

Organoactinide-Catalyzed Oligomerization of Terminal Acetylenes

Thomas Straub, Ariel Haskel, and Moris S. Eisen*

Department of Chemistry
Technion-Israel Institute of Technology
Haifa 32000, Israel

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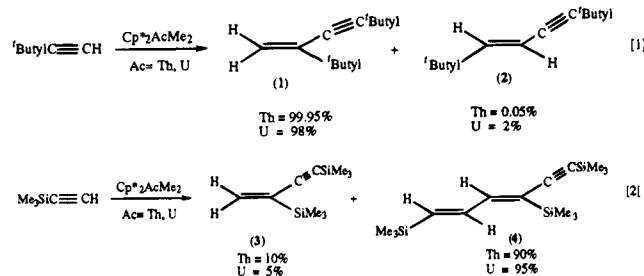
Various actinide alkyl and hydride metallocenes effectively and selectively catalyze a variety of C–H bond activation and hydrogenation reactions.¹ In their “cationic” form, these d⁰/f⁰ metallocene complexes have recently been shown to be very active catalysts for the polymerization of α -olefins;² however, very little is known about organoactinide-catalyzed alkyne oligomerization.³ The literature deals mainly with organolanthanides for selective dimerization and cyclodimerizations of alkynes,⁴ Ziegler–Natta-type systems for acetylene polymerization,⁵ and various transition metals for selective dimerization of alkynes.⁶ In this Communication, we report the reactivity and selectivity of some well-defined actinide alkyls with various monosubstituted acetylenes as well as the spectroscopic characterization of some of the key organometallic intermediates in the catalytic cycle.

Reaction of Cp*₂AcMe₂ (Cp* = C₅Me₅; Ac = Th, U) with an excess of *tert*-butylacetylene (benzene-*d*₆, alkyne/Cp*₂AcMe₂ ratio 330:1) results in the regioselective catalytic formation of the head-to-tail dimer 2,4-di-*tert*-butyl-1-buten-3-yne (**1**)⁷ and traces of the head-to-head dimer (*E*)-1,4-di-*tert*-butyl-1-buten-3-yne (**2**) (eq 1).⁷ In contrast, for HC≡CSiMe₃, the head-to-

change in regioselectivity for the last acetylenic insertion to yield, exclusively and regioselectively, the head-to-tail-to-head trimer (*E,E*)-1,4,6-tris(trimethylsilyl)-1,3-hexadien-5-yne (**4**) (eq 2).⁷ For HC≡CPh and HC≡C-*n*-C₄H₉, the Cp*₂AcMe₂-catalyzed oligomerization gives either mixtures of head-to-head and head-to-tail isomers or the formation of higher oligomers; however, allene compounds were not found (Table 1).⁸

A plausible reaction mechanism for the dimerization and trimerization of HC≡CSiMe₃ is given in Scheme 1. This mechanism consists of a sequence of well-established elementary reactions such as acetylene insertion into a M–C σ -bond and σ -bond metathesis. The first step in the catalytic cycle involves alkyne CH bond activation by the organoactinide⁹ and formation of the organoactinide bisacetylide complex Cp*₂Ac(C≡CR)₂ (**A**)¹⁰ together with CH₄ (step 1). Head-to-tail insertion of the alkyne into the actinide–carbon σ -bond yields a substituted alkenylactinide 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,^{11,12} into the organoactinide alkenyl complex **B**, yielding the bis(dienynyl)organoactinide complex **C**. The latter complex undergoes another σ -bond metathesis with an incoming alkyne, thus producing free dienyne and regenerating the active actinide bisacetylide complex. The organoactinide bisacetylide 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 (Figure 1). The ratio of the alkenyl chain groups to the Cp* groups in complex **C** was found spectroscopically to be 1:1, 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 complex **C**. This result argues that the rate for σ -bond metathesis between the actinide–carbonyls and the alkyne and the rate of insertion of the alkyne into the metal–carbonyl (steps 1 and 2) 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, is determined by the differences in activation energy ($\Delta\Delta G^*$) for CH bond activation and alkyne insertion in the last step (step 4) of the oligomerization mechanism. The effect of the solvents on this energy difference were found to be small (Table 1). It seems that the value of $\Delta\Delta G^*$ for dimerization processes depends on the size of the metal and the bulkiness of the alkyne substituent. For higher oligomerization reactions, there is a dependence also on the electronic effect of the alkyl substituent. For small metals, such as



head dimer is not formed; however, small amounts (<5%) of the head-to-tail dimer 2,4-bis(trimethylsilyl)-1-buten-3-yne (**3**) are formed, and catalytic trimerization takes place with dramatic

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(2) Jia, L.; Yang, X.; Stern, C.; Marks, T. J. *Organometallics* **1994**, *13*, 3755–3757 and references therein.

(3) For a stoichiometric thorium–ruthenium trimerization of a nitrile, see: Sternal, R. S.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7920–7921.

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(7) Compounds **1–4** were characterized by ¹H NMR, ¹³C NMR, and GC/MS spectroscopy; see supplementary material.

(8) Allenes have been observed for organolanthanide^{4b} and transition metal^{5c}-catalyzed oligomerization of acetylenes.

(9) Thermodynamically, the enthalpy for this step can be calculated to be exothermic for both actinides ($\Delta H(\text{Th}) \approx -18$ kcal/mol, $\Delta H(\text{U}) \approx -25$ kcal/mol): (a) Smith, G. M.; Susuki, H.; Sonnenberg, D. C.; Day, V. W.; Marks, T. J. *Organometallics* **1986**, *5*, 549–561. (b) Giardello, M. A.; King, W. A.; Nolan, S. P.; Porchia, M.; Sishta, C.; Marks, T. J. In *Energetics of Organometallic Species*; Martinho Simões, J. A., Ed.; Kluwer Academic Press: Dordrecht, The Netherlands, 1992; pp 35–51 and references therein.

(10) For **A** (R = Ph, Ac = U): ¹H NMR (THF-*d*₆, 293 K) δ 21.71 (d, 2H, ³J = 7.7 Hz, *o*-H), 13.14 (t, 1H, ³J = 7.7 Hz, *p*-H), 12.34 (t, 2H, ³J = 7.7 Hz, *m*-H), 3.02 (s, 30H, Cp*).

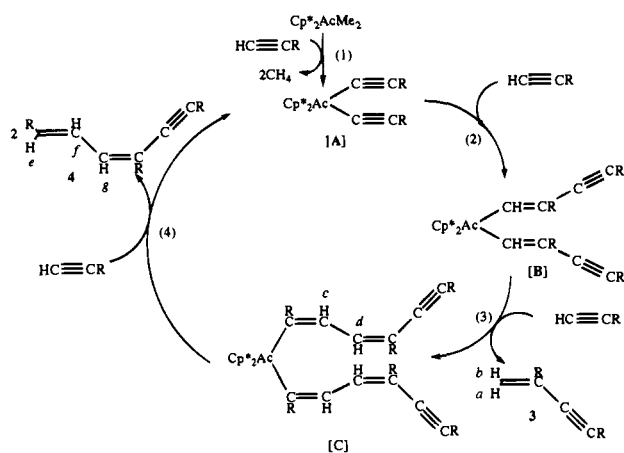
(11) Stockis and Hoffmann have performed calculations on the polarization of the π^* -orbitals in TMS-C≡CH and CH₃C≡CH. Different polarizations were found for both groups, showing the large effect of the substituent on the alkyne sp carbon atoms. These electronic effects are believed to be responsible for the difference in regioselectivities of the trimerization–dimerization results. Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952–2962.

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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	<i>t</i> -Bu	THF	99.95 (0.05)				2
2	U	<i>t</i> -Bu	THF	98 (2)				3
3	U	<i>t</i> -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	<i>n</i> -Bu ^b	THF	39	35	13	13	5
11	U	<i>n</i> -Bu ^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 GCMS data. ^c The number in parentheses corresponds to the oligomeric hexamers.

Scheme 1

yttrium,^{4b} dimers are formed exclusively by a similar mechanism, indicating that the energy of activation for insertion in step 3 is higher than that for the σ -bond metathesis. Larger lanthanides, such as lanthanum and cerium, form significant amounts of trimers, indicating a comparable CH bond activation and insertion energies. In the actinides, for R = *tert*-butyl, the metal resembles the small lanthanides, and for R = SiMe₃, the enthalpy of insertion is much lower than that of the CH activation due to the electronic effect of the silyl group.¹² For R = Ph and *n*-C₄H₉, we believe that the energy of insertion has decreased since insertion reactions are more sensitive to steric effects than CH σ -bond metathesis.¹³

Mechanistically, the presence of relatively low-lying empty metal σ -bonding orbitals, the relatively polar metal–ligand bonds, and the absence of energetically accessible metal oxidation states for oxidative addition/reductive elimination processes¹⁴ have implicated a “four-center” heterolytic metal–carbon transition bond cleavage, suggesting that the *cis* stereochemistry of the products should be preserved between the alkyl substituent and the acetylenic proton.

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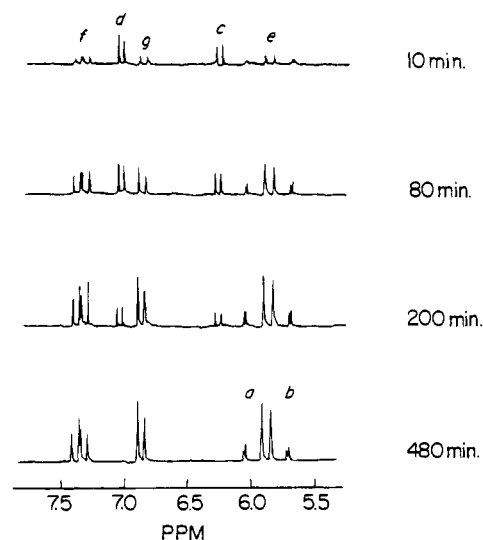


Figure 1. Vinylic region for the HC≡CSiMe₃ oligomerization reaction catalyzed by Cp*₂ThMe₂. Signals marked *c* and *d* correspond to the organoactinide bisacetylide complex C. The signals *f*, *g*, and *e* belong to the trimer 4, and the signals *a* and *b* belong to the corresponding dimer 3.

These results demonstrate that organoactinide centers are active catalysts for the 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 incorporation of these transformations into efficient and novel catalytic cycles is presently under investigation.

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Supplementary Material Available: Full experimental details; spectroscopic and analytical data for 1–4 (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions. JA950421U