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Designing new catalytic C–C and C–N bond formations promoted by organoactinides

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Abstract

Organoactinides of the type $Cp^*_2AnMe_2$ ($Cp^*=C_5Me_5$; An=Th; U) are active catalytic precursors for the oligomerization of terminal alkynes HC≡CR (R=alkyl, aryl, $SiMe_3$). The regioselectivity and the extent of oligomerization depend strongly on the alkyne substituent R, whereas the catalytic reactivity is similar for both organoactinides. Reaction with *tert*-butylacetylene yields regioselectively the E-2,4-disubstituted 1-buten-3-yne dimer whereas trimethylsilylacetylene is regioselective trimerized to the E,E-1,4,6-tris(trimethylsilyl)-1,3-hexadiene-5-yne, with small amounts (3–5%) of the corresponding E-2,4-disubstituted 1-buten-3-yne dimer. Oligomerization with less bulky alkyl and aryl substituted alkynes produces a mixture of higher oligomers with no regioselectivity. Using the $Cp^*_2ThMe_2$ catalyst, we have recently developed a strategic method to control the extent and in some cases the regioselectivity of the catalyzed oligomerization of nonbulky terminal alkynes to dimers and/or trimers. The metallocene catalytic precursors ensure the selective synthesis of small oligomers by the addition of specific amines. Catalytic ''tailoring'' to dimer and trimers can be achieved by using small or bulky amines, respectively. Kinetic and mechanistic data for the controlling experiments argue that the turnover-limiting step involves the acetylide actinide complex formation with the rapid insertion of the alkyne and protonolysis by the amine. The analog $Cp^*_2UMe_2$ in the presence of primary amines induce the selective C–N bond formation, producing enamines which are tautomerized to the corresponding imines. © 1998 Elsevier Science S.A.

Keywords: Organoactinides; Catalysis; C–C bond formation; C–N bond formation; Oligomerization; Hydroamination

1. Introduction

A critical and challenging goal in synthetic organic chemistry is the design of chemical reaction schemes to obtain selective and regiospecific products. The use of transition metals in this goal, with stoichiometric and catalytic reactions, has been widely studied, resulting in efficient, selective processes which operate under mild, easily controlled, conditions and which annually lead to the production of large amounts of ''fine chemicals'' [1]. These processes are based on the activation of chemical bonds by transition metals, often followed by transformations in the metal coordination sphere and product release. The selectivity and regiospecificity of the reactions are normally controlled by the electronic and steric effects of the starting materials, and in some cases by the organometallic moiety [2–4]. Despite the phenomenal growth of activity in this field [5–7], control on the regioselectivity and the extent of catalytic oligomerization/polymerization reactions, remains challenging. For example, in the catalytic Ziegler–Natta polymerization reaction, the added dihydrogen is used to control, to some extent, the molecular mass of the polymeric chains [8,9].

Various actinide alkyls and hydride metallocenes effectively and selectively catalyze a variety of C–H activation and hydrogenation reactions [10–13]. In their ''cationic'' form, these d^0/f^n ($n=0,2$) metallocene complexes have recently shown to be very active catalysts for the polymerization of α-olefins [14]. However, very little is known about organoactinide-catalyzed alkyne oligomerization [15], and the means to control the extent and the regiospecificity of the products was previously not available. The reported literature deals mainly with organolanthanides for selective dimerization and cyclodimerization of alkynes [16–18], with Ziegler–Natta type systems for acetylene polymerization [19–21] and with various transition metals for nonselective oligomerizations. Thus, we report here the reactivity and selectivity of some well-

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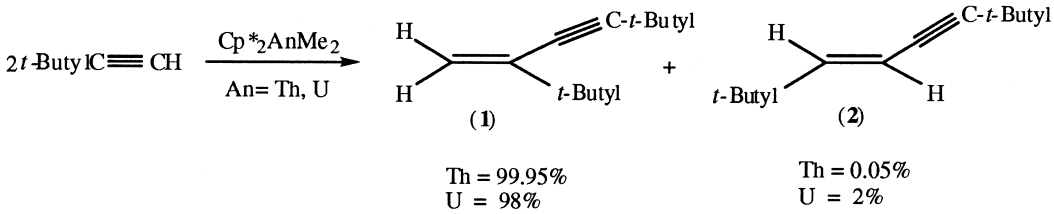
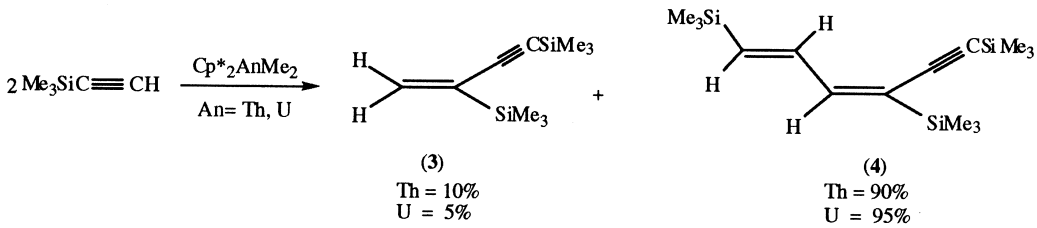
defined actinide alkyls with various monosubstituted acetylenes as well as the spectroscopic characterization of some of the organometallic intermediate complexes in the catalytic cycle. In addition we report a strategy to modify the nonselective catalytic cycle for the selective oligomerization of terminal acetylenes to produce, selectively and regiospecifically, dimers and/or trimers. The desired oligomeric product can be achieved a priori by adding the ''right'' amine into the catalytic cycle. This strategy provides a means of controlling, in principle, any oligomerization/polymerization reaction producing a specific eneyne product, for further chemical transformations [22–29]. The selectivity of the new catalytic cycle was achieved by considering the calculated difference in bond-disruption energies between an actinide–alkenyl- and an actinide–amido-bond, and the combination of the nonselective catalytic pathways with individual stoichiometric reactions. The regioselectivity of the process was tailored by the different organoactinide metals, the pK_a, and steric hindrance imparted by the amine.

Reaction of $Cp^*_2AnMe_2$ ($Cp^*=C_5Me_5$; An=Th; U) with an excess of *t*-butyl acetylene (benzene-*d*6 alkyne/$Cp^*_2AnMe_2$ ratio 330:1) results in the regioselective catalytic formation of the head to tail E-2,4-di-*t*-butyl-1-buten-3-yne dimer (**1**), and trace amounts of the head to head E-1,4-di-*t*-butyl-2-buten-4-yne (**2**) dimer (reaction 1). In contrast, for $HC\equiv CSiMe_3$, the head to head dimer is not formed, small amounts (5%>) of the head to tail E-1,4-bis(trimethylsilyl)-2-buten-4-yne dimer (**3**) is formed and catalytic trimerization takes place with dramatic change in regioselectivity for the last acetylenic insertion to yield exclusively and regioselectively the head to tail to head E,E-1,4,6-tris(trimethylsilyl)-1,3-hexadiene-5-yne trimer (**4**) (reaction 2) [30].





For $HC\equiv CPh$ and $HC\equiv C^nC_4H_9$ the $Cp^*_2AnMe_2$-catalyzed oligomerization gives either mixtures of head to head and head to tail isomeric dimers with the concomitant formation of higher — nonregiospecific — oligomers; however, allene-type compounds were not found [31] (Table 1).

A plausible reaction mechanism for the dimerization and trimerization of $HC\equiv CSiMe_3$ is given in Scheme 1. This mechanism consists on a sequence of well-established elementary reactions such as acetylene insertion into M–C σ-bond and σ-bond metathesis. The first step in the catalytic cycle involves alkyne CH bond activation by the organoactinides [32–34], and formation of the bis acetylide–organoactinide complex, $Cp^*_2An(C\equiv CR)_2$ (**A**) [35] together with CH_4 (step 1). Head to tail insertion of the alkyne into the actinide–carbon σ-bond yields a substituted alkenyl actinide complex (**B**). This complex undergoes either a σ-bond metathesis with an incoming alkyne to yield the corresponding dimer, or another tail to head insertion of an alkyne, with the expected regioselectivity [36–39], into the metal–carbon bond yielding the bis(dialkenyl)–organoactinide complex (**C**). This undergoes another σ-bond metathesis with an incoming alkyne, thus producing the free dieneynes and regenerating the active acetylide–actinide complex. The bis acetylide–organoactinide complex **A** can be detected and trapped by performing the first step of the catalytic oligomerization at room temperature. When heated to the reaction temperature (95°C), complex **A** disappears and complex **C** is the sole organoactinide that can be detected in the course of the catalytic trimerization as shown in situ by NMR experiments (Scheme 2, identification of each of the different protons is given in Scheme 1). The ratio of the alkenyl chain groups and the Cp^* groups in complex **C** is 1, arguing that both alkyl positions at the metal center are active sites with similar rates. The turnover limiting step for the catalytic trimerization is the elimination of the trimer compound from the organometallic–trimer complex (**C**). This result argues that the rate for σ-bond metathesis between the actinide–carbyls and the alkyne and the rate

Table 1
Distribution ratio and activity data for the oligomerization of terminal alkynes by organoactinide complexes

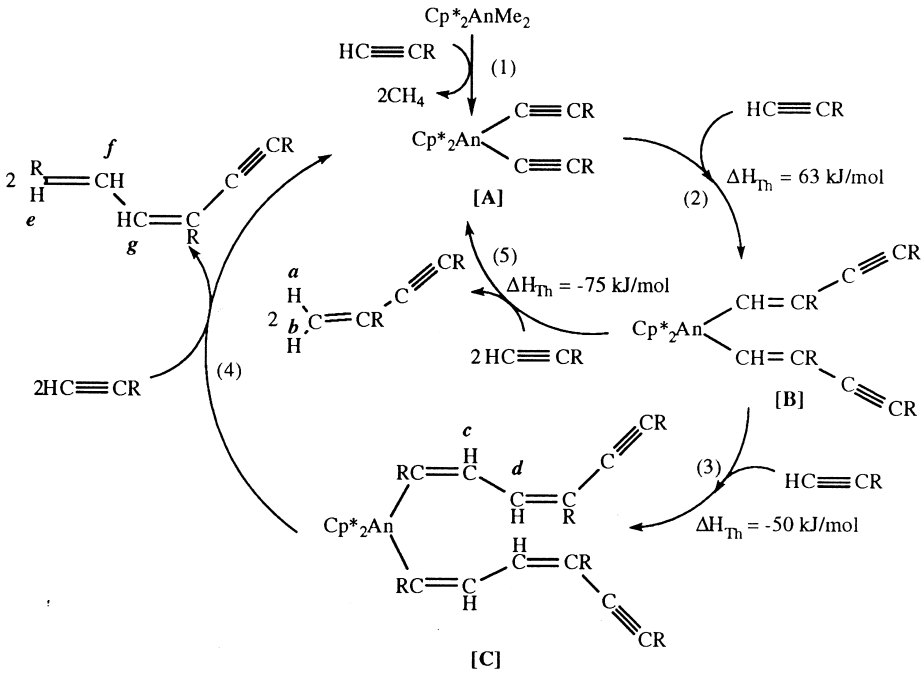
Entry	Catalyst	R	Solvent	Dimers (%)[a]	Trimers (%)	Tetramers (%)	Pentamers (%)[c]	N_t (h^{-1})
1	Th	*t*-butyl	THF	99.95 (0.05)				2
2	U	*t*-butyl	THF	98 (2)				3
3	U	*t*-butyl	C_6D_6	95 (5)				2
4	Th	$SiMe_3$	THF	12	88			7
5	Th	$SiMe_3$	C_6D_6	10	90			6
6	U	$SiMe_3$	THF	5	95			10
7	U	$SiMe_3$	C_6D_{12}	4	96			6
8	Th	Ph[b]	THF	28	57	15		6
9	U	Ph[b]	THF	30	50	20		6
10	Th	*n*-butyl[b]	THF	39	35	13	13	5
11	U	*n*-butyl[b]	THF		18	11	31 (40)	5

[a] The numbers in parentheses correspond to the dimer of type **2**.
[b] The percentage of the different oligomers was calculated from the GC–MS data.
[c] The numbers in parentheses correspond to the oligomeric hexamers.

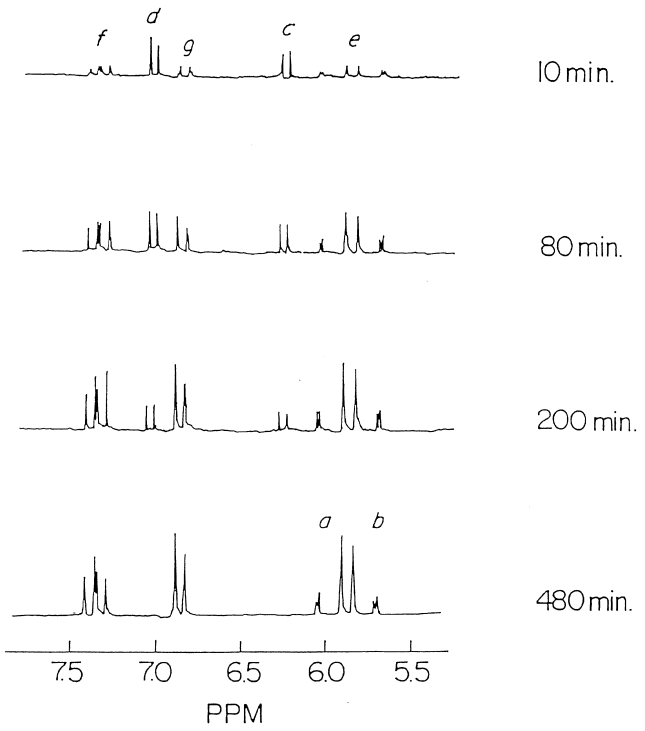
of insertion of the alkyne into the metal carbyl (step 1, 2 and 3) are faster than the rate for σ-bond metathesis of the alkyne with the metal–dialkenyl bond in the catalytic cycle (step 4).

The extent of oligomerization, i.e. the dimer/trimer-:higher oligomers ratio in the oligomerization reaction is determined by the differences in activation energy ($\Delta\Delta G^*$) for CH bond activation and alkyne insertion in the last step of the oligomerization which was found to be almost solvent dependence free (Table 1). It seems that the value of ($\Delta\Delta G^*$) for dimerization processes depends on the size of the metal and the bulk of the alkyl substituent. For higher oligomerization products there is a dependence also on the electronic effect of the alkyl substituent. For R=*t*-butyl, the metal resembles the small lanthanides and for R=$SiMe_3$, the energy of insertion is much lower than that of the CH activation due to the electronic effect of the silyl group [36]. For R=Ph and *n*-C_4H_9 we believe that the energy of insertion has decreased since insertion reactions are more sensitive to steric effects than CH σ-bond activations [40].

The calculated enthalpies for the different catalytic steps in the noncontrolled oligomerization of terminal alkynes show that the first insertion of a terminal alkyne into a thorium–acetylide complex, $Cp^*_2Th(C{\equiv}CR)_2$ (**A**), forming the complex **B** (step 2) is endothermic by 63 kJ mol^{-1} [30]. The formation of the organic dimer product and the starting acetylide complex **M–A**, which results from the protonolysis of complex **B** with the acidic hydrogen of the terminal alkyne, is exothermic by 75 kJ mol^{-1}. Thus, the



Scheme 1. Plausible cycle for the oligomerization of terminal alkynes catalyzed by organoactinide complexes.



Scheme 2. Vynilic region in the oligomerization of TMSC≡CH. Labeled signals correspond to the different compounds as marked in Scheme 1.

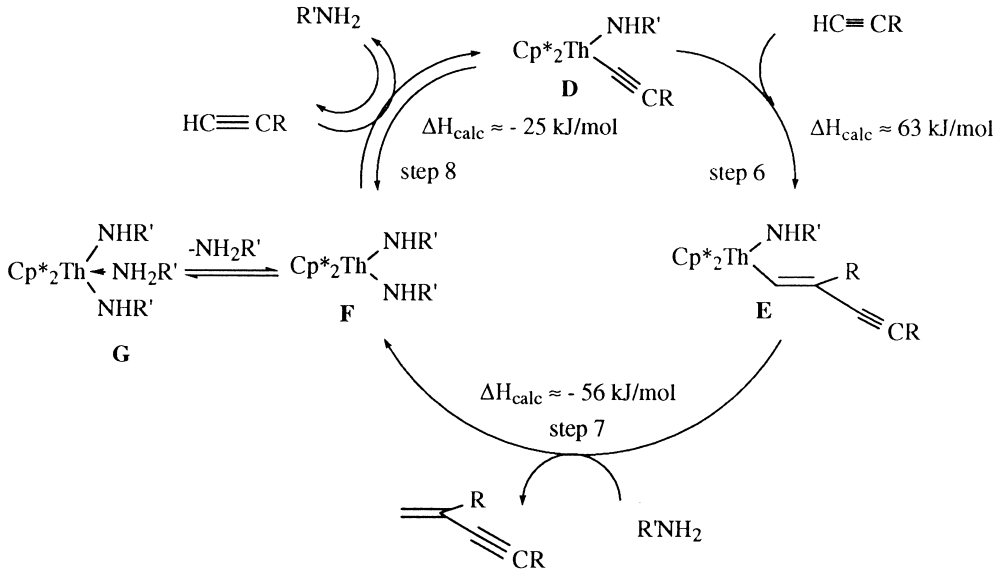
calculated enthalpy for the dimer formation reaction is exothermic by 12 kJ mol^{-1}. Interestingly, the insertion of a second alkyne into **B**, forming complex **C**, is calculated to be exothermic by 50 kJ mol^{-1}. Hence, the growing of the oligomeric chain is exothermic, leading to a nonselective oligomerization reaction [41,42].

We have developed a strategy which allows the production of oligomers with very high selectivity and regiospecificity. It is designed to allow a kinetic competition between the insertion of an alkyne into an actinide–alkenyl bond to lengthen the oligomeric chain (step 3), with the protonolysis of the growing oligomer with another source of acidic protons, instead of the same alkyne, thus preventing the formation of larger oligomers. True catalysis was achieved by transforming the new organometallic species back to the original active complex [43].

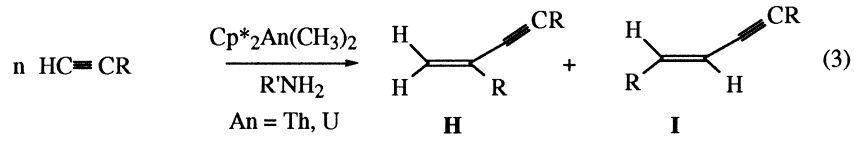
A plausible mechanism for this new strategy is described in Scheme 3, in which amines were used to achieve these two important goals [44].

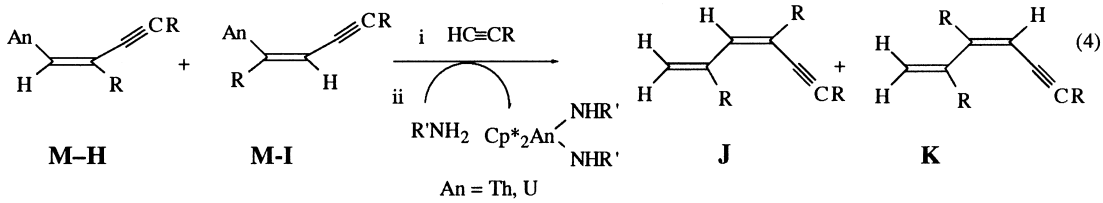
The presented mechanism in Scheme 3 consists of a sequence of well-established elementary reactions, such as insertion of acetylene into an M–C σ-bond, and σ-bond metathesis. The initial step in the catalytic cycle involves the insertion of an alkyne into an actinide–carbyl σ-bond, yielding the actinide–alkenyl amido complex **E** (step 6). This complex, may undergo either a σ-bond protonolysis with an amine to yield the corresponding dimer and the bisamido complex **F** (step 7), or another insertion of an alkyne and concomitant σ-bond protonolysis by the amine yielding the oligomeric trimer and the bisamido complex **F** [45–47]. Complex **F** may either be in rapid equilibrium with complex **G** [48], or in the presence of alkyne, converted in the rate determining step to the active complex **D** (step 8) [49].

The calculated enthalpies of the individual steps in the proposed catalytic cycle (Scheme 3) show that for organothorium complexes the bond strength follows the trend of: Th–acetylide>Th–NR_2>Th–alkenyl≈Th–dialkenyl [50,51]. The different selectivity and regiospecificity observed in the formation of dimers and trimers by the controlled oligomerization of terminal alkynes with amines can be resumed as shown in reactions 3 and 4.



Scheme 3. Plausible cycle for the controlled oligomerization of terminal alkynes catalyzed by organoactinide complexes.





The trimers obtained are those selectively formed by the regiospecific insertion of an alkyne into the **M**–**H** and **M**–**I** moieties, yielding only the regioselective trimers **J** and **K**, respectively. The yields obtained for each of the oligomers in the presence of the different amines are presented in Table 2; as can be seen, the thorium-catalyzed oligomerization in the presence of small amines ($MeNH_2$, $EtNH_2$) selectively yielded dimers with no formation of higher oligomers. This was confirmed by ^1H nuclear magnetic resonance (NMR) and by gas chromatography–mass spectrometry (entries 1, 2 in Table 2). For 1-hexyne, in the presence of isobutylamine, only one dimer was obtained (entry 3) [52]. However, in the absence of amine both dimers and a large number of higher oligomers were obtained [30]. This result indicates against the actinide–bisacetylide complex being an active species and provides corroborating evidence that the amine is the protonolysis agent.

Table 2
The effect of amines and catalytic precursors on the controlled catalytic oligomerization of terminal alkynes

Entry	Catalyst[a]	R[b]	Amine	Dimers (%)		Trimers (%)	
				H	I	J	K
1	Th	*n*-Bu	$MeNH_2$	45	48		
2	Th	*n*-Bu	$EtNH_2$	32	53		
3	Th	*n*-Bu	i-$BuNH_2$	89			
4	Th	*n*-Bu	*t*-$BuNH_2$	81		11	8
5	Th	*n*-Bu	2,6-DMA[c]	60		40	
6	Th	*n*-Bu	2,6-DMD[d]	42		58	
7	Th	C_5H_9[e]	$EtNH_2$	75	25		
8	Th	i-Pr	$EtNH_2$	57	43		
9	U	i-Pr	Me_2NH	10		90	
10	Th	*p*-*t*-BuPh	$EtNH_2$		10		
11	U	*p*-*t*-BuPh	Me_2NH		100		
12	U	*t*-Bu	*t*-$BuNH_2$[f]	40	60		

[a] [Catalyst] = 7.6×10^{-2} M, [alkyne] ≈ [amine] = 2.6 M. Solvent = benzene, T = 80°C. The remaining percentage to 100% conversion is the product formed in the intermolecular hydroamination of the corresponding alkyne and amine [30].
[b] R = substituent from the corresponding RC≡CH.
[c] 2,6-dimethylaniline.
[d] 2,6-dimethylaniline-d_2.
[e] Cyclopentyl.
[f] Slow catalytic oligomerization.

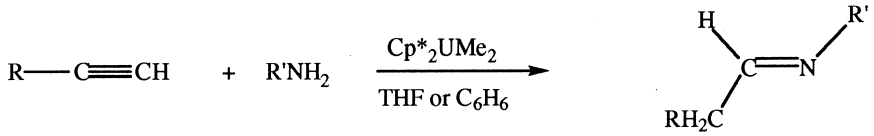
It is worth noting that for the analogous uranium complex, the comparison of the calculated enthalpy of the reaction for the growing oligomer chain ($\Delta H_U \approx -30$ kJ mol^{-1}) (step 3, Scheme 1) with the protonolysis by an amine ($\Delta H_U \approx 6$ kJ mol^{-1}) (step 7, Scheme 3) indicating that the uranium analog will not be as selective, as found experimentally, as the Th complex, where the corresponding calculated values are −50 and −56 kJ mol^{-1}, respectively. Thus, for the uranium equivalent, in the presence of small amines, bulky alkynes produce one dimer regioselectivity (entry 11), although for less bulky alkynes the best regioselectivity was found for isopropylacetylene, to yield a mixture of a dimer and trimer [53].

The steric effect of the different amines illustrated in Table 2 (entries 1 to 5) shows that increasing the bulkiness of the amine induces the formation of the two regiospecific trimers, **J** and **K**.

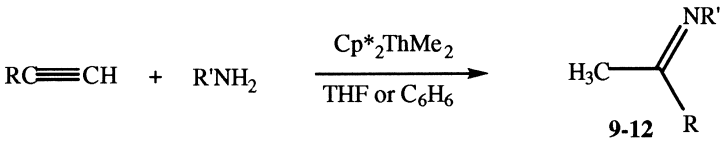
Kinetic measurements on the controlled oligomerization reaction yield the rate law Eq. (1), compatible with rapid, operationally irreversible alkyne insertion (step 6), rapid σ-bond protonolysis of the oligomer by the amine (step 7), a slow preequilibration involving the bis-amido (**F**) and the mono amido–acetylide complex (**D**) (step 8), and a rapid equilibrium between the bis-amido complex **F** and the bis-amido–amine complex **G**.

$$\nu = k[\mathrm{Th}]^1[\mathrm{alkyne}]^1[\mathrm{amine}]^{-1} \quad (1)$$

A new strategy was also implemented to increase the selectivity of the trimer. This was accomplished by providing a kinetic delay to the fast protonolysis by the amine (step 7) to allow more trimer formation. Step 7 is very rapid, and a small modification in the amine should allow a degree of fine control over the selectivity. This was achieved by replacement of the amine hydrogens by deuterium as shown in entry 5 and 6 in Table 2. The



R = TMS, R' = Me (95%) R = t-Bu, R' = Me (95%)
R = TMS, R' = Et (95%) R = t-Bu, R' = Et (95%)
R = n-Bu, R' = Me (70%) R = Ph, R' = Et (50%)
R = n-Bu, R' = Et (95%)



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R = H, R' = Et (80%)
R = *n*-Bu, R' = Me (7%)
R = *n*-Bu, R' = Et (15%)
R = Ph, R' = Et (33%)

competitive breaking of an N–D, versus the N–H bond, in the fast protonolysis reaction (step 7), which enabled us to change the selectivity of the reaction and to increase the ratio of trimer to dimer.

Interestingly, the uranium $Cp^*_2UMe_2$ with primary amines is able to induce the intermolecular hydroamination of the terminal alkynes with exclusive regiospecificity toward one enamine which is tautomerized to the corresponding imine (reaction 6). The thorium complex, under the same conditions, was found to be competing between the two processes (intermolecular hydroamination vs. dimer formation). The intermolecular hydroamination product was found to have the opposite regioselectivity as found for the uranium analog complex (reaction 7).

In conclusion, we have shown that it is possible to control the extent, the selectivity, and the regiospecificity of oligomerization reactions catalyzed by organoactinide complexes, by using selected amines. This led to the possibility of ensuring true catalysis by ''recycling'' the obtained organometallic complex back to the catalytically active species. For uranium, the selective intermolecular hydroamination process takes place instead of the oligomerization control due to the large difference in bond disruption energies among the two processes. A detailed understanding of the thermodynamics of the single steps in the desired reactions was the key to ''designing'' the catalytic cycles.

Acknowledgements

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References

[1] G.W. Parshall, S.D. Ittel, Homogeneous Catalysis, Wiley, New York, 2nd ed., 1992.
[2] R.R. Moser, D.W. Slocum, Homogeneous Transition Metal Catalyzed Reactions, American Chemical Society, Boston, MA, 1990.
[3] M.E. Davis, S.L. Suib, Selectivity in Catalysis, American Chemical Society, New York, 1991.
[4] J.A. Davies, P.L. Watson, J,F, Liebman, A. Greenberg, Selective Hydrocarbon Activation, VCH, New York, 1990.
[5] B.A. Arndtsen, R.G. Bergman, T.A. Mobley, T.H. Peterson, Acc. Chem. Res. 28 (1995) 154.
[6] E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, Vol. 12, Elsevier, New York, 1995.
[7] B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis: Selectivity, Strategy and Efficiency in Modern Organic Chemistry, Vols. 3 and 5, Pergamon Press, Oxford, 1991.
[8] T. Keii, K. Soga, Catalytic Olefin Polymerization, Elsevier, Amsterdam, 1990.
[9] W. Kaminsky, H. Sinn, Transition Metals and Organometallics as Catalysts for Olefin Polymerization, Springer-Verlag, Berlin, Heidelberg, 1988.
[10] G.M. Smith, J.D. Carpenter, T.J. Marks, J. Am. Chem. Soc. 108 (1986) 6805.
[11] J.W. Bruno, G.M. Smith, T.J. Marks, J. Am. Chem. Soc. 108 (1986) 40.
[12] C.M. Fendrick, L.D. Schertz, V.W. Day, T.J. Marks, J. Am. Chem. Soc. 7 (1988) 1828.
[13] Z. Lin, T.J. Marks, J. Am. Chem. Soc. 112 (1990) 5515.
[14] L. Jia, X. Yang, C. Stern, T.J. Marks, Organometallics 13 (1994) 3755.
[15] R.S. Sternal, M. Sabat, T.J. Marks, J. Am. Chem. Soc. 109 (1987) 4931.
[16] R. Duchateau, C.T. Van Wee, A. Meetsma, J.H. Teuben, J. Am. Chem. Soc. 115 (1994) 4931.
[17] H.J. Heeres, J.H. Tauben, Organometallics 10 (1991) 1980.
[18] H.J. Heeres, A. Heeres, J.H. Tauben, Organometallics 9 (1990) 1508.
[19] Z. Shen, Inorg. Chim. Acta 140 (1987) 7–13.
[20] M. Bruzzone, in: T.J. Marks, J.L. Fragala (Eds.), Fundamental and Technological Aspects of Organo-f-Element Chemistry, Reidel:Dodrecht, The Netherlands, 1985.
[21] M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan,

B.D. Santarsiero, W.P. Schaefer, J.E. Bercaw, J. Am. Chem. Soc. 109 (1987) 203.
[22] E. Negishi, M.D. Jensen, D.Y. Kondakov, Y. Wang, J. Am. Chem. Soc. 116 (1994) 8404.
[23] S.J. Miller, S.-H. Kim, Z.-R. Chen, R.H. Grubbs, J. Am. Chem. Soc. 117 (1995) 2108.
[24] A.F. Houri, Z. Xu, D.A. Cogan, A.H. Hoveyda, J. Am. Chem. Soc. 117 (1995) 2943.
[25] P.A. Wender, H. Takahashi, B. Witulski, J. Am. Chem. Soc. 117 (1995) 4720.
[26] S. Watanuki, M. Mori, Organometallics 14 (1995) 5054.
[27] B.M. Trost, M. Yanai, K. Hoogsteen, J. Am. Chem. Soc. 115 (1993) 5294.
[28] P.A. Magriotis, K.D. Kim, J. Am. Chem. Soc. 115 (1993) 2972.
[29] J.M. Nuss, R.A. Renneis, B.H. Levine, J. Am. Chem. Soc. 115 (1993) 6991.
[30] T. Straub, A. Haskel, M.S. Eisen, J. Am. Chem. Soc. 117 (1995) 6364.
[31] Allenes have been observed for organolanthanides and transition metals oligomerization of acetylenes.
[32] Thermodynamically the enthalpy for this step can be calculated to be exothermic for both actinides (ΔH(Th)≈ -18 kcal mol^{-1} and ΔH(U)≈ -25 kcal mol^{-1}).
[33] G.M. Smith, H. Susuki, D.C. Sonnenberg, V.W. Day, T.J. Marks, Organometallics 5 (1986) 549–561.
[34] M.A. Giardello, W.A. King, S.P. Nolan, M. Porchia, C. Sishta, T.J. Marks, In: J.A. Martinho Simòes (Ed.), Energetics of Organometallic Species, Kluwer Academic Press, Netherlands, 1992, pp. 35–51 and references therein.
[35] For **A** (Ac=U)^{1}H NMR (THF *d*8) δ 21.71 (d, 2H, $^{3}J=7.7$ Hz. *o*-H), 13.14 (t, 1H, $^{3}J=7.7$ Hz, *p*-H), 12.34 (t, 2H, $^{3}J=7.7$ Hz, *m*-H), 3.02 (s, 30H, Cp**).
[36] Stockis and Koffman have performed calculations on the polarization of the π* orbitals in TMSC≡CH and $CH_3C\equiv CH$. 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, R. Hoffman, J. Am. Chem. Soc., 102 (1980) 2952–2962.
[37] Y. Apeloig, R. Biton, A.A. Freih, J. Am. Chem. Soc. 114 (1993) 2522.
[38] J.B. Lambert, Tetrahedron 46 (1990) 2677.
[39] T.A. Blumenkopf, L.E. Overman, Chem. Rev. 86 (1986) 857.
[40] B.J. Burger, M.E. Thompson, W.D. Cotton, J.E. Bercaw, J. Am. Chem. Soc. 112 (1990) 1566.
[41] G.M. Smith, H. Susuki, D.C. Sonnenberg, V.W. Day, T.J. Marks, Organometallics 5 (1986) 549.
[42] M.A. Giardello, W.A. King, S.P. Nolan, M. Porchia, C. Sishta, T.J. Marks, in: J.A. Martinho-Simòes (Ed.), Energetics of Organometallic Species, Kluwer Academic Press, Dodrecht, The Netherlands, 1992, pp. 35–51.
[43] This strategy will work on catalytic schemes where the competing reactions are not the rate determining steps.
[44] Uranium complexes in the presence of terminal alkynes and primary amines do not produce oligomers, although they do bring about the intermolecular hydroamination of terminal alkynes to the corresponding imines. See Ref. .
[45] T. Straub, G. Reiss, W. Frank, M.S. Eisen, Paper Presented at the XIth FECHEM, Conference on Organometallic Chemistry, Parma, Italy, 10 September 1995.
[46] T. Straub, W. Frank, G. Reiss, M.S. Eisen, J. Chem. Soc., Dalton Trans. 0 (1996) 2541.
[47] For similar bisamido complexes of hafnium see: G.L. Hilhouse, A.R. Bulls, B.D. Santarsiero, J.E. Bercaw, Organometallics, 7 (1988) 1309.
[48] A. Haskel, T. Straub, M.S. Eisen, Organometallics 15 (1996) 3773.
[49] Steps 6 and 7 in Scheme 3 are very fast, thus preventing us to characterize complexes **D** and **E**. The similar alkylamido complex of thorium $Cp^*_2Th(NHR)CH_3$ (R=t-Bu) complex has been characterized in solution spectroscopically: ^{1}H NMR δ 2.02 (s 30H, Cp**), 1.08 (s, 9H, *t*-Bu), -0.22 (s, 3H, Th–CH_3).
[50] J.A. Martinho Simòes, J.L. Beauchamp, Chem. Rev. 90 (1990) 629.
[51] J.W. Bruno, T.J. Marks, L.R. Morss, Am. Chem. Soc. 105 (1983) 6824.
[52] Increasing the concentration of the amine causes the formation of the corresponding trans dimer. A. Haskel, Thesis, Technion, 1996.
[53] For $Cp^*_2U(NR_2)_2$ (R=Me) with other alkynes the oligomerization gives a mixture of oligomers. The selectivity is notoriously biased towards the smaller oligomers in comparison to the noncontrolled oligomerization.