Catalytic Coupling of Terminal Alkynes with Isonitrides 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 hydroisilylation of terminal alkynes. 1-4 Isonitrides are known to undergo a 1,1-insertion into the metal—acyclic 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, isonitrides, 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 isonitrides to form substituted 1-aza-1,3-enynes, which contain conjugated acetylenic and azomethine fragments R1C==N(aryl) (step 1). 15 This catalytic conversion of the isonitrile and alkene 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)-acyclic imine 4 as the major product (eq 1), from the monoinsertion reaction of [BuNC] into the terminal alkene, along with some minor byproducts (oligomerization of the terminal alkene and isomerization 16 of the isonitrile to the nitrile).

Interestingly, reaction with Cp3Uime affords product 5 in addition to compound 4 from the double insertion of two isonitrile molecules into one molecule of the terminal alkene. 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, 'Bu) and 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 Cp3UME2 crystals with 50% probability and atomic numbering. Hydrogen atoms are omitted for clarity.

Figure 2. Mechanism of the reaction catalyzed by Cp3UIME2.
The corresponding intermediate of the triple bond of 4 is then obtained by the protonolysis with a terminal alkyne (step 7). This is the first example of an insertion into the Th carbon bond. For complex 1, permitting complex B to undergo an additional 1,1-insertion of an internal triple bond 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 (An = Th) can react with product 4 to yield complex 6 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 acetylide–carbon bond. For organoactinides we have shown that the insertion of terminal alkynes into a metal–acetylide bond produces dimers or higher oligomers, 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 complex 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 (Bu–N=C=–), which induces polarization of the internal triple bond.

\[(\text{Et}_2\text{N})_3\text{U}^+ + \text{H} \rightleftharpoons \text{R} \rightleftharpoons (\text{Et}_2\text{N})_2\text{U} \rightleftharpoons \text{R} + \text{Et}_2\text{NH} \quad (4)\]

We have demonstrated that complex 1 reacts with terminal alkynes to form the acetylide complex (E) and Et₂NH via an equilibrium process (eq 4). 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 ¹H and ¹³C 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
(11) For complex 2: space group tetragonal, I41/acd; a = 31.830(3) Å, b = 31.830(3) Å, c = 8.4380(2) Å, α = 90°, β = 90°, γ = 90°, V = 8561.3(2) Å³, T = 230.0(2) K, Z = 16, R₁ = 0.0288 (T > 2σ(I)), wR₂ (all data) = 0.0575.
(13) For examples of stoichiometric 1,1-insertion of isonitriles into an actinide–carbon bond, see: (a) Dormond, A.; Aaliti, A.; Elbouadili, A.; Meise, J. Organometallics Chem. 1987, 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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* R in RC=C=CH₂.

Scheme 1. Plausible Mechanism for the Catalytic Coupling of tBuNC and Terminal Alkynes Mediated by Cp*²AmMe₂⁺⁺

For clarity we use R⁺ instead of RC=C=CH₂ and R' = Bu.