Controlling the Catalytic Oligomerization of Terminal Alkynes Promoted by Organoactinides: A Strategy to Short Oligomers

Ariel Haskel, Ji Quan Wang, Thomas Straub, Tal Gueta Neyroud, and Moris S. Eisen*

Contribution from the Department of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel

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Abstract: A novel strategy has been developed for the catalytic synthesis of short oligomers, dimers and/or trimers, of terminal alkynes. The method allows control of the extent of and, in some cases, the regiospecificity in the catalyzed oligomerization of terminal alkynes promoted by bis(pentamethylcyclopentadienyl)actinide dimethyl complexes ($Cp^*_2AnMe_2$; $Cp^* = C_5Me_5$, An = Th, U). These metallocene precursors are known to promote the simultaneous production of a large number of differently sized oligomers in the presence of terminal alkynes. However, the addition of specific amines ensures the selective synthesis of short oligomers. Catalytic "tailoring" to dimers or a mixture of dimers and trimers can be achieved by using nonbulky or bulky amines, respectively. The kinetics in the catalytic oligomerization of 1-hexyne, in the presence of *i*-$BuNH_2$, mediated by $Cp^*_2ThMe_2$ are first order in [alkyne], first order in [Th], and inverse first order in [amine]. Kinetic, spectroscopic, and mechanistic data argue that the turnover-limiting step involves the formation of the mono(amido)thorium acetylide complex with rapid insertion of the alkyne and protonolysis by the amine.

Introduction

In the design of chemical reaction schemes to obtain selective and regiospecific products, transition metals have been widely studied, with stoichiometric and catalytic reactions, and in many cases have resulted in efficient, selective processes which operate under mild and easily controlled conditions.[1,2] Despite the rapid growth of activity in this field,[3] controlling the extent of catalytic oligomerization/polymerization reactions remains challenging. For example, in the catalytic Ziegler−Natta polymerization reaction, dihydrogen is added to control, to some extent, the molecular weight of the polymeric chains,[4] or, in the polymerization of alkenes by cationic group 4 metallocenes, the counterion affects the molecular weight of the observed polymers.[5] For the catalytic oligomerization of alkynes, *the means to control the selectivity* (extent of the oligomerization) of the products was previously not available. It is noteworthy to point out that highly regioselective catalysts (early and late transition metals) for the specific *dimerization* of terminal alkynes have been reported but provide no means to generate or to control the formation of higher oligomers.[6,7]

In the preceding contribution,[8] we noted that organoactinide complexes of the type $(C_5Me_5)_2AnMe_2$ (An = Th (**1**), U (**2**)) were found to be effective precatalysts for the oligomerization of terminal alkynes. We have shown that for bulky acetylenes, such as *t*-BuC≡CH or (TMS)C≡CH, selective dimerization (eq 1) and trimerization (eq 2) were achieved, producing the head-to-tail dimer and the specific head-to-tail-to-head trimer, respectively.[9]

For nonbulky terminal alkynes, the oligomerization leads to a mixture of dimers to heptamers with no regioselectivity among the different oligomers.[9] The plausible mechanism based on kinetic experiments and accomplished by trapping some key

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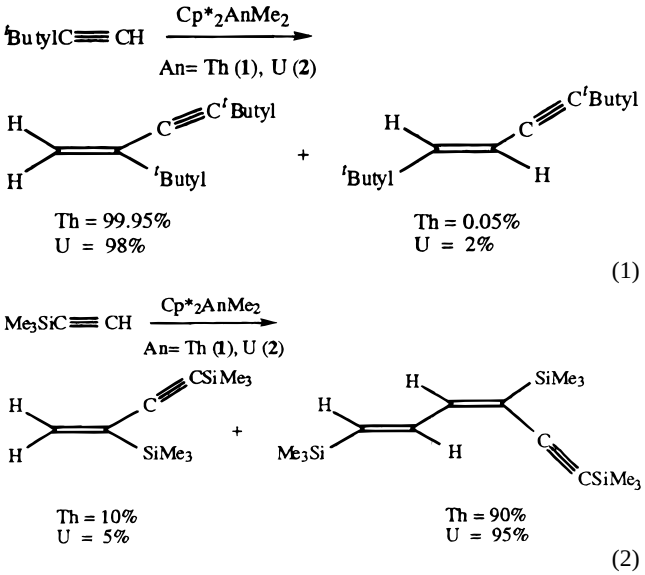

intermediate complexes, **3** and **4** (see Figure 1), was outlined in Scheme 1 in the preceding contribution.[8] The turnover-limiting step for the catalytic trimerization of (TMS)C≡CH was found to be the elimination of the organic trimer from the bis-(dieneyne)thorium complex **4**. This result argues that the rate for σ-bond metathesis between the actinide carbyls and the alkyne, eliminating methane, and the rate of insertion of the C≡C triple bond of the terminal alkyne into the metal acetylide moiety (steps 1 and 2 in Scheme 1, ref 8) are much faster than the rate for C−H σ-bond metathesis of the terminal alkyne bond with the metal−dialkenyl complex in the catalytic cycle (step 4).

An interesting conceptual consideration is the ability to control the proposed mechanism in such a manner as to allow the formation of specific dimer or trimer, restraining the formation of higher oligomers, that is, to block routes 3 and 4 (Scheme 1, preceding contribution[8]) and constrain the catalyst to follow pathways 2 and 5.

We report herein a *principle* for the selective control of the extent of oligomerization of terminal alkynes, by an acidic chain-transfer agent, as a basic *strategy* to modify the nonselective oligomerization toward small oligomers (dimers and trimers). This approach uses a chain-transfer reagent that does not end up in the product (in contrast to, e.g., H_2) and is also novel since it does not require subsequent elimination from the product to release the unsaturated oligomer (in contrast to, e.g., ethene oligomerization by metallocene catalysts or magnesium reagents).[10] The catalytic oligomerization is promoted by organoactinide complexes with the addition of the chain-transfer agent, producing *selective dimers and regiospecific trimers* with no other higher oligomers (tetramers to heptamers) as observed for the compared nonselective oligomerization without the added reagent. The oligomerization control was achieved by adding an amine (primary or secondary) to the catalytic cycle, without much altering of the turnover frequencies as compared with those of the noncontrolled process. The selectivity control, which is the amount of the different oligomers obtained by the different complexes (Th, U), of the new catalytic cycle was achieved by considering the difference in the calculated bond-disruption energies between an actinide−alkenyl and an actinide−amido bond and the combination of the nonselective catalytic pathways

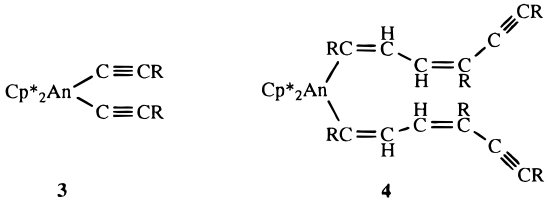

Figure 1. Trapped intermediate complexes in the oligomerization of terminal alkynes promoted by organoactinide complexes.

with individual stoichiometric reactions. The regioselectivity of the different oligomers can be tailored, to some extent, by the different organoactinide metals, the pK_a, and steric hindrance imparted by the amine. This strategy provides a route to control, in principle, oligomerization/polymerization reactions of terminal alkynes producing specific enynes for further chemical transformations toward antitumor antibiotics containing dieneynes or fused bicyclic [*n.m.*0] structural frameworks which represent primordial substructures in many biologically interesting molecules.[11]

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. Ether solvents were distilled under argon from sodium benzophenone ketyl. Hydrocarbon solvents (THF-d_8, toluene-d_8, benzene-d_6, C_6D_{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. Amines (Fluka) were dried over Na/K alloy and stored over activated molecular sieves (4 Å), degassed, and freshly vacuum-distilled. 2,6-dimethylaniline-d_2 was synthesized by repeated deuterium exchange with D_2O under N_2 and was found to be ≥99% ND_2 (^{1}H NMR and ^{2}H NMR integrations). $Cp^*_2AnMe_2$ (Th, U)[12] and $Cp^*_2U(NHR)_2$ (R = 2,6-dimethylphenyl, *t*-Bu, Ph, C≡C(TMS)) were prepared according to published procedures.[13] NMR spectra were recorded on Bruker AM 200 and Bruker AM 400 spectrometers. Chemical shifts for ^{1}H NMR and ^{13}C NMR are referenced to internal solvent resonances and are reported relative to tetramethylsilane. GC/MS experiments were conducted in a GC/MS (Finnigan Magnum) spectrometer. The NMR experiments were conducted in Teflon valve-sealed tubes (J. Young) after vacuum transfer of the liquids in a high-vacuum line.

Kinetic Study of Controlled Oligomerization. In a typical experiment, an NMR sample was prepared as described in the typical NMR-scale catalytic reactions section but maintained at −78 °C until kinetic measurements were initiated. The sealed tube was heated in a temperature-controlled oil bath, and at time intervals NMR data were acquired using eight scans per time interval with a long pulse delay to avoid saturation of the signal. The kinetics were usually monitored by the intensity changes in the substrate resonances and in the product resonances over 3 or more half-lives. The substrate concentration (C) was measured from the area (A_s) of the ^{1}H-normalized signal of the

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solvent (A_b). All the data collected could convincingly be least-squares-fit ($R > 0.98$) to eq 3 or 4, where C_0 ($C_0 = A_{s0}/A_{b0}$) is the initial concentration of substrate and C (A_s/A_b) is the substrate concentration at time t.

$$mt = \log(C/C_0) \tag{3}$$

$$\frac{1}{C} = \frac{1}{C_0} + mt \tag{4}$$

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 amine concentrations were in the range 0.035−0.49 M, initial alkyne concentrations were in the range 0.097−3.84 M, and typical catalyst concentrations were in the range 8.7−53 mM.

Synthesis of Cp*$_2$ThMe(NH-2,6-Me$_2$Ph) (15). A 50 mL Schlenk tube was charged in the glovebox with 50 mg (0.0939 mmol) of Cp*$_2$-ThMe$_2$. An 8 mL portion of THF was added to the Schlenk tube by vacuum transfer at −78 °C, and then 0.09 mL (0.0939 mmol) of 2,6-dimethylaniline was syringed into the Schlenk tube. The solution was stirred at −78 °C for 4 h and at room temperature for an additional 5 h. The reaction was monitored to completion by following the disappearance of the methyl signal of the starting complex at $\delta = -0.5$ ppm. The solvent was removed by vacuum distillation, the mixture was redissolved in 20 mL of toluene, the solution was filtered, and crystallization was accomplished by the addition of 5 mL of hexane at −78 °C overnight.

Ir: $\nu = 3253$ cm^{-1} (N−H). ^{1}H NMR (THF-d_8): δ 6.98 (d, 4H, ^3J = 7.4 Hz, *m-H*), 6.45 (t, 2H, ^3J = 7.4 Hz, *p-H*), 2. 28 (s, 31H, Cp + N*H*), 0.16 (s, 3H, CH_3). Anal. Calcd for $C_{29}H_{43}NTh$ (MW = 637.6966): C, 54.62; H, 6.80; N, 2.20. Found: C, 54.39; H, 6.89; N, 2.40. HRMS, *m*/*z*: 637.6970. Mp (dec) = 95−100 °C.

Synthesis of Cp*$_2$Th(NH-2,6-Me$_2$Ph)$_2$ (13). A 50 mL Schlenk tube was charged in the glovebox with 50 mg (0.0939 mmol) of Cp*$_2$ThMe$_2$. An 8 mL portion of THF was added to the Schlenk tube by vacuum transfer at −78 °C, and then 0.022 mL (0.229 mmol) of 2,6-dimethylaniline was syringed into the Schlenk tube. The solution was stirred for 4 h at −78 °C and for an additional 15 h at room temperature. The reaction was monitored to completion by following the disappearance of the methyl signals of the starting complex and of the intermediate methylamido complex at $\delta = -0.5$ and 0.16 ppm, respectively. The solvent was removed by vacuum distillation at low temperature, the mixture was redissolved in 20 mL of toluene, the solution was filtered, and crystallization was accomplished by the addition of 15 mL of hexane at −78 °C overnight.

Ir: $\nu = 3219$ cm^{-1} (N−H). ^{1}H NMR (THF-d_8): δ 7.08 (d, 4H, ^3J = 7.6 Hz, *m-H*), 6.39 (t, 2H, ^3J = 7.6 Hz, *p-H*), 2.10 (br, 32H, Cp + N*H*). Anal. Calcd for $C_{36}H_{50}N_2Th$ (MW = 742.8338): C, 58.21; H, 6.78; N, 3.77. Found: C, 54.25; H, 6.98; N, 3.58. HRMS, *m*/*z*: 742.8342. Mp (dec) = 97−113 °C.

Controlled Catalytic Oligomerization of HC≡CR by Cp*$_2$AnMe$_2$ (An = Th, U) in the Presence of Amines. (a) General Procedure. In a typical procedure, alkyne and amine were added to an NMR tube containing ≈7 mg (0.013 mmol) of the catalyst in ca. 0.3 mL of solvent (C_6D_6 where not stated otherwise) by vacuum transfer in a high-vacuum line. The sealed tube was heated in an oil bath (oil temperature 100 °C). For thorium, the formation of the metal bis(amido) complexes was indicated by the change of color of the reaction mixture from transparent to pale yellow. For uranium, the color of the reaction mixture changed from orange to red-brown during the formation of the metal bis(amido) complexes. After 100% conversion of the alkyne (detected by ^{1}H NMR), the organic products were vacuum-transferred to another NMR tube and identified by ^{1}H, ^{13}C, COSY, NOESY, and C−H correlation NMR spectroscopy and by GC/MS. Different geometrical isomers were identified by comparing the signals of one clean isomer and subtracting the data from those of the mixture.

(b) Dimerization of 3-Methyl-1-butyne by Cp*$_2$ThMe$_2$ and EtNH$_2$. According to the general procedure described above, 0.08 mL (0.78 mmol) of 3-methyl-1-butyne was dimerized (100% conversion after 66 h) with 0.4 mL (6.1 mmol) of $EtNH_2$ and 8 mg (0.015 mmol) of Cp*$_2$ThMe$_2$ to a mixture of the geminal head-to-tail **5A** (57%) and trans head-to-head **5B** (43%) dimers, respectively.

^{1}H NMR (400 MHz, C_6D_6) of **5A**: δ 5.23 (d, 1H, $^3J_{HH}$ = 1.95 Hz, H*H*C=C), 5.06 (d, 1H, $^3J_{HH}$ = 1.95 Hz, H*H*C=C), 2.31 (septet, 1H, $^3J_{HH}$ = 6.84 Hz, Me_2CHC=C), 2.30 (septet, 1H, $^3J_{HH}$ = 6.84 Hz, C≡CC*H*Me_2), 1.10 (d, 6H, $^3J_{HH}$ = 6.84 Hz, *Me*$_2$CHC=C), 1.05 (d, 6H, $^3J_{HH}$ = 6.84 Hz, *Me*$_2$CHC≡C).

^{13}C NMR (100 MHz, C_6D_6) of **5A**: δ 139.2 (s, *C*=C), 117.1 (t, $^1J_{CH}$ = 157.6 Hz, H_2C=C), 96.5 (s, C=C*C*≡C), 79.6 (s, C≡*C*CHMe$_2$), 35.7 (d, $^1J_{CH}$ = 136.3 Hz, C=C*C*HMe$_2$), 29.5 (d, $^1J_{CH}$ = 142 Hz, C≡C*C*HMe$_2$), 22.3 (q, $^1J_{CH}$ = 127.8 Hz, C=CCH*Me*$_2$), 21.4 (q, $^1J_{CH}$ = 126.3 Hz, C≡CCH*Me*$_2$).

^{1}H NMR (400 MHz, C_6D_6) of **5B**: δ 5.44 (dd, 1H, $^3J_{HH}$ = 7.81 Hz, $^3J_{HH}$ = 10.74 Hz, Me_2CH*H*C=CH), 5.16 (d, 1H, $^3J_{HH}$ = 10.74 Hz, Me_2CHHC=C*H*), 3.07 (m, 1H, Me_2C*H*CH=C), 2.13 (m, 1H, C≡CC*H*Me_2), 1.12 (d, 6H, $^3J_{HH}$ = 6.84 Hz, *Me*$_2$CHC=C), 1.05 (d, 6H, $^3J_{HH}$ = 6.84 Hz, *Me*$_2$CHC≡C).

^{13}C NMR (100 MHz, C_6D_6) of **5B**: δ 149.1 (d, $^1J_{CH}$ = 154.7 Hz, C≡C*C*H=C), 108.0 (d, $^1J_{CH}$ = 163.2 Hz, C=*C*HCHMe$_2$), 99.5 (s, C=C*C*≡C), 76.4 (s, C≡*C*CHMe$_2$), 35.9 (d, $^1J_{CH}$ = 136.3 Hz, C=C*C*HMe$_2$), 29.7 (d, $^1J_{CH}$ = 142 Hz, C≡C*C*HMe$_2$), 23.2 (q, $^1J_{CH}$ = 127.8 Hz, C=CCH*Me*$_2$), 21.8 (q, $^1J_{CH}$ = 126.3 Hz, C≡CCH*Me*$_2$).

m/*z*: 137 ($M^+ + 1$; 100%), 121 ($M^+ - CH_3$), 109 ($M^+ - CHCH_3$), 91 ($M^+ - 3CH_3$). High-resolution mass spectrum, *m*/*z*: calcd for C_8H_{16} (M^+), 136.2390; found, 136.2367.

(c) Oligomerization of 3-Methyl-1-butyne by Cp*$_2$UMe$_2$ and Me$_2$NH. As described above, in 0.25 mL of THF, 0.7 mL (6.8 mmol) of 3-methyl-1-butyne was oligomerized (90% conversion after 43 h) with 0.15 mL (2.3 mmol) of Me_2NH and 5 mg (0.01 mmol) of Cp*$_2$-UMe$_2$ to a mixture of the geminal head-to-tail dimer **5A** (10%) and the head-to-tail-to-tail trimer **5C** (90%), respectively. Vacuum-transfer distillation (50 °C; 1×10^{-3} mmHg) afforded clean separation of the two compounds.

^{1}H NMR (400 MHz, C_6D_6) of the head-to-tail-to-tail trimer **5C**: δ 6.00 (s, br, 1H, H_2C=CR*H*C=CR), 4.90 (m, br, 2H, *H*$_2$C=CRHC=), 3.02 (septet, 1H, $^3J_{HH}$ = 6.8 Hz, Me_2CHC=C), 2.83 (septet, 1H, $^3J_{HH}$ = 6.84 Hz, C≡CC*H*Me_2), 2.50 (septet, 1H, $^3J_{HH}$ = 6.84 Hz, C=CC*H*Me_2), 1.05 (d, 6H, $^3J_{HH}$ = 6.84 Hz, *Me*$_2$CHC≡C), 1.05 (d, 12H, $^3J_{HH}$ = 6.84 Hz, *Me*$_2$CHC=C).

^{13}C NMR (100 MHz, C_6D_6) of the head-to-tail-to-tail trimer **5C**: δ 153.3 (s, C≡C*C*=C), 134.7 (s, H_2C=*C*), 134.5 (d, H_2C=C*C*H=C), 112.1 (t, $^1J_{CH}$ = 156.0 Hz, H_2C=CCH=C), 97.6 (s, *C*≡CCHMe$_2$), 81.2 (s, C≡*C*CHMe$_2$), 36.9 (d, $^1J_{CH}$ = 127.5 Hz, C=C*C*HMe$_2$), 30.7 (d, $^1J_{CH}$ = 125 Hz, C≡C*C*HMe$_2$), 26.1 (q, $^1J_{CH}$ = 125.5 Hz, C=CCH*Me*$_2$), 23.5 (q, $^1J_{CH}$ = 125.5 Hz, C=CCH*Me*$_2$), 23.1 (q, $^1J_{CH}$ = 125.5 Hz, C≡CCH*Me*$_2$).

m/*z*: 204 (M^+), 189 ($M^+ - CH_3$), 175 ($M^+ - CH_2 - CH_3$), 9161 ($M^+ - CHMe_2$, 100%), 147 ($M^+ - CHMe_2 - CH_2$). High-resolution mass spectrum *m*/*z*: calcd for $C_{15}H_{24}$ (M^+), 204.3585; found, 204.3556.

(d) Dimerization of 1-Hexyne by Cp*$_2$ThMe$_2$ and MeNH$_2$. According to the general procedure described above, 12 mg (0.023 mmol) of Cp*$_2$ThMe$_2$ was mixed with 0.2 mL (1.7 mmol) of 1-hexyne and 0.2 mL (4.5 mmol) of $MeNH_2$ to yield a mixture (93%) of dimers (45% geminal (**6A**); 48% trans (**6B**)) after 46 h.

^{1}H NMR (400 MHz, C_6D_6) of **6A**: δ 5.40 (d, 1H, $^2J_{HH}$ = 1.95 Hz, *H*HC=C), 5.09 (d, 1H, $^2J_{HH}$ = 1.95 Hz, *H*HC=C), 2.16 (t, 2H, $^3J_{HH}$ = 6.84 Hz, H_2CC=C), 2.14 (t, 2H, $^3J_{HH}$ = 6.84 Hz, H_2CC≡C), 1.59 (quintet, 2H, $^3J_{HH}$ = 6.84 Hz, $^3J_{HH}$ = 6.84 Hz, H_2CCH_2C=C), 1.50−1.20 (m, 6H, CH_2), 0.86 (t, 3H, $^3J_{HH}$ = 6.84 Hz, CH_2CH_3), 0.76 (t, 3H, $^3J_{HH}$ = 6.84 Hz, CH_2CH_3).

^{13}C NMR (100 MHz, C_6D_6) of **6A**: δ 126.7 (s, *C*=), 119.5 (t, $^1J_{CH}$ = 158 Hz, H_2C=C), 94.4 (s, ≡*C*C=C), 78.1 (s, ≡*C*CH$_2$), 37.8 (t, $^1J_{CH}$ = 124 Hz, C≡CCH$_2$), 31.1 (t, $^1J_{CH}$ = 128 Hz, *C*H$_2$C=C), 30.7 (t, $^1J_{CH}$ = 131 Hz, ≡CCH$_2$*C*H$_2$CH$_2$), 22.3 (t, $^1J_{CH}$ = 132 Hz, C=CCH$_2$*C*H$_2$-CH$_2$), 22.2 (t, $^1J_{CH}$ = 125 Hz, *C*H$_2$CH$_3$), 19.2 (t, $^1J_{CH}$ = 122 Hz, *C*H$_2$CH$_3$), 14.0 (q, $^1J_{CH}$ = 124 Hz, CH_2CH_3), 13.6 (q, $^1J_{CH}$ = 124 Hz, CH_2CH_3).

m/*z*: 164 (M^+), 135 ($M^+ - CH_2 - CH_3$), 121 ($M^+ - CH_2 - CH_2 - CH_3$), 107 ($M^+ - C_4H_9$), 93 ($M^+ - C_4H_9 - CH_3$; 100%) High-resolution mass spectrum, *m*/*z*: calcd for $C_{12}H_{20}$, 164.2932; found, 164.2915.

^{1}H NMR (400 MHz, C_6D_6) of **6B**: δ 5.62 (dt, 1H, $^3J_{HH}$ = 10.94 Hz, $^3J_{HH}$ = 7.32 Hz, HC=C*H*CH$_2$), 5.33 (d, 1H, $^3J_{HH}$ = 10.94 Hz, HC=C*H*C≡C), 2.17 (t, 2H, $^3J_{HH}$ = 7.32 Hz, C*H*$_2$C=C), 2.10 (t, 2H, $^3J_{HH}$ = 7.32 Hz, C*H*$_2$C≡C), 1.65−1.11 (m, 8H, C*H*$_2$), 0.83 (t, 3H, $^3J_{HH}$ = 7.32 Hz, CH$_2$C*H*$_3$), 0.79 (t, 3H, $^3J_{HH}$ = 7.32 Hz, CH$_2$C*H*$_3$).

^{13}C NMR (100 MHz, C_6D_6) of **6B**: δ 142.1 (d, $^1J_{CH}$ = 155 Hz, ≡CH*C*=), 110.3 (d, $^1J_{CH}$ = 163 Hz, =*C*HCH$_2$), 90.1 (s, ≡*C*C=C), 81.6 (s, ≡C*C*H$_2$), 37.5 (t, $^1J_{CH}$ = 124 Hz, C≡C*C*H$_2$), 31.3 (t, $^1J_{CH}$ = 128 Hz, *C*H$_2$C=C), 31.2 (t, $^1J_{CH}$ = 131 Hz, C≡CCH$_2$*C*H$_2$CH$_2$), 22.6 (t, $^1J_{CH}$ = 132 Hz, C=CCH$_2$*C*H$_2$CH$_2$), 22.2 (t, $^1J_{CH}$ = 125 Hz, *C*H$_2$CH$_3$), 19.2 (t, $^1J_{CH}$ = 122 Hz, *C*H$_2$CH$_3$), 14.1 (q, $^1J_{CH}$ = 124 Hz, CH$_2$*C*H$_3$), 13.5 (q, $^1J_{CH}$ = 124 Hz, CH$_2$*C*H$_3$).

(e) Dimerization of 1-Hexyne by Cp*$_2$ThMe$_2$ and EtNH$_2$. As described above, 0.08 mL (0.70 mmol) of 1-hexyne was dimerized (85% conversion after 48 h) with 0.06 mL (0.91 mmol) of EtNH$_2$ and 15 mg (0.028 mmol) of Cp*$_2$ThMe$_2$ to a mixture of dimers (32% **6A** and 53% **6B**).

(f) Dimerization of 1-Hexyne by Cp*$_2$ThMe$_2$ and *i*-BuNH$_2$. As described above, 0.04 mL (0.35 mmol) of 1-hexyne was dimerized (89% conversion after 23 h) with 0.08 mL (0.81 mmol) of *i*-BuNH$_2$ and 5 mg (0.01 mmol) of Cp*$_2$ThMe$_2$ to the geminal dimer **6A**, selectively.

(g) Oligomerization of 1-Hexyne by Cp*$_2$ThMe$_2$ and 2,6-Dimethylaniline. In 0.2 mL of THF, 0.1 mL (0.85 mmol) of 1-hexyne was oligomerized (100% conversion after 72 h) with 0.14 mL (1.14 mmol) of 2,6-dimethylaniline and 10 mg (0.018 mmol) of Cp*$_2$ThMe$_2$ to a mixture of the geminal dimer **6A** (60%) and the head-to-tail-to-tail trimer **6C** (40%), respectively.

^{1}H NMR (400 MHz, C_6D_6) of **6C**: δ 6.80 (s, 1H, C≡CC*H*=C), 4.97 (d, 1H, $^2J_{HH}$ = 1.95 Hz, *H*C=C), 4.88 (d, 1H, $^2J_{HH}$ = 1.95 Hz, *H*C=C), 2.50 (t, 4H, $^3J_{HH}$ = 7.81 Hz, C*H*$_2$C=C), 2.45 (t, 2H, $^3J_{HH}$ = 6.84 Hz, C*H*$_2$C≡C), 1.70 (q, 2H, $^3J_{HH}$ = 7.81 Hz, C*H*$_2$CH$_2$C=C), 1.59−1.12 (m, 10H), 0.98 (t, 6H, $^3J_{HH}$ = 6.84 Hz, CH$_2$C*H*$_3$), 0.87 (t, 3H, $^3J_{HH}$ = 6.84 Hz, CH$_2$C*H*$_3$).

^{13}C NMR (100 MHz, C_6D_6) of **6C**: δ 125.3 (s, *C*=CH), 122.7 (d, $^1J_{CH}$ = 130.6 Hz, C=*C*H), 115 (t, $^1J_{CH}$ = 158 Hz, *C*H$_2$=C), 93.7 (s, ≡*C*C=C), 88.0 (s, ≡*C*CH$_2$), 40.5 (t, $^1J_{CH}$ = 127 Hz, C≡C*C*H$_2$), 36.1 (t, $^1J_{CH}$ = 128 Hz, *C*H$_2$C=C), 32.2 (t, $^1J_{CH}$ = 128 Hz, C=C*C*H$_2$CH$_2$-CH$_2$), 31.3 (t, $^1J_{CH}$ = 128 Hz, C≡CCH$_2$*C*H$_2$CH$_2$), 31.1 (t, $^1J_{CH}$ = 128 Hz, C=CCH$_2$*C*H$_2$CH$_2$), 30.5 (t, $^1J_{CH}$ = 128 Hz, C=CCH$_2$*C*H$_2$CH$_2$), 22.6 (t, $^1J_{CH}$ = 122 Hz, *C*H$_2$CH$_3$), 19.6 (t, $^1J_{CH}$ = 122 Hz, *C*H$_2$CH$_3$), 17.5 (t, $^1J_{CH}$ = 125 Hz, *C*H$_2$CH$_3$), 14.2 (q, $^1J_{CH}$ = 121 Hz, CH$_2$*C*H$_3$), 13.9 (q, $^1J_{CH}$ = 121 Hz, 2 × CH$_2$*C*H$_3$).

m/*z*: 246 (M$^+$), 231 (M$^+$ − CH$_3$), 217 (M$^+$ − CH$_2$ − CH$_3$), 204 (M$^+$ − C$_3$H$_8$), 189 (M$^+$ − C$_4$H$_9$; 100%). High-resolution mass spectrum, *m*/*z*: calcd for $C_{18}H_{30}$ (M$^+$), 246.4398; found, 246.4407.

(h) Oligomerization of 1-Hexyne by Cp*$_2$ThMe$_2$ and 2,6-Dimethylaniline-*d*$_2$. As described above, 0.06 mL (0.52 mmol) of 1-hexyne was oligomerized (100% conversion after 94 h) in 0.5 mL of THF with 0.06 mL (0.48 mmol) of 2,6 dimethylaniline-d_2 and 12 mg (0.023 mmol) of Cp*$_2$ThMe$_2$ to a mixture of the geminal dimer **6A** (42%) and the head-to-tail-to-tail trimer **6C** (58%), respectively The same reaction with 10 times excess (0.23 mmol) of the deuterated amine was completely inhibited.

(i) Oligomerization of 1-Hexyne by Cp*$_2$ThMe$_2$ and *t*-BuNH$_2$. As described above, 0.08 mL (0.70 mmol) of 1-hexyne was oligomerized (100% conversion after 62 h) with 0.08 mL (0.81 mmol) of *t*-BuNH$_2$ and 12 mg (0.023 mmol) of Cp*$_2$ThMe$_2$ to a mixture of the geminal dimer **6A** (81%) and the head-to-tail-to-tail trimer **6C** (19%), respectively. Vacuum-transfer distillation (50 °C; 1 × 10^{-3} mmHg) afforded the separation of the dimer from the trimer.

(j) Dimerization of Cyclopentylacetylene by Cp*$_2$ThMe$_2$ and EtNH$_2$. According to the general procedure above, 0.12 mL (1.10 mmol) of C_5H_9C≡CH was dimerized (100% conversion after 138 h) with 0.08 mL (1.2 mmol) of EtNH$_2$ and 7 mg (0.013 mmol) of Cp*$_2$-ThMe$_2$ to a mixture of the geminal head-to-tail **7A** (75%) and trans head-to-head **7B** (25%) dimers, respectively.

^{1}H NMR (400 MHz, C_6D_6) of the geminal head-to-tail isomer **7A**: δ 5.17 (d, 1H, $^3J_{HH}$ = 1.95 Hz, H*H*C=), 5.06 (d, 1H, $^3J_{HH}$ = 1.95 Hz, H*H*C=), 1.9−1.3 (m, 18H, C$_5$*H*$_9$).

^{13}C NMR (100 MHz, C_6D_6) of the geminal head-to-tail isomer **7A**: δ 136.9 (s, CH$_2$=*C*), 117.7 (t, $^1J_{CH}$ = 159.0 Hz, *C*H$_2$=C), 94.9 (s, C=C*C*≡C), 77.7 (s, ≡*C*C$_5$H$_9$), 47.6 (d, $^1J_{CH}$ = 126.3 Hz, C=C*C*HC$_4$H$_8$), 41.3 (d, $^1J_{CH}$ = 142 Hz, C≡C*C*HC$_4$H$_8$), 33.4 (t, $^1J_{CH}$ = 126.4 Hz, C=CCH*C*$_2$H$_4$C$_2$H$_4$), 31.2 (t, $^1J_{CH}$ = 134.9 Hz, C≡CCH*C*$_2$H$_4$C$_2$H$_4$), 25.9 (t, $^1J_{CH}$ = 132.0 Hz, C=CCHC$_2$H$_4$*C*$_2$H$_4$), 25.1 (t, $^1J_{CH}$ = 129.2 Hz, C≡CCHC$_2$H$_4$*C*$_2$H$_4$).

^{1}H NMR (400 MHz, C_6D_6) of the trans isomer **7B**: δ 5.54 (dd, 1H, $^3J_{HH}$ = 6.84 Hz, $^3J_{HH}$ 10.74 Hz, C$_5$H$_9$*H*C=CH), 5.38 (d, 1H, $^3J_{HH}$ = 10.74 Hz, =C*H*C≡C), 3.1 (m, 2H, C*H*C$_4$H$_8$), 1.9−1.3 (m, 16H, CHC$_4$*H*$_8$).

^{13}C NMR (100 MHz, C_6D_6) of the trans isomer **7B**: δ 147.0 (d, $^1J_{CH}$ = 156.1 Hz, C$_5$H$_9$*C*H=CH), 108.8 (d, $^1J_{CH}$ = 163.2 Hz, C=*C*H-C≡C), 98.4 (s, C=C*C*≡C), 80.1 (s, ≡*C*C$_5$H$_9$), 51.8 (d, $^1J_{CH}$ = 127.7 Hz, C=C*C*HC$_4$H$_8$), 41.3 (d, $^1J_{CH}$ = 142 Hz, C≡C*C*HC$_4$H$_8$), 34.3 (t, $^1J_{CH}$ = 134.9 Hz, C=CCH*C*$_2$H$_4$C$_2$H$_4$), 32.3 (t, $^1J_{CH}$ = 127.0 Hz, C≡CCH*C*$_2$H$_4$C$_2$H$_4$), 29.9 (t, $^1J_{CH}$ = 130.6 Hz, C=CCHC$_2$H$_4$*C*$_2$H$_4$), 25.8 (t, $^1J_{CH}$ = 132 Hz, C≡CCHC$_2$H$_4$*C*$_2$H$_4$).

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%). High-resolution mass spectrum, *m*/*z*: calcd for $C_{14}H_{20}$ (M$^+$), 188.3155; found, 188.3108.

(k) Dimerization of 4-*tert*-Butylphenylacetylene by Cp*$_2$ThMe$_2$ and EtNH$_2$. As described above, 0.14 mL (0.8 mmol) of 4-*t*-BuPh-C≡CH was dimerized (100% conversion after 69 h) with 0.08 mL (1.12 mmol) of EtNH$_2$ and 8 mg (0.015 mmol) of Cp*$_2$ThMe$_2$ to the trans head-to-head dimer **8B**, exclusively.

^{1}H NMR (400 MHz, C_6D_6) of the trans head-to-head dimer **8B**: δ 8.00 (d, 2H, $^3J_{HH}$ = 7.81 Hz, *o*-*H* of Ar−C≡C), 7.50 (d, 2H, $^3J_{HH}$ = 7.81 Hz, *o*-*H* of ArC=C), 7.35 (d, 2H, $^3J_{HH}$ = 7.81 Hz, *m*-*H* of Ar-C≡C), 7.18 (d, 2H, $^3J_{HH}$ = 7.81 Hz, *m*-*H* of ArC=C), 6.54 (d, 1H, $^3J_{HH}$ = 11.72 Hz, ArC*H*=CH), 5.87 (d, 1H, $^3J_{HH}$ = 11.72 Hz, Ar-CH=C*H*C≡C), 1.27 (s, 9H, *t*-*Bu*ArC=C), 1.18 (s, 9H, *t*-*Bu*ArC≡C).

^{13}C NMR (100 MHz, C_6D_6) of the trans head-to-head dimer **8B**: δ 151.7 (s, *C*C=C), 151.6 (s, *C*C≡C), 138.6 (d, $^1J_{CH}$ = 156.1 Hz, *o*-*C*HC≡C), 134.6 (s, *p*-*C*C≡C), 131.6 (d, $^1J_{CH}$ = 161.8 Hz, *o*-*C*H-C=C), 129.1 (d, $^1J_{CH}$ = 158.8 Hz, C≡C*C*H=C), 125.7 (d, $^1J_{CH}$ = 160.4 Hz, *m*-*C*HC≡C), 125.5 (d, $^1J_{CH}$ = 161.8 Hz, *m*-*C*HC=C), 121.3 (s, *p*-*C*C=C), 107.0 (d, $^1J_{CH}$ = 159.0 Hz, C=*C*HAr), 96.6 (s, C≡*C*Ar), 88.7 (s, C=C*C*≡C), 31.5 (s, C≡CPh*C*Me$_3$), 31.2 (s, C=CPh*C*Me$_3$), 19.4 (q, $^1J_{CH}$ = 124.9 Hz, C≡CPhC*Me*$_3$), 12.3 (q, $^1J_{CH}$ = 126.3 Hz, C=CPhC*Me*$_3$).

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$_2$). High-resolution mass spectrum, *m*/*z*: calcd for $C_{15}H_{24}$ (M$^+$), 316.4907; found, 316.4901.

(l) Dimerization of 4-*tert*-Butylphenylacetylene by Cp*$_2$UMe$_2$ and Me$_2$NH. As described above, in 0.4 mL of THF, 0.15 mL (0.9 mmol) of 4-*t*-BuPhC≡CH was dimerized (100% conversion after 43 h) with 0.15 mL (2.3 mmol) of Me$_2$NH and 5 mg (0.01 mmol) of Cp*$_2$UMe$_2$ to the trans head-to-head dimer **8B**, exclusively.

(m) Dimerization of Phenylacetylene by Cp*$_2$ThMe$_2$ and EtNH$_2$. As described above, 0.04 mL (0.4 mmol) of PhC≡CH was dimerized (67% conversion after 3 h) with 0.04 mL (0.61 mmol) of EtNH$_2$ and 13 mg (0.024 mmol) of Cp*$_2$ThMe$_2$ to the trans head-to-head dimer **9B**, exclusively.

^{1}H NMR (400 MHz, THF-d_8) of the trans head-to-head dimer **9B**: δ 7.94 (d, 2H, $^3J_{HH}$ = 8.79 Hz, *o*-*H* of ArCC≡C), 7.55−7.25 (m, 8H), 6.73 (d, 1H, $^3J_{HH}$ = 11.72 Hz, *H*C=CH), 5.93 (d, 1H, $^3J_{HH}$ = 11.72 Hz, HC=C*H*C≡C).

^{13}C NMR (100 MHz, THF-d_8) of the trans head-to-head dimer **9B**: δ 140.5 (d, *o*-*C*H of ArCC≡C, $^1J_{CH}$ = 156.1 Hz), 138.6 (s, *C*C≡C), 133.1 (d, $^1J_{CH}$ = 167.5 Hz, *o*-*C*H of ArC=C), 130.6 (d, $^1J_{CH}$ = 161.8 Hz, *m*-*C*H of ArCC≡C), 130.3 (d, $^1J_{CH}$ = 160.4 Hz, *p*-*C*H of Ar-C=C), 130.2 (d, $^1J_{CH}$ = 160.4 Hz, *m*-*C*H of ArCC≡C), 130.0 (d, $^1J_{CH}$ = 160.4 Hz, *p*-*C*H of ArC=C), 128.1 (d, $^1J_{CH}$ = 156.1 Hz, *C*H=CH), 126.8 (s, *C*C=C), 108.9 (d, $^1J_{CH}$ = 164.7 Hz, C=*C*HC≡), 97.5 (s, C≡*C*), 90.7 (s, C=C*C*≡C).

m/*z*: 204 (M$^+$; 100%), 126 (M$^+$ − C$_6$H$_5$), 101 (M$^+$ − CH$_2$CH$_2$ − C$_6$H$_5$). High-resolution mass spectrum, *m*/*z*: calcd for $C_{16}H_{12}$ (M$^+$), 204.0939; found, 204.0901.

(n) Dimerization of *t*-BuC≡CH by Cp*$_2$UMe$_2$ and t-BuNH$_2$. As above, in 0.4 mL of THF, 0.1 mL (0.8 mmol) of *t*-BuC≡CH was

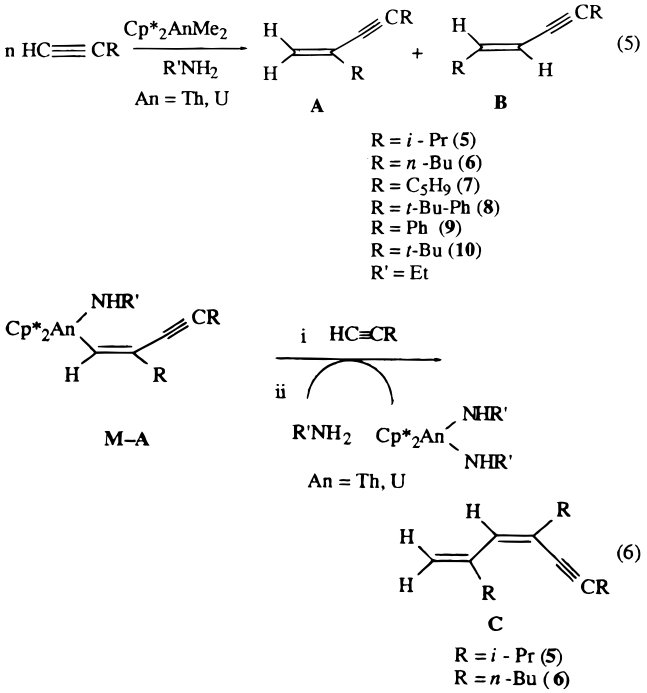
dimerized (50% conversion after 264 h) with 0.1 mL (1.0 mmol) of *t*-$BuNH_2$ and 5 mg (0.01 mmol) of $Cp^*_2UMe_2$ to a mixture of the geminal head-to-tail dimer **10A** (40%) and the trans head-to-head **10B** dimer (60%), respectively. For characterization of the geminal head-to-tail dimer, see ref 8.

^{1}H NMR (200 MHz, C_6D_6) of the trans head-to-head dimer **10B**: δ 5.68 (d, 1H, $^3J_{HH}$ = 11.9 Hz), 5.32 (d, 1H, $^3J_{HH}$ = 11.9 Hz), 1.15 (s, 9H), 1.00 (s, 9H).

Results

The goal of this investigation was to examine the scope, chemoselectivity, regioselectivity, actinide metal sensitivity, kinetics, and mechanism of the selective oligomerization of terminal alkynes controlled by the specific addition of amines. This study represents an extension of, and comparison to, our previous investigation of the oligomerization of terminal alkynes promoted by organoactinides.[8] In the following discussion, we focus on the reaction scope, metal effect, kinetics, rate law, and thermodynamics.

Reaction Scope of the Controlled Oligomerization. Organoactinide complexes of the type $(C_5Me_5)_2AnMe_2$ (An = Th, U) react with terminal alkynes in the presence of primary amines, yielding only dimers (eq 5) and, in some cases, an additional specific trimer (eq 6) (Table 1), contrasting the



oligomerization chemoselectivity and regioselectivity that has been observed under the same conditions in the absence of amines.[8] The reactions are conveniently monitored by ^{1}H NMR spectroscopy. In general, the initial reaction of $(C_5Me_5)_2AnMe_2$ (An = Th, U) with an alkyne yields the bis(acetylide) complex, though, in the presence of amines, for the thorium complex, the corresponding $(C_5Me_5)_2Th(NHR)_2$ (**13**) is formed whereas, for the uranium complex, no bis(amido) complex is observed unless a large excess of the amine is used.[13]

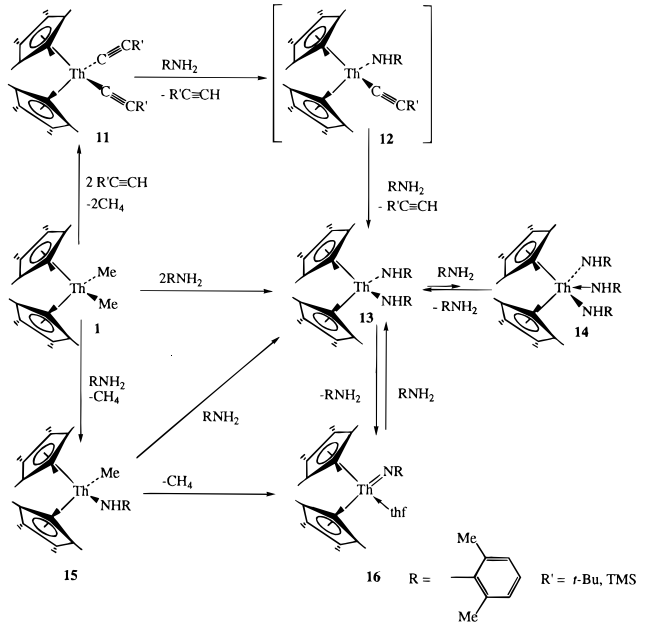
Stoichiometric Reactivity of Organoactinide Complexes. The different catalytic reactivities found for similar organoactinides (see Table 1), which is unprecedented in the chemistry of organoactinides, prompted us to study the stoichiometric reactivity of these organoactinide complexes to understand the resting state of the complexes in the catalytic cycle. The

Table 1. Controlled Catalytic Oligomerization of Terminal Alkynes Promoted by Organoactinides in the Presence of Amines[a]

				% dimers		% trimer
entry	catalyst[b]	R[c]	amine	**A**	**B**	**C**
1	Th	*i*-Pr	$EtNH_2$	57	43	
2	U	*i*-Pr	Me_2NH	10		90
3	Th	*n*-Bu	$MeNH_2$	45	48	
4	Th	*n*-Bu	$EtNH_2$	32	53	
5	Th	*n*-Bu	*i*-$BuNH_2$	89		
6	Th	*n*-Bu	2,6 DMA[d]	60		40
7	Th	*n*-Bu	2,6 DMD[e]	42		58
8	Th	*n*-Bu	*t*-$BuNH_2$	81		19
9	Th	C_5H_9[f]	$EtNH_2$	75	25	
10	Th	*p*-*t*-BuPh	$EtNH_2$		100	
11	U	*p*-*t*-BuPh	Me_2NH[g]		100	
11	Th	Ph	$EtNH_2$		67	
13	Th	Ph	*i*-$BuNH_2$		85	
14	Th	Ph	*t*-$BuNH_2$		100	
15	U	*t*-Bu	*t*-$BuNH_2$	40	60	

[a] Solvent C_6H_6; [cat] = 7.6×10^{-2} M; [alkyne] = 2.6 M; 80 °C; [amine] = 2.6 M; turnover frequency range 5−18 h^{-1}. The remaining percentage to 100% conversion is the product formed in the intermolecular hydroamination of the corresponding alkyne and amine.[15] [b] Precatalyst $Cp^*_2AnMe_2$ (An = Th, U). [c] R = substituent from the corresponding RC≡CH. [d] 2,6-Dimethylaniline. [e] 2,6-Dimethylaniline-d_2. [f] Cyclopentyl. [g] The same result was obtained without amine.

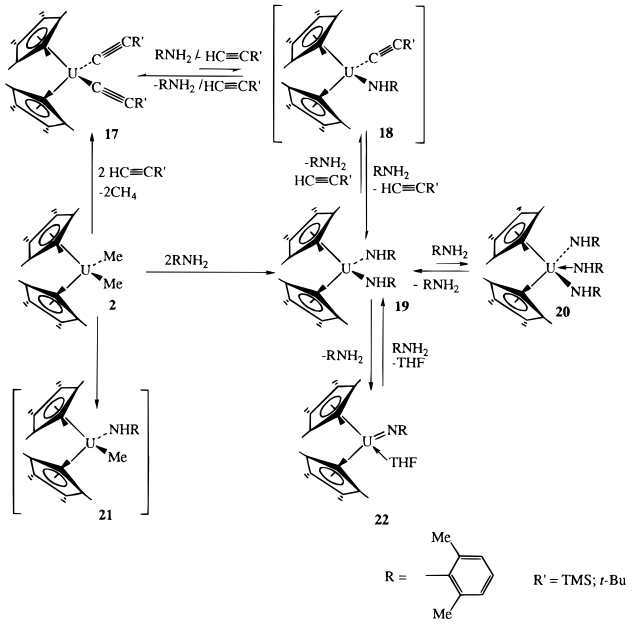
Scheme 1. Stoichiometric Reactivity of $(C_5Me_5)_2ThMe_2$ with Amines and Terminal Alkynes



reactivity for each actinide complex toward alkynes or/and amines is outlined in Schemes 1 and 2, for Th and U, respectively.

$(C_5Me_5)_2ThMe_2$ (**1**) reacts with *t*-BuC≡CH and (TMS)-C≡CH, producing the bis(acetylide) complexes $(C_5Me_5)_2Th(C{\equiv}CR)_2$ (**11**) (R = *t*-Bu, TMS).[8] The reaction of these bis(acetylide) complexes (**11**) with equimolar amounts of 2,6-dimethylaniline yields the corresponding bis(amido) complexes $(C_5Me_5)_2Th(NHR)_2$ (**13**). This result argues that the second amine insertion into the thorium mono(amido)−mono(acetylide) complex **12** is faster than the first insertion, thwarting its isolation. Interestingly, the reaction of $(C_5Me_5)_2ThMe_2$ (**1**) with an equimolar amount of 2,6-dimethylaniline allows the formation of the mono(amido)thorium methyl complex **15**, which can be reacted subsequently with another equivalent of 2,6-dimethylaniline, yielding the corresponding bis(amido) complex

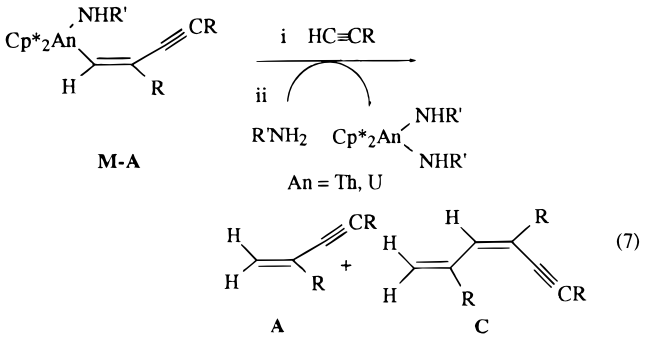
Scheme 2. Stoichiometric Reactivity of $(C_5Me_5)_2UMe_2$ with Amines and Terminal Alkynes



13. Heating the bis(amido) complex **13**, in THF, eliminates an amine molecule, allowing the formation of the thorium imido complex **16**. This complex can also be formed by eliminating methane by heating complex **15**.[14] In an excess of amine, the bis(amido) complex **13** seems to be in rapid equilibrium with the bis(amido)−amine complex **14**,[15] though the equilibrium lies toward the bis(amido) complex (vide infra).

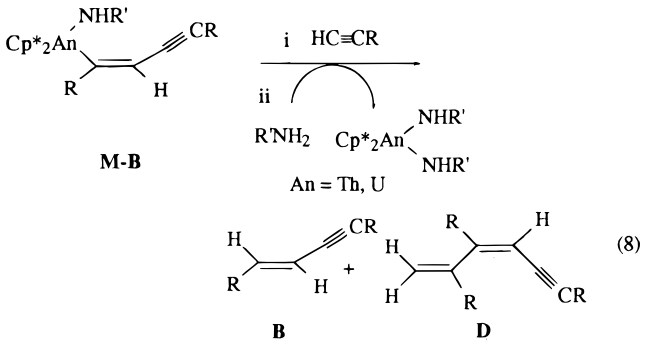
For the corresponding uranium complex **2**, a similar reactivity has been found. Thus, the reactions with PhC≡CH and (TMS)C≡CH produced the bis(acetylide) complexes $(C_5Me_5)_2U(C{\equiv}CR)_2$ (**17**) (R = Ph, TMS).[8] In contrast to the thorium complexes, these bis(acetylide) complexes are extremely stable and the bis(amido) complex **19** can be formed only by adding a large excess of the amine.[13] This result argues that the equilibrium between complexes **17** and **19** lies preferentially toward the bis(acetylide) complexes instead of either the mono(amido)−mono(acetylide) complex **18** or the bis(amido) complex **19**. Attempts to isolate the monomethyl−amido complex **21**, by reacting 1 equivalent of 2,6-dimethylamine with complex **2**, yield only 0.5 equiv of the bis(amido) complex **19**. Similar to the thorium bis(amido) complex, in the presence of an excess of amine, complex **19** is in fast equilibrium with complex **20**. Again, this equilibrium favors the bis(amido) complex (vide infra).[14] When the bis(amido) complex **19** is heated in THF, elimination of an amine molecule is observed, allowing the formation of the corresponding uranium imido complex **22**.[16,17]

Actinide, Amine, and Alkyne Effects on the Catalytic Process. For the thorium-catalyzed oligomerization of terminal alkynes in the presence of primary amines, as compared to the results in the absence of amines, a dramatic effect of reducing the extent of oligomerization is observed. For an aliphatic alkyne, nonbulky primary amines produce mixtures of the corresponding geminal dimer (**A**) and trans dimer (**B**) (entries 1 and 3 in Table 1; eq 5),[18] whereas for aromatic alkynes, only the trans dimer (**B**) is formed (entries 10−14 in Table 1). Increasing the bulkiness of the primary amine for aliphatic alkynes, using, for example, 2,6-dimethylaniline or *t*-$BuNH_2$, allows the formation only of the geminal dimer **A** and the specific trimer **C** with no traces of the trans dimer **B** (entries 6−8 in Table 1; eq 7). This result argues that the insertion of



(7)

the second alkyne into the metalla−eneyne complex **M**−**A**, which is presumably in the preferred stereochemistry due to the bulky amine, and the subsequent trimer elimination (eq 7) are much faster than either the insertion of an alkyne into the intermediate complex **M**−**B** or the protonolysis of **M**−**B** by either the alkyne or the amine, eliminating trimer **D** or dimer **B**, respectively (eq 8).[19] It is important to point out that the



(8)

reactions of the thorium precursor with nonbulky secondary amines, such as Et_2NH and Me_2NH, and *i*-PrC≡CH allow the formation of higher oligomers (up to pentamers); however, the obtained higher oligomers are produced in lower yields, as compared with the results obtained in the reactions in the absence of amines. In similar oligomerization reactions, with bulky secondary amines, such as Ph_2NH, no major changes are observed for these oligomerizations, as compared to the blank reactions in the absence of amines. These results argue that, for secondary amines, the rate of severing the growing oligomer from the metal is much slower than the rate of insertion of alkynes and severing the oligomer chain by the alkyne itself, producing the bis(acetylide) complex. (vide infra).

(14) Haskel, A.; Straub, T.; Eisen, M. S. *Organometallics* **1996**, *15*, 3770.

(15) The intermolecular hydroaminations of terminal alkynes promoted by these types of organoactinide complexes follow different reactivities.[14] However, in both cases, the kinetics exhibit an inverse first order in amine, which has been corroborated to be effective due to the rapid equilibrium between the bis(amido) complex and the bis(amido)−amine complex. This type of equilibrium has also been observed in organolanthanide chemistry in the presence of amines: (a) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241. (b) Gagné, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275. (c) Gagné, M. R.; Brard, L.; Conticello, V. P.; Giardello, M. A.; Stern, C. L.; Marks, T. J. *Organometallics* **1992**, *11*, 2003.

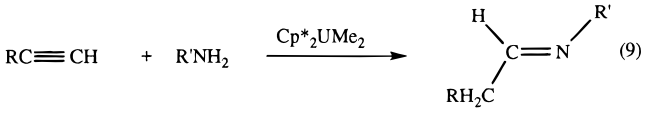
(16) (a) Eisen, M. S.; Straub, T.; Haskel, A. *J. Alloys Compd.* **1998**, *271*, 116. (b) Straub, T.; Haskel, A.; Eisen, M. S. Manuscript in Preparation.

(17) Imido structures of uranium(IV) and -(VI) have been characterized: (a) Warner, B. P.; Scott, B. L.; Burns, C. J. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 959. (b) Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 9448 and references therein.

(18) In the absence of amines, from dimers to heptamers are observed. See Table 1 in ref 8.

(19) The plausible equilibrium between **M**−**A** and **M**−**B** has been shown to be nonoperative under the reaction conditions.[8]

In the uranium-controlled oligomerization of *nonbulky* alkynes with secondary amines (primary amines yield only the intermolecular hydroamination product (eq 9)), no major chemo-

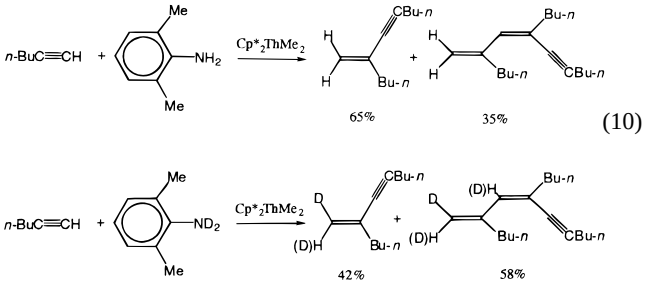


(9)

selectivity is observed, but the amount of the smaller oligomers increases as compared with that of the reactions performed in the absence of the amines (except for entry 2 in Table 1).[20] Interestingly, for *tert*-butylacetylene, in the absence of amine, the geminal dimer is obtained, regioselectively, whereas in the presence of *tert*-butylamine, a mixture of the two dimers is obtained (entry 15, Table 1). This result strongly suggests that the amine should be attached to the metal center at the time of the alkyne insertion to induce different regioselectivities.

Previously, for the noncontrolled oligomerization reactions, we showed that the actinide−bis(acetylide) complex is the active species in the catalytic cycle. In the new controlled oligomerization reaction, the formation of the organoactinide bis(amido) complex, which is the predominant species as observed in the NMR,[21] argues against this actinide−bis(acetylide) complex as being the active species and provides strong evidence that the amine is the major protonolytic agent.

To corroborate this protonolytic theory, besides the different regioselectivities observed and besides the kinetics of the reaction (vide infra), and to corroborate that the amine is the major protonolytic agent, a novel strategy was implemented to increase the selectivity toward the *trimer*. This was accomplished by providing a kinetic delay for the fast protonolysis by the amine, to allow more trimer formation, in a reaction producing both dimer and trimer through replacement of the amine hydrogens by deuterium (eq 10; and entries 6 and 7 in Table



(10)

42% 58%

1). This strategy indeed enabled us to influence the chemoselectivity of the oligomerization and to increase the trimer:dimer ratio.

Following the reaction, we observed the first deuterium at the geminal position but, at larger conversions, we observed more olefinic proton signals exchanged by deuterium, implicating that the alkyne and the deuterated amine were in equilibrium through the metal complex, only exchanging hydrogen/deuterium atoms.[22]

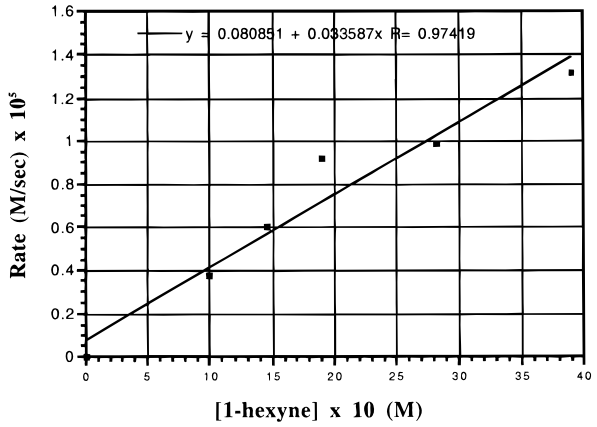


Figure 2. Plot of the observed reaction rate vs alkyne concentration for the controlled dimerization of 1-hexyne with *i*-BuNH$_2$ using Cp*$_2$ThMe$_2$ as the precatalyst in benzene-d_6. The line represents the least-squares fit to the data points.

Kinetic Studies of the Controlled Oligomerization of Terminal Alkynes. Kinetic measurements on the controlled oligomerization reaction of *n*-BuC≡CH with *i*-BuNH$_2$ were undertaken by in-situ ^{1}H NMR spectroscopy. The reaction of an ≈70-fold excess of *n*-BuC≡CH and *i*-PrNH$_2$ with (C$_5$Me$_5$)$_2$ThMe$_2$ was monitored with constant catalyst concentration until complete substrate consumption. The disappearance of the C≡CH (δ = 2.28 ppm) ^{1}H resonance was normalized. The turnover frequency of the reaction was calculated from the slope of the kinetic plots of substrate-to-catalyst ratio vs time. The kinetic plots as shown in Figure 2 reveal a linear dependence of the rate of the reaction on alkyne substrate concentration over a ∼40-fold substrate concentration range, which indicates a first-order dependence of the catalytic rate on substrate concentration under these conditions, in analogy to the nonselective oligomerization of terminal alkynes in the absence of amines.

Considering the rapidity of the An−C protonolysis by primary amines, it seems unreasonable that intermolecular proton transfer from either the alkyne or the amine could be turnover-limiting under most catalytic conditions. When the concentration of the alkyne is maintained constant and the concentration of the amine is varied over 14-fold concentration range (Figure 3) a plot of the rate of the reaction vs amine concentration exhibits an inverse proportionality, indicating that the reaction is inverse first order in amine. An inverse proportionality in catalytic systems is well-known and consistent with a rapid equilibrium before the rate-limiting step. Our case is consistent with the equilibrium between the bis(amido) complex and the bis(amido)-amine complex, as found in the hydroamination of terminal alkynes promoted by organoactinides[14,16] and early transition metal complexes[23] and in the hydroamination of olefins promoted by organolanthanide complexes.[15]

When the initial concentrations of the terminal alkyne and the amine are held constant and the concentration of the catalytic precursor is varied over a ∼10-fold concentration range (Figure 4), a plot of reaction rate vs precatalyst concentration indicates that the reaction is first-order-dependent in precatalyst. Thus,

(20) For Cp*$_2$U(NR$_2$)$_2$ (R = Me) control is observed only toward isopropylacetylene whereas, for other alkynes, a mixture of oligomers is obtained. The selectivity, though, is notoriously biased toward the smaller oligomers in comparison to that of the noncontrolled oligomerization.

(21) Cp*$_2$U{NH[C$_6$H$_3$(CH$_3$)$_2$]}$_2$ ^{1}H NMR (cyclohexane-d_{12}, 296 K): δ 8.85 (d, (4/2)H, ^3J = 7.0 Hz, *m-H*), 5.44 (s, 30H, Cp*), 4.10 (d, (4/2)H, ^3J = 7.0 Hz, *m-H*), 2.70 (t, 2H, $^3J_{HH}$ = 7.0 Hz, *p-H*), −0.78 (s, (6/3)H, C*H*$_3$), −22.4 (s, (6/3)H, C*H*$_3$), −52.0 (s, br, 2H, N*H*). Cp*$_2$Th(NH(*t*-Bu))$_2$ ^{1}H NMR (THF-d_8, 296 K): δ 2.02 (s, 32H, Cp* + N*H*), 1.08 (s, 18H, *t*-Bu). Cp*$_2$U(NHEt)$_2$ ^{1}H NMR (THF-d_8, 296 K): δ 1.18 (s, 30H, Cp*), 0.05 (t, 6H, $^3J_{HH}$ = 7.1 Hz, CH$_2$C*H*$_3$), −4.7 (br, 4H, C*H*$_2$CH$_3$), −76.50 (s, br, 2H, N*H*). Cp*$_2$U(NH(*t*-Bu))$_2$ ^{1}H NMR (THF-d_8, 296 K): δ 2.49 (s, 30H, Cp*), −3.74 (s, 18H, *t*-Bu), −64.30 (s, br, 2H, N*H*).

(22) Blank reactions of deuterated amines and alkynes at 80 °C in the absence of the organoactinide complexes did not induce the hydrogen/deuterium exchange.

(23) (a) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708. (b) Baranger, A. M.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 2753.

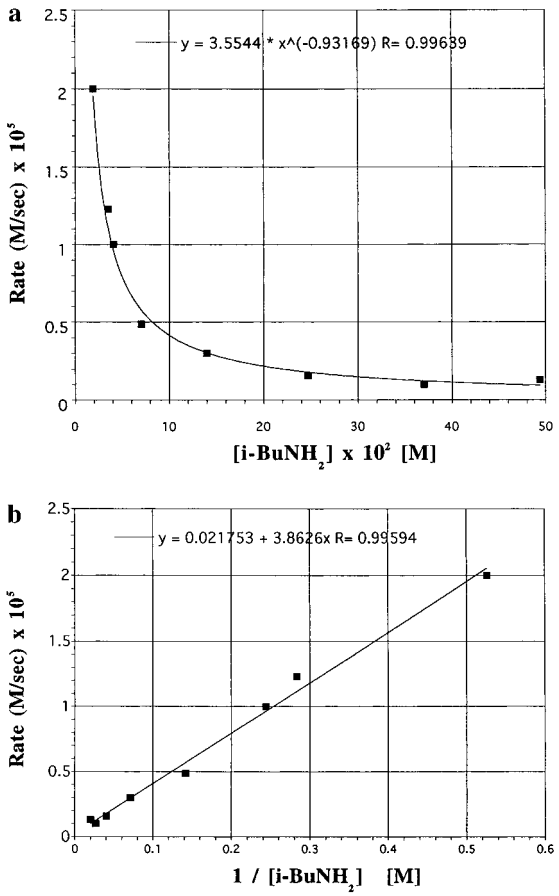


Figure 3. Plots of the observed reaction rate vs (a) amine concentration and (b) 1/amine concentration for the controlled dimerization of 1-hexyne with *i*-$BuNH_2$ using $Cp^*_2ThMe_2$ as the precatalyst in benzene-d_6. The line represents the least-squares fit to the data points.

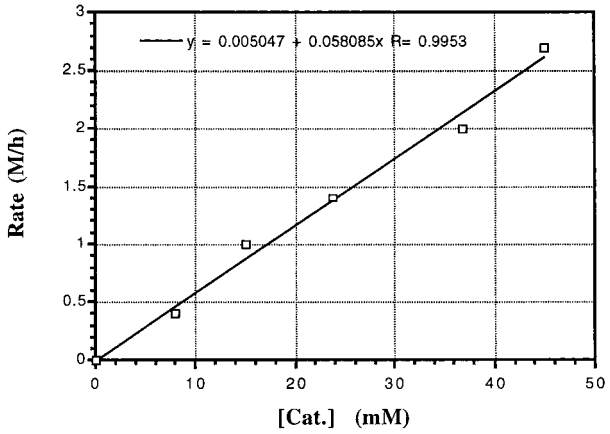


Figure 4. Plot of the observed reaction rate vs catalyst concentration for the controlled dimerization of 1-hexyne with *i*-$BuNH_2$ using $Cp^*_2ThMe_2$ as the precatalyst in benzene-d_6. The line represents the least-squares fit to the data points.

the rate law for the controlled oligomerization of terminal alkynes promoted by organoactinides is given by eq 11. The

$$v = k[\mathrm{Th}][\mathrm{alkyne}][\mathrm{amine}]^{-1} \qquad (11)$$

derived $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values from an Eyring analysis (Figure 5) are 15.1(3) kcal mol^{-1} and −41.2(6) eu, respectively.

Discussion

Catalytic Reaction Scope and Mechanism. The present catalytic results for the controlled oligomerization of terminal alkynes by amines producing dimers and, depending on the bulkiness of the amine, trimers with the absence of higher oligomers as compared to those for the noncontrolled catalytic cycle (tetramers−heptamers) demonstrate the ability to tailor the extent of oligomerization catalyzed by organoactinide complexes.[24] This *strategy* is based on an acidic chain-transfer mechanism as a competing reaction, modifying the nonselective oligomerization mechanism toward small oligomers. Using this approach, the chain-transfer reagent does not end up in the product and does not require subsequent elimination from the product to release the unsaturated oligomer. A substantial range of substrates can be selectively dimerized, including bulky and nonbulky aliphatic and aromatic terminal alkynes. Regarding the amine effect, with aliphatic alkynes and in the thorium case, nonbulky primary amines are able to produce a mixture of two of the three possible dimers with no discrimination between them, whereas bulky amines allow the production of one dimer and one trimer. Interestingly, the formed trimer contains the same regiochemistry as the dimer complex before it was protonated, indicating that, for bulky primary amines, the rate for releasing the dimer from the organometallic complex with the regiochemistry of **M**−**B** (eq 12) is much slower than the

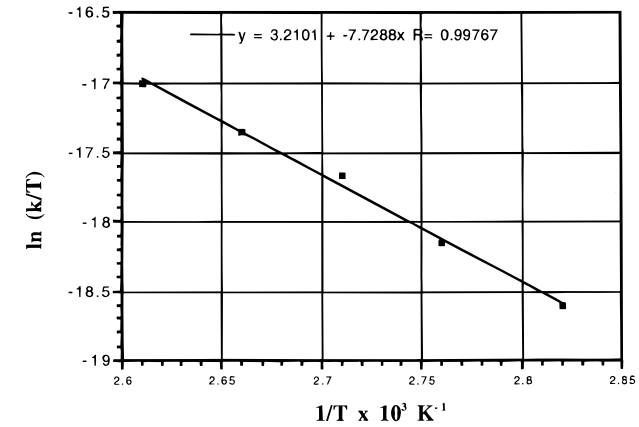
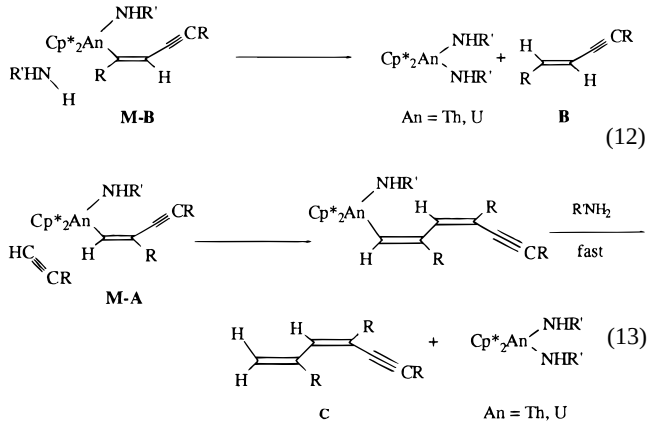


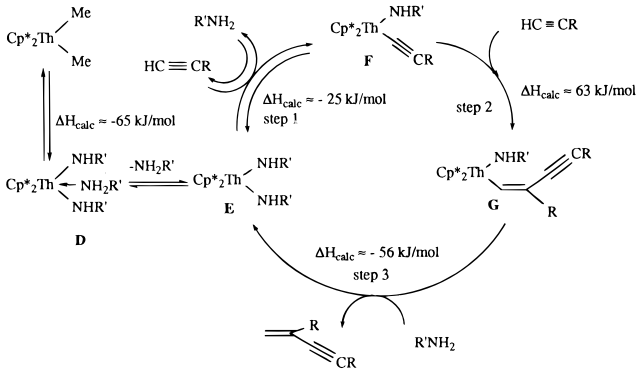
Figure 5. Eyring plot for the controlled dimerization of 1-hexyne with *i*-$BuNH_2$ using $Cp^*_2ThMe_2$ as the precatalyst in toluene-d_8. The line represents the least-squares fit to the data points.



rate of alkyne insertion into the metal complex with the regiochemistry **M**−**A** and subsequent protonolysis to the trimer (eq 13). This result also corroborates that the insertion of the alkyne yielding either **M**−**A** or **M**−**B** is not reversible.

(24) Other controlling reagents such as silanes (primary−tertiary) have been demonstrated to be effective as well: (a) Eisen, M. S. *Proceedings of the XVIIIth International Conference on Organometallic Chemistry*, Munich, Germany, August 1998; Abstract BI1. (b) Wang, J. Q; Eisen, M. S. Unpublished results.

Scheme 3. Plausible Cycle for the Controlled Oligomerization of Terminal Alkynes Catalyzed by Organothorium Complexes in the Presence of Primary Amines



Since the stereochemical approach of either the amine or the alkyne is a side approach,[25] it seems plausible that, for bulky primary amines, the steric hindrance imparted by the pentamethylcyclopentadienyl rings prevents the amine from closely approaching the metalla−eneyne complex, impeding the rapid severance of the dimer but allowing, at the same time, the insertion of one more alkyne with the specific regiochemistry, in which the alkyne substituent is pointing away from the metal center.[26] For nonbulky primary amines, no major steric hindrance is exhibited at the metal center, allowing the formation of both dimers. For secondary bulky amines, no real control is achieved, indicating that the amine is unable to rapidly sever the growing oligomeric chain, allowing a protonolysis competition with the terminal alkyne, forming the bis(acetylide) complexes. In addition, Et_2NH is able to reduce the amount of higher oligomers, though it is unable to control the chemo- and regioselectivity of the reaction. It seems that the equilibrium thorium bis(acetylide) ⇌ thorium mono(amide) mono(acetylide) is strongly affected by the bulkiness of the amine and the pK_a of its hydrogens.

Regarding the rate, the present oligomerization processes exhibit rates ($N_t = 5-18\ h^{-1}$) similar to those of the nonselective oligomerization ($N_t = 3-10\ h^{-1}$). The activation entropy $\Delta S^{\ddagger} = -41.2(6)$ eu for the dimerization of 1-hexyne in the presence of *t*-BuNH$_2$ can be compared to $\Delta S^{\ddagger} = -45.2(6)$ eu obtained for the trimerization of (TMS)C≡CH (eq 2). It appears that both processes proceed with similar degrees of entropic reorganization on approaching the transition state. Since in both oligomerization processes the rate-limiting steps are different, the activation enthalpy values are not compared.

A plausible mechanism for the controlled oligomerization of terminal alkynes is shown in Scheme 3. The mechanism consists of a sequence of well-established elementary reactions, such as insertion of acetylene into an M−C σ-bond and σ-bond metathesis. The precatalyst $(C_5Me_5)_2ThMe_2$ in the presence of amine and alkyne is converted to the bis(amido) complex **E** and the bis(amido)−amine complex **D**. These complexes were found to be in rapid equilibrium and are responsible for the inverse kinetic dependence on the amine. Complex **E**, which is the catalytic resting form of the complex under the catalytic conditions, reacts with 1 equiv of alkyne, as the rate-limiting step, producing complex **F** (step 1).[27] The formulation of complex **F** and not the bis(acetylide) complex is based on the different dimer and trimer ratios obtained with different amines, implying that at least one amine should be coordinated to the actinide complex. Likewise, with amines, the oligomerization of *t*-BuC≡CH by $Cp^*_2UMe_2$ produces both dimers whereas, in the absence of amine, only the geminal dimer is formed. Moreover, regarding the acetylenic substrates, for aromatic alkynes, the regiochemistry of the trans dimer is preferentially obtained whereas, for aliphatic alkynes, both dimers are obtained. Furthermore, comparison of the results obtained for the oligomerization of phenylacetylene in the absence of amines (with amines, only a dimer is obtained), in which both dimers and higher oligomers are obtained, argues that an amido−acetylide complex and not the bis(acetylide) complex is responsible for this fine regiodifferentiation. It is noteworthy to point out that, for the latter case, the observed regioselectivity can be explained not only by the higher partial charge ($\delta-$) of the α-carbon from the aromatic ring as compared with aliphatic alkynes[28] but also by the effective partial charge ($\delta+$) at the metal center due to the coordinated amine. The following rapid step in the catalytic cycle is the insertion of an alkyne into an actinide−carbyl σ-bond, yielding the actinide−alkenyl−amido complex **G** (step 2). This complex may undergo either a σ-bond protonolysis with the amine, to yield the corresponding dimer and the bis(amido) complex **E** (step 3), or another insertion of an alkyne and concomitant σ-bond protonolysis by the amine, yielding the oligomeric trimer and the bis(amido) complex **E**.[14] Thus the reaction rate law presented in eq 11 is compatible with rapid, operationally irreversible alkyne insertion (step 2), rapid σ-bond protonolysis of the oligomer by the amine (step 3), a slow preequilibration involving the bis(amido) (**E**) and the mono(amido)−acetylide complex (**F**) (step 1), and a rapid equilibrium between the bis(amido) complex **E** and the bis(amido)−amine complex **D**.

Metal Effect on the Catalytic Process. Controlling the oligomerization has been achieved by allowing a kinetic competition between the insertion of a new alkyne molecule into the metal−alkenyl bond (eq 14) with the protonolysis by the amine (eq 15). Hence, The insertion reaction produces a larger metalla−oligomer complex, whereas the competing protonolysis produces the organic product and the bis(amido) organometallic complex.[29] The difference in selectivity as found for the two similar organoactinide complexes can be cor-

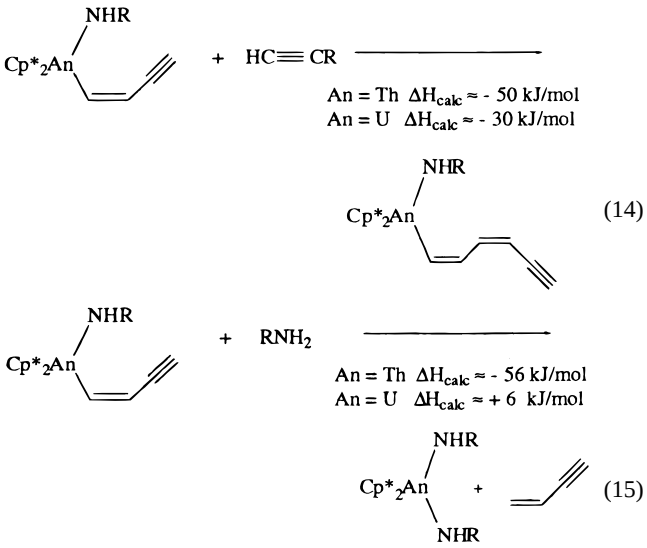
(25) (a) Fagan, P. J.; Manriquez, J. M.; Volmer, S. H.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206. (b) Elschenbrich, Ch.; Salzer, A. *Organometallics*, 1st ed.; VCH: Weinheim, Germany, 1989; Chapters 15 and 17.

(26) For (TMS)C≡CH, a different regiochemistry is obtained due to the polarization effect of the silicon atom. Stockis and Hoffman have performed calculations on the polarization of the π^* orbitals in (TMS)C≡CH and C*H*$_3$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: (a) Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952. (b) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806. (c) Allen, A. D.; Krishanmunti, R.; Surya Prakash, G. K.; Tidwell, T. T. *J. Am. Chem. Soc.* **1990**, *112*, 1291. (d) Apeloig, Y.; Biton, R.; Abu-Freih, A. *J. Am. Chem. Soc.* **1993**, *115*, 5, 2522. (e) Frey, J.; Schottland, E.; Rappoport, Z.; Bravo-Zhivotovskii, D.; Nakash, M.; Botoshansky, M.; Kaftory, M.; Apeloig, Y. *J. Chem. Soc., Perkin Trans 2* **1994**, 2555.

(27) Steps 2 and 3 in Scheme 1 are very fast, preventing the characterization of complexes **F** and **G**. Under the experimental conditions, the only observable complex during the catalytic reaction is the bis(amido) complex for either the thorium or the uranium complex. However, we have been able to spectroscopically characterize in solution a similar alkylamido complex of thorium, $Cp^*_2Th(NHR)CH_3$ (R = *t*-Bu): ^{1}H NMR δ 2.08 (s, 31H, Cp* + N*H*), 1.13 (s, 9H, *t*-Bu), −0.22 (s, 3H, Th−C*H*$_3$).

(28) The ^{13}C NMR spectra of phenylacetylene and *n*-BuC≡CH for the acetylenic carbons are extremely similar.

(29) The amine concentration range should be large enough to avoid formation of larger oligomers (the alkyne will compete for protonolysis). We have found that a 1:1 alkyne:amine ratio allows better control. Excess of amine will preferentially form complex **D**, making the reaction extremely slow.



roborated using bond disruption energy data.[30] Thus, for thorium, both reactions (eqs 14 and 15) are calculated to be exothermic by almost equal amounts, allowing the control, whereas, for uranium, the formation of the bis(amido) complex is endothermic, impeding the control of the extent of oligomerization. It is important to point out that all the alkyne substrates presented in Table 1 were reacted with both organoactinides and only those cases in which a controlling effect was found are presented in Table 1. For the majority of the substrates in the uranium case, no real controlling effect was found. Hence, the theoretical thermodynamic calculations are in agreement with our observed results, and it seems that the results found for the uranium complex (entries 2, 11, and 15 in Table 1) are the outcome of a kinetic effect presumably due to the bulkiness of the alkyne.

(30) (a) Smith, G. M.; Susuki, H.; Sonnenberg, D. C.; Day, V. W.; Marks, T. J. *Organometallics* **1986**, *5*, 549. (b) Giardello, M. A.; King, W. A.; Nolan, S. P.; Porchia, M.; Sishta, C.; Marks, T. J. In *Energetics of Organometallic Species*; Martinho-Simòes, J. A., Ed.; Kluwer Academic Press: Dodrecht, The Netherlands, 1992; pp 35−51. (c) Martinho Simòes, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629. (d) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824.

Conclusions

In conclusion, we have shown that it is possible to control the extent of the oligomerization of terminal alkynes catalyzed by organoactinide complexes, by using selected amines. This led to the possibility of ensuring catalysis by "recycling" the obtained organometallic bis(amido) complex back to the starting catalytically active mono(amido)thorium acetylide species. A detailed understanding of the thermodynamics of the single steps in the desired reactions was the key to "designing" the catalytic cycles. The use of different protonolytic sources are under investigation.

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