ArCH=CHC≡C), 1.27 (s, 9H, t-BuArC≡C), 1.18 (s, 9H, t-BuArC≡C). ^{13}C NMR (100 MHz, C$_6$D$_6$): δ 151.7 (s, CC≡C), 151.6 (s, CC=C), 138.6 (d, $^1J_{CH}$ = 156.1 Hz, o-CHC≡C), 134.6 (s, p-CC≡C), 131.6 (d, $^1J_{CH}$ = 161.8 Hz, o-CHC=C), 129.1 (d, $^1J_{CH}$ = 158.8 Hz, C≡CCH=C), 125.7 (d, $^1J_{CH}$ = 160.4 Hz, m-CHC≡C), 125.5 (d, $^1J_{CH}$ = 161.8 Hz, m-CHC=C), 121.3 (s, p-CC=C), 107.0 (d, $^1J_{CH}$ = 159.0 Hz, C=CHAr), 96.6 (s, C≡CAr), 88.7 (s, C≡CC≡C), 31.5 (s, C≡CPhCMe$_3$), 31.2 (s, C=CPhCMe$_3$), 19.4 (q, $^1J_{CH}$ = 124.9 Hz, C≡CPhCMe_3), 12.3 (q, $^1J_{CH}$ = 126.3 Hz, C=CPhCMe_3).

GC/MS data: m/z 316 (M$^+$; 100%), 301 (M$^+$ − CH$_3$), 245 (M$^+$ − CH$_2$CMe$_2$ − CH$_3$), 203 (M$^+$ − CMe$_3$ − CH$_2$CMe$_2$), 115 (M$^+$ − t-BuC$_6$H$_4$ − C$_2$H$_2$CMe$_2$).

(o) Oligomerization of 4-*tert*-Butylphenylacetylene by Cp*$_2$ThMe$_2$. A 0.1 mL (0.056 mmol) quantity of 4-*tert*-butylphenylacetylene in 0.5 mL of benzene was 100% oligomerized after 21 h, yielding a mixture of dimers (87%) and trimers (13%).

GC/MS data: trimer m/z 474 (M$^+$), 341 (M$^+$ − BuC$_6$H$_4$), 316 (M$^+$ − C$_2$H$_2$ − BuC$_6$H$_4$), 301 (M$^+$ − CH$_3$ − C$_2$H$_2$ − BuC$_6$H$_4$), 245 (M$^+$ − C$_4$H$_8$ − C$_2$H$_2$ − BuC$_6$H$_4$; 100%).

(p) Cross-Oligomerization of (Trimethylsilyl)acetylene and *tert*-Butylacetylene by Cp*$_2$UMe$_2$. A 0.35 mL (2.4 mmol) portion of (trimethylsilyl)acetylene and 0.3 mL (2.4 mmol) of *tert*-butylacetylene were vacuum-transferred into a J. Young NMR tube containing 5 mg (0.01 mmol) of Cp*$_2$UMe$_2$ in 0.3 mL of THF-d_8. The alkynes were oligomerized (100% in (trimethylsilyl)acetylene and 25% in *tert*-butylacetylene) after 66 h, yielding a mixture of dimers (14%), which were vacuum-transferred from the reaction mixture (383 K, 5.2 × 10^{-5} mmHg), and a mixture of trimers (86%). The obtained dimers were the geminal dimer **9** (10%) and the cross geminal dimer **12** (4%). The obtained trimers were the plain trimer **10** (43%), trimer **13** (27%), and trimer **14** (16%).

^{1}H NMR (200 MHz, THF-d_8) for **12**: δ 5.28 (dd, 2H, $^2J_{HH}$ = 1.5 Hz, C=CH_2), 1.25 (s, 9H, t-Bu), 0.9 (s, 9H, SiMe_3). GC/MS data: m/z 180 (M$^+$), 165 (100%) (M$^+$ − CH$_3$), 135 (M$^+$ − 3CH$_3$), 123 (M$^+$ − t-Bu), 97 (C≡CSiMe$_3$), 73 (SiMe$_3$). ^{1}H NMR (200 MHz, THF-d_8) for **13**: δ 7.15 (dd, 1H, $^3J_{HH}$ = 14.0 Hz, 11.5 Hz, BuC=CHCH=), 6.60

(d, 1H, $^3J_{HH}$ = 11.5 Hz, BuC=CHC*H*=), 5.65 (d, 1H, $^3J_{HH}$ = 14.0 Hz, BuC*H*=C*H*), 1.22 (s, 9H, C(C*H$_3$*)$_3$), 0.03 (s, 18H, SiMe$_3$). ^{13}C NMR (100 MHz, C$_6$D$_6$): δ 145.3 (d, $^1J_{CH}$ = 156 Hz, *CH*), 144.6 (d, $^1J_{CH}$ = 154 Hz, *CH*), 137.6 (d, $^1J_{CH}$ = 137 Hz, *CH*), 130.1 (s), 110.7 (s, *C*≡C(TMS)), 94.5 (s, C≡*C*(TMS)), 32.5 (q, $^1J_{CH}$ = 120 Hz, *C*Me$_3$), 29.0 (s, C*C*Me$_3$), 2.0 (q, $^1J_{CH}$ = 120 Hz, Si*Me$_3$*). GC/MS data: *m/z* 278 (M$^+$; 100%), 263 (M$^+$ − CH$_3$), 247 (M$^+$ − 2CH$_3$), 221 (M$^+$ − *t*-Bu), 206 (M$^+$ − *t*-Bu − CH$_3$), 97 (C≡CSiMe$_3$), 73 (SiMe$_3$), 57 (*t*-Bu). ^{1}H NMR (200 MHz, THF-d_8) for **14**: δ 7.02 (dd, 1H, $^3J_{HH}$ = 11.9 Hz, $^4J_{HH}$ = 0.9 Hz, (TMS)C=C*H*CH=), 6.30 (d, 1H, $^3J_{HH}$ = 11.9 Hz, (TMS)C=CHC*H*=), 5.44 (dd, 1H, $^3J_{HH}$ = 11.9 Hz, $^4J_{HH}$ = 0.9 Hz, (TMS)C*H*=CH), 1.10 (s, 9H, C(C*H$_3$*)$_3$), 0.04 (s, 9H, SiMe$_3$), 0.04 (s, 9H, SiMe$_3$). ^{13}C NMR (100 MHz, C$_6$D$_6$): δ 144.3 (d, $^1J_{CH}$ = 158 Hz, *CH*), 143.6 (d, $^1J_{CH}$ = 155 Hz, *CH*), 135.6 (d, $^1J_{CH}$ = 138 Hz, *CH*), 128.1 (s), 108.6 (s), 105.5 (s), 33.5 (q, $^1J_{CH}$ = 120 Hz, *C*Me$_3$), 2.0 (s, $^3J_{CH}$ = 120 Hz, Si*Me$_3$*), −2.5 (q, $^1J_{CH}$ = 120 Hz, Si*Me$_3$*). GC/MS data: *m/z* 278 (M$^+$; 100%), 263 (M$^+$ − CH$_3$), 247 (M$^+$ − 2CH$_3$), 221 (M$^+$ − *t*-Bu), 206 (M$^+$ − *t*-Bu − CH$_3$), 97 (C≡CSiMe$_3$), 73 (SiMe$_3$), 57 (*t*-Bu).

Kinetic Study of the Oligomerization of (TMS)C≡CH. In a representative experiment, an NMR sample was prepared as described in the typical NMR-scale catalytic reaction section but maintained at −78 °C until kinetic measurements were initiated. The sealed tube was heated in a temperature-controlled oil bath, and at time intervals NMR data were acquired using eight scans per time interval with a long pulse delay to avoid saturation of the signal. The kinetics were usually monitored by the intensity changes in the substrate resonances and in the product resonances over 3 or more half-lives. The substrate concentration (*C*) was measured from the area (A_s) of the ^{1}H-normalized signal of the solvent (A_b). All the data collected could convincingly least-squares-fit (*R* > 0.98) to eq 5, where C_0 ($C_0 = A_{s0}/A_{b0}$) is the

$$mt = \log(C/C_0) \qquad (5)$$

initial concentration of substrate and *C* (A_s/A_b) is the substrate concentration at time *t*.

The ratio of catalyst to substrate was accurately measured by calibration with internal FeCp$_2$. Turnover frequencies (N_t, h^{-1}) were calculated from the least-squares-determined slopes (*m*) of the resulting plots. Typical initial alkyne concentrations were in the range 0.7−7.2 M, and typical catalyst concentrations were in the range 25−240 mM.

Results

Synthesis and Properties of Bis(acetylide)−Organoactinide Complexes. Bis(acetylide)−organoactinide complexes can be synthesized in multigram quantities at room temperature via the reaction of Cp*$_2$AnMe$_2$ (Cp* = Me$_5$C$_5$; An = Th, U) with stoichiometric or excess amounts of the corresponding terminal alkynes (eq 6). For thorium, the formation of the metal bis-
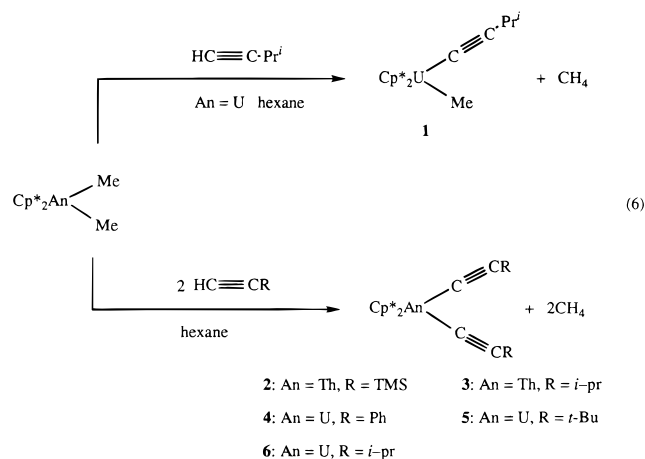
(acetylide) complexes was indicated by a change in color of the reaction mixture, from transparent to pale yellow. For
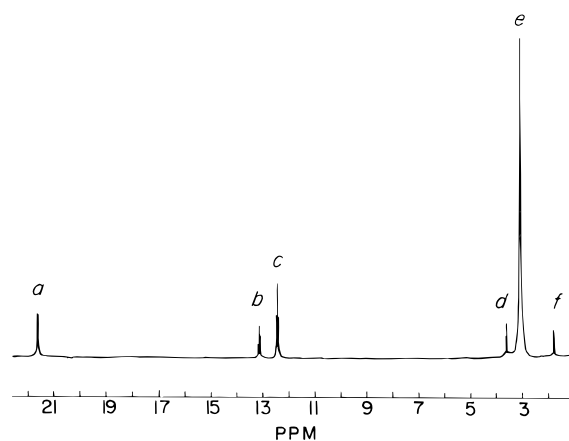
Figure 1. ^{1}H NMR spectrum of the paramagnetic Cp*$_2$U(C≡CPh)$_2$ in THF-d_8 (signals marked as d and f). Signals *a*−*c* correspond to the aromatic *o*-, *p*-, and *m*-hydrogens, respectively, whereas signal e corresponds to the Cp* hydrogens.

uranium, the color of the reaction mixture changed from orange to deep red-brown during the formation of the metal bis-(acetylide) complexes. The reaction which can be followed by ^{1}H NMR is much faster (30 min) for the organoactinide uranium complex than for the corresponding thorium complex (few hours). Attempts to trap the mono(acetylide)−methyl complex were successful only for the uranium isopropylacetylide complex (**1**) (eq 6). Attempts to trap, spectroscopically, any other organoactinide−mono(acetylide)−methyl complex were unsuccessful; only the starting materials or the bis(acetylide) complexes were observed. This result strongly argues, at least for the organothorium complexes, that the metathesis substitution of the second methyl ligand by the terminal alkyne is much faster than the first σ-bond metathesis.[25]

All newly synthesized organoactinides were characterized by standard spectroscopic/analytical techniques (see Experimental Section for details). Due to the paramagnetic chemical shifts of the 5f^5 uranium(IV) center and the rapid electron spin−lattice relaxation times, magnetically nonequivalent ligand protons generally exhibit sharp, well-separated signals and can be readily resolved in the ^{1}H NMR spectra as shown for complex **4** (Figure 1).

Organoactinide-Catalyzed Oligomerization of Terminal Alkynes. The reaction of Cp*$_2$AnMe$_2$ (An = Th, U) with an excess of *tert*-butylacetylene in benzene (alkyne:Cp*$_2$AnMe$_2$ ratio 330:1) at 80 °C results in the regioselective catalytic formation of the head-to-tail dimer 2,4-di-*tert*-butyl-1-butene-3-yne (**7**) and a trace amount of the corresponding head-to-head dimer (*E*)-1,4-di-*tert*-butyl-1-butene-3-yne (**8**) (eq 7).

The reaction of Cp*$_2$AnMe$_2$ with (trimethylsilyl)acetylene produces the head-to-tail geminal dimer 2,4-bis(trimethylsilyl)-1-butene-3-yne (**9**) and the head-to-tail-to-head trimer (*E,E*)-1,4,6-tris(trimethylsilyl)-1,3-hexadiene-5-yne (**10**) as the major products without any trace formation (checked by GC/MS) of the corresponding trans dimer or any other higher oligomers (eq 8).

For other terminal alkynes such as HC≡CPh, HC≡C(*i*-Pr), and HC≡CC$_5$H$_9$, the Cp*$_2$AnMe$_2$ complexes yield mixtures of

(25) In principle, the initial insertion step could also proceed by the opposite regiochemistry to yield the corresponding hydrides Cp*$_2$An(H)$_x$-(CH$_3$)$_{2-x}$ (*x* = 1, 2) and the internal alkyne. This reaction is actually estimated to be slightly exothermic (∼ 2 kcal/mol) although, by far, less exothermic than the reaction for the evolution of methane. Furthermore, no internal alkyne compounds were observed in the ^{1}H NMR spectra of the bis(acetylide) complexes. This pathway was indeed carefully probed since, in the presence of silanes, the organometallic hydride and the corresponding silaacetylide were observed.[13]

t-Bu—C≡C—H $\xrightarrow{\text{Cp*}_2\text{AnMe}_2}$ (An = Th, U)

(7)

7
An = Th: 99.95%
An = U: 98%

8
An = Th: 0.05%
An = U: 2%

TMS—C≡C—H $\xrightarrow{\text{Cp*}_2\text{AnMe}_2}$ (An = Th, U)

(8)

9
An = Th: 10%
An = U: 5%

10
An = Th: 90%
An = U: 95%
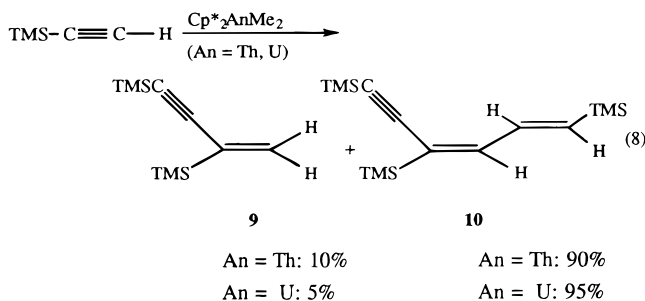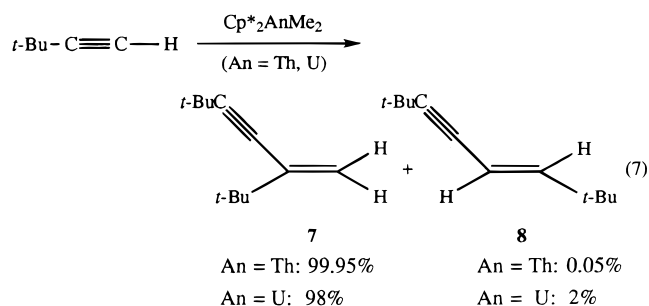
the head-to-head and head-to-tail isomeric dimers and higher oligomers with no specific regioselectivity (Table 1). For the bulky HC≡CPh-Me-4, different reactivities are found for the different organoactinide complexes. Whereas Cp*$_2$ThMe$_2$ yields a mixture of dimers and trimers, the corresponding Cp*$_2$UMe$_2$ affords *only* the head-to-head trans dimer **11** (eq 9). It is

Me—⟨ ⟩—C≡C—H $\xrightarrow{\text{Cp*}_2\text{UMe}_2}$

(9)

11
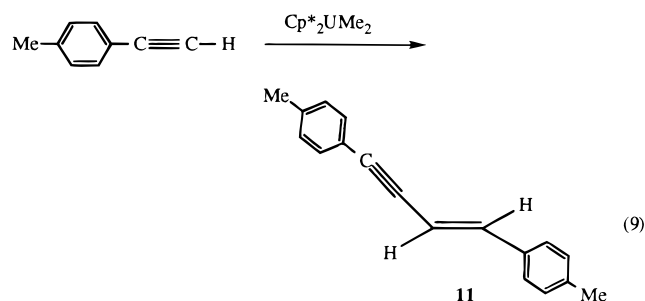
important to point out that no allenic compounds were formed in any of the oligomerization reactions, in contrast to the oligomerization of alkynes by organolanthanide complexes.[4e,19]

Interestingly, the utilization of different solvents does not cause major changes in the oligomerization reaction rates (Table 1, entries 2−7), arguing that no major solvent stabilization is required in the rate-determining transition state. Although the turnover frequencies for both of the organoactinide complexes are in the range 1−10 h^{-1}, the turnover number is high and is normally in the range 200−400. Moreover, in the absence of moisture and oxygen, these complexes are able to react continuously. Hence, the reaction of Cp*$_2$UMe$_2$ with (TMS)C≡CH (1:400) was run repeatedly four times with the same catalyst after vacuum transfer of the reaction products arguing for a high thermal and chemical stability for the uranium complex.

Cross-Oligomerization of t-BuC≡CH and (TMS)C≡CH by Cp*$_2$UMe$_2$. Since the oligomerization of t-BuC≡CH with Cp*$_2$UMe$_2$ (entry 3, Table 1) produced the geminal dimer, as the major product, indicating that the addition of the alkyne to the metal acetilide is regioselective, with the bulky group pointing away from the cyclopentadienyl groups (Figure 2), it was interesting to induce some competition between t-BuC≡CH and (TMS)C≡CH to allow, if possible, the formation of a specific oligomer. Thus, the reaction of equimolar amounts of

t-BuC≡CH and (TMS)C≡CH with Cp*$_2$UMe$_2$ produces two dimers (14%) and three specific trimers (86%). The obtained dimers are the geminal dimer **9** (10%) and the cross geminal dimer **12** (4%), resulting from the insertion of a t-BuC≡CH, with the same regioselectivity as observed in Figure 2, into the uranium bis(trimethylsilyl)acetylide complex. The trimers obtained are the head-to-tail-to-head trimer (*E,E*)-1,4,6-tris(trimethylsilyl)-1,3-hexadiene-5-yne (**10**) as the major product (43%), the trimer **14** (15%), resulting from the insertions of two (TMS)C≡CH groups into the *tert*-butylacetylide complex, and the unexpected trimer **13** (27%) (eq 10). Trimer **13** is formed

TMS—C≡CH + ^{t}BuC≡CH $\xrightarrow{\text{Cp*}_2\text{UMe}_2}$

(10)

9   **12**   **10**

14   **13**
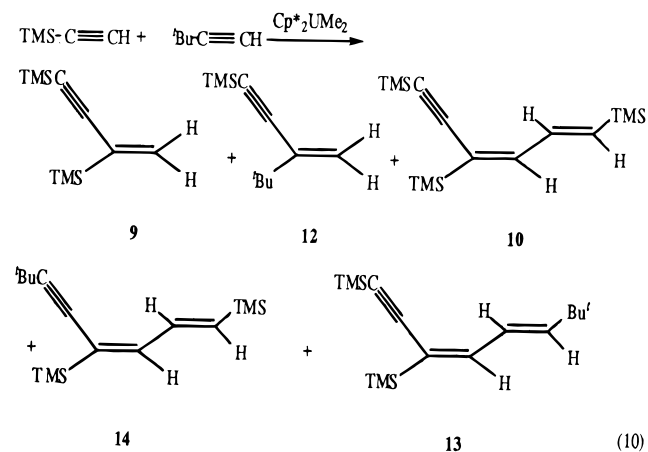
by the consecutive insertion of *tert*-butylacetylene after the (TMS)C≡CH insertion. This result argues that, in the formation of trimers, the last insertion rate is fast and competitive for both alkynes and that the metathesis of the free alkyne is the rate-determining step. Regarding the yields of the different products, in the presence of the second alkyne (t-BuC≡CH), the total amount of trimers was reduced, as compared with the simple oligomerization of (TMS)C≡CH, producing higher yields of dimers.

Trapping of the Key Intermediate Complex. Following the reaction of (TMS)C≡CH with Cp*$_2$UMe$_2$ spectroscopically shows two different domains. The first domain is at room temperature where the only compound obtained is the bis-(acetylide) complex. The oligomerization reaction is initiated by heating the reaction mixture to 70 °C, upon which the bis-(acetylide) complex signals disappear almost immediately and a new set of two doublets (δ = 7.13 and 6.25, ^3J = 9.03 Hz, in THF-d_8) are observed in the ^{1}H NMR spectrum, besides signals for the starting formation of the dimer and trimer. These signals are maintained constant during the course of the reaction, whereas the organic product signals increase (Figure 3). Poisoning experiments using equimolar amounts of water and D$_2$O show that the set of doublet signals disappear, arguing that the signals arise from the formation of an organoactinide intermediate and their integration is exclusively added to the integration of the obtained trimer. This result suggests a bis-(dieneyne) organoactinide complex (Figure 4) as the most plausible intermediate and as the resting state of the catalyst under the catalytic conditions. Corroborating this structure, the measured integration ratio, 2:15, between the vinylic signals of the plausible organometallic intermediate and the pentamethyl-cyclopentadienyl ancillary ligands argues for a ligand ratio of 1:1 between the Cp and dieneyne moieties, indicating that both acetylide positions at the metal center are active sites.

Kinetic Studies on the Oligomerization of (TMS)C≡CH. A kinetic study of the 3(TMS)C≡CH → **10** transformation was undertaken by in situ ^{1}H NMR spectroscopy. The reaction of a
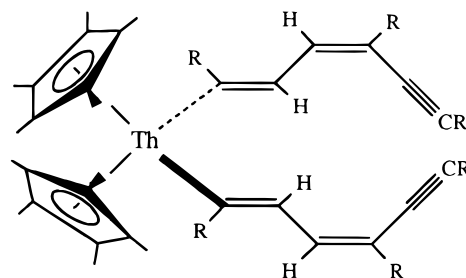
Table 1. Distribution Ratios and Activity Data for the Oligomerization of Terminal Alkynes by Organoactinide Complexes

entry	cat.	R	solvent	% dimers[a]	trimers	tetramers	pentamers	hexamers	heptamers	N_t (h^{-1})
1	Th	t-Bu	THF	99.95 (0.05)						2
2	U	t-Bu	THF	98 (2)						3
3	U	t-Bu	C$_6$D$_6$	95 (5)						2
4	Th	SiMe$_3$	THF	12	88					7
5	Th	SiMe$_3$	C$_6$D$_6$	10	90					6
6	U	SiMe$_3$	THF	5	95					10
7	U	SiMe$_3$	C$_6$D$_{12}$	4	96					6
8	Th	Ph[b]	THF	28	57	15				6
9	U	Ph[b]	THF	30	50	20				6
10	Th	n-Bu[b]	THF	39	35	13	13			5
11	U	n-Bu[b]	THF		18	11	31	40		5
12	U	C$_5$H$_9$	THF	17 (11)	47	15	10			9
13	Th	C$_5$H$_9$	C$_6$D$_6$	13	57	30				0.6
14	U	i−Pr	THF		35	60	4	1		15
15	Th	i−Pr	C$_6$D$_6$	1	6	2	72	9	10	4
16	U	4-MePh	THF	100						0.07
17	Th	4-MePh	C$_6$D$_6$	87	13					0.2

[a] The number in parentheses corresponds to the dimer of type **8**. [b] The percentage of the different oligomers was calculated from the GC/MS data.
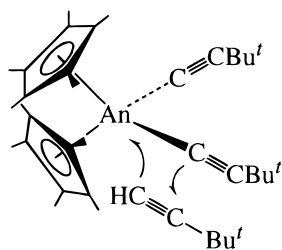
Figure 2. Regioselectivity of the insertion of a terminal alkyne into an organoactinide−acetylide bond.

R = TMS

Figure 4. The bis(dieneyne) organoactinide complex in the linear oligomerization of terminal alkynes, the most plausible intermediate.

Figure 3. Vinylic region for the Me$_3$SiC≡CH oligomerization reaction catalyzed by Cp$_2$*ThMe$_2$. Signals c and d correspond to the organoactinide bis(acetylide) complex **C** (Scheme 1). Signals f, g, and e belong to the trimer **10**, and signals a and b belong to the corresponding dimer **9**.
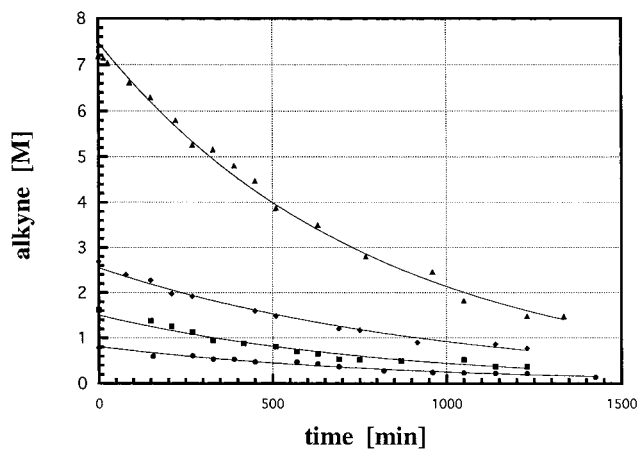
Figure 5. Plot of (TMS)C≡CH concentration as a function of time for the trimerization of (TMS)C≡CH (3(TMS)C≡CH → **10**) using Cp$_2$*UMe$_2$ as the precatalyst in benzene-d_6 at 25 °C.

(280−300)-fold molar excess of (trimethylsilyl)acetylene with Cp$_2$*UMe$_2$ was monitored with constant catalyst concentration until complete substrate consumption. The appearance of the vinylic signal, at $\delta = 7.60$ ppm, was normalized with the solvent signal as an internal standard. The kinetic plots as shown in Figure 5 reveal a logarithmic dependence of the alkyne substrate concentration on time over a ∼10-fold substrate concentration range, which indicates an essentially first-order dependence of the catalytic rate on substrate concentration under these conditions.

Considering the rapid protonolysis of the metal−alkyl bond by acidic hydrogens, it seems unreasonable that the formation of the acetylide complex could be the turnover-limiting step under most catalytic conditions. This first-order kinetic dependence on alkyne can be obtained by either of two pathways where (a) the insertion of an alkyne into the metal−acetylide bond is the rate-limiting step or (b) the σ-bond metathesis of the
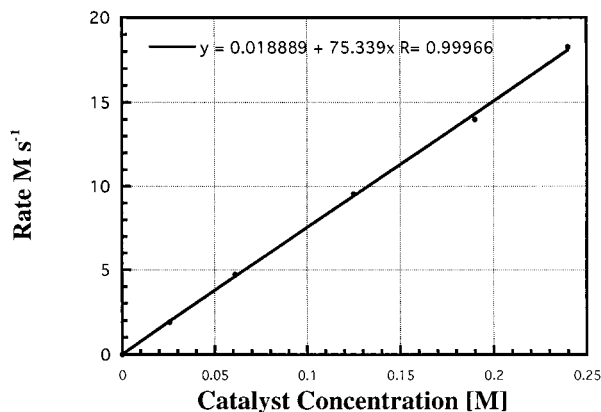
Figure 6. Determination of the reaction order in actinide concentration for the trimerization of $(TMS)C\equiv CH$ ($3(TMS)C\equiv CH \rightarrow$ **10**) mediated by $Cp^*_2UMe_2$ as the precatalyst in benzene-d_6 at 25 °C.

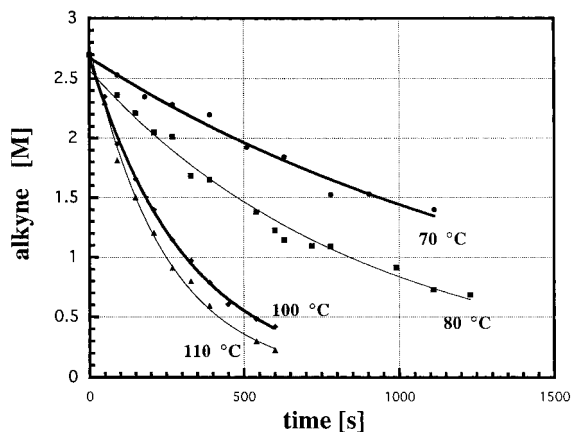**Figure 7.** Plot of $(TMS)C\equiv CH$ concentration as a function of time and temperature for the trimerization of $(TMS)C\equiv CH$ ($3(TMS)C\equiv CH \rightarrow$ **10**) using $Cp^*_2UMe_2$ as the precatalyst in toluene-d_8. Starting alkyne and catalyst concentrations are identical in each experiment.

oligomer by another alkyne is the rate-determining step. The first pathway can be excluded since no bis(acetylide) organometallic complex is observed during the course of the reaction even when high catalyst:alkyne ratios are used. When the initial concentration of the alkyne is held constant and the concentration of the catalyst precursor is varied over a 10-fold concentration range (Figure 6), a plot of reaction rate vs precatalyst concentration indicates the reaction to be first-order in catalyst.

The empirical rate law for the organoactinide-catalyzed oligomerization $3(TMS)C\equiv CH \rightarrow$ **10** is given by eq 11. The derived rate constant for the production of **10** at 70 °C is $k = 7.6(6) \times 10^{-4} \text{ s}^{-1}$.

$$\nu = k[\text{alkyne}][\text{U}] \tag{11}$$

A similar kinetic dependence on alkyne and catalyst concentrations is observed over a 70−110 °C temperature range (Figure 7). The derived activation parameters E_a, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ from an Eyring analysis (Figure 8) are 11.8(3) kcal mol^{-1}, 11.1(3) kcal mol^{-1}, and −45.2(6) eu, respectively.

Discussion

Synthesis of Bis(acetylide) Complexes. The σ-bond metathesis reaction of the acidic proton of a terminal alkyne with an organoactinide complex of the type $Cp^*_2AnMe_2$ (An = Th, U) is a rapid reaction which is thermodynamically driven by the elimination of methane. Thus, a number of bis(acetylide)
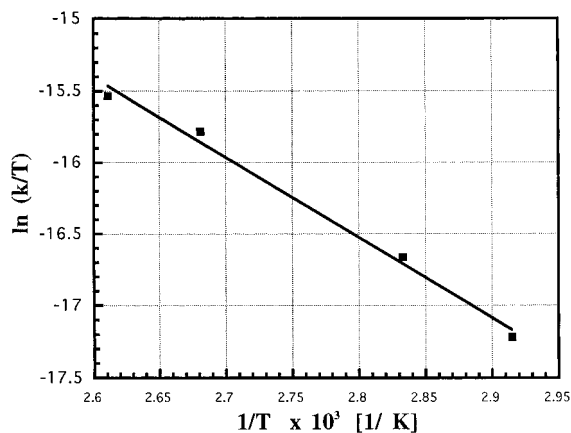
Figure 8. Eyring plot for the trimerization of $(TMS)C\equiv CH$ ($3(TMS)C\equiv CH \rightarrow$ **10**) using $Cp^*_2UMe_2$ as the precatalyst in toluene-d_8. The line represents the least-squares fit to the data points.

complexes can be easily prepared and characterized. The enthalpy of reaction for the formation of the bis(acetylide) complex is highly exothermic and can be calculated from tabulated bond disruption energies which have been measured for these organoactinide complexes (eq 12).[16]

$$\Delta H_{\text{Th (calc)}} = -18 \text{ kcal mol}^{-1}$$
$$\Delta H_{\text{U (calc)}} = -48 \text{ kcal mol}^{-1}$$
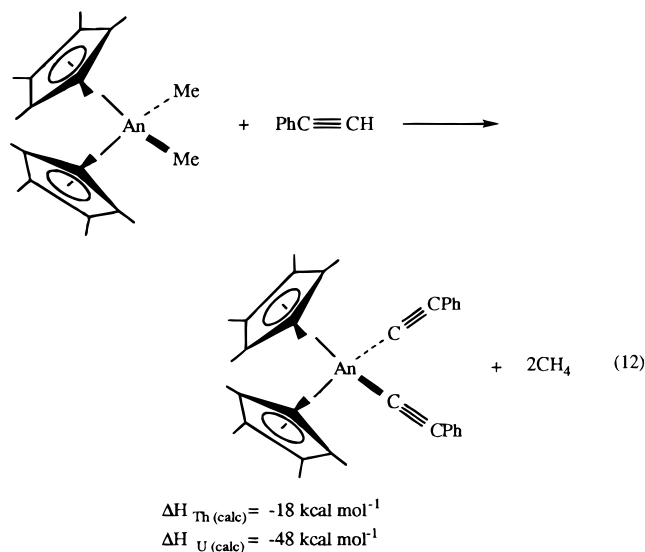
Interestingly, only the mono(acetylide) complex was observed, as a transient organometallic moiety, for the uranium complex with isopropylacetylene (**1**). Stoichiometric reactions, even at low temperatures, for other alkynes did not form the mono(acetylide) but rather formed the bis(acetylide) complexes, indicating that the second σ-bond metathesis has a much lower energy of activation than that of the corresponding first σ-bond metathesis. The symmetric NMR spectra which are obtained for these bis(acetylide) complexes, similar to those of other early transition metal bis(acetylide) complexes,[26] indicate that they do not form bridging acetylide complexes as in the group 3−organolanthanide complexes. Interestingly, only when $Cp^*_2HfCl_2$ is reacted with an excess of $NaC\equiv CH$, is the mono-(acetylide) bridging complex $Cp^*_2(C\equiv CH)HfC\equiv CHf(C\equiv CH)-Cp^*_2$ obtained.[27]

(26) For related group 4−bis(acetylide) compounds, see: (a) Erker, G.; Frömberg, W.; Benn, R.; Mynott, R.; Augermund, K.; Krüger, C. *Organometallics* **1989**, *8*, 911. (b) Lang, H.; Herres, M.; Zsolnai, L.; Imhof, W. *J. Organomet. Chem.* **1991**, *409*, C7.

(27) Southard, G. E.; Curtis, M. D.; Kampf, J. W. *Organometallics* **1996**, *15*, 4667.

Scheme 1. Plausible Mechanism for the Linear Oligomerization of Terminal Alkynes Promoted by Organoactinide Bis(acetylide) Complexes

Cp*$_2$AnMe$_2$

2 HC≡CR

2 CH$_4$ (1)

Cp*$_2$An
C≡CR
C≡CR
A

2 HC≡CR   (2)

Cp*$_2$An
CH=CR—C≡CR
CH=CR—C≡CR
B

b H—CR
a H
C≡CR
9

2 HC≡CR

(3)   2 HC≡CR

Cp*$_2$An
RC=CH—CH=CR—C≡CR
RC=CH—CH=CR—C≡CR
C

c H   *d* H R
RC=C—C=C—C≡CR
H   H R

(4)

2 HC≡CR

R *f*
=CH
H
HC=CR—C≡CR
e *g*
10

2
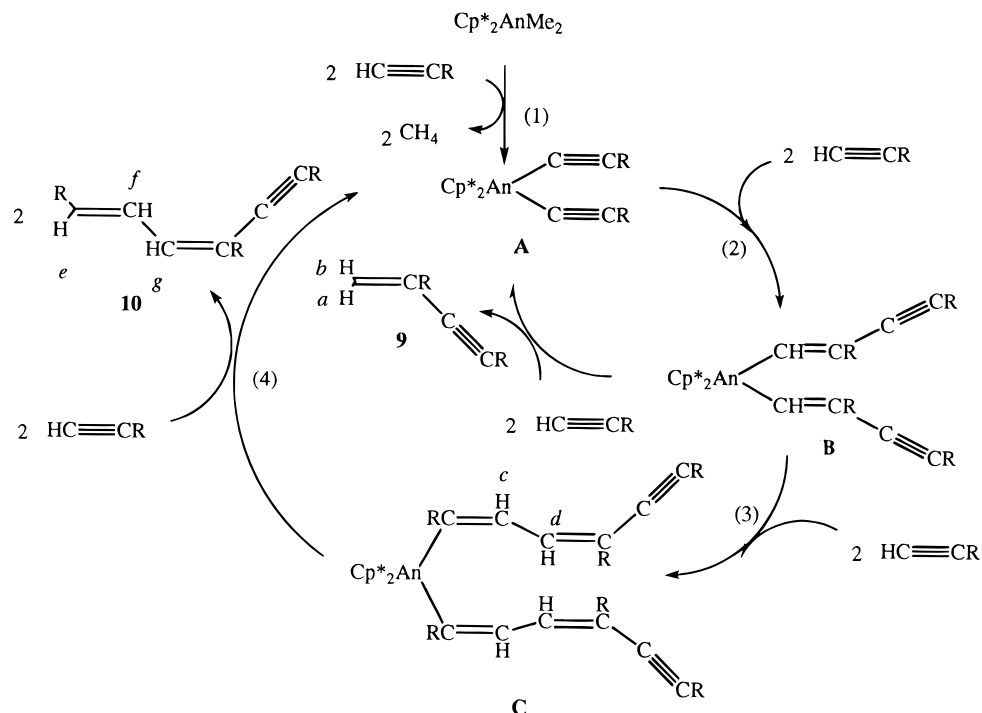
Catalytic Reaction Scope and Mechanism. The present catalytic results for the linear oligomerizations of terminal alkynes demonstrate that a substantial range of substrates can be oligomerized. The oligomerizations proceed either to a specific dimer and trimer for bulky terminal alkyne substituents or to a myriad of oligomers, with no specific chemoselectivity and regioselectivity, beyond the conventional syn addition to the metal−acetylide bond, for nonbulky terminal alkynes.[28] For *t*-BuC≡CH, the oligomerization with organoactinide complexes is highly regiospecific toward the geminal dimer **7**, as found for organolanthanides and isolobal group 4 complexes.[4e,28d] **7** is obtained by the regioselective addition of the alkyne to the metal acetylide complex with the substituent group pointing away from the cyclopentadienyl ligands (Figure 2), in contrast to late transition metal complexes. For example, ruthenium complexes are effective catalysts for the dimerization of terminal alkynes, producing all of the three type of dimers depending the nature of the ligand.[28b,29] For early transition metal aryloxy group 4 complexes, mixtures of compounds are obtained comprising the geminal dimer, linear trimer, and trimers of either the aromatic or fulvene compounds depending the alkyne substituent.[30] In those systems, a Ti[II] or Zr[II] complex is the most plausible expected key intermediate. For (TMS)C≡CH, in the presence of organoactinides, small amounts of the geminal dimer and *only* the regiospecific trimer **10** are obtained. Interestingly, the dimer has the same 1,2-insertion regioselectivity as found for *t*-BuC≡CH. For the oligomeric trimer, a dramatic change for the second insertion is observed, in which the last alkyne

insertion is in a 2,1-mode. The 2,1-insertion mode of (TMS)C≡CH is indeed electronically favored, as expected for the of polarization of its π^* orbital.[31] Thus, it seems that the first insertion in the oligomerization of terminal bulky alkynes with organoactinide complexes is driven by steric factors (entries 1−7 and 16−17 in Table 1), whereas the second insertion is electronically governed.[32] In comparison to organolanthanides complexes of the type Cp*$_2$LnCH(TMS)$_2$ (Ln = Ce, La), these organolanthanide complexes are by far more reactive and less regioselective, producing, in addition to the geminal dimer, the 2,1-insertion trans dimer product, two trimers, and two allene compounds.[4e] For the isolobal group 3 yttrium complex Cp*$_2$YCH(TMS)$_2$, only two dimers have been obtained,[17c] contrasting the reactivity of the (aryloxy)yttrium complex, from which only the head-to-head 2,1-insertion trans dimer was produced.[4d] A plausible pathway for the organoactinide oligomerization of terminal alkynes is shown in Scheme 1.

This mechanism consists of a sequence of well-established elementary reactions such as insertion of an alkyne into an M−C σ-bond and σ-bond metathesis. The first step in the catalytic cycle involves the protonation, at room temperature, of the alkyl groups in the organoactinide precatalyst, yielding the bis-(acetylide) complexes Cp*$_2$An(C≡CR)$_2$ (**A**), with the concomitant elimination of methane (step 1). The 1,2-head-to-tail-insertion of the alkyne into the actinide−carbon σ-bond yields the plausible bis(alkenyl)actinide complex **B**. Complex **B** undergoes either a σ-bond metathesis with the C−H bond of

(28) For ^{1}H and ^{13}C NMR of eneynes, see ref 4e and: (a) Horton, A. D. *J. Chem. Soc., Chem. Commun.* **1992**, 185. (b) Yi, C. S.; Liu, N. *Organometallics* **1996**, *15*, 3968. (c) Horton, A. D.; Orpen, A. G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 876. (d) Yoshida, M.; Jordan, R. F. *Organometallics* **1997**, *16*, 4508.

(29) Slugovc, C.; Mereiter, K.; Zobetz, E.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 5275.

(30) (a) Johnson, E.; Balaich, G. J.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 11086. (b) van der Linden, A.; Schaverien, C. J.; Meijboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008.

(31) For reviews, see: (a) Fleming, I. *Chemtracts: Org. Chem.* **1993**, *6*, 113. (b) Lambert, J. B. *Tetrahedron* **1988**, *46*, 2677. (c) Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: New York, 1989; pp 57−225. (d) Gabelica, V.; Kresge, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 3838 and references cited therein.

(32) Stockis and Hoffman have performed calculations on the polarization of the π^* orbitals in (TMS)C≡CH and CH$_3$C≡CH. Different polarizations were found for both groups, showing the large effect of the substituent on the alkyne sp-carbon atoms. These electronic effects are believed to be responsible for the difference in regioselectivities of the trimerization−dimerization results. Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952.

Scheme 2. Calculated Enthalpies of Reaction for the Oligomerization of Terminal Alkynes Promoted by Organothorium Complexes
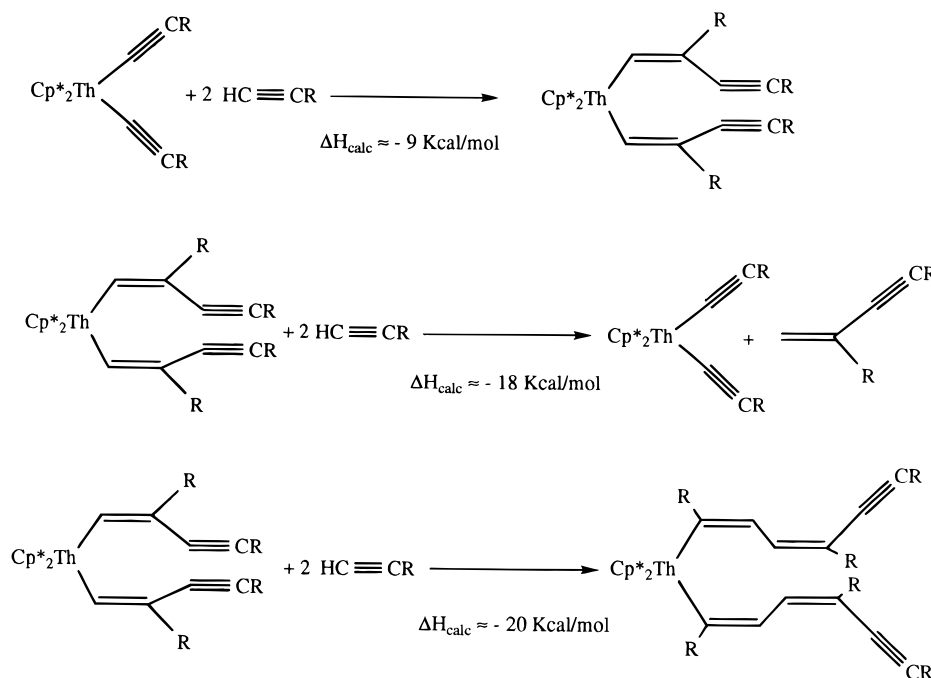
another alkyne, producing the corresponding geminal dimer and **A**, or an additional 2,1-tail-to-head-insertion of an alkyne, with the expected regioselectivity, into the organoactinide alkenyl complex **B**, yielding the bis(dienyl)organoactinide complex **C**. The latter complex, **C**, undergoes another σ-bond metathesis with an incoming alkyne, yielding the corresponding trimer and regenerating the active actinide bis(acetylide) complex. The turnover-limiting step for the catalytic trimerization is the elimination of the trimer compound from the organometallic complex **C**, indicating that the rate for σ-bond metathesis between the actinide carbyls and the alkyne and the rate of insertion of the alkyne into the metal–acetylide bond (steps 1 and 2) are, by far, much faster than the rate for σ-bond metathesis of the alkyne with the metal–dialkenyl bond in the catalytic cycle (step 4).

The activation parameters for the organothorium oligomerization of (TMS)C≡CH are characterized by a rather small enthalpy of activation (11.1(3) kcal mol^{-1}) and a large negative (even for an intermolecular reaction) entropy of activation (−45.2(6) eu; $\Delta G^{\ddagger} = 24(1)$ kcal mol^{-1} at 298 K). These parameters suggest a highly ordered transition state with considerable bond making to compensate for bond breaking. Interestingly, organoactinide-centered hydrogenolysis processes, which proceed via a four-centered transition state (Figure 2), exhibit rather similar activation parameters ($\Delta H^{\ddagger} = 9(2)$ kcal mol^{-1}; $\Delta S^{\ddagger} = -45(5)$ eu).[33]

Thermodynamically, higher oligomers and even polymers are expected,[34,35] as calculated for the enthalpy of reaction, for the addition of triple bonds in a conjugated manner (Scheme 2). ΔH_{calc} for dimer formation is exothermic by 27 kcal mol^{-1} for

either organoactinide, whereas every additional insertion is calculated to be exothermic by an additional 20 kcal mol^{-1}. Thus, ΔH_{calc} for trimer formation is exothermic by 47 kcal mol^{-1}, corroborating the results in Table 1 (entries 8−15), in which it is shown that nonbulky terminal alkynes are oligomerized with no chemoselectivity.

Regarding the cross-oligomerization of (TMS)C≡CH with *t*-BuC≡CH by Cp*$_2$UMe$_2$, besides the expected geminal dimer **9** and trimer **10**, three more compounds **12**−**14** are observed, reflecting the different reactivities of the two alkynes. The chemoselectivity of the products toward (TMS)C≡CH indicates that the protonolysis of Cp*$_2$UMe$_2$ or either the organoactinide eneyne or dieneyne moieties by (TMS)C≡CH is much faster than that of *t*-BuC≡CH. The kinetic competition among the alkynes, for the first insertion, yielding the organoactinide eneyne complex, favors the (TMS)C≡CH alkyne (compounds **9**, **10**, **13**, and **14**). Since no trimer was obtained for the oligomerization of plain *t*-BuC≡CH, we expected to obtain only trimers with a TMS group in the terminal vinylic position due to the putative polarization of the (TMS)C≡CH toward the metal center (Figure 9). The unexpected formation of compound **13** indicates that (TMS)C≡CH or *t*-BuC≡CH is able to insert in a competitive fashion, allowing the formation of **10** or **13**, respectively. It seems that the bulky effect of the *tert*-butyl group is by far larger than that of the TMS group in this specific organometallic environment.[36] This result also argues against an equilibrium between the bis(alkenyl) complex **C** and the

(33) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5515.

(34) The reaction of either organoactinide complex with acetylene (HC≡CH) produced the precipitation of black *cis*-polyacetylene. The *cis*-polyacetylene was thermally converted to the *trans*-polyacetylene at 80 °C, as shown by the IR spectrum in which the typical absorption at about 1015 cm^{-1} given by *trans*-polyacetylene rises slowly and the characteristic absorptions at 445, 740, and 1329 cm^{-1} of the cis polymer disappear. Wang, J. Q.; Eisen, M. S. Unpublished results.

(35) Ohff, A.; Burlakov, V. V.; Rosenthal, U *J. Mol. Catal.* **1996**, *108*, 119.

(36) The effective size of a substituent is expected to depend on the specific environment in which the group is placed.[37] The Me$_3$Si and CH$_3$ groups have been found to have similar effective sizes,[38] albeit the van der Waals size of the silyl group is much larger considering that the Si−C bond is much longer than a C−C or a C−H bond.

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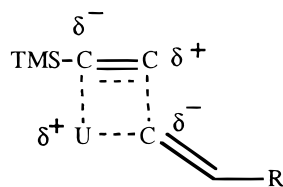
Figure 9. Expected polarization of (trimethylsilyl)acetylene toward organoactinide complexes in the oligomerization of terminal alkynes.

alkenyl organoactinide **B** since no trimer containing two *t*-Bu groups was observed.

The extent of oligomerization, i.e., the dimer/trimer:higher oligomer ratio, is determined by the differences in activation energy ($\Delta\Delta G^{\ddagger}$) for the CH σ-bond activation and alkyne insertion in the last catalytic step (step 4) of the oligomerization mechanism. The effect of the solvents on this energy difference were found to be small as compared to those of other four-centered transition state processes catalyzed by organoactinides (Table 1).[12,13,24] It seems that the values $\Delta\Delta G^{\ddagger}$ for the dimerization processes depend on the size of the metal and the bulkiness of the alkyne substituent. For higher oligomers, there is an additional dependence on the electronic effect of the alkyl substituent. For small alkynes, it seems that the energy of insertion decreases since the insertion reactions are more sensitive to steric effects than are the CH σ-bond metatheses.

Conclusions

The results presented here demonstrate that organoactinide complexes are active catalysts for the linear oligomerization of terminal alkynes by a mechanism that consists of several insertions and σ-bond metathesis. A delicate balance between alkyne insertion and alkyne CH σ-bond metathesis determines the dimer:higher oligomer ratio. The present work represent the first study of the synthetic, spectroscopic, kinetic, and reactivity properties of bis(acetylide) organoactinide complexes. It provides insights into the mechanistic process and stability of the key intermediate compounds, providing a basis for the rational modification of the metallocene complexes of future organo-actinide arrays. It also lays the groundwork necessary to understand the approach for controlling the oligomerization reaction to obtain selectively and catalytically only dimers.[22]