Organoactinide-Catalyzed Intermolecular Hydroamination of Terminal Alkynes

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

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

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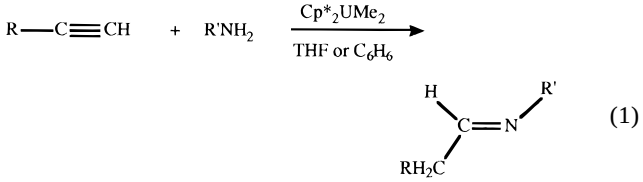
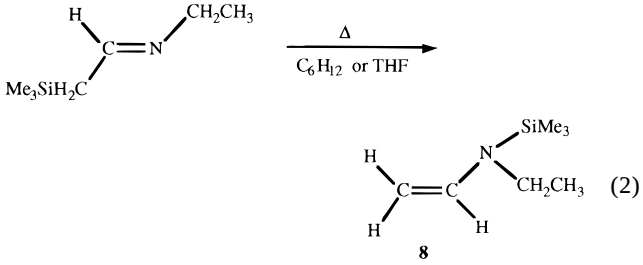
Summary: Organoactinide complexes of the type $Cp^*_2AcR_2$ (Ac = Th, U) catalyze the intermolecular hydroamination of terminal alkynes with aliphatic amines. The regioselectivity of the products can be tuned by the alkyne and the metal. Mechanistic studies shows that the rate-limiting step is the formation of an actinide imido complex. For thorium, the imido intermediate has been characterized by standard techniques, including X-ray diffraction.

The addition of an N−H bond to an alkene or alkyne to form an alkylated amine, enamine, or imine is a fundamental process in organic chemistry.[1,2] The catalytic *intramolecular* hydroamination/cyclization of aminoolefins,[3] and recently aminoalkynes,[4] has been achieved with a variety number of catalysts under mild conditions. However, *intermolecular* catalytic processes for olefins was only been observed for one system[5] whereas, for internal alkynes, catalytic intermolecular hydroamination has been accomplished only with aromatic amines and zirconocene bis(amides).[6] Marks et al. have shown in the accompanying article that organolanthanides are effective catalysts for the alkene and internal alkyne *intermolecular* hydroamination with aliphatic amines.[7] For terminal alkynes, the intermolecular hydroamination was previously not available. We recently reported that organoactinide carbyl complexes are efficient catalysts for the selective oligomerization of terminal alkynes.[8] Expanding this rich homogeneous catalytic chemistry, we report here the reactivity and selectivity of some well-defined actinide-carbyl catalysts with various monosubstituted alkynes and aliphatic amines as well as the solid-state characterization of the actinide−imido complex, a key intermediate in the catalytic cycle for the intermolecular hydroamination of terminal alkynes. Reaction of $Cp^*_2UMe_2$ ($Cp^* = C_5Me_5$) with an excess of amine and alkyne (benzene-d_6, 80 °C, ∼24 h, 420:420:1 amine:alkyne:$Cp^*_2UMe_2$ ratio) results in the regioselective catalytic formation of imines (**1**−**7**)[9] and traces of alkyne oligomerization products (eq 1).[10] For $HC{\equiv}CSiMe_3$, the



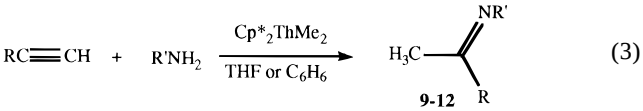
(1)

1 R = TMS, R' = Me (95%) **5** R = t-Bu, R' = Me (95%)
2 R = TMS, R' = Et (95%) **6** R = t-Bu, R' = Et (95%)
3 R = n-Bu, R' = Me (70%) **7** R = Ph, R' = Et (50%)
4 R = n-Bu, R' = Et (95%)



(2)

8



(3)

9-12

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

organic imine undergoes an uncatalized 1,3-shift of the silyl group producing enamine **8** (eq 2).[11] The $Cp^*_2ThMe_2$ analogue reacts similarly with $Me_3SiC{\equiv}CH$ and $MeNH_2$ or $EtNH_2$, producing imines **1** and **2**, respectively. With $HC{\equiv}CH$ and $EtNH_2$, imine **9** is obtained with traces of the oligomerization products. However, with *n*-$BuC{\equiv}CH$ or $PhC{\equiv}CH$ and methyl- or ethylamine, a dramatic change in the regioselectivity takes place yielding the unexpected imines **10**−**12**, respectively, with various amounts of the dimerized alkyne (eq 3).[10]

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1996.

(1) (a) For a review of additions of amines to alkenes, see: Gasc, M. B.; Latties, A.; Perie, J. J. *Tetrahedron* **1983**, *339*, 703. (b) For a review of addition of amines to alkynes, see: Jäger, V.; Viehe, H. G. *Houben-Weyl, Methoden der Organischen Chemie*; Thieme Verlag: Stuttgart, Germany, 1977; Vol. 5/2a, p 713.

(2) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapters 7.4, 17.1 and references therein. (b) Nugent, W. A.; Mayer, J. A. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

(3) (a) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241−10234. (b) Gagné, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275−294. (c) Hegedus, L. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1113−1114.

(4) (a) Li, Y.; Fu, P.-F.; Marks, T. J. *Organometallics* **1994**, *13*, 439−440. (b) McGrane, P. L.; Livinghouse, T. *J. Am. Chem. Soc.* **1993**, *115*, 11485−11489. (c) McGrane, P. L.; Jensen, M.; Livinghouse, T. *J. Am. Chem. Soc.* **1992**, *114*, 5459−5460.

(5) Casalnuovo, A. L.; Calabbreses, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738−6740.

(6) (a) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708−1719. (b) Baranger, A. M.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 2753−2763 and references therein.

(7) Li, Y.; Marks, T. J. *Organometallics* **1996**, *15*, 3770.

(8) Straub, T.; Haskel, A.; Eisen, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 6364−6365.

(9) In compounds **1**−**12**, known products were identified by comparison with literature data[9a,b] and new compounds were characterized by ^1H, ^{13}C, GC/MS, and high-resolution MS spectroscopy; see Supporting Information. (a) Fry, J. L. *J. Chem. Soc., Chem. Commun.* **1974**, 45. (b) Karabatsos, G. L.; Lande, S. S. *Tetrahedron* **1968**, *24*, 3907−3922.

(10) Haskel, A.; Straub, T.; Eisen, M. S. Manuscript in preparation.

(11) (a) Hitchcock, P. B.; Lappert, M. F.; Liu, D. S. *J. Chem. Soc., Chem. Commun.* **1994**, 1699. (b) Eisen, M. S.; Kapon, M. *J. Chem. Soc., Dalton Trans.* **1994**, 3507.

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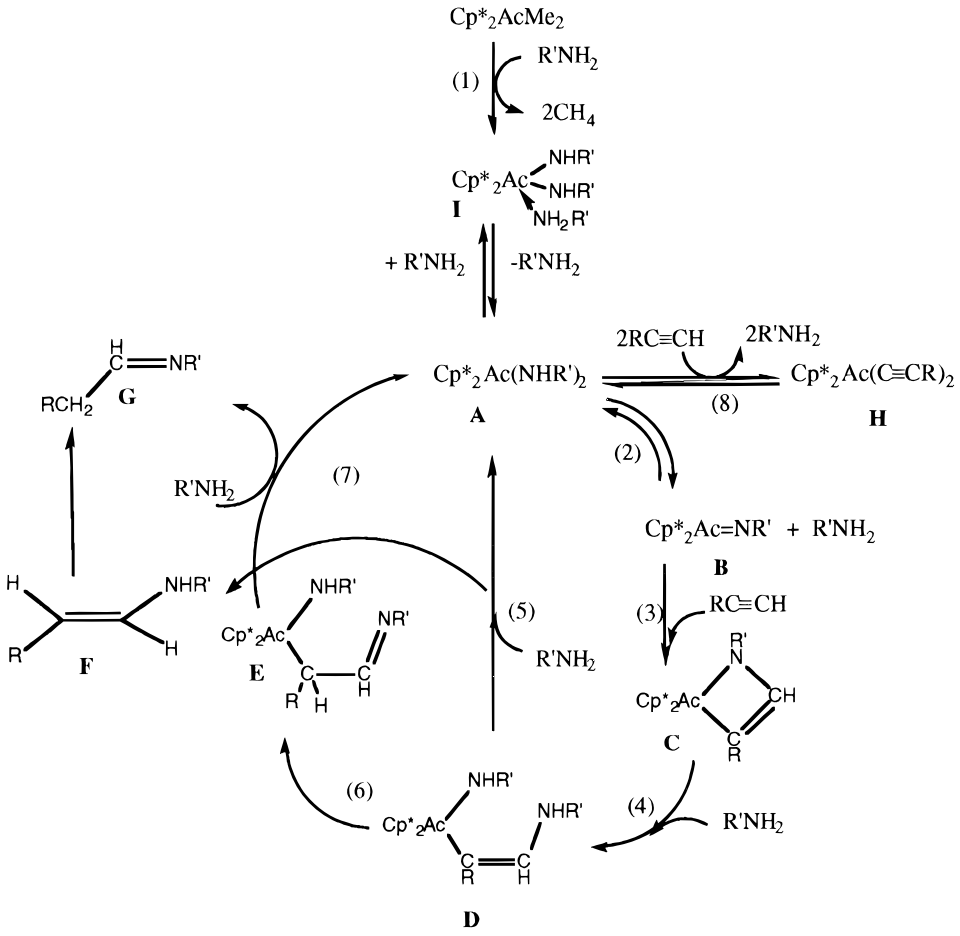
Scheme 1



A plausible reaction mechanism for the intermolecular hydroamination of terminal alkynes with aliphatic amines is given in Scheme 1. The first step in the catalytic cycle involves N−H σ-bond activation by the organoactinide[12] and formation of CH_4 as observed by NMR together with an organoactinide bis(amido)−amine complex $Cp^*_2Ac(NHR)_2{\cdot}H_2NR$ (**I**)[13] (step 1) which is in rapid equilibrium with the bis(amido) complex (**A**).[14] Complex **A** may follow two competitive equilibration pathways. The first, σ-bond metathesis with the terminal alkyne to yield complex **H** (step 8) will induce the production of oligomerization products.[15] In the second, *as the rate-determining step*, the elimination of an amine molecule produces the corresponding imido complex $Cp^*_2Ac{=}NR'$ (**B**) (step 2). Although crystals of a base-free imido complex suitable for diffraction were not obtained, crystals of a mono-THF adduct (**13**) could be grown in a toluene/hexane mixture using a bulky R′ group (R′ = 2,6-dimethylphenyl) (Figure 1).[16] Interestingly, the structure of complex **13** shows that the imido ligand is essentially linear with a Th−N−C bond angle of 171.5(7)°. This indicates that the ligand is acting as a four-electron donor making complex **13** formally a 20-electron complex. As a result, the Th−N bond length of 2.045(8) Å is ∼0.22 Å shorter than in the corresponding bis(amido) analogue, although it is ∼0.093 Å longer than a similar base-free uranium imido.[13,17] Imido complex **B** undergoes a rapid double bond metathesis with an incoming alkyne with the substituent group oriented toward the metal (*anti* fashion) to yields metallacycle **C** (step 3). Rapid protonolytic ring-opening

(12) Thermodynamically, the enthalpy for this step can be calculated to be exothermic for both actinides (ΔH(Th) ≈ −17 kcal/mol and ΔU(U) ≈ −9 kcal/mol). (a) Giardello, M. A.; King, W. A.; Nolan, S. P.; Porchia, M.; Sishta, C.; Marks, T. J. In *Energetics of Organometallic Species*; Simões, M. J. A., Ed.; Kluwer Academic Press: Dordrecht, The Netherlands, 1992; pp 35−51 and references therein. (b) Simões, M. J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629−688.

(13) For lanthanides, analog complexes have been characterized, see refs 3a,b. Attempts of trapping complex **I** at low temperatures have been unsuccessful.

(14) (a) Characterization, solid-state structure, and reactivity toward alkynes of a bis(amido) complex **A** (Ac = U; R = 2,6-dimethylphenyl): Straub, T.; Frank, W.; Reiss, G. J.; Eisen, M. S. *J. Chem. Soc., Dalton Trans.*, in press. (b) Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206−2220.

(15) Pathway to complex **H** (step 8) was observed for Th complexes inducing the production of selective oligomers. For uranium complexes, this equilibrium pathway involving the bis(amido)/bis(acetylide) complex is not observed.

(16) To a stirred solution of $Cp^*_2ThMe_2$ (0.5 g, 9.4×10^{-4} mol) in 20 mL of THF was added 2,6-dimethylaniline (0.136 g, 9.4×10^{-4} mol) at −78 °C. The yellow solution was allowed to warm to room temperature (55 min) and refluxed for 14 h. The THF was removed under reduced pressure leaving a yellow microcrystalline solid. The solid was dissolved in 10 mL of toluene and layered with 30 mL of hexane at 65 °C. Slow cooling to room temperature yields (48%) yellow crystals of **13** (310 mg, 4.47×10^{-4} mol) after 2 h. ^{1}H-NMR data for **13** [C_6D_6, 293 K, δ]: 7.32 (d, 2 H, $^3J_{HH}$ = 7.3 Hz), 6.66 (t, 1 H, $^3J_{HH}$ = 7.3 Hz), 3.78 (br, 4 H, THF), 1.99 (s, 30 H, Cp*-Me), 1.93 (s, 6 H, Ar-*Me*), 1.30 (br, 4 H, THF). ^{13}C-NMR data [benzene-d_6 and THF-d_8, 293 K, δ]: 128.2, 127.3, 123.0, 113.6, 73.1 (THF), 25.5 (Cp*-Me), 22.4 (THF), 11.6 (CH_3). Anal. Calcd for $C_{32}H_{47}NOTh$: C, 55.41; H, 6.78. Found: C, 55.22; H, 6.81. Cryoscopic measurements on compound **13** in C_6H_6 gave M_r = 857 (calcd = 693). Crystal data for monomeric imido complex **13**: *C*2/*c*, V = 11969(3) Å^3, Mo Kα (λ = 0.710 69 Å) μ = 50.33 cm^{-1}, d_{calc} = 1.540 g cm^{-1}, a = 63.911(8) Å, b = 11.041(2) Å, c = 16.987(4) Å, T = −120.0 °C, Z = 8; the final residuals for 631 variables refined against the 5748 data for which $I > 3\sigma(I)$ were R = 0.037, R_w = 0.033, and GOF = 1.53.

(17) For a base-free uranium−imido complex see: Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 9448−9460.

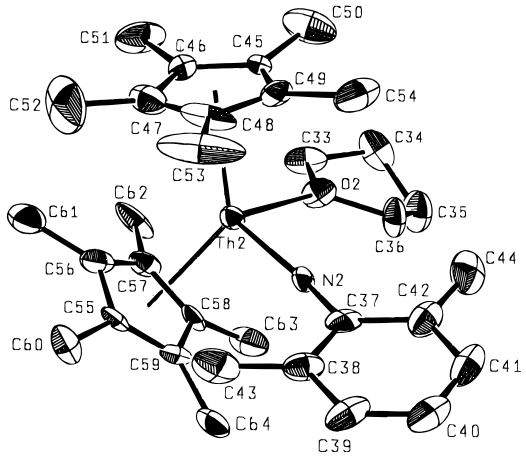


Figure 1. Perspective ORTEP drawing of the non-hydrogen atoms of Cp*Th=NR·THF (R = 2,6-dimethylphenyl) (**13**). All atoms are represented by thermal ellipsoids drawn to encompass 50% of the electron density.

of complex **C** by an amine yields the enamine amido organoactinide complex **D** (step 4).[18] Complex **D** may either react with an amine to yield the starting bis(amido) complex **A** by elimination of enamine (**F**) (step 5) that will rapidly isomerize to the more stable imine (**G**)[19] or form complex **E** by a 1,3 shift of the hydrogen atom of the amine in the enamine complex (step 6). The subsequent reaction of complex **E** with amine eliminates the imine (**G**) reproducing the bis(amido) complex **A** (step 7). Both σ-M−C(sp^2) and σ-M−C(sp^3) protonolytic processes (steps 5 and 7) have catalytic precedents.[8,20] For the intermolecular hydroamination of terminal alkynes these pathways are rapid and cannot be distinguished.

For the thorium cycle, the regioselectivity of insertion in step 3 is dependent on the alkyne yielding the *unexpected imine* formed by the insertion of the alkyne with the substituent group pointing away from the metal (*syn* fashion) with large amounts of oligomeric dimer formation (eq 3).[8] This result argues that, for thorium, the equilibrium constant for the imido formation (step 2) is much smaller than the competing acetylide formation constant (step 8) in Scheme 1.[10]

Kinetic measurements[21] for the uranium-catalyzed processes for ethylamine and TMSC≡CH yield rate law (4),

$$v = k[\mathrm{Ac(NHR')_2}]^1[\mathrm{alkyne}]^0[\mathrm{amine}]^{-1} \qquad (4)$$

which is compatible with rapid reversible bis(amido)−amine−bis(amido) equilibrium, turnover-limiting imido formation (step 2), and rapid operationally irreversible N−H bond activation (steps 4 and 5 or 7).[10] Mechanistically, the absence of accessible metal oxidation states for oxidative addition/reduction elimination processes implicate a "four-center" heterolytic metal−carbon transition bond cleavage.

The combined observation of our group and Marks' indicate that organo-f-elements exhibit rich, complementary, and potentially useful ranges of catalytic hydroamination chemistries. These studies also suggest that it may be possible to generate different isolobal actinides which are likely to be even more reactive than their imido analogues. Efforts aimed at achieving these goals are underway.

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Supporting Information Available: Text describing synthetic, spectroscopic, and analytical data for compounds **1**−**12**, figures showing kinetic data and plots, and X-ray experimental details for complex **13** including tables of positional and anisotropic displacement parameters and bond lengths and angles (39 pages). Ordering information is given on any current masthead page.

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(18) The Th−alkenyl bond is stronger than the Th−N bond by ≈10 kcal/mol; see ref 10.

(19) ΔH_f data are not available to compare the thermodynamics of amine addition to olefins versus that to alkynes. However, the addition of NH_3 to acetylene is estimated to be ≈14 kcal more exothermic than that to ethylene. AM1 semi-empirical calculations show that the imine formed with $MeNH_2$ by the *anti*-addition of the alkyne is more stable than the corresponding enamine by the following: TMSC≡CH, ≈2.1 kcal/mol; *n*-BuC≡CH, ≈3.5 kcal/mol; PhC≡CH, ≈1.4 kcal/mol.

(20) (a) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *7*, 1828−1838. (b) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5515−5525.

(21) The same kinetic order in catalyst is obtained starting from the $Cp^*_2U(Me)_2$ or $Cp^*_2U(NHR')_2$ complexes. [Catalyst] = 0.015−0.078 M; [amine] = 0.70−4.26 M; [alkyne] = 0.75−4.20 M.