Articles

Intermolecular Hydroamination of Terminal Alkynes Catalyzed by Organoactinide Complexes. Scope and Mechanistic Studies

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Organoactinide complexes of the type $Cp^*_2AnMe_2$ (An = Th, U) have been found to be efficient catalysts for the hydroamination of terminal alkynes with aliphatic primary amines. The chemoselectivity and regioselectivity of the reactions depend strongly on the nature of the catalyst and the nature of the amine and show no major dependence on the nature of the alkyne. The hydroamination reaction of the terminal alkynes with aliphatic primary amines catalyzed by the organouranium complexes produces the corresponding imines where the amine and the alkyne are regioselectively disposed in a *syn*-regiochemistry, whereas for similar reactions with the organothorium complex besides the methyl alkylated imine, dimeric and trimeric alkyne oligomers are also produced. For (TMS)C≡CH and $EtNH_2$ both organoactinides produced the same imine compounds when the reaction is carried out in THF or toluene. In benzene, both imines *E* and *Z* $(TMS)CH_2CHN{=}Et$ are obtained, the earlier undergo a 1,3-silyl Brook sigmatropic rearrangement toward the enamine, whereas the latter remains unchanged. Mechanistic studies on the hydroamination of (TMS)C≡CH and $EtNH_2$ promoted by the organouranium complex show that the first step in the catalytic reaction is the formation of the bis(amido) complex, found in equilibrium with the corresponding bisamido−amine complex, which loses an amine, yielding a uranium−imido complex. Insertion of the alkyne into the imido bond with subsequent amine protonolysis, isomerization, and product release comprise the primary steps in the catalytic cycle. The kinetic rate law was found to follow an inverse kinetic order in amine, a first order in complex, and a zero order in alkyne, with $\Delta H^{\ddagger} = 11.7(3)$ kcal mol^{-1}, $\Delta S^{\ddagger} = -44.5(8)$ eu. The turnover-limiting step is the release of an amine from the bisamido complex yielding the imido complex. The key organoactinide intermediate for the intermolecular hydroamination reaction was found to be the corresponding actinide−imido complexes. For both actinides the complexes have been characterized, and for thorium the single-crystal X-ray diffraction was studied. A plausible mechanistic scenario is proposed for the hydroamination of terminal alkynes and aliphatic primary amines.

Introduction

During the past decade the chemistry of electrophilic d^0/f^n lanthanide and actinide metallocene complexes has been under intense investigation.[1−3] The use of these organo-f-complexes as catalysts to promote synthetically important organic transformations, where the crucial step is an insertion of an olefinic (alkene or alkyne) functionality into a metal−alkyl, metal−hydride, or metal−heteroatom bond, has grown exhibiting unique features.[3] For organolanthanides, such processes include hydrogenation,[4−6] oligomerization/polymerizations,[2,7−9] hydrosilylation,[10] hydrophosphination,[11] hydrobora-

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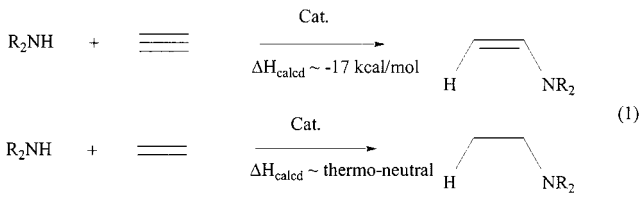
tion,[12] ring-opening Ziegler polymerization,[9,13] and silanolytic chain transfer in olefin polymerization.[8,14] For organoactinides, C−H activation,[15,16] hydrogenation,[17] dimerization,[18,19] oligomerization,[20] and hydrosilylation of terminal alkynes[21,22] comprise such processes. The catalytic C−N bond formation processes are of cardinal importance in organic chemistry, and olefin or alkyne hydroamination by catalytic N−H bond addition to unsaturated carbon−carbon multiple bonds represents a challenge and remains a highly desirable transformation (eq 1). The hydroamination reaction as presented in eq 1 is an atom-economic route with no byproducts.



(1)

Regarding thermodynamic considerations, the addition of amines to alkenes is approximately thermoneutral, whereas the corresponding addition to alkynes is calculated to be more favorable.[22,23] The negative entropy balance of the reaction hampers the use of high temperatures. Hence, a catalyst is required to accomplish such organic transformations. Two major routes have been utilized involving either amine or unsaturated carbon−carbon bond activations.[24] The amine activation route employs alkali and alkaline-earth metals to form nucleophilic moieties, which will then undergo addition to the unsaturated species. This first route achieves modest yields and low selectivities.[25] The second route uses late transition metals (e.g., Pd^{2+}, Rh^{+}), which activate the olefinic moiety by complexation, allowing a facile nucleophilic attack by the amine.[26] The transition-metal hydroamination route exhibits in general short catalyst lifetimes, low turnover frequencies, and/or limited reaction scope.[27−29]

In contrast to transition-metal complexes, organo-f-element complexes exhibit unique characteristics for the activation not only of unsaturated carbon−carbon multiple bonds but of amine groups as well. These characteristics include high electrophilicity of the metal centers, large ionic radii allowing high coordination numbers and coordinative unsaturation, spectator ancillary ligation, absence of the conventional oxidative-addition/reductive-elimination mechanism route, and facile bond activation through a concerted four-centered σ-bond metathesis. Organolanthanide complexes have been found to be extremely good catalysts for the *intramolecular* hydroamination/cyclization of aminoalkenes,[5,6,30]

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aminoalkynes,[31−33] and recently of aminoallenes.[34] Even enantioselective intramolecular aminations have been performed using chiral organolanthanide precatalysts.[6] The *intermolecular* hydroamination of olefins and alkynes, in principle, is the most enticing organic transformation. Such processes have not generally proven to be efficient and frequently lack generality and regioselectivity. Hence, the intermolecular functionalization of olefins and alkynes with amines in a regioselective mode has been mentioned as one of the 10 most important challenges in catalysis.[35] Among the studied intermolecular hydroamination processes of internal alkynes with aliphatic amines,[36] organolanthanides have shown to be active catalysts, although proceeding with very low turnover numbers (TON = 2).[33] Early transition titanocene- and zirconocene-(bisamide) complexes also have been used for the hydroamination of internal alkynes with aromatic amines,[28,29] whereas for terminal alkynes and aliphatic amines, the intermolecular hydroamination was previously not available.

We recently reported that organoactinide hydrocarbyl complexes are efficient catalysts for the oligomerization and cross oligomerization of terminal alkynes.[20,37] In addition, we have shown that the addition of a chain transfer agent during the catalytic oligomerization allows the selective and regiospecific production of dimers and/or trimers.[18,19] Expanding this rich homogeneous catalytic chemistry, in this contribution we report the synthesis and characterization of well-defined amido and imido organoactinide complexes and their reactivity for the intermolecular hydroamination of terminal alkynes with primary amines.[38,39] We present a full account of the reaction scope, substrate substituent effect, metal effect, trapping of the key organometallic intermediate in the catalytic cycle, and the kinetics and mechanistic aspects of the catalytic process.

Experimental Section

Materials and Methods. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line or interfaced to a high-vacuum (10^{-5} Torr) line or in a nitrogen-filled Vacuum Atmospheres glovebox with a medium capacity recirculator (1−2 ppm O_2). Argon, acetylene, and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieves column. Ether solvents were distilled under argon from sodium benzophenone ketyl. Hydrocarbon and deuterated solvents (THF-d_8, toluene-d_8, benzene-d_6, cyclohexane, and cyclohexane-d_{12}) were distilled under nitrogen from Na/K alloy. All solvents for vacuum line manipulations were stored in vacuo over Na/K alloy in resealable bulbs. Acetylenic compounds (Aldrich) were dried and stored over activated molecular sieves (4 Å), degassed, and freshly vacuum-distilled. Amines (Fluka) were dried over Na/K alloy and stored over activated molecular sieves (4 Å). $Cp^*_2AnMe_2$ (Th, U), Cp^*_2-Th(Cl)Me, $Cp^*_2U(NHR)_2$ (R = 2,6-dimethylphenyl, *t*-Bu, Et, Ph), and $Cp^*_2An(C{\equiv}CR)_2$ (R = TMS, *t*-Bu, Ph) were prepared according to published procedures.[18,20,22,40] NMR spectra were recorded on Bruker AM 200 MHz and Bruker AM 400 MHz spectrometers. Chemical shifts for ^{1}H NMR and ^{13}C NMR are referenced to internal solvent resonances and are reported relative to tetramethylsilane. GC/MS experiments were conducted in a GC/MS (Finnigan Magnum) spectrometer. Preparative GC was conducted in a Varian GC equipped with a 0.25 in. diameter copper column with 20% Carbowax 20M on Cromosorb W. Molecular weight determinations were performed using a cryoscopic Knauer Cryo equipment, in benzene. The NMR experiments were conducted in Teflon valve-sealed tubes (J-Young) after vacuum transfer of the liquids in a high-vacuum line. All toxic materials were disposed in accordance with *Prudent Practices for Disposal of Chemicals from Laboratories*; National Academy Press: Washington, DC, 1983.

General Procedure for the Catalytic Intermolecular Hydroamination of Terminal Alkynes. In a typical procedure, the specific amount of an alkyne and an equimolar amount of the respective amine were vacuum transferred in a high-vacuum line into a Schlenk tube containing a given amount of the precatalysts, $Cp^*_2AnMe_2$ (An = U, Th), in a denoted amount of the corresponding solvent. For $MeNH_2$ and $EtNH_2$ (low boiling point amines), a heavy glass Schlenk flask, suitable for high-pressure reactions, was used and a J-Young stopcock sealed the reaction vessel. Amounts of gaseous amines and alkynes were measured in their liquid state by cooling the gases on a (high-pressure) buret before transferring to the reaction Schlenk flask. The Schlenk tube was heated by means of a thermostatic oil bath (±0.1 °C), during a particular amount of time. The solvent was removed by vacuum, and the products were isolated through vacuum distillation (preparative yields are also reported). J-Young NMR tubes were filled into the glovebox. The percentage of the converted products is given related to the starting alkyne as measured either by preparatory or by analytical GC chromatography and by NMR spectroscopy depending on the number of products before the distillation of the product. In all the reactions, the volatiles and the residue were identified by ^{1}H, ^{13}C, and 2D (COSY, C−H correlation, NOESY) NMR spectroscopy and GC/MS spectroscopy and by comparing with compounds known in the literature.

Kinetic Study of the Hydroamination Reaction. In a typical experiment, a J-Young NMR sample was prepared by transferring the specific amounts of amine, alkyne, and the organoactinide into the tube containing the appropriate amount of the corresponding solvent. The sealed tube was maintained at −78 °C until kinetic measurements were initiated. The sealed tube was heated in a temperature-controlled oil bath, and at time intervals NMR data were acquired using eight scans per time interval with a long pulse delay to avoid saturation of the signal. The conversion was measured by following the intensity of the acetylenic hydrogen of the alkyne. The kinetic studies were usually monitored by the intensity changes in both the substrate resonances and in the product resonances over 3 or more half-lives. The substrate concentration [*C*] was measured from the area (A_s) of the ^{1}H-normalized signal of the solvent (A_b). All the data collected could be convincingly fitted ($R > 0.98$) by least-squares to eqs 2 or 3, where C_0 ($C_0 = A_{so}/A_{bo}$) is the initial concentration of substrate, and $C(A_s/A_b)$ is the substrate concentration at time *t*.

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$$mt = \log(C/C_0) \quad (2)$$

$$\frac{1}{C} = \frac{1}{C_0} + mt \quad (3)$$

The ratio of catalyst to substrate was accurately measured by calibration with internal $FeCp_2$. Turnover frequencies (N_t, h^{-1}) were calculated from the least-squares determined slopes (m) of the resulting plots. The range of concentrations that were kinetically studied for the initial amine concentrations was between 0.029 and 0.31 M, initial alkyne concentrations were in the range 0.097−3.84 M, and typical initial catalyst concentrations were in the range 1.0−150.0 mM.

(1) Hydroamination of TMSC≡CH with $MeNH_2$ by $Cp^*_2UMe_2$. According to the general procedure, 1.0 mL (7.0 mmol) of TMSC≡CH and 0.3 mL (7.0 mmol) of $MeNH_2$ were reacted with 53 mg (0.1 mmol) of $Cp^*_2UMe_2$ in 5 mL of benzene. The reaction mixture was heated to 78 °C for 22 h to obtain the imine **1** in 97% conversion and 95% yield. Bp_{20} = 71−74 °C. NMR data of **1**. ^{1}H NMR {400 MHz, benzene-d_6, 293 K}: δ 7.45 (m, 1 H, $^3J_{HH}$ = 4.9 Hz; $^4J_{HH}$ = 1.3 Hz, C≡CH), 3.00 (m, 3H, $^4J_{HH}$ = 1.3 Hz; $^5J_{HH}$ = 1.3 Hz, NCH_3,), 1.70 (m, 2 H, $^3J_{HH}$ = 4.9 Hz; $^5J_{HH}$ = 1.3 Hz, CH_2−SiMe$_3$), 0.02 (s, 9 H, SiMe$_3$). ^{13}C NMR {100 MHz, benzene-d_6, 293 K}: δ 161.0 (d, J_{CH} = 152 Hz, *C*H), 47.4 (q, J_{CH} = 134 Hz, N*C*H$_3$), 21.7 (t, J_{CH} = 128 Hz, Si*C*H$_2$), 1.9 (q, J_{CH} = 118 Hz, Si*C*H$_3$). HRMS (*m*/*z*): {M$^+$} calcd for $C_6H_{15}NSi$ 129.0973, found 129.0959. Anal. Calcd for $C_6H_{15}NSi$: C, 55.74; H, 11.70; N, 10.83. Found: C, 55.94; H, 11.46; N, 10.47.

(2) Hydroamination of TMSC≡CH with $EtNH_2$ by $Cp^*_2UMe_2$. (a) According to the general procedure, 1.0 mL (7.0 mmol) of TMSC≡CH and 0.5 mL (7.5 mmol) of $EtNH_2$ were reacted with 53 mg (0.1 mmol) of $Cp^*_2UMe_2$ in 5 mL of THF. The reaction mixture was heated to 65 °C for 24 h to obtain the imine **2A** as the sole product in 97% conversion and 90% yield. Bp_{15} = 64−66 °C. NMR data of **2A**. ^{1}H NMR {400 MHz, THF-d_8, 293 K}: δ 7.65 (m, 1 H, $^3J_{HH}$ = 4.8 Hz; $^4J_{HH}$ = 1.2 Hz, C≡CH), 3.36 (m, 2 H, $^3J_{HH}$ = 7.1 Hz; $^4J_{HH}$ = 1.2 Hz, CH_2-CH$_3$), 1.87 (m, 2 H, $^3J_{HH}$ = 4.8 Hz; $^5J_{HH}$ = 1.2 Hz, CH_2−SiMe$_3$,), 1.04 (t, 3 H, $^3J_{HH}$ = 7.1 Hz, *C*H$_2$-*C*H$_3$), 0.07 (s, 9 H, SiMe$_3$). ^{13}C NMR {100 MHz, benzene-d_6, 293 K}: δ 158.0 (d, J_{CH} = 152 Hz, *C*H), 55.9 (t, J_{CH} = 137 Hz, CH_2-CH$_3$), 22.0 (t, J_{CH} = 136 Hz, SiCH$_2$), 16.5 (q, J_{CH} = 127 Hz, CH$_2$-*C*H$_3$), 1.8 (q, J_{CH} = 120 Hz, SiCH$_3$). HRMS (*m*/*z*): {M$^+$} calcd for $C_7H_{17}NSi$ 143.1130, found 143.1122. Anal. Calcd for $C_7H_{17}NSi$: C, 58.67; H, 11.96; N, 9.77. Found: C, 58.39; H, 11.66; N, 9.93.

(b) According to the general procedure, 2.0 mL (14.0 mmol) of TMSC≡CH and 1.0 mL (15 mmol) of $EtNH_2$ were reacted with 53 mg (0.1 mmol) of $Cp^*_2UMe_2$ in 5 mL of benzene. The reaction mixture was heated to 78 °C for 64 h to obtain a mixture of compounds **2A** and **2B** with 97% conversion containing 90% and 10% of **2A** and **2B**, respectively. The two isomers are separated using preparatory GC chromatography. The characterization for the *E* and *Z* isomers was obtained by two separate procedures: (1) NOE experiments between the vinylic hydrogen and the CH_2 group of the amine were performed; (2) both isomers were heated jointly and separately to obtain the rearrangement product **2C**, leaving the compound **2B** unchanged.

After the distillation less than 3% remains as a mixture of the TMSC≡CH dimer (**7A**) and trimer (**7B**), in a ratio of 5:1, respectively. These oligomers were characterized based on GC/MS and by comparison with clean compounds that were prepared as reported in the literature.[20] ^{1}H NMR of **2B** {400 MHz, THF-d_8, 293K}: δ 7.69 (m, 1 H, $^3J_{HH}$ = 4.8 Hz; $^4J_{HH}$ = 1.3 Hz, C≡CH), 2.77 (m, 2 H, $^3J_{HH}$ = 7.1 Hz, CH_2-CH$_3$), 1.95 (m, 2 H, $^3J_{HH}$ = 4.8 Hz, CH_2-SiMe$_3$), 1.05 (t, 3 H, $^3J_{HH}$ = 7.1 Hz, *C*H$_2$-*C*H$_3$), 0.08 (s, 9 H, SiMe$_3$). HRMS (*m*/*z*): {M$^+$} calcd for $C_7H_{17}NSi$ 143.1130, found 143.1119 Anal. Calcd for C_7H_{17}-NSi: C, 58.67; H, 11.96; N, 9.77. Found: C, 58.39; H, 11.68; N, 9.89.

(c) According to the general procedure, 6.0 mL (42.0 mmol) of TMSC≡CH and 3.0 mL (45 mmol) of $EtNH_2$ were reacted with 53 mg (0.1 mmol) of $Cp^*_2UMe_2$ in 10 mL of cyclohexane. The reaction mixture was heated to 78 °C for 237 h to obtain 97% conversion (95% yield) of **2A**.

(d) According to the general procedure, 3.0 mL (21.0 mmol) of TMSC≡CH and 1.5 mL (22 mmol) of $EtNH_2$ were reacted with 53 mg (0.1 mmol) of $Cp^*_2UMe_2$ in 5 mL of toluene. The reaction mixture was heated to 95 °C for 73 h to obtain 97% conversion (85:10:5% yield for **2A**:**2B**:**7B**, respectively).

(e) According to the general procedure, 1.0 mL (7.0 mmol) of TMSC≡CH and 0.5 mL (7.5 mmol) of $EtNH_2$ were reacted with 60 mg (0.1 mmol) of $Cp^*_2U(NHEt)_2$ in 5 mL of THF. The reaction mixture was heated to 65 °C for 24 h to obtain the imine **2A** as the sole product in 95% conversion and 89% yield.

(f) According to the general procedure, 1.0 mL (7.0 mmol) of TMSC≡CH and 0.5 mL (7.5 mmol) of $EtNH_2$ were reacted with 70 mg (0.1 mmol) of Cp^*_2U═NR(THF) (NR = 2,6-dimethylaniline) in 5 mL of THF. The reaction mixture was heated to 65 °C for 24 h to obtain the imine **2A** as the sole product in 94% conversion and 85% yield.

(3) Sigmatropic Rearrangement of the Imine 2A into the Enamine 2C. A Schlenk flask was charged with 1.2 g (8.37 mmol) of **2A** and 5 mL of THF. The reaction was refluxed and followed by GC chromatography. An aliquot of 10 μL was removed periodically and the normalized signal concentration of **2A** measured. The reaction was found to proceed slowly in THF, forming 60% of the rearrangement product after 41 days. Compound **2C** was purified by fractional distillation under reduced pressure. Bp_{20} = 47−52 °C. NMR data of **2C**. ^{1}H NMR {400 MHz, THF-d_8, 293 K}: δ 6.31 (dd, 1 H, $^3J_{HH}$ = 12.4 Hz, 7.9 Hz, C≡CH), 3.80 (d, 1 H, $^3J_{HH}$ = 12.4 Hz CH_2), 3.68 (d, 1 H, $^3J_{HH}$ = 7.9 Hz, CH_2), 3.13 (m, 2 H, $^3J_{HH}$ = 7.1 Hz; $^4J_{HH}$ = 1.2 Hz, CH_2−CH$_3$), 1.10 (t, 3 H, $^3J_{HH}$ = 7.1 Hz, *C*H$_2$-CH_3), 0.26 (s, 9 H, SiMe$_3$). ^{13}C NMR {100 MHz, benzene-d_6, 293 K}: δ 137.0 (d, J_{CH} = 164 Hz, *C*H), 95.9 (t, J_{CH} = 167 Hz, C = *C*H$_2$), 55.9 (t, J_{CH} = 127 Hz, *C*H$_2$CH$_3$), 16.5 (q, J_{CH} = 127 Hz, CH$_2$-*C*H$_3$), 1.8 (q, J_{CH} = 120 Hz, SiCH$_3$). HRMS (*m*/*z*): {M$^+$} calcd for $C_7H_{17}NSi$ 143.1130, found 143.1127. Anal. Calcd for C_7H_{17}-NSi: C, 58.67; H, 11.96; N, 9.77. Found: C, 58.24; H, 11.76; N, 9.59.

(4) Hydroamination of TMSC≡CH with *n*-$PrNH_2$ by $Cp^*_2UMe_2$. According to the general procedure, 3.0 mL (21 mmol) of TMSC≡CH and 2.0 mL (24 mmol) of *n*-$PrNH_2$ were reacted with 54 mg (0.1 mmol) of $Cp^*_2UMe_2$ in 6 mL of benzene. The reaction mixture was heated to 78 °C for 58 h to obtain the imine **3** as the sole product in 98% conversion and 95% yield. Bp_{25} = 74−76 °C. NMR data of **3**. ^{1}H NMR {400 MHz, THF-d_8, 293 K}: δ 7.45 (m, 1 H, $^3J_{HH}$ = 5.8 Hz; $^4J_{HH}$ = 1.2 Hz, C≡CH), 3.30 (m, 2 H, $^3J_{HH}$ = 7.1 Hz; $^4J_{HH}$ = 1.2 Hz, CH_2CH$_2$CH$_3$), 1.69 (d, 2 H, $^3J_{HH}$ = 5.8 Hz, CH_2-SiMe$_3$), 1.51 (m, 2 H, 3J_{HH} = 6.9 Hz, $^3J_{HH}$ = 6.4 Hz, CH$_2$*CH$_2$*CH$_3$), 0.85 (t, 3 H, $^3J_{HH}$ = 6.4 Hz, *C*H$_2$CH_3), 0.01 (s, 9 H, SiMe$_3$). ^{13}C NMR {100 MHz, benzene-d_6, 293 K}: δ 159.0 (d, J_{CH} = 151 Hz, *C*H), 64.5 (t, J_{CH} = 131 Hz, *C*H$_2$CH$_2$CH$_3$), 28.0 (t, J_{CH} = 129 Hz, CH$_2$*C*H$_2$CH$_3$), 25.0 (t, J_{CH} = 129 Hz, *C*H$_2$Si), 12.0 (q, J_{CH} = 125 Hz, CH$_2$CH$_2$*C*H$_3$), −1.0 (q, J_{CH} = 123 Hz, SiMe$_3$). HRMS (*m*/*z*): {M$^+$} calcd for $C_8H_{19}NSi$ 157.1286, found 157.1274. Anal. Calcd for $C_8H_{19}NSi$: C, 61.07; H, 12.17; N, 8.90. Found: C, 61.42; H, 11.88; N, 8.74.

(5) Hydroamination of TMSC≡CH with *i*-$PrNH_2$ by $Cp^*_2UMe_2$. According to the general procedure, 1.5 mL (10 mmol) of TMSC≡CH and 1.0 mL (11 mmol) of *i*-$PrNH_2$ were reacted with 52 mg (0.1 mmol) of $Cp^*_2UMe_2$ in 6 mL of benzene. The reaction mixture was heated to 78 °C for 190 h to obtain imine **4** in 98% conversion and 95% yield. Bp_{14} = 46−50 °C. NMR data of **4**. ^{1}H NMR {400 MHz, benzene-d_6}: δ 7.48 (t, 1 H, $^3J_{HH}$ = 6.0 Hz, C≡CH), 3.10 (h, 1 H, $^3J_{HH}$ = 6.3 Hz, CH(CH$_3$)$_2$), 1.67 (d, 2 H, $^3J_{HH}$ = 6.0 Hz, CH_2-SiMe$_3$), 1.12 (d, 6 H, $^3J_{HH}$ = 6.3 Hz, CH(CH_3)$_2$), −0.05 (s, 9 H, SiMe$_3$). ^{13}C NMR {100 MHz, benzene-d_6, 293 K}: δ157.4 (d, J_{CH} = 150

Hz, *C*H), 61.7 (d, J_{CH} = 134 Hz, *C*H(CH_3)$_2$), 26.4 (t, J_{CH} = 125 Hz, *C*H_2Si), 24.6 (q, J_{CH} = 127 Hz, CH(*C*H_3)$_2$), −1.0 (q, J_{CH} = 124 Hz, $SiMe_3$). HRMS (*m*/*z*): {M^+} calcd for $C_8H_{19}NSi$ 157.1286, found 157.1274. Anal. Calcd for $C_8H_{19}NSi$: C, 61.07; H, 12.17; N, 8.90. Found: C, 61.42; H, 12.48; N, 8.72.

(6) Hydroamination of TMSC≡CH with *n*-BuNH$_2$ by Cp*$_2$UMe$_2$. According to the general procedure, 1.0 mL (7.0 mmol) of TMSC≡CH and 0.7 mL (7.0 mmol) of *n*-BuNH$_2$ were reacted with 53 mg (0.1 mmol) of Cp*$_2$UMe$_2$ in 3 mL of THF. The reaction mixture was heated to 65 °C for 28 h to obtain imine **5** in 98% conversion and 93% yield. Bp_{10} = 59−63 °C. NMR data of **5**. ^{1}H NMR {200 MHz, THF-d_8}: δ 7.33 (t, 1 H, $^3J_{HH}$ = 5.7 Hz, C≡CH), 3.12 (t, 2 H, $^3J_{HH}$ = 6.4 Hz, CH_2(CH_2)$_2$-CH_3), 1.52 (d, 2 H, $^3J_{HH}$ = 5.7 Hz, CH_2-SiMe$_3$), 1.39 (m, 2 H, CH$_2$CH_2CH$_2$CH$_3$), 1.14 (m, 2 H, CH$_2$CH$_2$CH_2CH$_3$), 0.68 (t, 3 H, $^3J_{HH}$ = 7.2 Hz, (CH$_2$)$_3$CH_3), −0.15 (s, 9 H, $SiMe_3$). ^{13}C NMR {50 MHz, THF-d_8, 293 K}: δ 160.0 (d, J_{CH} = 151 Hz, *C*H), 61.5 (t, J_{CH} = 130 Hz, *C*H$_2$-SiMe$_3$), 33.7 (t, J_{CH} = 126 Hz, *C*H$_2$(CH$_2$)$_2$CH$_3$), 27.6, 20.7 (2t, J_{CH} = 126 Hz, CH$_2$(*C*H$_2$)$_2$CH$_3$), 14.0 (q, J_{CH} = 124 Hz, (CH$_2$)$_3$*C*H$_3$), −1.8 (q, J_{CH} = 123 Hz $SiMe_3$). HRMS (*m*/*z*): {M^+} calcd for $C_9H_{21}NSi$ 171.1443, found 171.1424. Anal. Calcd for $C_9H_{21}NSi$: C, 63.08; H, 12.35; N, 8.17. Found: C, 63.46; H, 12.01; N, 8.33.

(7) Hydroamination of TMSC≡CH with *i*-BuNH$_2$ by Cp*$_2$UMe$_2$. According to the general procedure, 1.5 mL (10.0 mmol) of TMSC≡CH and 1.0 mL (10.0 mmol) of *i*-BuNH$_2$ were reacted with 51 mg (0.1 mmol) of Cp*$_2$UMe$_2$ in 6 mL of benzene. The reaction mixture was heated to 78 °C for 110 h to obtain imine **6** in 95% conversion and 90% yield. Bp_{10} = 54−58 °C. NMR data of **6**. ^{1}H NMR {200 MHz, THF-d_8, 293 K}: δ 7.56 (t, 1 H, $^3J_{HH}$ = 5.6 Hz, C≡CH) 3.05 (d, 2 H $^3J_{HH}$ = 6.1 Hz, *CH*$_2$-*i*-Pr), 1.75 (m, 1 H, $^3J_{HH}$ = 6.4 Hz, C*H*(CH$_3$)$_2$), 1.69 (d, 2 H, $^3J_{HH}$ = 5.6 Hz, CH_2-SiMe$_3$), 0.82 (d, 6 H, $3J_{HH}$ = 6.3 Hz, CH(CH_3)$_2$), 0.0 (s, 9 H, $SiMe_3$). ^{13}C NMR data {50 MHz, THF-d_8, 293 K}: δ 162.0 (d, J_{CH} = 151 Hz, *C*H), 71.5 (t, J_{CH} = 132 Hz, *C*H$_2$-CH(CH$_3$)$_3$), 31.6 (d, J_{CH} = 127 Hz, CH$_2$*C*H(CH$_3$)$_3$), 29.0 (t, J_{CH} = 123 Hz, *C*H$_2$SiMe$_3$), 22.2 (q, J_{CH} = 125 Hz, CH-(*C*H$_3$)$_2$), −0.06 (q, J_{CH} = 121 Hz, $SiMe_3$). HRMS (*m*/*z*): {M^+} calcd for $C_9H_{21}NSi$ 171.1443, found 171.1441. Anal. Calcd for $C_9H_{21}NSi$: C, 63.08; H, 12.35; N, 8.17. Found: C, 63.22; H, 12.25; N, 8.06.

(8) Oligomerization of TMSC≡CH to 7A and 8A by Cp*$_2$UMe$_2$. According to the general procedure, 4.0 mL (28.0 mmol) of TMSC≡CH and 2.5 mL (25.0 mmol) of *t*-BuNH$_2$ were reacted with 54 mg (0.1 mmol) of Cp*$_2$UMe$_2$ in 10 mL of THF. The reaction mixture was heated to 65 °C for 28 h to obtain a mixture of dimer (**7A**) and trimer (**8A**) in a 1:9 ratio, respectively. For full characterization of the products see ref 20.

(9) Hydroamination of *t*-BuC≡CH with MeNH$_2$ by Cp*$_2$UMe$_2$. As described in the general procedure, 0.9 mL (7.0 mmol) of *t*-BuC≡CH and 0.3 mL (7.0 mmol) of MeNH$_2$ were reacted with 51 mg (0.1 mmol) of Cp*$_2$UMe$_2$ in 6 mL of benzene. The reaction mixture was heated to 78 °C for 17 h to obtain imine **9** in 95% conversion and 90% yield. Bp_{15} = 57−58 °C. NMR data of **9**. ^{1}H NMR {400 MHz, benzene-d_6, 293 K}: δ 7.52 (m, 1 H, $^3J_{HH}$ = 5.4 Hz; $^4J_{HH}$ = 1.5 Hz, C≡CH), 3.16 (m, 3 H, $^4J_{HH}$ = 1.5 Hz; $^5J_{HH}$ = 1.0 Hz, NCH_3), 2.07 (d, 2 H, $^3J_{HH}$ = 5.4 Hz, CH_2), 0.89 (s, 9 H, *t*-Bu). ^{13}C NMR {100 MHz, benzene-d_6, 293 K}: δ 163.3 (d, J_{CH} = 151 Hz, *C*H), 49.6 (t, J_{CH} = 132 Hz, *C*H$_2$), 48.0 (q, J_{CH} = 132 Hz, NCH_3), 30.8 (s, *C*CH$_3$), 29.7 (q, C*C*H$_3$, J_{CH} = 125 Hz). HRMS (*m*/*z*): {M^+} calcd for $C_7H_{15}N$ 113.1204, found 113.1195. Anal. Calcd for $C_7H_{15}N$: C, 74.27; H, 13.36; N, 12.37. Found: C, 74.04; H, 13.54; N, 12.40.

(10) Hydroamination of *t*-BuC≡CH with EtNH$_2$ by Cp*$_2$UMe$_2$. As described in the general procedure, 2.5 mL (20.0 mmol) of *t*-BuC≡CH and 1.5 mL (22.0 mmol) of EtNH$_2$ were reacted with 53 mg (0.1 mmol) of Cp*$_2$UMe$_2$ in 6 mL of THF. The reaction mixture was heated to 65 °C for 58 h to obtain imine **10** in 98% conversion and 93% yield. Bp_{18} = 65−69 °C. NMR data of **10**. ^{1}H NMR {200 MHz, THF-d_8, 293 K}: δ 7.75 (t, 1 H, $^3J_{HH}$ = 5.4 Hz, C≡C*H*), 3.38 (q, 2 H, $^3J_{HH}$ = 7.1 Hz, CH_2CH$_3$), 2.13 (d, 2 H, $^3J_{HH}$ = 5.4 Hz, CH_2-*t*-Bu), 1.18 (t, 3 H, $^3J_{HH}$ = 7.1 Hz, CH$_2$CH_3), 1.00 (s, 9 H, C(CH_3)$_3$). ^{13}C NMR {50 MHz, THF-d_8, 293 K}: δ 151.0 (d, J_{CH} = 162.2 Hz, *C*H), 57.6 (t, J_{CH} = 132 Hz, *C*H$_2$CH$_3$), 50.9 (t, J_{CH} = 129 Hz, *t*-Bu-*C*H$_2$), 32.6 (s, *C*), 31.0 (q, J_{CH} = 125 Hz, C(*C*H$_3$)$_3$), 26.5 (q, J_{CH} = 126 Hz, CH$_2$*C*H$_3$). HRMS (*m*/*z*): {M^+} calcd for $C_8H_{17}N$ = 127.1361, found 127.1349. Anal. Calcd for $C_8H_{17}N$: C, 75.52; H, 13.47; N, 11.01. Found: C, 75.43; H, 13.65; N, 10.91.

(b) As described in the general procedure, 2.5 mL (20.0 mmol) of *t*-BuC≡CH and 1.5 mL (22.0 mmol) of EtNH$_2$ were reacted with 58 mg (0.1 mmol) of Cp*$_2$U(NHEt)$_2$ in 6 mL of THF. The reaction mixture was heated to 65 °C for 58 h to obtain imine **10** in 93% conversion and 86% yield.

(c) As described in the general procedure, 2.5 mL (20.0 mmol) of *t*-BuC≡CH and 1.5 mL (22.0 mmol) of EtNH$_2$ were reacted with 70 mg (0.1 mmol) of Cp*$_2$U═NR·(THF) (NR = 2,6-dimethylanilide) in 6 mL of THF. The reaction mixture was heated to 65 °C for 58 h to obtain imine **10** in 91% conversion and 82% yield.

(11) Hydroamination of *t*-BuC≡CH with *n*-PrNH$_2$ by Cp*$_2$UMe$_2$. As described in the general procedure, 1.2 mL (10.0 mmol) of *t*-BuC≡CH and 0.8 mL (10.0 mmol) of *n*-PrNH$_2$ were reacted with 52 mg (0.1 mmol) of Cp*$_2$UMe$_2$ in 6 mL of benzene. The reaction mixture was heated to 78 °C for 41 h to obtain imine **11** in 98% conversion and 91% yield. Bp_{20} = 77−84 °C. NMR data of **11**. ^{1}H NMR {400 MHz, benzene-d_6, 293 K}: δ 7.48 (m, 1 H, $^3J_{HH}$ = 5.4 Hz; $^4J_{HH}$ = 1.3 Hz, C≡C*H*), 3.32 (m, 2 H, $^3J_{HH}$ = 7.4 Hz; $^4J_{HH}$ = 1.3 Hz, CH_2CH$_2$CH$_3$), 2.05 (d, 2 H, $^3J_{HH}$ = 5.4 Hz, CH_2-*t*-Bu), 1.55 (m, 2 H, $3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 6.7 Hz, CH$_2$CH_2CH$_3$), 0.89 (s, 9 H, CMe$_3$), 0.87 (t, 3 H, $^3J_{HH}$ = 6.7 Hz, CH$_2$CH_3). ^{13}C NMR {100 MHz, benzene-d_6, 293 K}: δ 161.0 (d, J_{CH} = 151 Hz, *C*H), 63.8 (t, J_{CH} = 134 Hz, *C*H$_2$CH$_2$CH$_3$), 49.5 (t, J_{CH} = 134 Hz, *C*H$_2$-*t*-Bu), 30.9 (s, *C*CH$_3$), 29.5(q, J_{CH} = 124 Hz, C*C*H$_3$), 24.5 (t, J_{CH} = 126 Hz, CH$_2$*C*H$_2$CH$_3$), 12.0 (q, J_{CH} = 126 Hz, CH$_2$CH$_2$*C*H$_3$). HRMS (*m*/*z*): {M^+} calcd for $C_9H_{19}N$ 141.1517, found 141.1510. Anal. Calcd for $C_9H_{19}N$: C, 76.53; H, 13.56; N, 9.92. Found: C, 76.79; H, 13.70; N, 10.01.

(12) Hydroamination of *t*-BuC≡CH with *i*-PrNH$_2$ by Cp*$_2$UMe$_2$. (a) As described in the general procedure, 1.6 mL (13.0 mmol) of *t*-BuC≡CH and 1.0 mL (12.0 mmol) of *i*-PrNH$_2$ were reacted with 53 mg (0.1 mmol) of Cp*$_2$UMe$_2$ in 6 mL of THF. The reaction mixture was heated to 65 °C for 210 h to obtain imine **12** in 65% conversion and 55% yield. Bp_{25} = 78−80 °C. NMR data of **12**. ^{1}H NMR {200 MHz, THF-d_8, 293 K}: δ 7.49 (t, 1 H, $^3J_{HH}$ = 5.6 Hz, C≡C*H*), 3.05 (h, 1 H, $^3J_{HH}$ = 6.4 Hz, C*H*(CH$_3$)$_2$), 1.95 (d, 2 H, $^3J_{HH}$ = 5.6 Hz, CH_2-*t*-Bu), 0.93 (s, 9 H, CMe$_3$), 0.79 (d, 6 H, $^3J_{HH}$ = 6.4 Hz, CH(CH_3)$_2$). ^{13}C NMR {50 MHz, THF-d_8, 293 K}: δ 160.0 (d, J_{CH} = 152 Hz, *C*H), 63.0 (d, J_{CH} = 134 Hz, *C*H(CH$_3$)$_3$), 50.4 (t, J_{CH} = 126 Hz, *C*H$_2$-*t*-Bu), 32.1 (s, *C*CH$_3$), 29.7 (q, J_{CH} = 125 Hz, C*C*H$_3$), 27.2 (q, J_{CH} = 128 Hz, CH(*C*H$_3$)$_2$). HRMS (*m*/*z*): {M^+} calcd for $C_9H_{19}N$ 141.1517, found 141.1504. Anal. Calcd for $C_9H_{19}N$: C, 76.53; H, 13.56; N, 9.92. Found: C, 76.21; H, 13.32; N, 9.77.

(b) When the same reaction as in (a) is carried out in benzene, and the reaction mixture was heated to 78 °C for 130 h to obtain the imine **12** in 55% conversion.

(13) Hydroamination of *t*-BuC≡CH with *n*-BuNH$_2$ by Cp*$_2$UMe$_2$. (a) As described in the general procedure, 0.9 mL (7.0 mmol) of *t*-BuC≡CH and 0.7 mL (7.0 mmol) of *n*-BuNH$_2$ were reacted with 50 mg (0.1 mmol) of Cp*$_2$UMe$_2$ in 6 mL of THF. The reaction mixture was heated to 65 °C for 38 h to obtain imine **13** in 95% conversion and 84% yield. Bp_{25} = 86−94 °C. NMR data of **13**. ^{1}H NMR {400 MHz, THF-d_8}: δ 7.51 (m, 1 H, $^3J_{HH}$ = 5.4 Hz, $^4J_{HH}$ = 1.3 Hz, C≡C*H*), 3.32 (t, 2 H, $^3J_{HH}$ = 6.7 Hz, CH_2(CH$_2$)$_2$CH$_3$), 2.08 (d, 2 H, $^3J_{HH}$ = 5.4 Hz, CH_2-*t*-Bu), 1.60 (m, 2 H, CH$_2$CH_2CH$_2$CH$_3$), 1.32 (m, 2 H, CH$_2$-CH$_2$CH_2CH$_3$), 0.88 (s, 9 H, *t*-Bu), 0.87 (t, 3 H, $^3J_{HH}$ = 7.0 Hz, (CH$_2$)$_3$CH_3). ^{13}C NMR {50 MHz, THF-d_8, 293 K}: δ 161.5 (d, J_{CH} = 151 Hz, *C*H), 61.7 (t, J_{CH} = 132 Hz, *C*H$_2$-*t*-Bu), 49.5 (t,

J_{CH} = 127 Hz, $CH_2(CH_2)_2CH_3$), 33.6, 20.7 (2t, J_{CH} = 125 Hz, $CH_2(CH_2)_2CH_3$), 29.7 (q, *t*-Bu), 14.0 (q, J_{CH} = 120 Hz, $(CH_2)_3CH_3$). HRMS (*m*/*z*): {M^+} calcd for $C_{10}H_{21}N$ 155.1674, found 155.1653. Anal. Calcd for $C_{10}H_{21}N$: C, 77.35; H, 13.63; N, 9.02. Found: C, 77.17; H, 13.47; N, 8.84.

(14) Hydroamination of *t*-BuC≡CH with *i*-BuNH$_2$ by Cp*$_2$UMe$_2$. As described in the general procedure, 2.1 mL (17.0 mmol) of *t*-BuC≡CH and 1.8 mL (18.0 mmol) of *i*-BuNH$_2$ were reacted with 54 mg (0.1 mmol) of Cp*$_2$UMe$_2$ in 5 mL of THF. The reaction mixture was heated to 65 °C for 425 h to obtain imine **14** in 95% conversion and 87% yield. Bp_{15} = 65−70 °C. NMR data of **14**. ^{1}H NMR {400 MHz, THF-d_8, 293 K}: δ 7.52 (m, 1 H, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 1.4 Hz, C≡C*H*), 3.04 (d, 2 H, $^3J_{HH}$ = 6.4 Hz, CH_2CH(CH$_3$)$_3$), 1.97 (d, 2 H, $^3J_{HH}$ = 5.6 Hz, CH_2-*t*-Bu), 1.75 (m, 1 H, $^3J_{HH}$ = 6.4 Hz, C*H*(CH$_3$)$_2$), 0.90 (s, 9 H, CMe$_3$), 0.80 (d, 6 H, $3J_{HH}$ = 6.4 Hz, CH(CH_3)$_2$). ^{13}C NMR {100 MHz, THF-d_8, 293 K}: δ 163.0 (d, J_{CH} = 152 Hz, *C*H), 72.0 (t, J_{CH} = 132 Hz, *C*H$_2$−CH(CH$_3$)$_3$), 60.0 (d, J_{CH} = 125 Hz, CH$_2$*C*H(CH$_3$)$_3$), 51.5 (t, J_{CH} = 126 Hz, *C*H$_2$-*t*-Bu), 32.1 (s, *C*CH$_3$), 32.0 (q, J_{CH} = 125 Hz, CCH_3), 23.0 (q, J_{CH} = 124 Hz, CH(CH_3)$_2$). HRMS (*m*/*z*): {M^+} calcd for $C_{10}H_{21}N$ 155.1674, found 155.1671. Anal. Calcd for $C_{10}H_{21}N$: C, 77.35; H, 13.63; N, 9.02. Found: C, 77.21; H, 13.47; N, 8.90.

(15) Dimerization of *t*-BuC≡CH to 7B by Cp*$_2$UMe$_2$. According to the general procedure, 1.0 mL (8.0 mmol) of *t*-BuC≡CH and 1.0 mL (10.0 mmol) of *t*-BuNH$_2$ were reacted with 51 mg (0.1 mmol) of Cp*$_2$UMe$_2$ in 4 mL of benzene. The reaction mixture was heated to 78 °C for 8 h to obtain the geminal dimer **7B**. For full characterization see ref 20.

(16) Hydroamination of *n*-BuC≡CH with MeNH$_2$ by Cp*$_2$UMe$_2$. As described above in the general procedure, 1.7 mL (14.0 mmol) of *n*-BuC≡CH and 0.7 mL (15.0 mmol) of MeNH$_2$ were reacted with 53 mg (0.1 mmol) of Cp*$_2$UMe$_2$ in 6 mL of benzene. The reaction mixture was heated to 78 °C for 34 h to obtain imine **15** in 96% conversion and 92% yield. Bp_{20} = 92−98 °C. NMR data of **15**: ^{1}H NMR {400 MHz, benzene-d_6, 293 K}: δ 7.37 (m, 1 H, CH, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 1.3 Hz, C≡C*H*), 3.12 (m, 1 H, $^4J_{HH}$ = 1.3 Hz, NCH_3), 2.05 (m, 2 H, CH-CH_2), 2.22, 1.48, 1.20 (m, 6 H, CH_2 chain), 1.09 (br, 3 H, CH$_2$CH_3). ^{13}C NMR {100 MHz, THF-d_8, 293 K}: δ 167.0 (d, J_{CH} = 163 Hz, *C*H), 56.0 (t, J_{CH} = 134 Hz, *C*H$_2$-CH$_2$), 39.0 (q, J_{CH} = 125 Hz, NCH_3), 33.1, 32.6, 27.4 (*C*H$_2$), 20.0 (q, J_{CH} = 124 Hz, CH$_2$*C*H$_3$). HRMS (*m*/*z*): {M^+} calcd for $C_7H_{15}N$ 113.1204, found 113.1186. Anal. Calcd for $C_7H_{15}N$: C, 74.27; H, 13.36; N, 12.37. Found: C, 74.65; H, 13.09; N, 12.22.

(17) Hydroamination of *n*-BuC≡CH with EtNH$_2$ by Cp*$_2$UMe$_2$. As described above in the general procedure, 2.3 mL (19.0 mmol) of *n*-BuC≡CH and 1.5 mL (22.0 mmol) of EtNH$_2$ were reacted with 51 mg (0.1 mmol) of Cp*$_2$UMe$_2$ in 6 mL of THF. The reaction mixture was heated to 65 °C for 44 h to obtain imine **16** in 96% conversion and 88% yield. Bp_{10} = 63−66 °C. NMR data of **16**: ^{1}H NMR {200 MHz, THF-d_8, 293 K}: δ 7.43 (t, 1 H, $^3J_{HH}$ = 5.5 Hz, C*H*), 3.33 (q, 2 H, $3J_{HH}$ = 7.1 Hz, NCH_2CH$_3$), 2.18 (m, 2 H, CHCH_2), 1.50 (m, 2 H, CHCH$_2$CH_2), 1.30 (m, 4 H, CH_2 chain), 1.22 (t, 3 H, $^3J_{HH}$ = 7.1 Hz NCH$_2$CH_3), 0.87 (t, 3 H, CH$_3$ chain). ^{13}C NMR {50 MHz, benzene-d_6, 293 K}: δ162.0 (d, J_{CH} = 152 Hz, *C*H), 55.7 (t, J_{CH} = 133 Hz, NCH$_2$CH$_3$), 35.8, 31.7, 25.8, and 22.7 (t, CH$_2$ chain), 16.4 (q, J_{CH} = 121 Hz, NCH$_2$*C*H$_3$), 14.0 (q J_{CH} = 124 Hz, CH$_2$*C*H$_3$). HRMS (*m*/*z*): {M^+} calcd for $C_8H_{17}N$ 127.1361, found 127.1354. Anal. Calcd for $C_8H_{17}N$: C, 75.52; H, 13.47; N, 11.01. Found: C, 75.81; H, 13.61; N, 10.81.

(18) Hydroamination of *n*-BuC≡CH with *n*-PrNH$_2$ by Cp*$_2$UMe$_2$. As described in the general procedure, 2.3 mL (19.0 mmol) of *n*-BuC≡CH and 1.5 mL (19.0 mmol) of *n*-PrNH$_2$ were reacted with 53 mg (0.1 mmol) of Cp*$_2$UMe$_2$ in 6 mL of benzene. The reaction mixture was heated to 78 °C for 54 h to obtain imine **17** in 65% conversion and 91% yield. Bp = 168−171 °C. NMR data of **17**. ^{1}H NMR, see ref 41. ^{13}C NMR {50 MHz, benzene-d_6, 293 K}: δ 161.0 (d, J_{CH} = 152 Hz, *C*H), 64.2 (N-CH$_2$) 46.3 32.3, 31.4, 29.2. 28.6, 24.5 (q, J_{CH} = 126 Hz, NCH$_2$*C*H$_2$CH$_3$), 12.0 (q, J_{CH} = 126 Hz, CH$_2$CH$_2$*C*H$_3$). HRMS (*m*/*z*): {M^+} calcd for $C_9H_{19}N$ 141.1517, found 141.1501. Anal. Calcd for $C_9H_{19}N$: C, 76.53; H, 13.56; N, 9.92. Found: C, 76.22; H, 13.49; N, 9.87.

(19) Hydroamination of *n*-BuC≡CH with *i*-PrNH$_2$ by Cp*$_2$UMe$_2$. As described in the general procedure, 0.9 mL (7.0 mmol) of *n*-BuC≡CH and 0.6 mL (7.0 mmol) of *i*-PrNH$_2$ were reacted with 54 mg (0.1 mmol) of Cp*$_2$UMe$_2$ in 6 mL of benzene. The reaction mixture was heated to 78 °C for 116 h to obtain imine **18** in 65% conversion and 91% yield. Bp = 157−159 °C. NMR data of **18**: ^{1}H NMR {200 MHz, benzene-d_6, 293 K}: δ 7.41 (t, 1 H, $^3J_{HH}$ = 4.9 Hz, C*H*), 3.12 (h, 1 H, $3J_{HH}$ = 6.0 Hz, CH(CH$_3$)$_2$), 2.05 (m, 2 H, CH-CH_2), 1.90, 1.82, 1.70 (m, 6 H, CH$_2$ chain), 1.17 (d, 6 H, $^3J_{HH}$ = 6.0 Hz, CH-(CH_3)$_2$), 0.88 (t, 3 H, $^3J_{HH}$ = 6.0 Hz, CH$_2$CH$_3$). ^{13}C NMR {50 MHz, benzene-d_6, 293 K}: δ 160.5 (d, J_{CH} = 151 Hz, *C*H), 64.0 (d, J_{CH} = 133 Hz, *C*H(CH$_3$)$_3$), 46.2, 30.2, 29.7, 28.3, 27.2 (q, J_{CH} = 128 Hz, CH(*C*H$_3$)$_2$), 12.0 (q, J_{CH} = 156 Hz, CH$_2$CH$_2$*C*H$_3$). HRMS (*m*/*z*): {M^+} calcd for $C_9H_{19}N$ 141.1517, found 141.1496. Anal. Calcd for $C_9H_{19}N$: C, 76.53; H, 13.56; N, 9.92. Found: C, 76.19; H, 13.26; N, 9.78.

(20) Hydroamination of *n*-BuC≡CH with *i*-BuNH$_2$ by Cp*$_2$UMe$_2$. As described in the general procedure, 1.3 mL (10.0 mmol) of *n*-BuC≡CH and 1.0 mL (10.0 mmol) of *i*-BuNH$_2$ were reacted with 52 mg (0.1 mmol) of Cp*$_2$UMe$_2$ in 5 mL of benzene. The reaction mixture was heated to 78 °C for 27 h to obtain the imine **19** in 95% conversion and 92% yield. Bp_{10} = 67−70 °C. NMR data of **19**: NMR see ref 42. HRMS (*m*/*z*): {M^+} calcd for $C_{10}H_{21}N$ 155.1674, found 155.1670. Anal. Calcd for $C_{10}H_{21}N$: C, 77.35; H, 13.63; N, 9.02. Found: C, 77.02; H, 13.34; N, 8.83.

(21) Oligomerization of *n*-BuC≡CH by Cp*$_2$UMe$_2$. According to the general procedure, 4.0 mL (33.0 mmol) of *n*-BuC≡CH and 3.0 mL (30.0 mmol) of *t*-BuNH$_2$ were reacted with 51 mg (0.1 mmol) of Cp*$_2$UMe$_2$ in 5 mL of THF. The reaction mixture was heated to 65 °C for 8 h to obtain the geminal dimer **7C** (60%) and additional trimers. For full characterization of **7C**, see ref 18.

(22) Hydroamination of PhC≡CH and MeNH$_2$ by Cp*$_2$UMe$_2$. According to the general procedure, 1.5 mL (14.0 mmol) of PhC≡CH and 0.7 mL (15.0 mmol) of MeNH$_2$ were reacted with 54 mg (0.1 mmol) of Cp*$_2$UMe$_2$ in 5 mL of THF. The reaction mixture was heated to 65 °C for 33 h to obtain imine **20** in 95% conversion and 85% yield. Bp_{12} = 67−72 °C. NMR data of **20**: NMR see ref 43. HRMS (*m*/*z*): {M^+} calcd for $C_9H_{11}N$ 133.0891, found 133.0867. Anal. Calcd for $C_9H_{11}N$: C, 81.16; H, 8.32; N, 10.52. Found: C, 80.89; H, 8.07; N, 10.74.

(23) Hydroamination of PhC≡CH and EtNH$_2$ by Cp*$_2$UMe$_2$. According to the general procedure, 1.5 mL (14.0 mmol) of PhC≡CH and 1.0 mL (15.0 mmol) of EtNH$_2$ were reacted with 52 mg (0.1 mmol) of Cp*$_2$UMe$_2$ in 6 mL of THF. The reaction mixture was heated to 65 °C for 67 h to obtain imine **21** in 72% conversion and 66% yield with the concomitant formation of other nontraceable compounds. $Bp_{0.3}$ = 43−49 °C. NMR data of **21**: NMR, see ref 44. HRMS (*m*/*z*): {M^+} calcd for $C_{10}H_{13}N$ 147.1048, found 147.1027. Anal. Calcd for $C_{10}H_{13}N$: C, 81.59; H, 8.90; N, 9.51. Found: C, 81.23; H, 8.74; N, 9.32.

(24) Hydroamination of *i*-PrC≡CH and EtNH$_2$ by Cp*$_2$UMe$_2$. According to a general procedure, 1.5 mL (15.0

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mmol) of *i*-PrC≡CH and 1.0 mL (15.0 mmol) of $EtNH_2$ were reacted with 54 mg (0.1 mmol) of $Cp^*_2UMe_2$ in 5 mL of THF. The reaction mixture was heated to 65 °C for 50 h to obtain imine **22** in 95% conversion and 86% yield. Bp = 128−130 °C. NMR data of **22**. ^{1}H NMR {400 MHz, THF-d_8, 293 K}: δ 7.60 (m, 1 H, $^3J_{HH}$ = 5.0 Hz, $^4J_{HH}$ = 1.2 Hz, C≡C*H*), 3.30 (m, 2 H, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.2 Hz, CH_2CH$_3$), 2.05 (dd, 2 H, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 5.0 Hz, CH_2CH(CH$_3$)$_2$), 1.90 (m, 1 H,, $^3J_{HH}$ = 7.6 Hz, C*H*(CH$_3$)$_2$), 1.15 (t, 2 H, $^3J_{HH}$ = 7.3 Hz, CH$_2$CH_3), 0.92 (d, 6 H, $^3J_{HH}$ = 7.6 Hz, CH(CH$_3$)$_2$). ^{13}C NMR {50 MHz, THF-d_8, 293 K}: δ 163.7 (d, J_{CH} = 161 Hz, *C*H═), 55.6 (t, J_{CH} = 127 Hz, *C*H$_2$), 52.5 (t, J_{CH} = 131 Hz, NCH$_2$CH$_3$), 24.1 (d, J_{CH} = 161 Hz, *C*H), 22.1 (q, J_{CH} = 124 Hz, *C*H$_3$), 16.4 (q, J_{CH} = 124 Hz, NCH$_2$*C*H$_3$). HRMS (*m*/*z*): {M$^+$} calcd for $C_7H_{15}N$ 113.1204, found 113.1200. Anal. Calcd for $C_7H_{15}N$: C, 74.27; H, 13.36; N, 12.37. Found: C, 74.07; H, 13.45; N, 12.28.

(25) Hydroamination of $C_5H_{11}C$≡CH and $EtNH_2$ by $Cp^*_2UMe_2$. According to a general procedure, 0.7 mL (6.0 mmol) of $C_5H_{11}C$≡CH and 0.5 mL (7.0 mmol) of $EtNH_2$ were reacted with 51 mg (0.1 mmol) of $Cp^*_2UMe_2$ in 7 mL of THF. The reaction mixture was heated to 65 °C for 20 h to obtain imine **23** in 92% conversion and 80% yield. Bp_5 = 73−89 °C. NMR data of **23**. ^{1}H NMR {200 MHz, THF-d_8, 293 K}: δ 7.49 (t, 1 H, $^3J_{HH}$ = 4.9 Hz, C*H*), 3.28 (q, 2 H, $^3J_{HH}$ = 7.1 Hz, CH_2-CH$_3$), 2.15 (d, 2 H, $^3J_{HH}$ = 4.9 Hz, CH_2C$_5$H$_{11}$), 2.10−1.50 (m, 11 H C$_5$H$_{11}$), 1.20 (q, 2 H, $^3J_{HH}$ = 7.1 Hz, CH$_2$CH_3). ^{13}C NMR {50 MHz, THF-d_8, 293 K}: δ 164.2 (d, J_{CH} = 154 Hz, *C*H═), 54.2 (t, J_{CH} = 127 Hz, *C*H$_2$C$_5$H$_{11}$), 53.7 (t, J_{CH} = 131 Hz, N*C*H$_2$-CH$_3$), 32.1 (d, J_{CH}= 127 Hz, *C*HCH$_2$CH═), 22.1 (CH$_2$ ring) 23.4 (CH$_2$ ring), 14.3 (q, J_{CH}= 124 Hz, NCH$_2$*C*H$_3$). HRMS (*m*/*z*): {M$^+$} calcd for $C_9H_{17}N$ 139.1361, found 139.1349. Anal. Calcd for $C_7H_{15}N$: C, 77.63; H, 12.31; N, 10.06. Found: C, 77.28; H, 12.191; N, 9.92.

(26) Hydroamination of TMSC≡CH and $MeNH_2$ by $Cp^*_2ThMe_2$. According to the general procedure, 2.0 mL (14.0 mmol) of TMSC≡CH and 0.6 mL (14.0 mmol) of $MeNH_2$ were reacted with 140 mg (0.26 mmol) of $Cp^*_2ThMe_2$ in 7 mL of benzene. The reaction mixture was heated to 78 °C for 36 h to obtain a conversion of the alkyne in 97% and the imine **1** in 27% yield. The dimer **7A** was obtained in 70%.

(27) Hydroamination of TMSC≡CH and $EtNH_2$ by $Cp^*_2ThMe_2$. (a) According to the general procedure, 1.0 mL (7.0 mmol) of TMSC≡CH and 0.45 mL (7.0 mmol) of $EtNH_2$ were reacted with 129 mg (0.26 mmol) of $Cp^*_2ThMe_2$ in 7 mL of benzene. The reaction mixture was heated to 78 °C for 15 h to obtain a conversion of the alkyne in 97% but forming only the imine **2A** in 35% yield. The dimer **7A** was obtained in 62% yield.

(b) According to the general procedure, 1.0 mL (7.0 mmol) of TMSC≡CH and 0.45 mL (7.0 mmol) of $EtNH_2$ were reacted with 180 mg (0.25 mmol) of Cp^*_2Th═NR(THF) (NR = 2,6-dimethylamilide) (**33**) in 7 mL of benzene. The reaction mixture was heated to 78 °C for 15 h to obtain a conversion of the alkyne in 95% but forming only the imine **2A** in 30% yield. The dimer **7A** was obtained in 60% yield.

(28) Hydroamination of HC≡CH with $EtNH_2$ by $Cp^*_2ThMe_2$. As described above in the general procedure, 0.5 mL (12 mmol) of HC≡CH and 0.7 mL (11.0 mmol) of $EtNH_2$ were reacted with 120 mg (0.26 mmol) of $Cp^*_2ThMe_2$ in 6 mL of benzene in a high-pressure Schlenk flask. The reaction mixture was heated to 48 °C for 4.5 h and the flask cooled and opened slow in a well-ventilated hood to remove any excess of acetylene. The mixture was submitted to distillation to obtain 80% (based on the amine) of imine **24**. Bp = 58−60 °C. NMR data of **24**. NMR see ref 45. HRMS (*m*/*z*): {M$^+$} calcd for C_4H_9N 71.073, found 71.048. Anal. Calcd for C_4H_9N: C, 67.55; H, 12.75; N, 19.69. Found: C, 67.05; H, 12.45; N, 19.37.

(29) Hydroamination of *n*-BuC≡CH with $MeNH_2$ by $Cp^*_2ThMe_2$. As described above in the general procedure, 2.0 mL (17.0 mmol) of *n*-BuC≡CH and 2.0 mL (45.0 mmol) of $MeNH_2$ were reacted with 120 mg (0.26 mmol) of $Cp^*_2ThMe_2$ in 6 mL of benzene. The reaction mixture was heated to 78 °C for 46 h to obtain a full conversion of the alkyne, but only 7% was characterized to be the imine **25**. 90% was found to be the geminal **7C** and the trans dimer of *n*-BuC≡CH in a percentage ratio of 45:48, respectively. Bp_{23} = 52−56 °C. NMR data of **25**. ^{1}H NMR {200 MHz, benzene-d_6, 293 K}: δ 2.94 (s, 3 H, CH_3N), 2.20 (q, 2 H, $^3J_{HH}$ = 6.8 Hz, CH_2CH$_2$), 1.80−1.20 (m, 7H, CH_2 chain + CH_3), 0.81 (t, 3 H, $^3J_{HH}$ = 6.8 Hz, CH$_2$CH_3). ^{13}C NMR {50 MHz, benzene-d_6, 293 K}: δ 164.6 (s, *C*), 55.7 (q, J_{CH} = 127 Hz, NCH$_3$), 35.8, 31.7, 25.8 and (t, CH$_2$ chain), 18.9 (q, J_{CH} = 124 Hz, ≡C*C*H$_3$), 13.2 (q J_{CH} = 124 Hz, CH$_2$*C*H$_3$). HRMS (*m*/*z*): {M$^+$} calcd for $C_7H_{15}N$ 113.1204, found 113.1194. Anal. Calcd for $C_7H_{15}N$: C, 74.27; H, 13.36; N, 12.37. Found: C, 74.02; H, 13.67; N, 12.09.

(30) Hydroamination of *n*-BuC≡CH with $EtNH_2$ by $Cp^*_2ThMe_2$. (a) As described above in the general procedure, 2.3 mL (19.0 mmol) of *n*-BuC≡CH and 1.5 mL (22.0 mmol) of $EtNH_2$ were reacted with 51 mg (0.1 mmol) of $Cp^*_2ThMe_2$ in 6 mL of THF. The reaction mixture was heated to 65 °C for 44 h to obtain a full conversion of the alkyne, but only 10% was characterized to be the imine **26**. 87% was found to be a mixture of the geminal **7C** and the trans dimer of *n*-BuC≡CH in a percentage ratio of 32:53, respectively. Bp_{12} = 67−72 °C. NMR data of **26**. ^{1}H NMR {200 MHz, benzene-d_6, 293 K}: δ 3.14 (q, 2H, $^3J_{HH}$ = 7.8 Hz, NCH_2CH$_3$), 2.09 (t, 2 H, 3J_{HH} = 8.5 Hz, CH_2CH$_2$), 1.80−1.20 (m, 7H, CH_2 chain + CH_3), 1.02 (t, 3 H, $^3J_{HH}$ = 7.8 Hz, NCH$_2$CH_3) 0.77 (t, 3 H, $^3J_{HH}$ = 7.8 Hz, CH$_2$CH_3). ^{13}C NMR {50 MHz, benzene-d_6, 293 K}: δ 165.7 (s, *C*), 50.5 (t, J_{CH} = 127 Hz, NCH$_2$CH$_3$), 35.8, 31.7, 25.8 and (t, CH$_2$ chain), 18.9 (q, J_{CH} = 124 Hz, ≡C*C*H$_3$), 15.1 (q, J_{CH} = 121 Hz, NCH$_2$*C*H$_3$), 13.2 (q, J_{CH} = 124 Hz, CH$_2$*C*H$_3$). HRMS (*m*/*z*): {M$^+$} calcd for $C_8H_{17}N$ 127.1361, found 127.1349. Anal. Calcd for $C_8H_{17}N$: C, 75.52; H, 13.47; N, 11.01. Found: C, 75.25; H, 13.27; N, 10.72.

(b) As described above in the general procedure, 2.3 mL (19.0 mmol) of *n*-BuC≡CH and 1.5 mL (22.0 mmol) of $EtNH_2$ were reacted with 70 mg (0.1 mmol) of Cp^*_2Th═NR(THF) (NR = 2,6-dimethylanilide) in 6 mL of THF. The reaction mixture was heated to 65 °C for 44 h to obtain a full conversion of the alkyne, but only 13% was characterized to be the imine **26**. 82% was found to be the geminal **7C** and the trans dimer of *n*-BuC≡CH in a percentage ratio of 31:51, respectively.

(31) Hydroamination of PhC≡CH and $EtNH_2$ by $Cp^*_2ThMe_2$. According to the general procedure, 2.0 mL (20.0 mmol) of PhC≡CH and 1.5 mL (22.0 mmol) of $EtNH_2$ were reacted with 130 mg (0.24 mmol) of $Cp^*_2ThMe_2$ in 6 mL of benzene. The reaction mixture was heated to 78 °C for 3 h to obtain a quantitative conversion of the alkyne, forming the imine **27** (33%) with the concomitant formation of a mixture of the phenyl acetylene dimers (64%). $Bp_{0.5}$ = 54−59 °C. NMR data of **27**: ^{1}H NMR {200 MHz, THF-d_8, 293 K}: δ 6.9−7.5 (m, 5 H, Ph), 3.36 (q, 2 H $^3J_{HH}$ = 6.8 Hz, NCH_2), 2.17 (s, 3H, CCH_3), 1.16 (t, 3 H, 3J_{HH} = 6.8 Hz, NCH$_2$CH_3). ^{13}C NMR {50 MHz, THF-d_8, 293 K}: δ 164.4 (s, *C*═), 130.8, 129.5, 128.3 (CH-aromatic) 49.3 (t, J_{CH} = 126 Hz, N*C*H$_2$CH$_3$), 16.4 (q, J_{CH}= 124 Hz, NCH$_2$*C*H$_3$), 13.1 (q, J_{CH} = 124 Hz, *C*H$_3$). HRMS (*m*/*z*): {M$^+$} calcd for $C_{10}H_{13}N$ 147.1048, found 147.1043. Anal. Calcd for $C_{10}H_{13}N$: C, 81.59; H, 8.90; N, 9.51. Found: C, 81.75; H, 8.54; N, 9.61.

(32) Hydroamination of *i*-PrC≡CH and $PhNH_2$ by $Cp^*_2ThMe_2$. According to the general procedure, 0.2 mL (2.5 mmol) of *i*-PrC≡CH and 0.25 mL (2.7 mmol) of $PhNH_2$ were reacted with 100 mg (0.20 mmol) of $Cp^*_2ThMe_2$ in 10 mL of benzene. The reaction mixture was heated to 78 °C for 170 h to obtain a quantitative conversion of the alkyne, forming the imine **28** in 95% and yielding 85% of the compound with trace formation of the geminal dimer. $Bp_{0.3}$ = 54−56 °C. NMR data of **28**: ^{1}H NMR {200 MHz, benzene-d_6, 293 K}: δ 6.85 (dd, 2 H, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 7.9 Hz, *m*-H-Ph), 6.63 (t, 1 H $^3J_{HH}$ =

(45) Stevens, C.; Kimpe, N. *J. Org. Chem.* **1993**, *58*, 132.

7.9 Hz, *p*-H−Ph), 6.31 (d, 2H, $^3J_{HH}$ = 6.8 Hz, *o*-H-Ph), 2.40−2.20 (m, 1 H, N≡C−CH), 1.42 (s, 3 H, N≡C−CH_3), 1.05 (d, 6 H, $^3J_{HH}$ = 8.3 Hz, CH-$(CH_3)_2$). ^{13}C NMR data {50 MHz, THF-d_8, 293 K}: δ 174.5 (N=*C*), 151.9 (N-C_{ipso}), 128.7, 124.6, 122.4 (Ar-*C*), 40.4 (*C*(Me_2), 20.1 (C(*C*$H_3)_2$), 15.8 (≡C*C*H_3). HRMS (*m*/*z*): {M^+} calcd for $C_{11}H_{15}N$ 161.1204, found 161.1198. Anal. Calcd for $C_{10}H_{13}N$: C, 81.94; H, 9.38; N, 8.69. Found: C, 81.70; H, 8.98; N, 8.42.

Synthesis of Complex 33. To a stirred solution of Cp*$_2$-$ThMe_2$ (0.5 g, 9.5 × 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 and refluxed for 15 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 **33** (310 mg, 4.47 × 10^{-4} mol) after 2 h. NMR data of **33**: ^{1}H NMR {200 MHz, C_6D_6, 293 K}: δ 7.32 (d, 2 H, $^3J_{HH}$ = 7.3 Hz), 6.66 (t, 1H, $^3J_{HH}$ = 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 {50 MHz, C_6D_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, 55.40; H, 6.83; N, 2.02. Found: C, 55.22; H, 6.81; N, 1.94. Cryoscopy measurements on compound **33** in benzene gave M_r = 857 (calcd = 693).

Synthesis of Complex 38. To a stirred solution of Cp*$_2$-UMe_2 (0.5 g, 9.2 × 10^{-4} mol) in 20 mL of THF was added 2,6-dimethylaniline (0.132 g, 9.2 × 10^{-4} mol) at −78 °C. The dark red solution was allowed to warm to room temperature and refluxed for 2 h. The THF was removed under reduced pressure, leaving a red 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 (88%) red crystals of **38** (566 mg, 8.1 × 10^{-4}mol) after 6 h. Complex **38** was subjected to single-crystal X-ray analysis; however severe disorder of the THF molecules prevented a successful refinement. The presence of the paramagnetic uranium (U(IV),f^2) electrons induced large shifts in the ^{1}H NMR signals. NMR data of **38**: ^{1}H NMR {200 MHz, $C_{12}D_{12}$, 293K}: δ 37.4 (s, $\nu_{1/2}$ = 15 Hz, 1 H,), 14.9 (s, $\nu_{1/2}$ = 15 Hz, 2 H), 5.5 (s, 6 H, Ar = Me), 1.4 (s, $C_{12}D_{11}H$), −2.4 (s, 30H, Cp*-Me), −15.4 (s, $\nu_{1/2}$ = 33 Hz, 2 H, THF), −28.4 (s, $\nu_{1/2}$ = 33 Hz, 2 H, THF). Anal. Calcd for $C_{32}H_{47}NOU$: C, 54.93; H, 6.77; N, 2.00. Found: C, 55.04; H, 6.54; N, 2.32. Cryoscopy measurements on compound **38** in benzene gave M_r = 765 (calcd = 699).

X-ray Measurements of Complex 31. A single crystal of the compound was fished from a batch immersed in Paratone oil-N under dry conditions and quickly mounted on the Philips PW1100/20 diffractometer under a cold stream of nitrogen at 150 K. Accurate cell parameters were derived from 25 carefully centered reflections using graphite-monochromatized Mo Kα radiation. Data collections were performed in the $\omega/2\theta$ mode.[46] Three reflections were measured each 120 min to monitor system instability, but variations no higher than 3.5% were observed.

Intensities were corrected for background Lorentz, polarization effects, and analytical absorptions and reduced to a list of structure factors.[47] The Th atom was located by the Patterson method using SHELXS97.[48] Anisotropic refinement of this atom gave R = 0.10. Fourier difference maps revealed the positions of four Cl(CH_3) atoms attached to the Th atom on the mirror plane at x = 0. Each of these Cl(CH_3) atoms was refined isotropically with an occupancy of 0.125. At this stage, difference maps showed 16 peaks, which could be interpreted in terms of a disordered Cp* molecule taking two distinct orientations. The whole organometallic complex being completed by the mirror plane at x = 0. This reasonable model could not be refined isotropically because of very low electron densities relative to the Th atom. To maintain reasonable geometry throughout refinement, an idealized Cp* was adopted for the two orientations using the SHELXL97 package.[49] Both orientations were refined isotropically as rigid groups until convergence was reached at R = 0.045. After refinement was completed, each pair of the Cl(CH_3) atoms could be easily ascribed to one of the complex orientations. The four Cl(CH_3) positions on the mirror plane give one full Cl and (CH_3) group per complex. It was also assumed that the methyl group is distributed among the chlorine sites to yield an average atom 0.125(Cl+C). This model could not be refined because of very low density as described before and was ignored. Molecular graphics were performed with the program package TEXSAN.[50]

X-ray Measurements of Complex 33. A yellow prismatic crystal of complex **33** having approximate dimensions 0.3 × 0.2 × 0.2 mm was cut from a clump of crystals, and the resultant was mounted using oil (Paratone-N) on a glass fiber. All measurements were made on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. The data were collected at −120 ± 1 °C using the $\omega-\theta$ scan technique to a maximum 2θ value of 47.9°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.25° with a takeoff angle of 2.8°. Scans of (1.00 + 0.35 tan θ)° were made at variable speeds between 3 and 16.0°/min (in omega). An empirical absorption correction using the program DIFABS[51] was applied which resulted in transmission factors ranging from 0.97 to 1.13. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques.[52] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[53]

Results

The goal of this investigation was to examine the scope, chemoselectivity, regioselectivity, actinide metal sensitivity, kinetics, and mechanism of the selective *intermolecular* hydroamination of terminal alkynes with aliphatic amines. This study represent an extension of the unique reactivities of organoactinide complexes with terminal alkynes in the presence of primary amines, and a complementary comparison to group 4 and organolanthanide chemistry in parallel processes. In the ensuing discussion, we focus on the reaction scope, alkyne substituents, amine substituents, metal effect, kinetics, and the rate law expression. In addition we report on the solid-state characterization of two organothorium complexes: the first, a monomethyl monochloride thorium complex, an intermediate toward the general formation of an organoimido thorium complexes, and the second, a thorium-imido complex, a key inter-

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(48) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
(49) Sheldrick, G. M. *SHELXL97*, Program for the Refinement of Crystal Structures; University of Gottingen: Germany, 1997.
(50) *ORTEP*, TEXRAY Structure Analysis Package; Molecular Structure Corporation: 3200 Research Forest Drive, The Woodlands, TX 77381, 1999.
(51) *DIFABS*: Walker, N.; Stuart. *Acta Crystallogr.* **1983**, *A39*, 158. An empirical program for absorption corrections.
(52) *DIRDIF92*: Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. Smykalla, C. *The DIRDIF program system*; Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1992..
(53) *teXsan*: Crystal Structure Package; Molecular Structure Corporation: The Woodlands, TX, 1985 and 1992.

Table 1. Crystal Data and Structure Refinement for the Complexes 31 and 33

	31	33
empirical formula	$C_{21}H_{33}ClTh$	$C_{64}H_{94}N_2O_2Th$
fw	552.96	1387.54
temperature	150(1) K	153(1) K
wavelength	0.71070 Å	0.71070 Å
cryst syst, space group	orthorombic, *Cmc*21	monoclinic, *C*2/*c*
unit cell dimens		
	$a = 17.607(4)$ Å, $\alpha = 90°$	$a = 63.911(8)$ Å, $\alpha = 90°$
	$b = 8.206(6)$ Å, $\beta = 90°$	$b = 11.041(2)$ Å, $\beta = 93.09(1)°$
	$c = 14.909(3)$ Å, $\gamma = 90°$	$c = 16.987(4)$ Å, $\gamma = 90°$
volume	2154.1(17) Å^3	11969(3) Å^3
Z, calcd density	4, 1.705 Mg/m^3	8, 1.540 Mg/m^3
abs coeff	0.7045 mm^{-1}	0.503 mm^{-1}
F(000)	1064	5504
crystal size	0.2 × 0.27 × 0.33 mm	0.3 × 0.2 × 0.2 mm
θ range for data collection	2.31−25.05°	1.25−23.60°
limiting indices	$-20 \le h \le 20, -9 \le k \le 0, -17 \le l \le 0$	$0 \le h \le 15, -20 \le k \le 22, -25 \le l \le 25$
no. of reflns collected/unique	1987/1033 [*R*(int)=0.0800]	11 309/9945 [*R*(int)=0.056]
completeness to highest θ	100.0	100.0
refinement method	full-matrix least-squares on F^2	full-matrix least-squares
no. of data/restraints/params	1033/1/54	9945/0/631
goodness-of-fit on F^2	1.195	1.53
final *R* indices [$I>2\sigma(I)$]	R1 = 0.0454, wR2 = 0.1092	R1 = 0.037, $R_w = 0.033$
R indices (all data)	R1 = 0.0482, wR2 = 0.1103	
largest diff peak and hole	3.941 and -−1.654 e Å^{-3}	−0.94 and 1.20 Å^{-3}

Table 2. Bond Lengths [Å] and Angles [deg] for Complex 31

Th−Cl(1A)	2.55(4)
Th−Cl(1B)	2.69(3)
Th−Cl(2A)	2.71(3)
Th−Cl(2B)	2.75(3)
Cl(1A)−Th−Cl(2A)	98.0(11)
Cl(1B)−Th−Cl(2B)	94.9(11)

Table 3. Bond Lengths [Å] and Angles [deg] for Complex 33

Th(1)−O(1)	2.526(7)
Th(2)−O(2)	2.520(7)
Th(1)−N(1)	2.045(8)
Th(2)−N(2)	2.066(7)
O(1)−Th(1)−N(1)	100.8(3)
Th(1)−N(1)−C(5)	171.5(7)
O(2)−Th(2)−N(2)	98.7(3)
Th(2)−N(2)−C(37)	170.8(7)

mediate in the catalytic cycle for the hydroamination of alkynes. We start the presentation of the results with the reaction scope for the organoactinide-catalyzed intermolecular hydroamination of terminal alkynes, followed by pertinent stoichiometry reactivity of the organoactinides.

Scope of Organoactinide-Catalyzed Intermolecular Hydroamination of Terminal Alkynes. The organoactinide complexes $Cp^*_2AnR_2$ ($Cp^* = C_5Me_5$, An = Th, U, R = Me, NHR′, R′ = alkyl) are precatalysts for the intermolecular hydroamination of terminal aliphatic and aromatic alkynes in the presence of primary aliphatic amines to yield the corresponding imido compounds, as shown for the uranium complexes in eq 4 and Table 4, and for the corresponding thorium complexes in eq 5 and Table 5. In each table, N_t is the turnover frequency at the temperature indicated in parentheses. The catalytic intermolecular reaction proceeds, in most cases, until completion at the corresponding reflux temperature of the solvents. The reactions were followed either by GC, GC/MS chromatography or ^{1}H NMR spectroscopy. For low-boiling alkyne or amines, a heavy glass high-pressure J-Young Schlenk flask was used. All the imine products were characterized by ^{1}H NMR (long-range couplings are sometimes observed and are reported), ^{13}C NMR, and 2D-NMR spectroscopy, GC/MS, high-resolution mass spectroscopy, and microanalysis or by comparison to literature ^{1}H/^{13}C NMR spectral data and data from authentic samples prepared accordingly to literature procedures. Isolation protocols for the products involved high-vacuum transfer of the products and volatiles with the subsequent elimination of the solvent and final distillation of the products. In general, at room temperature, the initial reaction of $Cp^*_2AnMe_2$ (An = Th, U) with an alkyne yields the corresponding bisacetylide complexes, although in the presence of amines, the corresponding bisamido complexes $Cp^*_2An(NHR)_2$ are obtained preferentially.[18,20,54]

Stoichiometric Reactivity of Organoactinide Complexes. The different catalytic reactivities found for such related organoactinides, which is unexpected in organoactinide chemistry, incited us to study some stoichiometric reactions between the organothorium starting complexes ($Cp^*_2ThCl_2$ (**29**) and $Cp^*_2ThMe_2$ (**30**)) with alkynes and amines. Stoichiometric characterizations for analogous organouranium complexes have been recently published.[18,55,56] When complexes **29** and **30** are mixed in equimolar amounts (Scheme 1) in toluene, as shown by Marks et al.,[40] a disproportionation reaction takes place forming (>97%) $Cp^*_2Th(Cl)Me$ (**31**) as followed by ^{1}H NMR spectroscopy. The X-ray solid-state study on complex **31** shows a normal disposed organoactinide metallocene with an ring centroid−metal−ring centroid angle of 135(2)°, metal to ring centroid distance of 2.56(9) Å, and Th−CH_3/Cl average distance of (∼2.67(8) Å), similarly to other organo-f-complexes.[40,56,57] The crystal exhibits a disorder between

(54) All toxic materials were disposed in accordance with *Prudent Practices for Disposal of Chemicals from Laboratories*; National Academy Press: Washington, DC, 1983.

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Table 4. Catalytic Intermolecular Hydroamination Catalyzed by the Organouranium Complexes $Cp^*_2UMe_2$ (36), $Cp^*_2U(NHEt)_2$ (37), and $Cp^*_2U{=}NR(THF)$ (NR = 2,6-dimethylanilide) (38)

entry	cat	RC≡CH R	R′NH$_2$	solvent[a]	product	conversion % (yield %)	N_t (h^{-1}) (temp °C)
1	**36**	TMS	Me	B	**1**	>97, (95)	3.1, (78)
2	**36**	TMS	Et	B	**2A** + **2B**	>97, (90:10)	2.2, (78)
3	**36**	TMS	Et	T	**2A**	>97, (90)	3.0, (65)
4	**36**	TMS	Et	C	**2A**	>97, (95)	1.8, (78)
5	**36**	TMS	Et	To	**2A**	>97, (85)	3.3, (95)
6	**36**	TMS	Et	Cl			
7	**37**	TMS	Et	T	**2A**	95, (89)	3.0, (65)
8	**38**	TMS	Et	T	**2A**	94, (85)	3.1, (65)
9	**36**	TMS	*n*-Pr	B	**3**	>98, (95)	3.6, (78)
10	**36**	TMS	*i*-Pr	B	**4**	>98, (95)	0.5, (78)
11	**36**	TMS	*n*-Bu	T	**5**	>98, (93)	2.5, (65)
12	**36**	TMS	*i*-Bu	B	**6**	95, (90)	0.9, (78)
13	**36**	TMS	*t*-Bu	B	**7A**, **8A**	95 (1:9)	10, (65)
14	**36**	*t*-Bu	Me	B	**9**	95, (95)	4.0, (78)
15	**36**	*t*-Bu	Et	T	**10**	>98, (93)	3.4, (65)
16	**37**	*t*-Bu	Et	T	**10**	93, (86)	3.5, (65)
17	**38**	*t*-Bu	Et	T	**10**	91, (82)	3.5, (65)
18	**36**	*t*-Bu	n-Pr	B	**11**	>98, (91)	2.4, (78)
19	**36**	*t*-Bu	i-Pr	T	**12**	65, (55)	0.4, (65)
20	**36**	*t*-Bu	i-Pr	B	**12**	55, (50)	0.05, (78)
21	**36**	*t*-Bu	n-Bu	T	**13**	95, (84)	1.8, (65)
22	**36**	*t*-Bu	i-Bu	T	**14**	95, (87)	0.4, (65)
23	**36**	*t*-Bu	t-Bu	B	**7B**	>99, (95)	11, (78)[c]
24	**36**	*n*-Bu	Me	B	**15**	96, (92)	4.1, (78)
25	**36**	*n*-Bu	Et	T	**16**	95, (88)	4.3, (65)
26	**36**	*n*-Bu	n-Pr	B	**17**	65, (91)	3.5, (78)
27	**36**	*n*-Bu	i-Pr	B	**18**	65, (91)	0.6, (78)
28	**36**	*n*-Bu	i-Bu	B	**19**	95, (92)	3.7, (78)
29	**36**	*n*-Bu	t-Bu	B	**7C**	90 (60)	8.0, (65)
30	**36**	Ph	Me	T	**20**	95, (85)	4.2, (65)
31	**36**	Ph	Et	T	**21**	72, (66)	1.5, (65)
32	**36**	Ph	*t*-Bu	B	**7D**	95, (90)	6.0, (78)
33	**36**	*i*-Pr	Et	T	**22**	95, (86)	3.0, (65)
34	**36**	C_5H_{11}	Et	T	**23**	92, (80)	3.0, (65)

[a] B = benzene, T = THF, C = cyclohexane, To = toluene, and Cl = chloroform.

Table 5. Catalytic Intermolecular Hydroamination Catalyzed by the Organothorium Complexes $Cp^*_2ThMe_2$ (30) and $Cp^*_2Th{=}NR''(THF)$ (R″ = 2,6-dimethylanilide) (33)

entry	cat	RC≡CH R	R′NH$_2$	solvent[a]	product	conversion % (yield %)	N_t (h^{-1}) (temp °C)
1	**30**	TMS	Me	B	**1**	>97, (27)	1.5, (78)
2	**30**	TMS	Et	B	**2A**	>97, (35)	1.8, (78)
3	**30**	TMS	Et	Cl			
4	**33**	TMS	Et	B	**2A**	>95, (30)	1.9, (78)
5	**30**	H	Et	B	**24**	>97, (80)	11.3, (48)
6	**30**	*n*-Bu	Me	B	**25**	>97, (7)	0.3, (78)
7	**30**	*n*-Bu	Et	B	**26**	>97, (10)	0.1, (65)
8	**33**	*n*-Bu	Et	B	**26**	>95, (13)	0.1, (65)
9	**30**	Ph	Et	B	**27**	>97, (33)	14, (78)
10	**30**	*i*-Pr	Ph	B	**28**	>95, (85)	0.07, (78)

[a] B = benzene, T = THF, C = cyclohexane, To = toluene, and Cl = chloroform.

the methyl and the chloride groups with equal statistical population at both equatorial sites (Figure 1), while Table 1 and Table 2 summarize the crystal and structural data. Complex **31** reacts with 1 equiv of the lithium amide salt LiNHR (RNH = 2,6-dimethylanilide), producing the monoamido methyl complex **32** in quantitative yield.[18] Heating a THF solution of complex **32** for 2 h allows the formation of the solvated imido complex **33** with the concomitant formation of methane. Eliminating an amine molecule from the bisamido complex **35** in a solution of refluxing THF allows an additional pathway toward the formation of complex **33** (Scheme 1). Complex **35** can be obtained from the reaction of the bisacetylide complex **34** with two equimolar amounts of the corresponding amine.[18,58]

The X-ray ORTEP picture of the imido complex **33** is presented in Figure 2, while Tables 1 and 3 summarize the crystal and structural data, respectively. Complex **33** crystallizes in a monoclinic C-centered space group having two independent molecules in the unit cell. The Th(1)−N(1) distance 2.045(8) Å is short, as expected for an imido metal double bond. This bond length agrees well with other organo-f-imido bond lengths when differences in ionic radii due to the distinctive metals, including oxidation states and coordination number, are taken into account.[59] The most important feature in complex **33** is the almost linear Th−N−C_{ipso} = 171.5-(7)°, as observed for various imido-transition metals[29] but in contrast for a similar uranium-imido complex (U−N−C_{ipso} = 162.3(10)°) having a slight distortion from linearity.[56] The oxygen of the THF solvent donates a

(58) Straub, T. R., G.; Frank, W.; Eisen, M. S. *J. Chem. Soc., Dalton Trans.* **1996**, 2541.

(59) (a) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751. (b) Spirlet, M. R.; Rebizant, J.; Apostolidis, C.; Kanellakopulos, B. *Acta Crystallogr.* **1992**, *C48*, 2135.

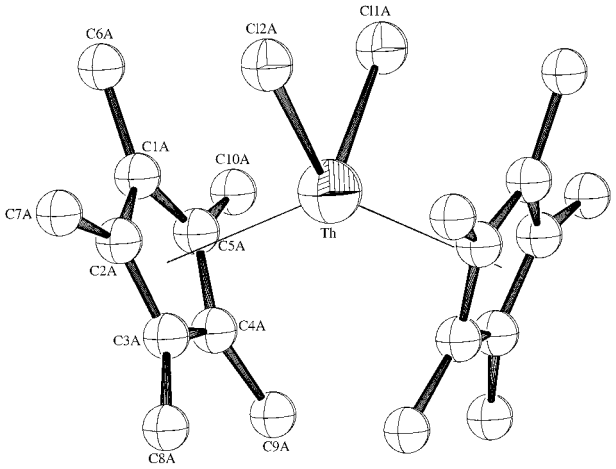


Figure 1. ORTEP plot of complex **31** showing ideal spheres for all atoms except the metal center.

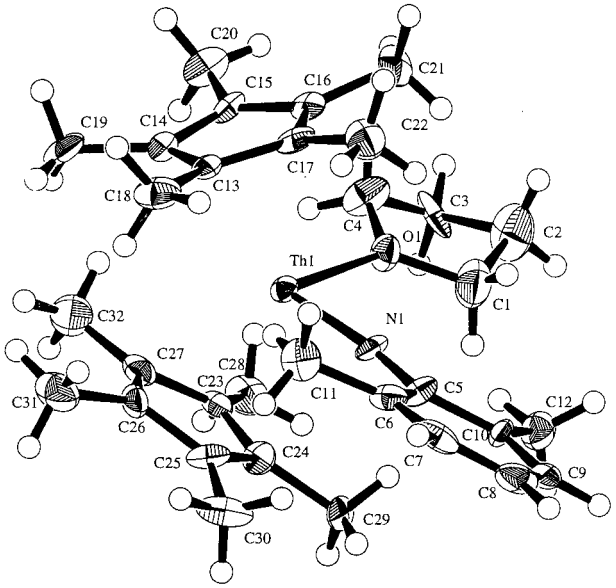
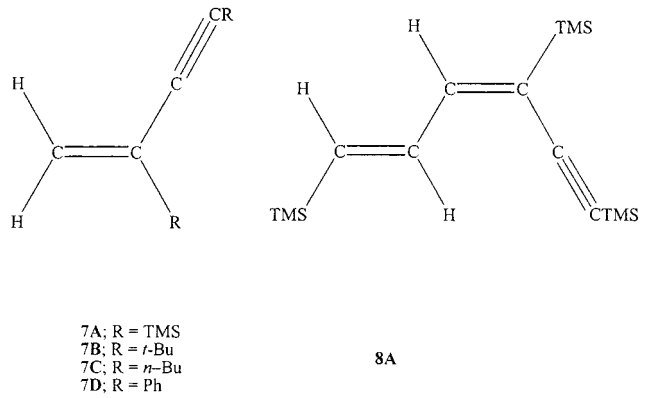


Figure 2. Perspective ORTEP drawing of the nonhydrogen atoms in complex **33**. All atoms are represented by thermal ellipsoids drawn to encompass 50% of the electron density.

pair of nonbonding electrons to the thorium metal (Th−O = 2.526(7) Å), causing a metal coordinative saturation stabilization. The ancillary ligations are disposed relative to the thorium center in a distorted tetrahedral fashion exhibiting a narrow angle between the equatorial ligands (N−Th−O = 100.8(3)°) and a wide angle between the cyclopentadienyl ligands (ring-centroid−Th−ring-centroid = 132.0(2)°).

Actinide, Amine, and Alkyne Effect on the Catalytic Process. The catalyzed intermolecular process as illustrated in eqs 4 and 5 shows two possible regioselectivities of the hydroamination products depending the used catalyst. The intermolecular hydroamination catalyzed by the uranium catalyst (Table 4) shows a large regio- and chemoselectivity toward only one type of imine products in which the amine and alkyne substituents are disposed, almost always, in a *E* regiochemistry, whereas for the thorium catalyst (Table 5), the methyl alkyl-substituted imines are obtained. These latter imines are produced in moderate yields due to the competing dimerization of the corresponding alkyne



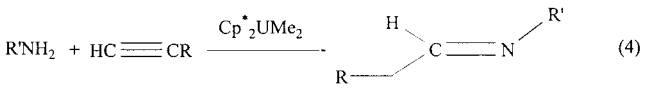
7A; R = TMS
7B; R = *t*-Bu
7C; R = *n*-Bu
7D; R = Ph

8A

Figure 3. Dimer and trimer observed in the hydroamination of terminal alkynes and primary amines promoted by organoactinide complexes.

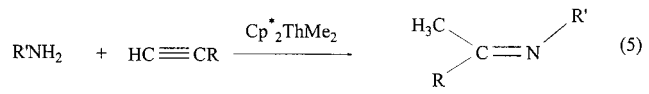
toward the geminal dimer. When the organouranium complexes catalyze the hydroamination reaction, for (TMS)C≡CH and $EtNH_2$ (entry 2, Table 4) both stereoisomers *E*-**2A** and *Z*-**2B** are obtained in a ratio of 90:10, respectively, in addition to some traces (<4%) of the geminal dimer **7A** and the trimer **8A** (Figure 3)**.** The *Z* isomer and the oligomeric traces are formed only when the reaction is carried out in benzene.[18,37] When the same reaction is carried out in THF, cyclohexane, or even toluene, the highly preferentially formed product is the isomeric *E*-imine, **2A** (entries 3−5, Table 4). In $CHCl_3$ (entry 6) no hydroamination reaction is observed, but the starting precatalyst reacts with the solvent, producing the corresponding dichloro organoactinide metallocene, $Cp^*_2UCl_2$. Thus, for terminal alkynes (RC≡CH, R = TMS, *t*-Bu, *n*-Bu, Ph, C_5H_{11}, *i*-Pr), a large variety of primary aliphatic amines (R′NH_2, R′ = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu) can be used to produce the intermolecular hydroamination products in a variety of polar or nonpolar solvents. When the different complexes $Cp^*_2UMe_2$ (**36**), $Cp^*_2U(NHEt)_2$ (**37**), and Cp^*_2U=NR(THF) (NR = 2,6-dimethylanilide) (**38**) are used as starting materials for the hydroamination of (TMS)C≡CH or *t*-BuC≡CH with $EtNH_2$, similar rates, stereochemistry, and yields of the imine products are obtained (entries 7, 8 and 16, 17 in Table 4). This result strongly argues for a shared active species for those three complexes.

Interestingly, for all the alkyne reactions catalyzed by the uranium complex, in which the bulky *t*-$BuNH_2$ was used as the primary aliphatic amine, no hydroamination products were observed. The products observed were only the selective geminal dimers corresponding to the starting alkyne (for (TMS)C≡CH the trimer **8A** was also observed), which were obtained quantitatively with high turnover frequencies (Table 4, entries 13, 23, 29, and 32). This result indicates that with *t*-$BuNH_2$ the active species for the intermolecular hydroamination is not obtained. Moreover, the only tracked catalytic compounds, observed in solution, are the uranium bis(acetylide) (**39**) and the uranium bis(amido) (**40**) complexes. We have already shown that the latter two compounds are in rapid equilibrium with the mono amido acetylide complex (**A**), responsible for the oligomerization of alkynes in the presence of amines (eq 6).[18] An attempt to perform the hydroamination reaction with secondary amines produces only oligomeric alkynes, indicating again the lack of formation of the active



(4)

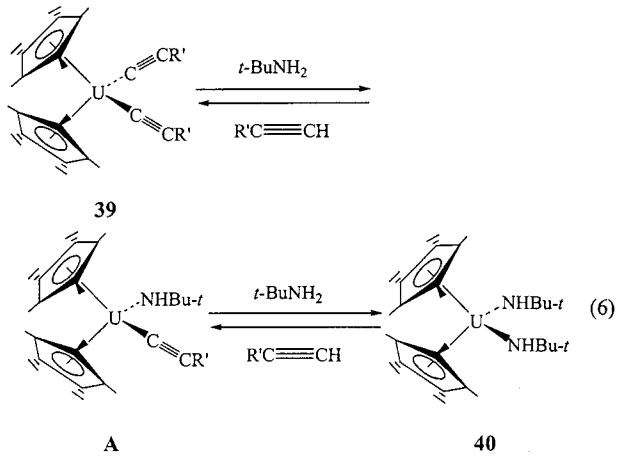
R =	TMS, R' = Me	(**1**)	R =	*n*-Bu, R' = Me	(**15**)
R =	TMS, R' = Et	(**2**)	R =	*n*-Bu, R' = Et	(**16**)
R =	TMS, R' = *n*-Pr	(**3**)	R =	*n*-Bu, R' = *n*-Pr	(**17**)
R =	TMS, R' = *i*-Pr	(**4**)	R =	*n*-Bu, R' = *i*-Pr	(**18**)
R =	TMS, R' = *n*-Bu	(**5**)	R =	*n*-Bu, R' = *i*-Bu	(**19**)
R =	TMS, R' = *i*-Bu	(**6**)	R =	Ph, R' = Me	(**20**)
R =	*t*-Bu, R' = Me	(**9**)	R =	Ph R' = Et	(**21**)
R =	*t*-Bu, R' = Et	(**10**)	R =	*i*-Bu, R' = Et	(**22**)
R =	*t*-Bu, R' = *n*-Pr	(**11**)	R =	C_5H_{11}, R' = Et	(**23**)
R =	*t*-Bu, R' = *i*-Pr	(**12**)			
R =	*t*-Bu, R' = *n*-Bu	(**13**)			
R =	*t*-Bu, R' = *i*-Bu	(**14**)			



(5)

R =	H, R' = Et	(**24**)
R =	*n*-Bu, R' = Me	(**25**)
R =	*n*-Bu, R' = Et	(**26**)
R =	Ph, R' = Et	(**27**)
R =	*i*-Pr, R' = Ph	(**28**)

hydroamination complex, whereas when carrying out the reaction with internal alkynes, no hydroamination or other products were observed.



(6)

When comparing the hydroamination rates for a specific alkyne utilizing the assorted amines, with their different substituent steric hindrances, we have observed that the use of bulkier amines dramatically induces a lower turnover frequency (N_t). When comparing the hydroamination rates for a particular amine ($MeNH_2$), using the diverse alkynes (compare entries 1, 14, 24, and 30 in Table 4), similar N_t values are observed. This result firmly indicates that the bulkiness of the terminal alkyne has a less important effect on the hydroamination rate as compared to the amine effect.

The intermolecular hydroamination catalyzed by the analogous organothorium complex $Cp^*_2ThMe_2$ (**30**) (eq 5, Table 5) exhibits similar reactivities with (TMS)C≡CH and $MeNH_2$ or $EtNH_2$, producing the imines **1** and **2A**, respectively (entries 1, 2 in Table 5). An attempt to perform the hydroamination reaction in chloroform produces only the corresponding thorium dichloride complex **29** (entry 3 in Table 5), in a similar fashion as obtained for the analogous uranium complex. With HC≡CH, the imine **24** is formed with traces of some oligomerization products. However, in the intermolecular hydroamination catalyzed by complex **30** with *n*-BuC≡CH or PhC≡CH and $MeNH_2$ or $EtNH_2$ a dramatic change in the regioselectivity takes place, yielding the unexpected imines **25**−**27** (entries 6, 7, 9, and 10 in Table 5), respectively, with assorted amounts of the corresponding alkyne geminal dimers. An effort to perform the hydroamination reaction with secondary amines allows only the chemoselective formation of alkyne dimer and trimers without any traceable hydroamination products (Figure 3).[18]

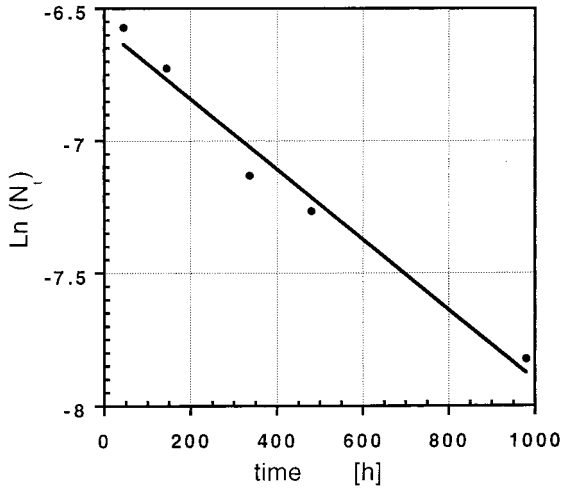


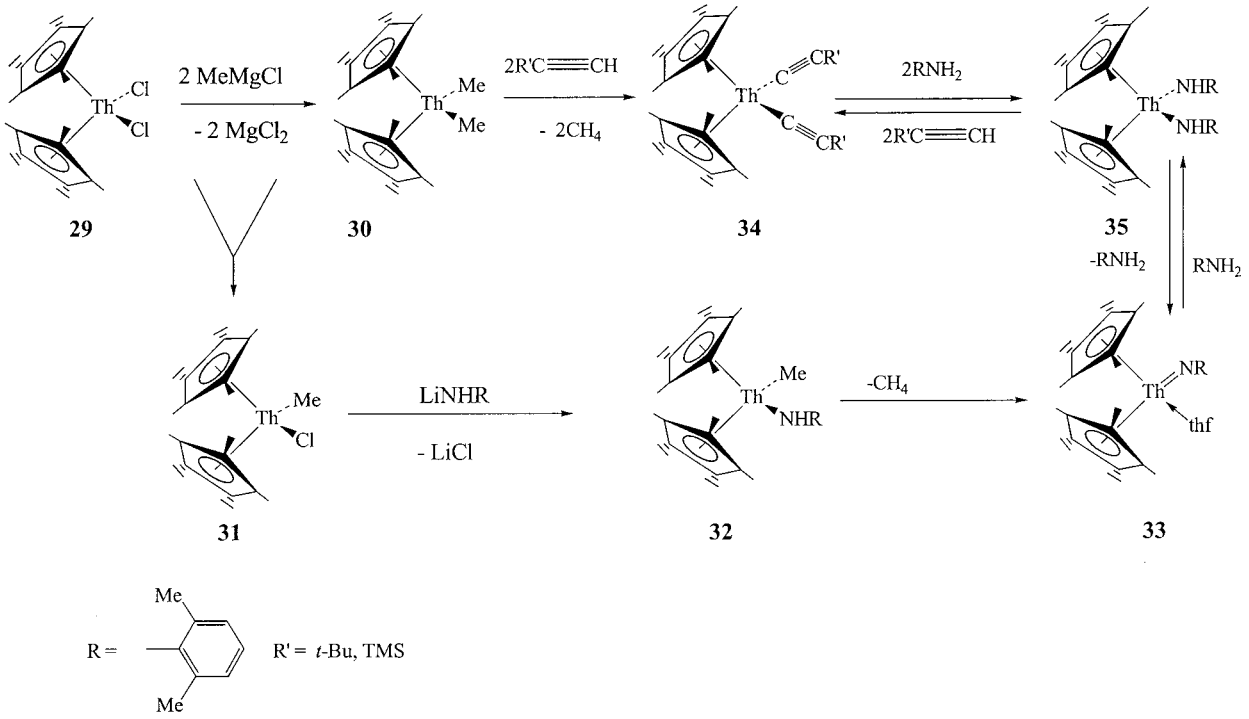
Figure 4. Linear first-order dependence for the 1,3-sigmatropic rearrangement of the imine **2A** into **2C** in toluene at 110 °C.

The catalytic hydroamination of *n*-BuC≡CH or (TMS)C≡CH with $EtNH_2$ with either complex **30** or the imido complex **33** gave similar rate, yields, stereochemistry of the products, and indistinguishable kinetic curves (compare entries 2, 4 and 7, 8 in Table 5), indicating that both complexes are routed through a mutual active species, in a manner similar to that observed for the different uranium complexes. Performing the reaction of *i*-PrC≡CH and aniline, $PhNH_2$, the imine **28** is obtained in high yield, as the sole product of the reaction, but with very low turnover frequency (N_t = 0.07 h^{-1}). This result is similar to the results obtained for the hydroamination of alkynes with aromatic amines by early transition-metal complexes.[28,29]

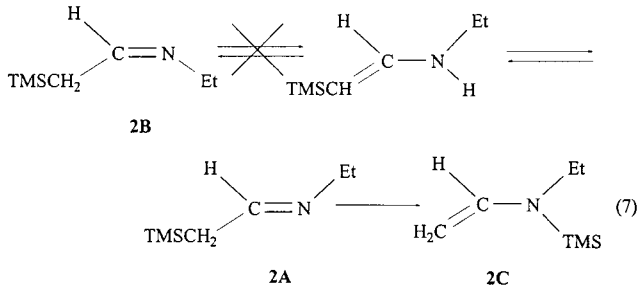
The imine **2A** was found to undergo a noncatalyzed silyl Brook rearrangement at 60 °C in THF to form the corresponding enamine **2C** (eq 7).[60] The rearrangement also follows a first order in imine at 110 °C in toluene, as indicated by a plot of the natural logarithm of the turnover frequencies as a function of time for different imine concentrations (Figure 4). The rearrangement was observed to proceed at similar turnover frequencies in either cyclohexane or THF, corroborating that the reaction is plausibly intramolecular via a concerted mechanism, displaying a lack of polar transition states during the rearrangement.[60] Interestingly, following by ^1H NMR spectroscopy the rearrangement of a mixture of isomers **2A** and **2B** in a ratio of 9:1, respectively, at

(60) (a) Brook, A. G.; Bassindale, A. R. In *Rearrangements in Ground and Exited States*; Academic Press: New York, 1980; Vol. 2. (b) Hitchock, P. B.; Lappert, M. F.; Liu, D.-S. *J. Chem. Soc., Chem. Commun.* **1994**, 1699.

Scheme 1. Stoichiometric Reactivity of $Cp^*_2Th(Cl)Me$ with Lithium Amide and $Cp^*_2ThMe_2$ with Primary Amines and Terminal Alkynes



60 °C in THF or at 110 °C in toluene (even if the crude mixture is used after the hydroamination reaction with catalyst and amine), shows that the isomer **2A** is fully rearranged to **2C**, leaving the concentration of **2B** unaffected. This result argues that an imine−enamine tautomerization is not highly operative in THF at 60 °C or in toluene at 110 °C for this specific imine. In the presence of such a tautomerization the imine **2B** would be equilibrated into a new mixture of **2A** and **2B**, resulting in the total conversion of **2B** into **2C** (eq 7).

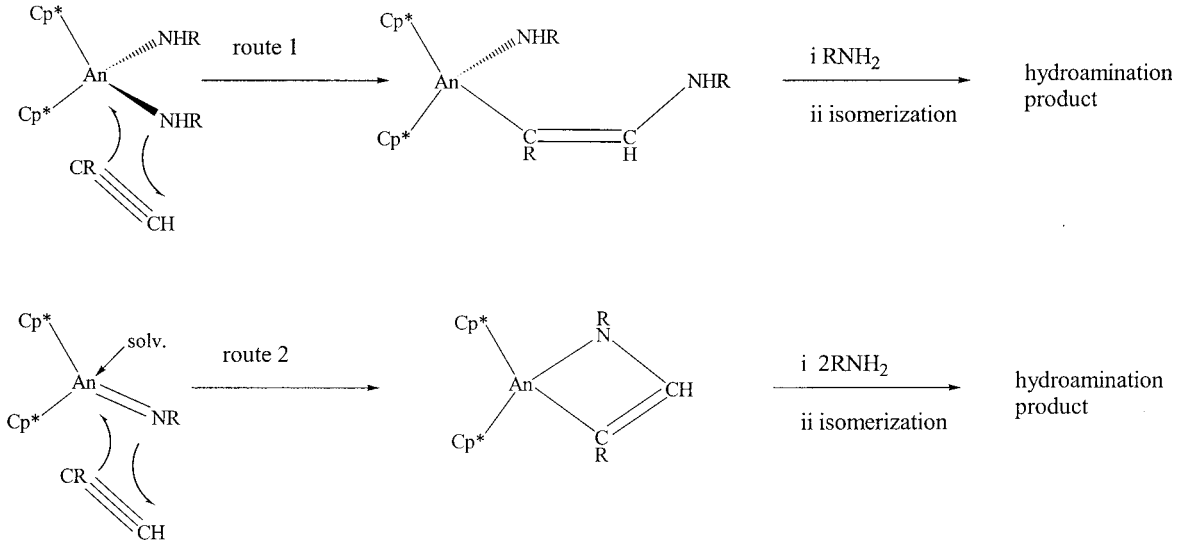


The formation of the concomitant oligomers observed in the hydroamination reactions catalyzed by both thorium complexes **30** and **33** indicates that two different complexes are active, in solution, plausibly interconverting, causing the formation of the two parallel processes. Since the characterization of active species responsible for the formation of dimer and trimers of terminal alkynes has been recently disclosed (eq 6, for thorium complexes this equation is also effective),[18] it was conceptually important to differentiate between two possible pathways for the key intermediate organometallic responsible for the hydroamination process (Scheme 2). The first route is an insertion of an alkyne into a metal−amido bond, as found in lanthanide chemistry.[31,33,61] The second route comprises the insertion of an alkyne into a metal−imido (M=N) bond, as observed for early transition-metal complexes.[29] To discriminate between these two routes, kinetic and thermodynamic studies have been performed.

Kinetic Studies of the Hydroamination Terminal Alkynes with Primary Amines. Kinetic measurements on the hydroamination of (TMS)C≡CH with $EtNH_2$ were undertaken by in-situ ^1H NMR spectroscopy. The reaction of an ≈70-fold excess of (TMS)C≡CH (3.0 M) with the precatalyst $(C_5Me_5)_2UMe_2$ (0.043 M) was monitored with constant alkyne and catalyst concentrations until complete amine consumption (range of amine concentrations = 0.029−0.31 M). Either the disappearance of the terminal alkyne's hydrogen C≡CH (δ = 2.280 ppm) or the appearance of the aldimine CH=NEt (δ = 7.65 ppm) ^1H resonances were normalized depending if the alkyne or the amine was constant during the kinetic measurements. The turnover frequency of the reaction was calculated from the slope of the kinetic plots of substrate-to-catalyst ratio vs time. Considering the rapidity of the actinide−alkyl protonolysis by primary amines,[39,58] it seems unreasonable that intermolecular proton transfer from either an alkyne or an amine toward the formation of the product could be the turnover-limiting step under most catalytic conditions. A plot of the imine concentration vs time (Figure 5a) exhibits the behavior for an inverse proportionality that is corroborated by the plot of $^1/_2$[amine]^2 vs time yielding a straight line (Figure 5b), indicating that the reaction is inverse first order in amine. An inverse proportionality in catalytic systems is well known and is consistent with a rapid equilibrium before the turnover-limiting step. In our case, this is consistent with an equilibrium between the bis(amido) and the bis-

(61) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 707.

Scheme 2. Plausible Expected Pathways for the Organoactinide-Catalyzed Intermolecular Hydroamination of Primary Amines with Terminal Alkynes



An = U;
For An= Th, the approach stereochemistry for some alkynes must be inverted before insertion

(amido)−amine complexes, as already found for the controlled oligomerization of terminal alkynes in the presence of amines by these organoactinides.[58,62] Similar equilibria have been observed in the hydroamination of olefins promoted by organolanthanide complexes.[6,63]

When the initial concentration of the alkyne and the amine are maintained constant and the concentration of the catalytic precursor is varied over a ~11-fold concentration range (Figure 6), a plot of the reaction rate vs precatalyst concentration indicates that the reaction is first-order dependent in precatalyst. When the concentration of the amine and the catalyst are held constant and the concentration of the alkyne is changed over a 39-fold concentration range, no difference in the kinetic rate is observed, indicating that the reaction is zero order in alkyne concentration. Thus, the rate law for the hydroamination of terminal alkynes promoted by organoactinides[64] can be formulated as presented in eq 8.

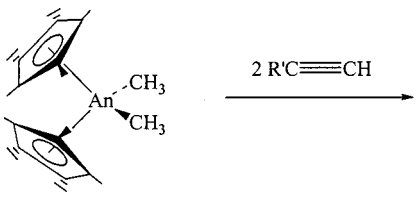
$$\nu = k[\mathrm{An}][\mathrm{amine}]^{-1}[\mathrm{alkyne}]^{0} \qquad (8)$$

The derived $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ parameter values (in the range 60−120 °C) (error values are in parentheses) from a thermal Eyring analysis (Figure 7) are 11.7(3) kcal mol^{-1} and −44.5 (8) eu, respectively.

Discussion

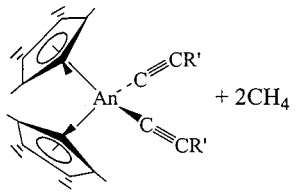
The discussion of the results will be presented by starting with some stoichiometric organoactinide reactions toward the formation of either the corresponding bis(acetylide) or bis(amido) complexes, the key organoactinide imido complex, the reaction scope, and the mechanistic implications.

Synthesis of Bis(acetylide) and Bis(amido) Organoactinide Complexes. One of the earliest primary reactions we need to appreciate is related to the resting state of the different organoactinides in the presence of alkynes and amines. Our discussion starts by presenting the reactions of organoactinides with stoichiometric amounts of terminal alkynes and then their consecutive reactions with amines. The σ-bond metathesis reaction of the acidic proton of a terminal alkyne with an organoactinide complex of the type $Cp^*_2AnMe_2$ (An = Th, U) is an extremely fast exothermic reaction driven by the elimination of methane. A series of these bis(acetylide) complexes have been prepared and characterized (eq 9).[18,22]



An = Th (**30**)
An = U (**36**)

$\Delta H_{\mathrm{Th\ (calc)}} = -18$ kcal mol^{-1}
$\Delta H_{\mathrm{U\ (calc)}} = -48$ kcal mol^{-1}



(9)

An = Th (**34**)
An = U (**39**)

The monoacetylide methyl complexes $Cp^*_2AnMe(C{\equiv}CR)$ (An = Th, U; R = alkyl) have been observed, as a

(62) Eisen, M. S.; Straub, T.; Haskel, A. *J. Alloys Compd.* **1998**, *271*, 116.

(63) This type of equilibrium has also been observed in organolanthanide chemistry in the presence of amines, see: (a) Gagnè, M. R.; Brard, L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275. (b) Gagnè, M.; Brard, L.; Conticello, V. P.; Giardello, M. A.; Stern, C. L.; Marks, T. J. *Organometallics* **1992**, *11*, 2003.

(64) The same rate law is observed for the corresponding organothorium complex.

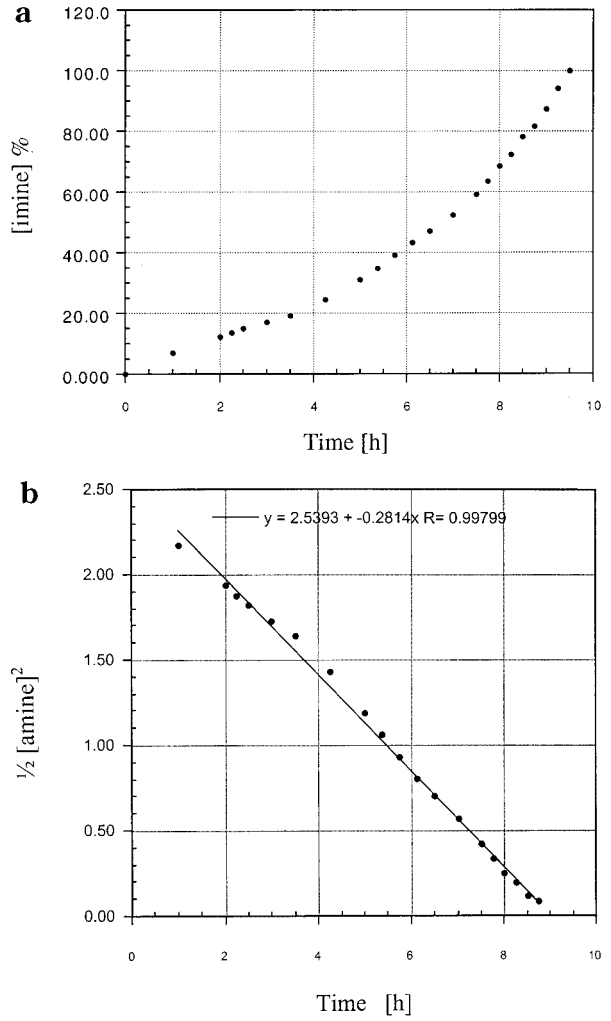


Figure 5. Determination of the reaction order in amine concentration for the hydroamination of TMSC≡CH and $EtNH_2$ mediated by $Cp^*_2UMe_2$ as the precatalyst in benzene-d_6 at 20 °C. Plot of imine concentration vs time (**5a**). Linear plot of $^1/_2$[amine]^2 vs time (**5b**).

transient organometallic, for the uranium complex only when the alkyne *i*-PrC≡CH was used. For the rest of the utilized alkynes or when using the thorium complex (**30**), the starting dimethyl or the bis(acetylide) organo-f-complexes are the exclusive products observed.[22] This result indicates that, in general, the second σ-bond metathesis has a lower energy of activation as compared to the activation energy needed to form the monoacetylide organoactinide complexes. One of the most remarkable behaviors of these bisacetylide organoactinides is their different unexpected performance in the presence of primary amines. We have shown that organoactinides of the type ($Cp^*_2AnMe_2$) in the presence of primary amines will form for thorium, the bis(amido) complexes $Cp^*_2Th(NHR)_2$ (RNH = 2,6-dimethylanilide (**35**)), and for uranium the imido complexes $Cp^*_2U{=}NR$ (RN = 2,6-dimethylanilide (**38**)).[18,20,22]

Catalytic Reaction Scope and Mechanism. The present catalytic results for the intermolecular hydroamination of terminal alkynes with primary amines produce imines, and depending on the starting organoactinide, alkyne oligomers (dimers and trimers) are observed as coproducts. A substantial range of substrates can be selectively hydroaminated including

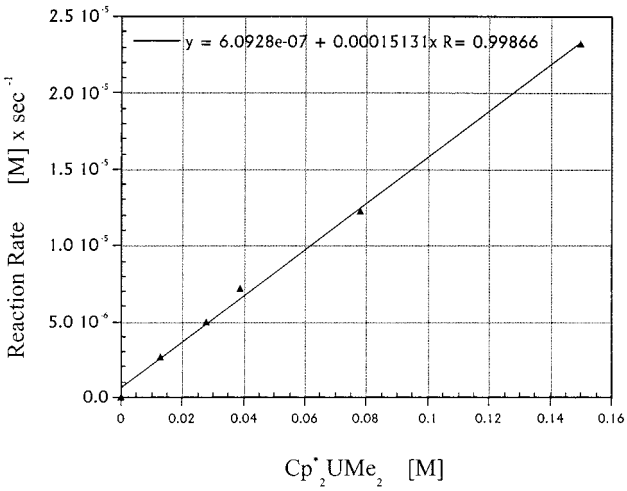


Figure 6. Determination of the reaction order in catalyst concentration for the hydroamination of TMSC≡CH and $EtNH_2$ mediated by $Cp^*_2UMe_2$ as the precatalyst in benzene-d_6 at 20 °C.

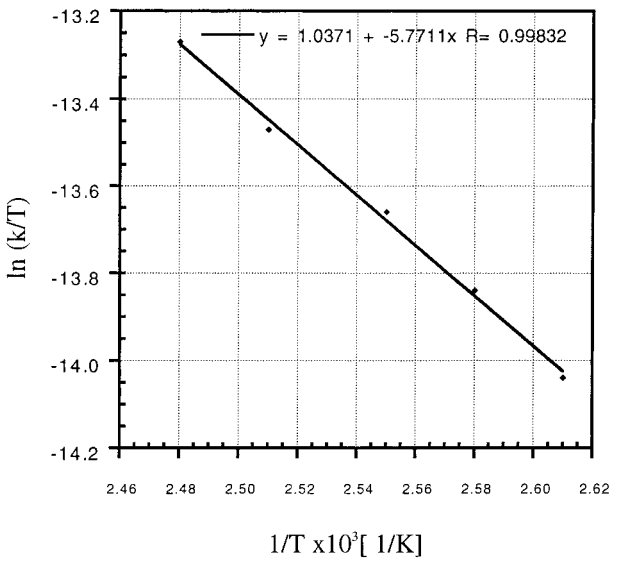
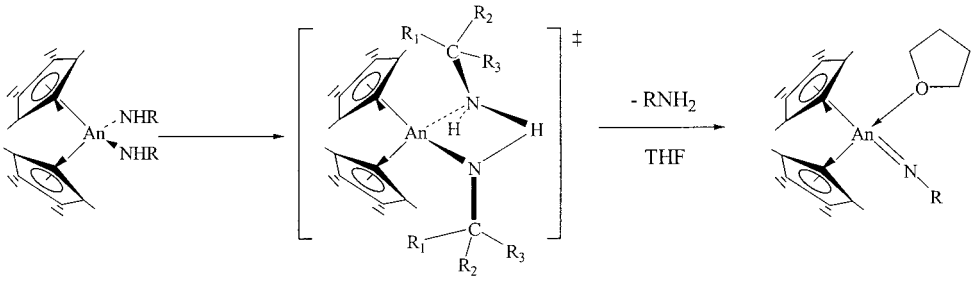


Figure 7. Eyring plot for the hydroamination of TMSC≡CH and $EtNH_2$ mediated by $Cp^*_2UMe_2$ as the precatalyst in toluene-d_8. The line represents the least-squares fit to the data points.

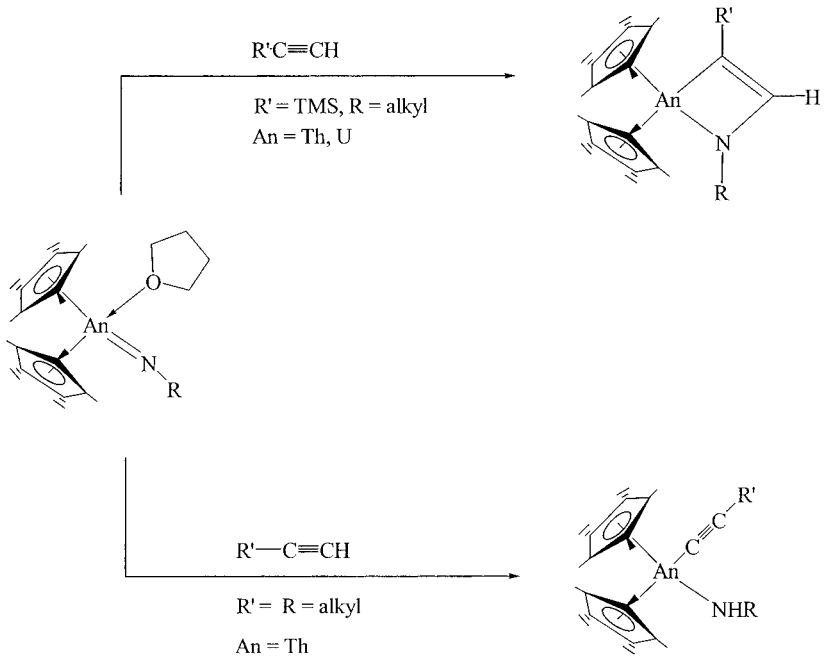
bulky and nonbulky aliphatic and aromatic alkynes. Regarding the amine effect and for the uranium case, we have found that the bulkier the amine substituent, the lower the rate of hydroamination, leading to a constraint with the bulkier *t*-$BuNH_2$, which allows only the production of dimeric alkynes. It is important to point out that increasing the bulkiness of the amine does not produce more dimeric compounds; thus with *t*-$BuNH_2$ the active hydroamination complex is not formed. Since the stereochemical approach of either an alkyne or an amine to the organometallic moiety is via a side approach,[40,65] its reasonable to consider that the lack of alkyne effect on the kinetic hydroamination rate suggests that the proposed route 1 (Scheme 2) is not a major operative pathway for the organoactinide-catalyzed hydroamination of terminal alkynes and amines. This particular route has been studied resulting only

(65) Elschenbroich, C.; Salzer, A. *Organometallics*, 1st ed.; VCH: Weinheim, Germany, 1989; Chapters 15 and 17.

Scheme 3. Plausible N−H Activation Pathway for the Formation of Imido Organoactinides (For *t*-BuNH$_2$ No Reaction Is Observed)



Scheme 4. Distinctive Modes of Activation for Organoactinide−Imido Complexes in the Presence of Terminal Alkynes

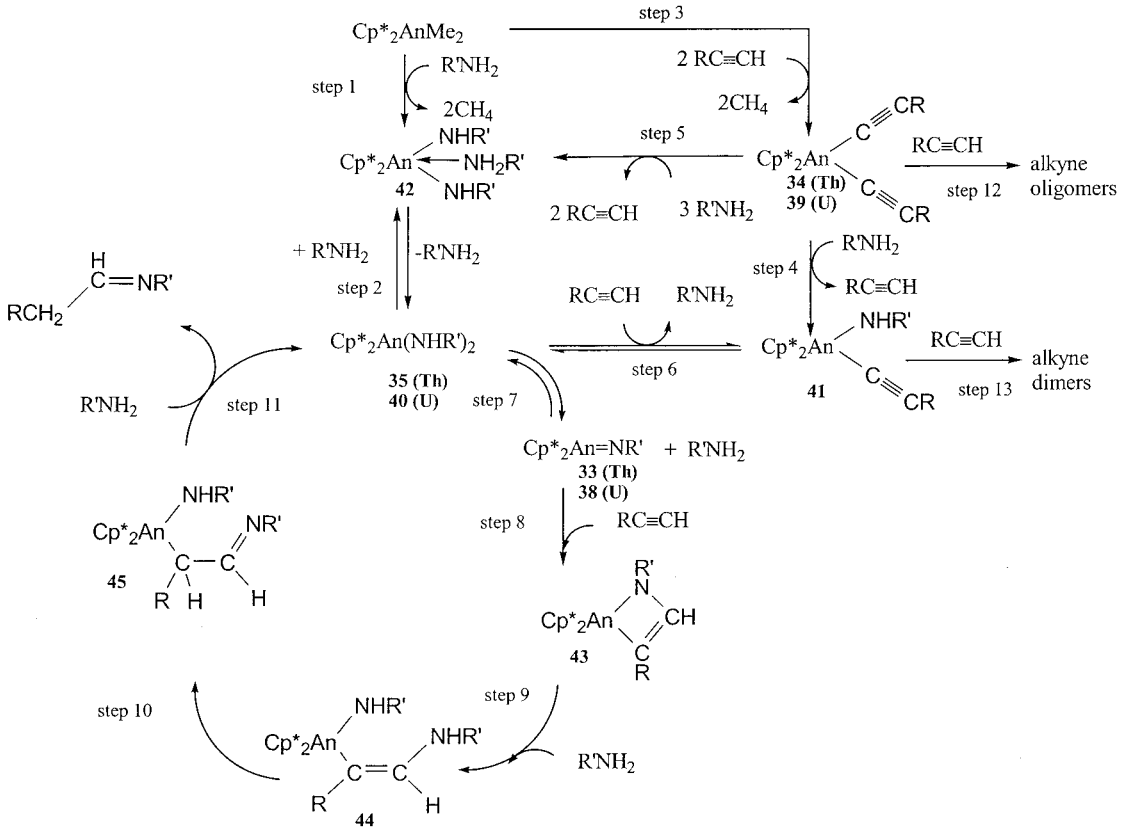


in the amido substitution by the alkyne producing the monoacetylide complex with no hydroamination products.[18,58,62] Moreover if this route would be operative, secondary amines should also induce the hydroamination reaction, which is not the present case. The zero kinetic order on alkyne supports route 2 (Scheme 2), corroborating the high coordinative unsaturation of the imido complexes under the reaction conditions allowing a fast insertion of the different alkynes with identical rates. Hence, when bulky amines are utilized, the rate of formation for the corresponding imido complexes is retarded due to the encumbered transition state, as described in Scheme 3, reaching the highest steric encumbrance with *t*-BuNH$_2$, where only the starting bisamido complex is obtained.

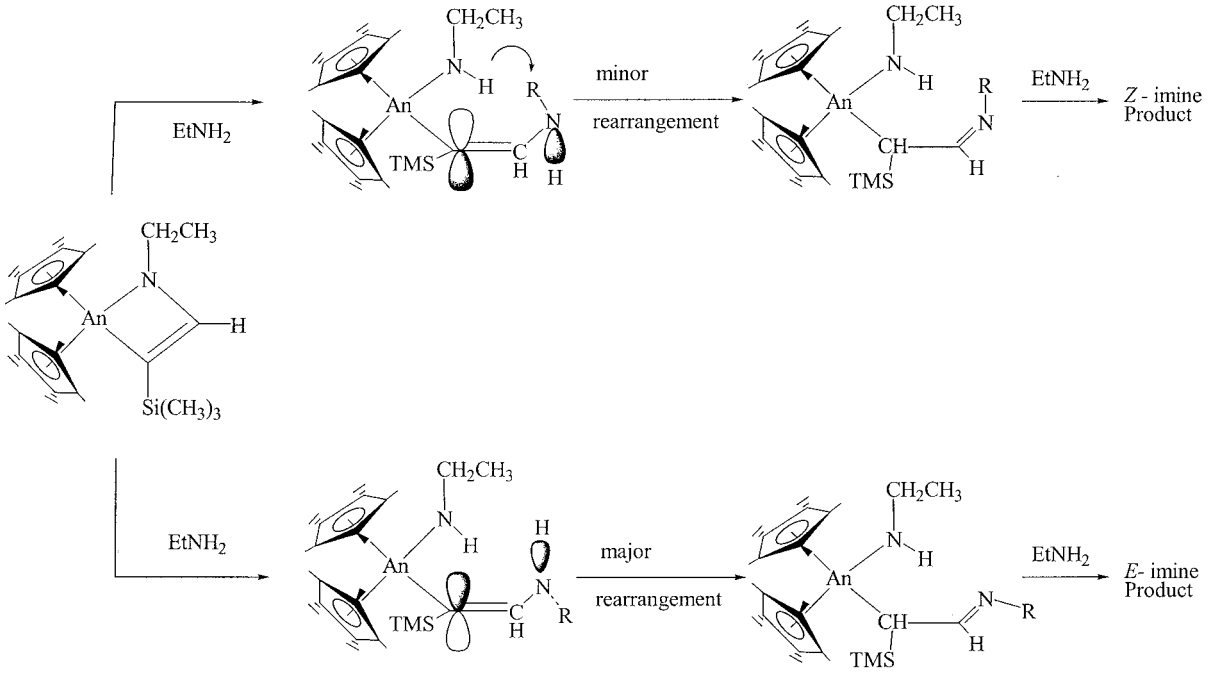
Interesting is the fate of the different imido complexes upon their reactions with terminal alkynes. For both organoactinide−imido complexes, a selective metathesis with the π-bond of the alkyne is likely operative (production of hydroamination products), whereas for the thorium complex a protonolysis reaction is encountered as a competing reaction concomitantly (Scheme 4). This competing reaction forms the active monoacetylide thorium amido complex (**41**) responsible for the selective dimerization of the terminal alkynes.

For secondary amines, no hydroamination reaction was noticed, indicating that a high-energy pathway should be necessary to prepare the corresponding imido complex, by eliminating a tertiary amine from the bis(dialkyl)amido complex. In contrast, a similar mono(dialkyl)amido monoacetylide complex, Cp*$_2$An(NR$_2$)(C≡CR′), similar to complexes **A** and **41** for the uranium and thorium complexes, respectively, yields the dimerization/oligomerization of the terminal alkynes, as already disclosed.[18] Regarding the rate, the present hydroamination reactions exhibit rates (N_t = 0.05−14 h^{-1}) that are lower than those observed for either the selective or nonselective oligomerization of alkynes (5−18 h^{-1}). The activation entropy $\Delta S^{\ddagger} = -44.5(8)$ eu for the hydroamination of (TMS)C≡CH with EtNH$_2$ can be compared to the entropy value of $\Delta S^{\ddagger} = -41.2(6)$ eu obtained for the dimerization of 1-hexyne in the presence of *t*-BuNH$_2$[18,20] or to the value of $\Delta S^{\ddagger} = -45.2(6)$ obtained for the trimerization of (TMS)C≡CH, promoted by Cp*$_2$ThMe$_2$.[37] It appears that all three processes proceed with similar degrees of entropic reorganization on approaching the transition state (four-centered transition pathway). Since in the hydroamination of terminal alkynes and the other well-known organoactinide-centered processes, the rate-limiting steps involve the

Scheme 5. Plausible Mechanism for the Intermolecular Hydroamination of Terminal Alkynes and Primary Amines Promoted by the Organoactinide Complexes



Scheme 6. Formation of Imines *E*-2A and *Z*-2B via the 1,3-Sigmatropic Hydrogen Shift from the Two Possible Organoactinide Complexes 44[a]

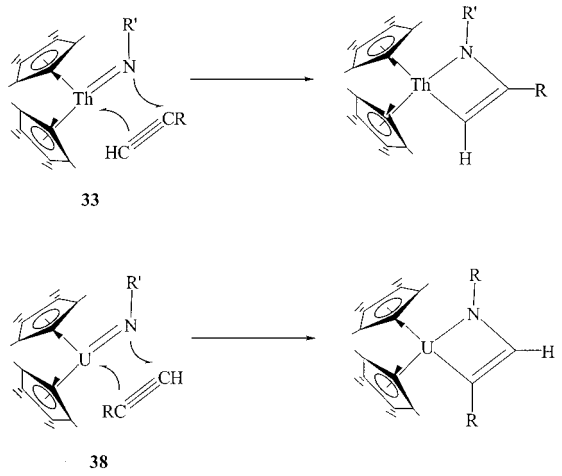


[a] The curved arrow shows the interaction among the amine substituents.

activation of different moieties, the activation enthalpy values are not compared.

A plausible mechanism for the intermolecular hydroamination of terminal alkynes promoted by the organothorium complex is shown in Scheme 5. The mechanism consists of well-established elementary reactions such as insertion of acetylene or amines into M−C or M−N σ-bonds and σ-bond metathesis. The first step in the catalytic cycle involves the N−H σ-bond activation of the primary amine by the starting organoactinide, yielding methane and the bisamido−amine complex $Cp^*_2Ac(NHR')_2 \cdot H_2NR'$ (**42**) (step 1), which is

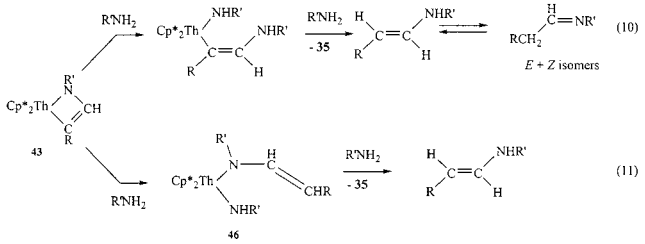
Scheme 7. Opposite Reactivity Exhibited in the Reaction of Organoactinide−Imido Complexes with Terminal Alkynes



in rapid equilibrium with the corresponding bis(amido) complex **35** (step 2).[58,62,63] An additional starting point involves a similar C−H σ-bond activation of an alkyne with the organoactinide, yielding methane and the bis(acetylide) complex **34** (step 3), This complex will react rapidly in the presence of amines either in equivalent amounts (step 4) or with an excess (step 5), yielding complexes **41** or **42**, respectively. Complex **35** may follow two competitive equilibrium pathways. The first pathway, a σ-bond equilibrium metathesis with a terminal alkyne yielding complex **41** (step 6), which will induce the production of selective dimers (step 13). The second pathway (step 7), and as the rate-limiting step, is an elimination of an amine molecule, producing the corresponding imido complex **33**. The imido complex **33** undergoes a rapid π-bond metathesis with an incoming alkyne, yielding the metallacycle **43** (step 8). Rapid protonolytic ring opening of complex **43**, by an amine, yields the actinide−enamine amido complex **44** (step 9). Complex **44** will rapidly isomerize to the actinide−alkyl(imine) amido, **45**, via an intramolecular 1,3-sigmatropic hydrogen shift (step 10), which upon a subsequent protonolysis by an additional amine (step 11) will produce the imine and regenerates the bis(amido) complex **35**.

Theoretically, an additional pathway toward the production of the imine can be proposed from complex **44** as described in eq 10. In this reaction path the protonolysis of the organic compound occurs before the enamine−imine tautomerization. Both σ-M−C(sp^2) (first step in eq 10) and σ-M−C(sp^3) (step 11 in Scheme 3) protonolytic processes have catalytic precedents in organoactinide chemistry.[15,17,37] Since by heating a mixture of the two imines *E*-**2A** and *Z*-**2B** only the imine *E*-**2A** undergoes a 1,3-silyl sigmatropic Brook rearrangement without change in the concentration of the *Z*-**2B** isomer (eq 7), it seems reliable to deduce that the pathway as expressed in eq 10 is not a major operational path and that the isomeric ratio between the *E* and *Z* isomers is governed by the reorganization at the metal complex **44** toward **45**, in distinction as observed for the intramolecular hydroamination of alkynes by organolanthanide complexes.[33,69]

In addition, the lack of enamine−imine isomerization also argues against the protonolysis of the metallacycle



complex **43** yielding the bisamido complex **46** (eq 11). A second protonolysis (either inter- or intramolecular) will be necessary to obtain the enamine (no direct pathway to the imine). The larger amount of the *E* isomer as compared to that of the *Z* isomer is basically a consequence of the steric hindrance of the amine substituents in the isomerization pathway (Scheme 6). It is important to point out that the nature of the different solvent effects observed in the production of imines **2A** and **2B** is as of yet unclear.

Metal Effect on the Catalytic Process. As observed in Tables 4 and 5 the organothorium complex promotes the intermolecular hydroamination in different regioselectivity (except for (TMS)C≡CH), presumably due to the polarization effect of the silicon atom[67]) as compared to the organouranium complex. The product distinction between these two catalysts is achieved due to a contrasting stereochemistry in the metathesis of the alkyne, toward the imido complex (Scheme 7). Since for both metal complexes the bond making and bond breaking are similar (breaking an alkyne π-bond, making a N−C and M−C(sp^2) bonds), it seems plausible that the regiochemistry of the intermolecular hydroamination is driven by the organometallic differences in their imido-electronic configurations rather than the difference in their thermodynamic characteristics (plausibly the f^2 electrons at the uranium complex). A similar difference between isolobal organouranium and organothorium complexes has been already observed for different catalytic processes such as in the oligomerization of alkynes, cross oligomerization of alkynes, and the hydrosilylation of terminal alkynes and olefins.[18,20] These results corroborate a plausible metal-electronic effect as the basis for the stereospecific formation of the hydroamination products.

The lack of reactivity of internal alkynes in the intermolecular hydroamination reaction cannot be ac-

(66) *ORTEP*, TEXRAY Structure Analysis Package; Molecular Structure Corporation: 3200 Research Forest Drive, The Woodlands, TX 77381, 1999.

(67) Stockis and Hoffman have performed calculations on the polarization of the π*-orbitals in (TMS)C≡CH and CH_3C≡CH. Different polarizations were found for both groups, showing the large effect of the substituent on the alkyne sp-carbon atoms. This electronic effect is believed to be responsible for the similar stereochemistry addition of TMSC≡CH to both organoactinides: (a) Stockis, A.; Hoffman, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952. (b) Apeloig, Y. Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806. (c) Allen, A. D.; Krishanmunti, R.; Surya Prakash, G. K.; Tidwell, T. T. *J. Am. Chem. Soc.* **1990**, *112*, 1291. (d) Apeloig, Y.; Biton, R.; Abu-Freih, A. *J. Am. Chem. Soc.* **1993**, *115*, 2522. (e) Frey, J.; Schottland, E.; Rappoport, Z.; Bravo-Zhivotovskii, D.; Nakash, M.; Botoshansky, M.; Kaftory, M.; Apeloig, Y. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2555.

(68) Manuscript in preparation.

(69) Since amine is always present in solution, a base-catalyzed mechanism can be proposed for such a rearrangement. The lack of ratio sensitivity among the *E* and *Z* isomers for the different solvents at the different temperatures (thf, toluene) indicates a preferential concerted reaction, see: Miller, B In *Advanced Organic Chemistry, Reactions and Mechanism;* Prentice Hall: NJ, 1998; Chapters 4−7.

counted for on steric interactions since for the different complexes different orientations of the terminal alkyne substituents have been found. It seems that the formation of the metallacycle for both complexes **33** and **38** (Scheme 7) with internal alkynes is a high-energy process. Remarkably, we have recently found that internal alkynes will undergo hydroamination with primary and secondary amines through a different mechanism with a cationic uranium complex.[68]

Conclusions

The evidence presented here shows that organoactinide complexes are capable of insertion of terminal alkynes into metal−imido bonds regioselectively, inducing the intermolecular hydroamination reaction. The present process provides a method for the catalytic synthesis of different imines based on the starting organoactinide. The catalytic reaction scope includes a large variety of terminal alkynes and primary amines. The turnover frequencies of this organoactinide-catalyzed intermolecular hydroamination are found to be highly dependent on the metal and the bulkiness of the amine but almost not dependent on the alkyne nature. The key intermediate organometallic in the hydroamination process has been recognized to be the imido compound, and the first organothorium imido complexes have been trapped and solid-state characterized. The use of these organoactinide reactivities is being incorporated into catalytic cycles for the synthesis of elaborate molecules.

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Supporting Information Available: Tables of crystallographic data for complexes **31** and **33**. This material is available free of charge via the Internet at http://pubs.acs.org.

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