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Catalytic Coupling of Terminal Alkynes with Isonitriles Promoted by Organoactinide Complexes

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Catalytic Coupling of Terminal Alkynes with Isonitriles Promoted by Organoactinide Complexes

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In the past decade, neutral and cationic organoactinide complexes have been studied as catalysts for several organic transformations. Such processes comprise the polymerization of alkenes, the oligomerization, intermolecular and intramolecular hydroamination, and hydrosilylation of terminal alkynes.[1−4] Isonitriles are known to undergo a 1,1-insertion into the metal−acetylide bond of early or late transition metals, under stoichiometric conditions.[5] Very recently, Odom et al. elegantly designed a three-component coupling of terminal alkynes, isonitriles, and primary amines catalyzed by titanium complexes to form α,β-unsaturated β-iminoamines.[6] The reactivity of isonitrile molecules is a result of the lone pair of electrons alike carbenes. A basic conceptual question regards the use of organoactinides as catalysts for the coupling of terminal alkynes with isonitriles to form substituted 1-aza-1,3-enynes, which contain conjugated acetylenic and azomethine fragments $R^1C{\equiv}C{-}CH{=}NR^2$ (α,β-acetylenic aldimines). These species have attracted large attention as important synthons in organic synthesis, since they possess three active reaction centers for constructing polyfunctional compounds.[7]

Herein, we report the coupling reaction of terminal alkynes and *tert*-butylisonitrile (^{t}BuNC) catalyzed by the actinide complexes $[(Et_2N)_3U][BPh_4]$ (**1**)[8] and $Cp^*_2AnMe_2$ [Cp* = C_5Me_5, An = U (**2**),[9] Th (**3**)[10]]. These compounds proved to be efficient catalysts for a variety of reactions;[1−4] the single-crystal structure of complex **2** is shown in Figure 1.[11]

The three complexes **1**, **2**, and **3** catalyzed the coupling of isonitrile and terminal acetylenes (eqs 1−3) via 1,1-insertion of the isonitrile terminal carbon atom into a metal−acetylide or a metal−imine bond.[12,13] The catalytic conversion of the isonitrile and alkyne to 1-aza-1,3-enynes was achieved in toluene or benzene at 90−100 °C, while no reaction was observed in the absence of catalyst.

The product distribution for the coupling reaction (Table 1) was found to depend strongly on both the catalyst and the alkyne/isonitrile ratio. The cationic catalyst **1** selectively produces the (*E*)-acetylenic imine **4** as the major product (eq 1), from the monoinsertion reaction of ^{t}BuNC into the terminal alkyne, along with some minor byproducts (oligomerization of the terminal alkyne and isomerization[14] of the isonitrile to the nitrile).

Interestingly, reaction with $Cp^*_2UMe_2$ affords product **5** in addition to compound **4** from the double insertion of two isonitrile molecules into one molecule of the terminal alkyne. The percentage of **5** was successfully raised by increasing the amount of isonitrile (Table 1, entry 7). The reaction between bulky terminal alkynes (R = TMS, ^{t}Bu) and ^{t}BuNC in the presence of **3** (Table 1, entries 9−11) produces **4** (eq 3) as the major product. When the reaction

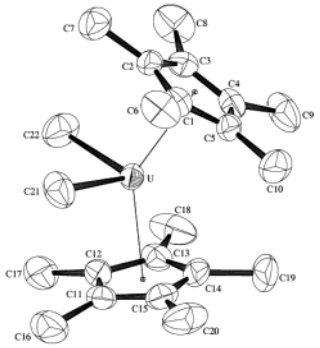

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Figure 1. Thermal ellipsoid plot of $Cp^*_2UMe_2$ crystals with 50% probability and atomic numbering. Hydrogen atoms are omitted for clarity.

is performed with smaller (nonbulky) terminal alkynes, the formation of the additional product **6** is observed. Product **6** results from the coupling of two acetylene molecules and one isonitrile molecule (Table 1, entry 13). The variation of the molar ratio of **4** and **6** over time suggests that **6** is formed only after the complete formation of **4**, by reaction of the latter with the remaining alkyne. The similar behavior of the three discussed catalysts strongly suggests a common mechanism for all of them to obtain compound **4**, with various branches forming products **5** and **6**. A plausible mechanism is described in Scheme 1.

The organoactinide complexes **2** and **3** react with the terminal alkynes to yield the bis(acetylide) complex **A** (step 1).[15] This complex undergoes a 1,1-insertion of the isonitrile into the metal−carbon bond to form the acetylenic imido complex **B** (step 2). Protonolysis by another terminal alkyne yields the monoinsertion product **4** and regenerates complex **A** as the active species in the catalytic cycle (step 3). For complex **2**, this protonolysis step is

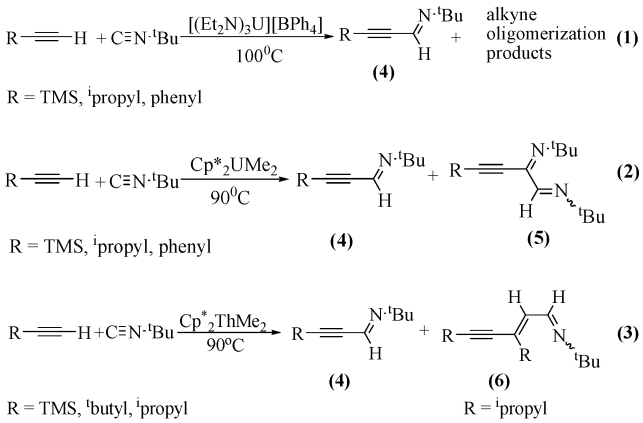

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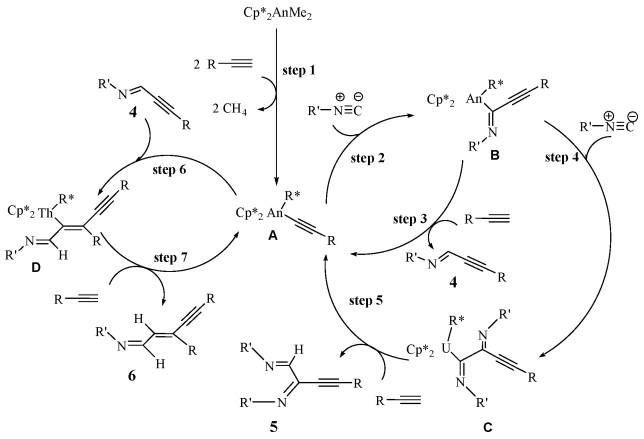
Table 1. Product Distribution for the Coupling Reaction of ^{t}BuNC and Terminal Alkynes Catalyzed by Different Organoactinide Complexes

entry	catalyst	R[a]	catalyst/^{t}BuNC/RC≡CH	time (h)	**4** (%)	**5** (%)	**6** (%)
1	**1**	TMS	1:40:50	48	80		
2	**1**	Ph	1:50:50	48	81		
3	**1**	^{i}Pr	1:40:55	48	81		
4	**2**	TMS	1:50:30	6	56	13	
				24	81	19	
5	**2**	Ph	1:40:60	48	90	10	
6	**2**	^{i}Pr	1:40:70	48	75	25	
7	**2**	^{i}Pr	1:50:20	48	50	50	
8	**3**	TMS	1:100:100	23	90		
9	**3**	TMS	1:100:180	18	85		
10	**3**	^{t}Bu	1:100:100	18	80		
11	**3**	^{t}Bu	1:100:200	18	90		
12	**3**	^{i}Pr	1:100:100	18	90		
13	**3**	^{i}Pr	1:100:200	2	19		0
				17	95		5
				64	60		40
				210	47		53

[a] R in RC≡CH.

Scheme 1. Plausible Mechanism for the Catalytic Coupling of ^{t}BuNC and Terminal Alkynes Mediated by $Cp^*_2AnMe_2$[a]



[a] For clarity we use R* instead of RC≡C and R′ = ^{t}Bu.

not as rapid as that for complex **3**, permitting complex **B** to undergo an additional 1,1-insertion of a second isonitrile molecule to yield the corresponding intermediate **C** (step 4). The double insertion product **5** is then obtained by the protonolysis with a terminal alkyne (step 5) regenerating the active bisacetylide complex **A**. With an excess of nonbulky terminal alkynes, the bisacetylide complex **A** (An = Th) can react with product **4** to yield complex **D**, by insertion of the triple bond of **4** into the Th−acetylide bond (step 6). Protonolysis of **D** by another terminal alkyne yields product **6** and the active species **A** (step 7). This is the first example of an insertion of an internal triple bond into an actinide−carbon bond. For organoactinides we have shown that the insertion of terminal alkynes into a metal−acetylide bond produces dimers or higher oligomers,[2] and when the reaction is performed in the presence of terminal and internal alkynes, only the products formed by the activation of the terminal alkyne are produced. These results showed that the insertion of an internal triple bond must be higher in energy in comparison with terminal alkynes. In contrast, the formation of **6** indicates that, even in the presence of a terminal alkyne, the insertion of the internal triple bond of **4** was preferred, presumably due to the electronic effects of the imine fragment (^{t}Bu−N=C−), which induces polarization of the internal triple bond.

$$\underset{\mathbf{1}}{(Et_2N)_3U^+} + H{-}{\equiv}{-}R \rightleftharpoons \underset{\mathbf{E}}{(Et_2N)_2U^+{-}{\equiv}{-}R} + Et_2NH \quad \mathbf{(4)}$$

We have demonstrated that complex **1** reacts with terminal alkynes to form the acetylide complex (**E**) and Et_2NH via an equilibrium process (eq 4).[3b] **E** is an analogue of **A** and catalyzes the coupling reaction like complexes **2** and **3** by steps 1−3 in Scheme 1. The protonolysis step 3 can be performed via a terminal alkyne to yield **4** and **E** or by the free amine to regenerate **1**.

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Supporting Information Available: Experimental section including the synthesis and ^{1}H and ^{13}C NMR analysis of compounds **4**−**6** and crystallographic data for the crystal structure of complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) For examples of catalytic activity of organoactinides in hydrogenation, see: Lin, Z.; Marks, T. J. *J. Am. Chem. Soc*. **1990**, *112*, 5515 and references therein.
(2) For examples of catalytic activity of organoactinides in oligomerizations, or controlled dimerizations, see: (a) Haskel, A.; Straub, T.; Dash, A. K.; Eisen, M. S. *J. Am. Chem. Soc*. **1999**, *121*, 3014 and references therein. (b) Haskel, A.; Wang, J. Q.; Straub, T.; Neyroud, T. G.; Eisen, M. S. *J. Am. Chem. Soc*. **1999**, *121*, 3025 and references therein.
(3) For recent examples of catalytic activity of organoactinides in hydroamination, see: (a) Stubbert, D. B.; Stern, C. L.; Marks, T. J. *Organometallics* **2003**, *22*, 836. (b) Wang, J.; Dash, A. K.; Kapon, M.; Berthet, J. C.; Ephritikhine, M.; Eisen, M. S. *Chem.—Eur. J*. **2002**, *8*, 5384. (c) Straub, T.; Haskel, A.; Neyroud, T. G.; Kapon, M.; Botoshansky, M.; Eisen, M. S. *Organometallics* **2001**, *20*, 5017 and references therein.
(4) For examples of catalytic activity of organoactinides in hydrosilylation, see: Dash, A. K.; Gourevich, I.; Wang, J. Q.; Wang, J.; Kapon, M.; Eisen, M. S. *Organometallics* **2001**, *20*, 5084.
(5) (a) Martins, A. M.; Ascenso, J. R.; De-Azevedo, C. G.; Dias, A. R.; Duarte, M. T.; Da-Silva, J. F.; Veiros, L. F.; Rodrigues, S. S. *Organometallics* **2003**, *22*, 4218. (b) Takei, F.; Yanai, K.; Onitsuka, K.; Takahashi, S. *Chem.—Eur. J*. **2000**, *6*, 983. (c) Ahlers, W.; Erker, G.; Fröhlich, R. *J. Organomet. Chem.* **1998**, *571*, 83.
(6) Cao, C.; Shi, Y.; Odom, A. L. *J. Am. Chem. Soc*. **2003**, *125*, 2880.
(7) Stadnichuk, M. D.; Khramchikhin, A. V.; Piterskaya, Y. L.; Suvorova, I. V. *Russ. J. Gen. Chem.* **1999**, *69*, 593.
(8) Berthet, J. C.; Boisson, C.; Lance, M.; Vigner J.; Nierlich, M.; Ephritikhine M. *J. Chem. Soc., Dalton Trans.* **1995**, 3019.
(9) Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3939.
(10) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40.
(11) For complex **2**: space group tetragonal, *I*41/*a*; a = 31.8530(3) Å, b = 31.8530(3) Å, c = 8.4380(2) Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, V = 8561.3(2) Å^3, T = 230.0(2) K, Z = 16, R_1 = 0.0288 ($I > 2\sigma(I)$), wR_2 (all data) = 0.0575.
(12) For a review on 1,1-insertions into a metal−carbon bond, see: Kayaki, Y.; Yamamoto, A. *Curr. Methods Inorg. Chem.* **2003**, *3*, 373.
(13) For examples of stoichiometric 1,1-insertion of isonitriles into an actinide−carbon bond, see: (a) Dormond, A.; Aaliti, A.; Elbouadili, A.; Moise, C. *J. Organomet. Chem.* **1987**, *329*, 187. (b) Moloy, K. G.; Fagan, P. J.; Manriquez, J. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 3939.
(14) Isomerization of isonitrile to nitrile was studied; see: Meier, M.; Muller, B.; Ruchart, C. *J. Org. Chem.* **1987**, *52*, 648.
(15) This complex has been characterized for both Th and U. See ref 3.

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