ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

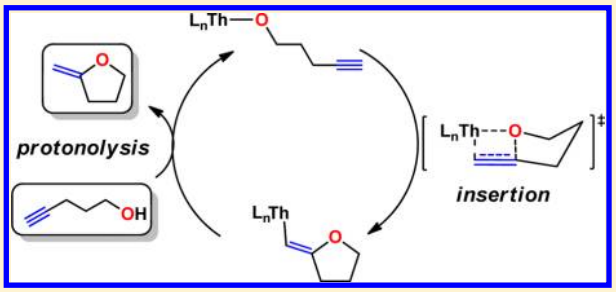
Organothorium-Catalyzed Hydroalkoxylation/Cyclization of Alkynyl Alcohols. Scope, Mechanism, and Ancillary Ligand Effects†

Stephen D. Wobser and Tobin J. Marks*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113, United States

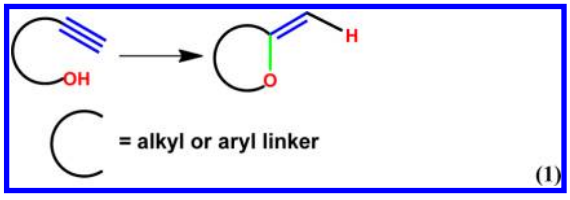
Supporting Information

ABSTRACT: Organothorium complexes bearing amide or alkyl proligands are active toward the highly selective hydroalkoxylation/cyclization of alkynyl alcohols. Substrates include primary and secondary alcohols, as well as terminal and internal alkynes. Catalysts with strongly binding ligation such as pentamethylcyclopentadienyl (Cp* = C_5Me_5) or "constrained geometry catalysts" (CGC = $Me_2Si(\eta^5\text{-}Me_4C_5)(^t BuN)$) remain soluble throughout the reaction, with the more sterically open (CGC)$Th(NMe_2)_2$ (**1**) exhibiting higher activity than $Cp^*_2Th(CH_2TMS)_2$ (**2**). The use of precatalyst $[(Me_3Si)_2N]_2Th[\kappa^2\text{-}(N,C)\text{-}CH_2Si(CH_3)_2N(SiMe_3)]$ (**3**) leads to precipitation upon the addition of alcohol substrates, although catalytic activity is retained. The substrate scope for **1** includes primary and secondary alcohols as well as terminal and internal alkynes. *In situ* ^{1}H NMR spectroscopic monitoring indicates that the rate law is zero-order in [substrate] and first-order in [catalyst]. The rates of primary alcohols and terminal alkynes are significantly more rapid than their more sterically hindered counterparts, suggesting that steric demands dominate the hydroalkoxylation/cyclization transition state. Turnover frequencies as high as 49 h^{-1} at 60 °C are observed, producing exclusively the *exo*-methylene products. For internal alkyne substrates, alkenes with *E*-orientation are formed with complete selectivity. Activation parameters $\Delta H^{\ddagger}$ = 27.9(0.4) kcal/mol, $\Delta S^{\ddagger}$ = −3.0(1.1) eu, and E_a = 28.6(0.4) kcal/mol are largely in accord with observations for other f-element-mediated insertive hydroelementation processes, and an ROH/ROD kinetic isotope effect of 0.97(0.02) is observed. The reactivity patterns, kinetics, and activation parameters are consistent with a pathway proceeding via turnover-limiting alkyne insertion into the Th−O bond, with subsequent, rapid Th−C protonolysis, regenerating the initial Th−OR species.



INTRODUCTION

Carbon oxygen linkages, particularly in oxygen-containing heterocycles, are ubiquitous in natural products and biologically active molecules and are important in fine chemicals.[1] For this reason, recent research efforts have been directed toward developing new methods of heterocycle syntheses and developing a better understanding of these synthetic processes.[2] One method with promising applicability is catalytic hydroalkoxylation. Hydroalkoxylation (eq 1), formally defined as the addition of a hydrogen−oxygen bond across a carbon−carbon unsaturation, offers several attractions compared to traditional carbon−oxygen bond-forming reactions. In contrast to alternative approaches, catalytic hydroalkoxylation requires relatively mild conditions and is highly atom-efficient, in principle producing no side products.[1e,3] Several methodologies for the catalytic alkyne hydroalkoxylation with alcohols have been reported in the literature, employing iridium,[4] rhodium,[5] gold,[6] mercury,[7] palladium,[8] molybdenum,[9] ruthenium,[10] tungsten,[11] silver,[12] platinum,[13] and other metal catalysts.[1d,14] However, these transformations are often necessarily coupled to other processes, including oxidation or isomerization. Furthermore, the rate and selectivity of these processes are often highly sensitive to the structural and electronic nature of the substrate. Therefore, pursuing alternative strategies to produce valuable oxygen-containing heterocycles in an efficient, atom-economical catalytic process is highly desirable.



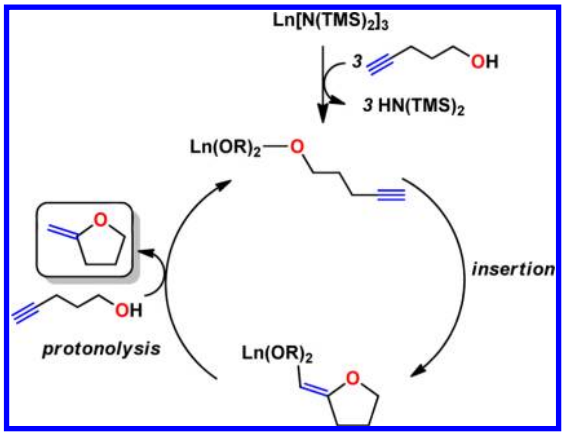
Organolanthanide catalysts are well known for their activity and selectivity in hydrofunctionalization processes,[15] and this laboratory recently reported the use of $Ln[N(TMS)_2]_3$ complexes (Ln = La, Sm, Y, Lu) as efficient precatalysts for intramolecular hydroalkoxylation/cyclization (Scheme 1). These Ln catalysts are active for a wide variety of mono- and disubstuted alkynes and allenes.[16] Moreover, this process was

†This paper was scheduled to appear in the Recent Advances in Organo-f-Element Chemistry special issue but was inadvertently omitted.

Special Issue: Recent Advances in Organo-f-Element Chemistry

Received: September 13, 2012
Published: November 14, 2012

Scheme 1. General Lanthanide-Mediated Hydroalkoxylation/Cyclization Process

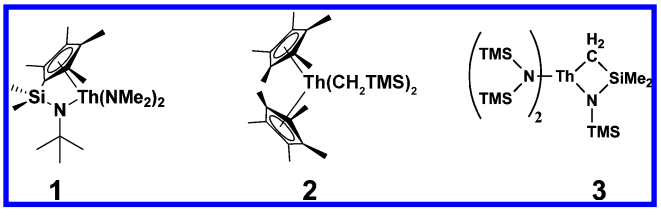


argued to proceed through a two-step mechanism involving alkyne insertion into a Ln−OR bond, followed by rapid protonolysis of the newly formed Ln−C bond by another molecule of the alcoholic substrate, simultaneously freeing the desired cyclic ether and regenerating the Ln−OR species.[17] While lanthanide catalysts have long been known to undergo a variety of rapid insertion processes into Ln−X bonds,[15e,r,18] this marked the first ever report of carbon−carbon bond insertion into a Ln−OR linkage. Inspired by the discovery of this new reactivity, we have examined several related metal centers differing substantially in charge and ionic radius (Th^{4+}, Sc^{3+}, Zr^{4+}, and Al^{3+}) and report the results of this study here.

Organoactinides have been employed to catalytically effect many demanding organic transformations.[19] The distinctive reactivity of the 4f lanthanide and 5f actinide series[20] is a result of several factors, including the high electrophilicity and kinetic lability of the metal centers, the general resistance toward oxidative-addition/reductive-elimination processes, and the large ionic radii with high coordination numbers. Actinides exhibit high reactivity for a variety of σ-bond metathesis and insertion processes and have demonstrated tolerance for an increasing variety of polar functionalities.[18a,19a,21] Indeed, the actinide literature over the last several years is rich in studies of the structure and reactivity of actinide-oxygen complexes.[22] This work contributes to a growing toolbox from which fundamental steps can be assembled into useful catalytic processes. The present report constitutes the first implementation of organoactinides in the catalytic hydroalkoxylation of alkynes by alcohols in a highly efficient and selective manner.

A variety of ligand architectures is examined in this study (Chart 1 below), and cyclopentadienyl-based (Cp) ligation is determined to be essential for catalyst solubility in the reaction mixture. The established efficacy of the "constrained geometry" ligand[23] (CGC) in many catalytic hydroelementation reactions is now demonstrated to be applicable to organothorium-catalyzed hydroalkoxylation. The empirical rate law, activation energetic parameters, and operative kinetic isotope effects are determined, and a mechanism is proposed. These results are then compared and contrasted with related organolanthanide systems, providing insight into the differences between the closely related 4f and 5f series. We also identify the substrate features affecting rate and selectivity and discuss them in relation to the proposed catalytic cycle.

Chart 1. Organoactinide Complexes Used As Precatalysts in the Present Work for Alkyne Hydroalkoxylation with Alcohols



The scope and activity of various substrates are examined, as is the effect of temperature on reaction rate. Activation parameters are determined empirically and discussed in relation to other hydroelementation processes and metal centers. This contribution, overall, broadens the scope of hydroelementation reactions mediated by f-elements and enhances the understanding of the unique reactivity of these metal ions in the context of a catalytic process. This insight should contribute to the understanding of the behavior of f-elements with polar substrates and assist in the rational design of new catalysts and catalytic processes.

EXPERIMENTAL SECTION

General Considerations. All manipulations of air-sensitive materials were carried out with rigorous exclusion of O_2 and moisture in flame- or oven-dried Schlenk-type glassware either on a dual-manifold Schlenk line, interfaced to a high-vacuum manifold (10^{-6} Torr), or in an N_2-filled MBraun glovebox with a high-capacity recirculator (<1 ppm O_2). Argon (Airgas) was purified by passage through a MnO column to remove O_2 and a column of Davison 4A molecular sieves to remove water immediately before use. Solvents used for catalytic reactions were stored over Na/K alloy in resealable containers and vacuum-transferred immediately prior to use. All liquid or volatile solid substrates for catalytic experiments were dried over a series of three or more beds of freshly activated Davison 4A molecular sieves as solutions in benzene-d_6 or toluene-d_8 (Cambridge Isotope Laboratories, 99+ atom % D). Substrate solutions were degassed by freeze−pump−thaw methods. Solid substrates were purified by sublimation under high vacuum and were stored at −35 °C in a glovebox. The NMR internal integration standard, methyltriphenylsilane, was sublimed and exposed to high vacuum overnight before storage in the glovebox. The precatalysts $Sc[N(TMS)_2]_3$,[24] $Cp^*_2Th(CH_2TMS)_2$,[19t] and (CGC)$Th(NMe_2)_2$[25] were prepared as reported in the literature. Precatalysts $[Al(NMe_2)_3]_2$ and $Zr(NMe_2)_4$ were purchased from Strem, purified by sublimation, and stored in a glovebox. Substrates **4**, **6**, **8**, **18**, and **20** were purchased from Sigma-Aldrich. Substrate **16** was purchased from TCI. Substrates **10**,[26] **12**,[27] **14**,[28] **20**,[29] and **22**[30] were prepared as reported in the literature. Product NMR spectroscopic data agree well with the published literature spectra.[16b,c]

Physical and Analytical Measurements. NMR spectra were recorded on a Mercury 400 (400 MHz, ^1H; 100 MHz, ^{13}C; 61 MHz, ^2H), an Inova 500 (500 MHz, ^1H; 125 MHz, ^{13}C), or a Bruker Avance III 500 (500 MHz, ^1H; 125, ^{13}C) instrument. Chemical shifts (δ) for ^1H, ^2H, and ^{13}C are referenced to internal solvent resonances and reported relative to $SiMe_4$. NMR scale experiments on air-sensitive samples were conducted in Teflon valve-sealed J. Young tubes.

$[(Me_3Si)_2N]_2Th[\kappa^2\text{-}(N,C)\text{-}CH_2Si(CH_3)_2N(SiMe_3)]$. The following modification of the procedure of Dormond et al.[31] was employed. A flip-frit apparatus with a magnetic stir bar was charged in the glovebox with $ThCl_4$ (3.0 g, 8.0 mmol) and $Na[N(SiMe_3)_2]$ (5.9 g, 32 mmol) and then removed from the glovebox. Approximately 100 mL of dry, deoxygenated toluene was added. The reaction mixture was next stirred for 1 h at 90 °C under Ar and then for 90 min at reflux, then allowed to cool to room temperature before flip filtration. The solid that collected was washed with toluene. All volatiles were removed by vacuum, and pentane was condensed onto the resulting residue. The

dx.doi.org/10.1021/om300881b | Organometallics 2013, 32, 2517−2528

mixture was stirred for several minutes, and then the volatiles were removed by vacuum. This process was repeated a second time, and the resulting off-white powder was exposed to high vacuum overnight before being taken into the glovebox. The powder was taken up in a minimal amount of pentane and filtered again. The resulting off-white powder, $[(Me_3Si)_2N]_2Th[\kappa^2\text{-}(N,C)\text{-}CH_2Si(CH_3)_2N(SiMe_3)]$, was obtained in 72% yield. The ^{1}H NMR spectral features correspond to the literature values.[31]

Kinetic Studies of Hydroalkoxylation Reactions. In a typical experiment, in the glovebox, a weighed amount of the precatalyst (ca. 10 μmol, 5.7 mg) and the internal standard Ph_3SiMe (ca. 50 μmol, 13.5 mg) were transferred to a glass vial and dissolved in a measured quantity of toluene-d_8. The resulting solution was then pipetted into a Teflon-valved J. Young NMR tube. In the case of solid substrates, the substrate (200 μmol, 20 equiv) was also dissolved in toluene-d_8 and added to the NMR tube in the glovebox. The NMR tube was then removed from the glovebox and interfaced to a high-vacuum manifold via a glass adapter with a secondary Teflon valve. The NMR tube was then cooled to −78 °C and exposed to high vacuum. In the case of liquid substrates, the upper portion of the valve was then backfilled with Ar, and a 1.0 M solution of the substrate in C_6D_6 or C_7D_8 was added by syringe. In cases where the substrate reacted within 24 h, the sample was immediately placed in an NMR spectrometer pre-equilibrated to the appropriate temperature (±0.1 °C, calibrated with an ethylene glycol standard). Data were obtained with a single transient to avoid signal saturation. In cases where substrate conversion required greater than 24 h, the reactions were heated in temperature-controlled oil baths and removed periodically for NMR spectroscopic analysis. Substrate and/or product concentrations were determined relative to the intensity of the internal standard resonance over three or more half-lives.

Data were fit by least-squares analysis according to eq 2, where t is time and [product] is the concentration of product at time t. The turnover frequency (N_t) was calculated according to eq 3, where $[\text{catalyst}]_0$ is the initial catalyst concentration.

$$[\text{product}] = mt \tag{2}$$

$$N_t(h^{-1}) = \frac{m}{[\text{catalyst}]_0} \tag{3}$$

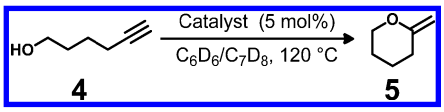
RESULTS

Initial screening of the various metal complexes assayed catalytic hydroalkoxylation activity using 5-hexyn-1-ol as a test substrate (Table 1). We find that $Zr(NMe_2)_4$ and $Sc[N(TMS)_2]_3$ exhibit moderate catalytic activity for the formation of 2-methylenetetrahydropyran (N_t = 0.03 and 0.017 h^{-1}, respectively), while $[Al(NMe_2)_3]_2$ shows no reaction over the course of 1 week at 120 °C. Thus, these complexes adhere to the general trend observed for lanthanide-mediated hydroalkoxylation and hydroamination, where smaller ionic radii correlate with lower turnover frequencies. While not lanthanide complexes, the extension of these observations to groups 3 and 4 d^0 complexes provides an informative comparison. The precatalyst $(CGC)Th(NMe_2)_2$ is also found to cleanly produce the desired cyclization product with N_t = 0.32 h^{-1}, prompting further investigation. In addition to metal ionic radii, formal oxidation states appear to have a significant influence on the hydroalkoxylation rate. While Zr(IV) is slightly smaller than Sc(III), under the same reaction conditions it exhibits a higher N_t for this reaction. Similarly, while Th(IV) has a slightly smaller ionic radius than La(III), it effects this reaction at the highest rate of any metal ion examined in the present study.

In typical lanthanide-catalyzed hydroalkoxylation/cyclizations, the active species was determined to be a homoleptic metal alkoxide, generated by the rapid cleavage of protonolytically labile amido proligands (Scheme 1).[16c] For the purpose of comparison to published f-element data, amido ligands were also used in the present study, with the exception of the Th precatalyst. Thorium is known to form oligomeric alkoxides, frequently insoluble in hydrocarbon solvents (*vide infra*).[33] Comparative hydroalkoxylation/cyclization rate data are compiled in Table 1.

Thorium-Mediated Hydroalkoxylation/Cyclization Experiments. The results of the catalytic hydroalkoxylation/cyclization of alkynyl alcohol substrates mediated by organothorium precatalysts bearing cyclopentadienyl and non-cyclopentadienyl ancillary ligation were next investigated. The transformation **6** → **7** (Table 2) was studied for precatalysts $(CGC)Th(NMe_2)_2$, **1**; $Cp^*_2Th(CH_2TMS)_2$ ($Cp^* = C_5Me_5$), **2**; and $[(Me_3Si)_2N]_2Th[\kappa^2\text{-}(N,C)\text{-}CH_2Si(CH_3)_2N(SiMe_3)]$, **3**.

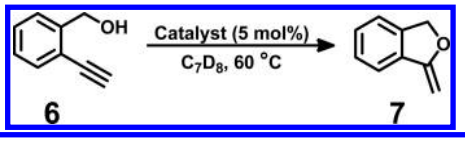
Table 1. Catalyst Screening for the Hydroalkoxylation/Cyclization of 5-Hexyn-1-ol[a]

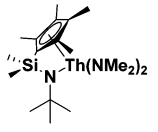
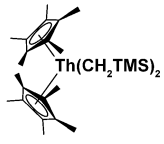
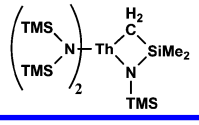


entry	precatalyst	ionic radius[b]	N_t (h^{-1}, 120 °C)
1	$La[N(TMS)_2]_3$	1.160	0.11[16c]
2	$(CGC)Th(NMe_2)_2$	1.05	0.32
3	$Sc[N(TMS)_2]_3$	0.870	0.017
4	$Zr(NMe_2)_4$	0.84	0.030
5	$[Al(NMe_2)_3]_2$	0.535	N.R.

[a]Reactions carried out in Teflon-valved J. Young NMR tubes with [metal] = 14.3 mM; $[\text{substrate}]_0$ = 286 mM. [b]Data are presented to indicate the relative metal ionic radii and were tabulated by Shannon.[32] Data are for eight-coordinate species, except for Al, which is reported for six-coordinate species.

Table 2. Comparison of Th-Mediated Hydroalkoxylation/Cyclization Rates as a Function of Th Ligation[a]



Entry	Precatalyst	Structure	N_t (h^{-1}, 60 °C)
1	**1** $(CGC)Th(NMe_2)_2$		49
2	**2** $Cp^*_2Th[CH_2TMS]_2$		26
3	**3** $[(Me_3Si)_2N]_2Th[\kappa^2\text{-}(N,C)\text{-}CH_2Si(CH_3)_2N(SiMe_3)]$[b]		37

[a]Reactions carried out in Teflon-valved J. Young NMR tubes with [Th] = 14.3 mM; $[\text{substrate}]_0$ = 286 mM. [b]Precipitate observed during reaction.

dx.doi.org/10.1021/om300881b | *Organometallics* 2013, 32, 2517−2528

In each case the reaction was complete by NMR spectroscopy in less than 1 h at 60 °C. None of the catalysts display any evidence of an induction period, indicating essentially instantaneous protonolysis of the monodentate amide ligands by the alcohol substrates. This is consistent with the known oxophilicity and kinetic lability of Th(IV) and the large difference in Th−O bond enthalpy versus the precatalyst Th−N bonds.[33a,34]

Where cyclopentadienyl-based ancillary ligands are employed (Table 2, entries 1 and 2), the reaction proceeds to completion as a homogeneous solution. However, when the more labile proligands[34] are used (Table 2, entry 3), small amounts of suspended solid are observed immediately upon mixing the substrate and precatalyst, with free $HN(TMS)_2$ observed by ^1H NMR spectroscopy. This suggests a classic σ-bond protonolysis reaction pattern for metal amides with alcohols.[16,34,35] By the end of the reaction using precatalyst **3**, copious pale yellow precipitate is observed. Despite the precipitate, NMR spectroscopic monitoring of the reaction was continued in this case, and a turnover frequency of 37 h^{-1} is obtained. In this case, N_t was derived using data only up to 50% theoretical conversion due to deviation from linearity toward the end of the reaction (Figure 1). Notably, in this case, the reaction

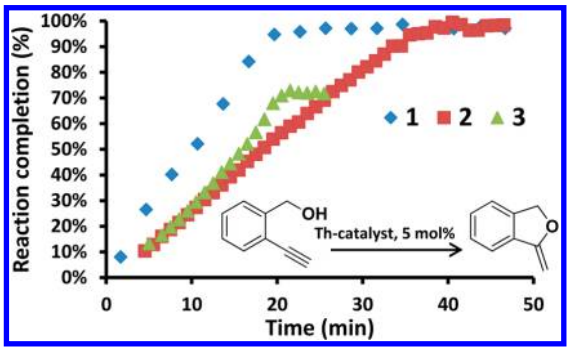


Figure 1. Conversion versus time plots for the hydroalkoxylation/cyclization of 2-ethynylbenzyl alcohol mediated by the indicated 5 mol % Th catalysts in toluene at 60 °C.

progress plateaus at ∼72% of the theoretical yield. Complex **1** was found to have the most active ancillary ligand set investigated and achieved a turnover frequency of N_t = 49 h^{-1}, exceeding the rate of the $La[N(TMS)_2]_3$-catalyzed process by ∼5×. The CGC ligand has two binding sites, one through an amide and the other through a heavily alkylated cyclopentadienyl ring. Note that, unlike CGC complex **1**, when either **2** or **3** is exposed to alcoholic substrates, ancillary ligand protonolysis is observable by ^1H NMR spectroscopy, arguing that the bidentate CGC ligand is essential for persistent ancillary ligation. In the case of each precatalyst, the monodentate amide and alkyl ligands are rapidly protonolyzed.

For the organothorium-catalyzed alkyne hydroalkoxylation/cyclization reactions, excepting those involving precatalyst **3**, where extensive precipitation is observed, a constant turnover rate is observed throughout the course of the reaction, demonstrating zero-order rate dependence on substrate concentration. This observation is consistent with results for related lanthanide-mediated hydroalkoxylation/cyclization and f-element-mediated hydroamination/cyclization processes, both of which are proposed to proceed via a rate-limiting intramolecular insertion step. Further support for this turnover-limiting step comes from the first-order dependence of the rate on catalyst concentration. Thus, a study of the hydroalkoxylation/cyclization of 4-pentyn-1-ol at various catalyst concentrations reveals first-order rate dependence on the concentration of catalyst **1** (Figure 2). In all cases, the reaction maintains a zero-order dependence on substrate and the reaction proceeds cleanly to completion. The overall empirical rate law is therefore expressed in eq 4.

$$\text{rate} = k[\text{substrate}]^0[\text{catalyst}]^1 \quad (4)$$

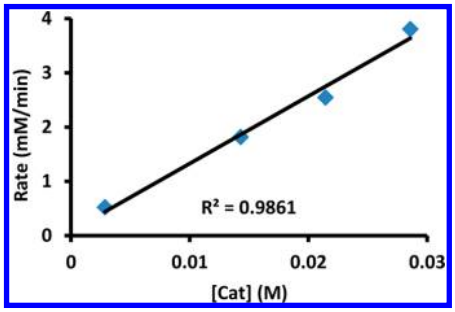


Figure 2. Reaction rates for the hydroalkoxylation/cyclization of 4-pentyn-1-ol by precatalyst **1** as a function of catalyst concentration.

Activation Parameters. Kinetic studies were conducted over a 60−100 °C temperature range. Reactions were monitored by *in situ* ^1H NMR spectroscopy for the hydroalkoxylation/cyclization of 4-pentyn-1-ol by **1**, and the results are displayed in Figure 3. The rate of product formation in each

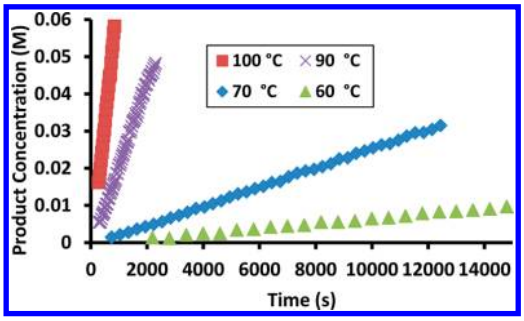


Figure 3. Time dependence of product formation for the catalytic hydroalkoxylation/cyclization of 4-pentyn-1-ol mediated by **1** at the indicated temperatures.

case is constant and indicates a zero-order rate dependence on substrate concentration over the given temperature range. Standard Eyring (Figure 4) and Arrhenius (Supporting Information) plots are then used to derive the activation parameters $\Delta H^{\ddagger}$ = 27.9(0.4) kcal/mol, $\Delta S^{\ddagger}$ = −3.0(1.1) eu, and E_a = 28.6(0.4) kcal/mol.[36] Furthermore, an −OH versus −OD isotopic labeling study assayed by ^1H and ^2H NMR spectroscopy indicates a kinetic isotope effect (KIE) of k_H/k_D = 0.97 (0.02) (Table 3, entries 9 and 10). Due to the known tendency of f-element catalysts to activate terminal alkynyl RC≡C−H bonds,[16b,21f,g,37] the kinetics of 2-(2-phenylethynyl)benzyl alcohol, an internal alkyne, were studied to avoid the complication of H/D scrambling between the alkynyl and alcoholic hydrogen atoms.

Proposed Catalytic Cycle. Scheme 2 illustrates the proposed catalytic cycle for organothorium-mediated alkynyl alcohol hydroalkoxylation/cyclization. The cycle is based on the rate law dependence on substrate and catalyst concentrations,

dx.doi.org/10.1021/om300881b | *Organometallics* 2013, 32, 2517−2528

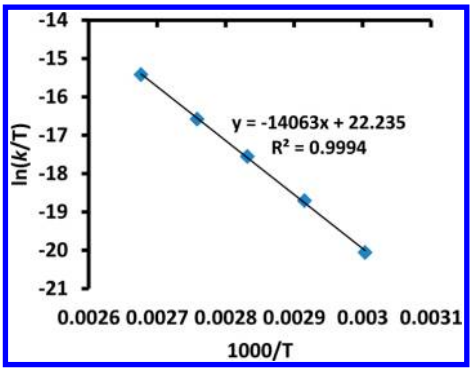
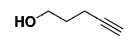
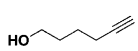
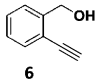
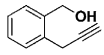
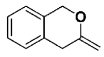
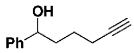
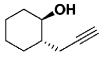
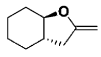
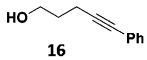
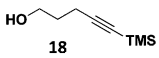
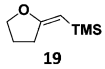
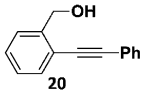
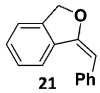
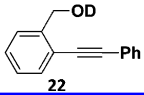
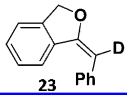


Figure 4. Eyring plot for the catalytic hydroalkoxylation/cyclization of 4-pentyn-1-ol mediated by **1** over a temperature range 60−100 °C.

Table 3. Scope of Hydroalkoxylation/Cyclization Reactions Catalyzed by Precatalyst 1[a]

Entry	Substrate	Product	N_t, h^{-1} (°C)
1	 **8**	 **9**	0.16 (60); 0.65 (70); 2.1 (80); 5.8 (90); 19 (100)
2	 **4**	 **5**	0.32 (120)
3	 **6**	 **7**	49 (60)
4	 **10**	 **11**	4.4 (120)
5	 **12**	 **13**	0.20 (120)
6	 **14**	 **15**	0.34 (60)
7	 **16**	 **17**	0.25 (120)
8	 **18**	 **19**	<0.01 (120)
9[b]	 **20**	 **21**	0.47 (120)
10[b]	 **22**	 **23**	0.48 (120)

[a]Reactions carried out in J. Young NMR tubes catalyzed by precatalyst **1** (5 mol %), using C_6D_6/C_7D_8 solvent. [b]*o*-Xylene-d_{10} solvent.

as well as the observed regiochemistry, KIE, and activation parameters. Upon activation of the precatalyst by protonolysis of the amide/alkyl bonds, the active Th−OR catalytic species is generated (Scheme 2, step *i*). Next, the alkyne approaches and undergoes insertion into the Th−O bond, via a four-center transition state (step *ii*).[17] This is expected to be the most thermodynamically demanding and the turnover-limiting step along the reaction coordinate. The newly generated Th−C bond is highly susceptible to protonolysis and is rapidly cleaved to generate the product and simultaneously regenerate the Th−O active species (step *iii*). This two-step insertion/protonolysis cycle is consistent with the empirical reaction rate shown in eq 4, where intramolecular step *ii* is turnover-limiting.

Hydroalkoxylation/Cyclization Substrate Scope. The scope of alkynyl alcohol substrates examined in the present study is summarized in Table 3. The intramolecular hydroalkoxylation/cyclization of alkynyl alcohols could, in principle, produce either of two distinct regioisomers (Chart 2). In one case the oxygen is fused to the proximate alkynyl carbon atom, generating a cyclic *exo*-methylene product. In the case of terminal alkynes, this is the Markovnikov product. Alternatively, the newly formed bond may be between the oxygen and the distal alkynyl carbon atom, generating a cyclic product with an *endocyclic* double bond. For terminal alkynes this is the anti-Markovnikov product. With all substrates in Table 3, the *exo* product is observed exclusively. The reactions are found to proceed to >95% completion in all cases and to have constant rates of product formation over three half-lives. Several interesting observations can be made from the data in Table 3. It can be seen that five-membered rings close more quickly than six-membered rings (Table 3, **8** → **9** vs **4** → **5** and **6** → **7** vs **10** → **11**). The data in Table 3 also demonstrate that either an aliphatic or aromatic linker may be incorporated between the alkyne and alcohol functionalities. Introducing an *ortho*-disubstituted aromatic linker enhances the rate up to 300-fold (Table 3, **8** → **9** vs **6** → **7** and **4** → **5** vs **10** → **11**). The substrate scope includes both primary and secondary alcoholic substrates, with primary alcohols cyclizing more rapidly than secondary alcohols (Table 3, **4** → **5** vs **12** → **13**).

Precatalyst **1** catalyzes both terminal alkynyl and internal alkynyl substrate conversions. However, the internal alkynyl substrates require elevated reaction temperatures of >120 °C to achieve catalytic rates comparable to those observed for terminal alkynyl substrates at 60−70 °C (**8** → **9** vs **16** → **17**). In the case of internal alkynyl substrates, the substituent can potentially be located in two different orientations (*E* or *Z*) at the newly formed C═C bond. For all internal alkyne substrates, the *E* isomer is generated exclusively, with no quantities of *Z*-oriented substitution detectable by ^{1}H NMR spectroscopy.

The TMS-substituted alkyne **18** is a unique case in which the reaction does not proceed cleanly to completion, and only trace product is detectable, even after 1 week at 120 °C. Several unidentified side products are detectable by ^{1}H NMR spectroscopy, in addition to trimethyl(5-(trimethylsilyl)pent-4-ynyloxy)silane. This observation is not unique to actinide catalysts, but is consistent with processes identified for lanthanide catalysts as well, doubtless facilitated by the formation of a reactive metal-alkynyl species (Scheme 3).[16b]

Diene Substrates. Allene hydoalkoxylation/cyclization has the potential to be a valuable tool for accessing various heterocyclic products.[1a,b,2c,38] Allene double bonds are known to lie 10 kcal/mol higher in energy than isolated double bonds,[39] and for this and possibly steric reasons, the hydroalkoxylation/cyclization of allenic double bonds is significantly more facile than for isolated alkenes.[15i,j] The reaction of 4,5-hexadiene-1-ol mediated with 5 mol % of (CGC)Th$(NMe_2)_2$ (**1**) in toluene-d_8 at 120 °C is found to produce 6-methyl-3,4-dihydro-2*H*-pyran and 2-methylenetetrahydropyran, the latter of which undergoes quantitative conversion to 6-methyl-3,4-dihydro-2*H*-pyran under the standard reaction conditions (Scheme 4). Although a colorless

dx.doi.org/10.1021/om300881b | *Organometallics* 2013, 32, 2517−2528

Scheme 2. Proposed Catalytic Cycle for Organothorium-Catalyzed Hydroalkoxylation/Cyclization

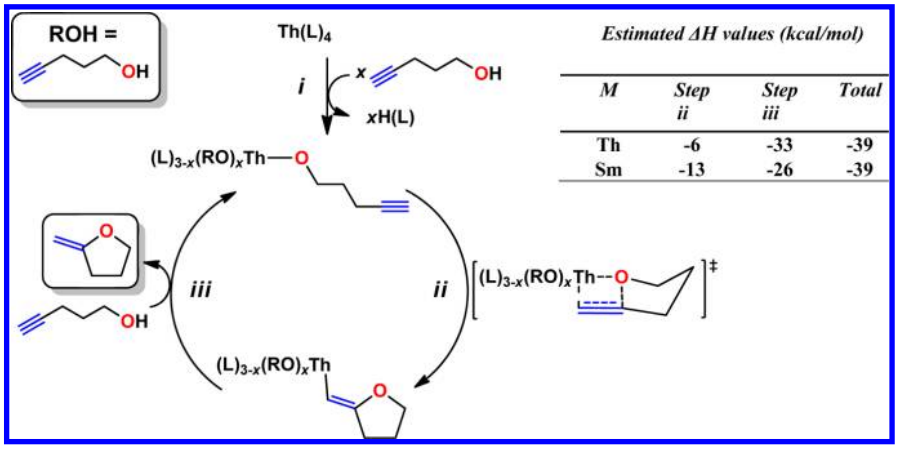
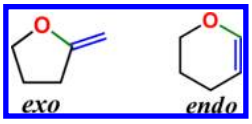


Chart 2. Possible *exo* and *endo* Products of Hydroalkoxylation/Cyclization



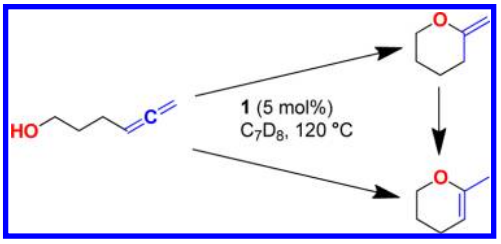
precipitate forms upon heating the reaction mixture, *in situ* ^{1}H NMR spectroscopy indicates that the hydroalkoxylation reaction continues, but that substrate consumption is nonlinear with time. After two days, the reaction reaches ~40% completion. In contrast to these results, a solution of 4,6-heptadiene-1-ol with 5 mol % of (CGC)Th(NMe$_2$)$_2$ (**1**) in *o*-xylene-d_{10} is found to be unreactive with respect to hydroalkoxylation, even at 145−155 °C over the course of 1 week. Again, a colorless precipitate is observed upon heating 4,6-heptadiene-1-ol with the catalyst. Precipitation has also been observed under similar reaction conditions in the hydroamination of both allenes and conjugated alkenes using catalyst **1**. This is likely an effect of the strong interaction of actinides with π-systems. For example, the electron-rich diene terminus of one ligand could conceivably coordinate to a second metal center, thus facilitating oligomerizaion and precipitation of intermediate species. No CGC ligand cleavage is observed by NMR spectroscopy.

DISCUSSION

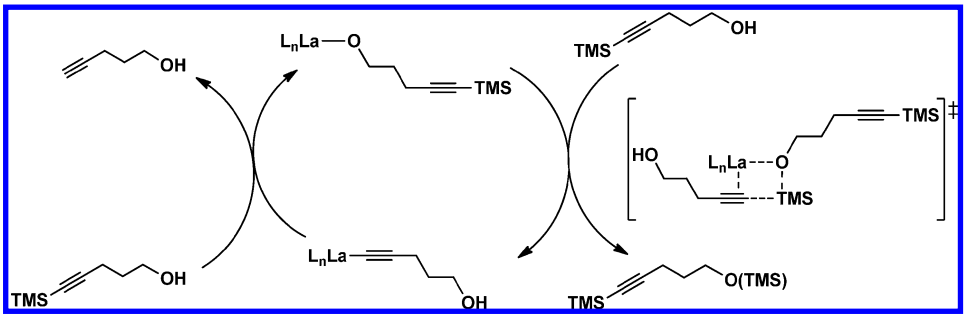
Metal Identity Effects on Turnover Frequency. The relative rates of hydroalkoxylation/cyclization depend heavily on the identity of the catalyst metal. It is found that in the conversion **4** → **5** the reaction rates mediated by M(NR$_2$)$_3$ species (M = La, Sc, or Al; R = Me or TMS) follow the trend La > Sc > Al. This trend approximately parallels the ordering in ionic radii of the metal ions (Table 1), indicating that larger, more sterically open metal sites are more reactive in hydroalkoxylation/cyclization. This trend is also observed within the lanthanide series Ln[N(TMS)$_2$]$_3$, where the effect is proposed to reflect steric demands in the four-center insertive transition state (Scheme 2, step *ii*).[17] The larger, more open metal centers more easily facilitate the approach and insertion of the unsaturation into the M−O bond. The insertion step is rate-limiting, so the relative steric openness of the metal centers dominates the overall reaction rate. Similarly, it is observed for the metals in oxidation state +4 that (CGC)Th(NMe$_2$)$_2$ catalyzes the reaction **4** → **5** far more rapidly than does Zr(NMe$_2$)$_4$ (N_t = 0.32 vs 0.030 h^{-1}, respectively). This difference is also observed in hydroamination/cyclizations mediated by group 4 and actinide ions with identical CGC, amide, and/or chloride ligands.[35b]

When comparing metals of similar size, but different formal oxidation states, for example Zr(IV) (IR = 0.84 Å) versus

Scheme 4. Course of 4,5-Hexadien-1-ol Hydroalkoxylation/Cyclization Mediated by Precatalyst 1



Scheme 3. Catalytic Cycle for Organolanthanide-Mediated Reaction of TMS-Alkynyl Alkynols



dx.doi.org/10.1021/om300881b | *Organometallics* 2013, 32, 2517−2528

Sc(III) (IR = 0.87 Å), note that Zr(IV) is a slightly more active hydroalkoxylation/cyclization catalyst than Sc(III). Among other factors,[35b] a plausible explanation is that alkoxide and alcohol ligands have roughly similar steric demands and that hard, oxophilic ions of similar size will likely have approximately the same total number of bound alkoxide/alcohol ligands. In this situation, it is reasonable that C≡C insertion processes would be favored at metal centers accommodating greater numbers of metal−alkoxide σ-bonds (four vs three here). Overall, the trends among catalyst metal ions in this study are consistent with related hydroamination results in which the general activity of tetravalent actinide catalysts is comparable to that of trivalent lanthanide catalysts and substantially exceeds that of tetravalent group 4 catalysts, regardless of the ancillary ligation.[35] These qualitative comparisons between groups 3 and 4, lanthanide, and actinide complexes should provide useful guidance to future efforts to design new hydroalkoxylation catalysts.

Diene Substrate Scope. Both 1,2- and 1,3-dienes were investigated as potential hydroalkoxylation substrates. These polyunsaturated substrates offer access to new product structures suitable for subsequent functionalization and, in some cases, higher turnover frequencies than olefins in f-element-catalyzed hydroamination.[35a,40] This is due to the greater thermodynamic driving force for additions to 1,2-dienes and the potential coordination of both C=C unsaturations in the case of 1,3-dienes.[41] Nevertheless, they are found to be poor substrates for the present organothorium-catalyzed hydroalkoxylation process. In both dieneol cases, a precipitate forms immediately upon heating the substrates with (CGC)-Th(NMe$_2$)$_2$. This may reflect stronger M−(C=C) π-interactions for actinides versus lanthanides,[42] leading to stronger intermolecular interactions (e.g., Figure 5), aggregation, and eventually precipitation. Free H$_2$CGC ligand is not observed in the ^{1}H NMR spectrum of the reaction mixture. Interestingly, similar precipitation is also noted in some cases for organothorium-catalyzed diene hydroamination.[35a] The difference in the present case versus similar lanthanide-catalyzed hydroamination and hydroalkoxylation processes provides an interesting distinction in Ln/An reactivity.

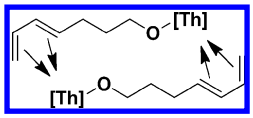
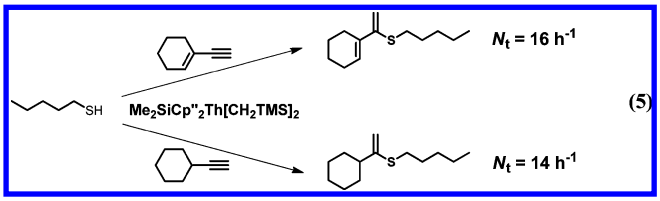


Figure 5. Possible mode of intermolecular coordination of dienyl alcohols to organothorium complexes.

Reaction Mechanism. Kinetic studies of the present hydroalkoxylation processes indicate that the rate law has zero-order dependence on substrate concentration and first-order dependence on catalyst concentration. This observation supports the catalytic cycle depicted in Scheme 2, in which turnover-limiting C≡C insertion into the Th−O bond is followed by rapid protonolysis by free or bound substrate. The observation that reaction rate is heavily influenced by substrate C≡C substituents and product ring size argues against rate-limiting protonolysis. The assertion is further supported by data indicating a negligible kinetic isotope effect (0.97). Additionally, note that steric demands tend to dominate the transition states of f-element insertive processes,[15c,e,17] so it is not unexpected that secondary alcohols turn over more slowly than primary alcohols, as in **4** → **5** vs **12** → **13** (Table 3). The precipitous fall in turnover frequency associated with proceeding from a primary to a secondary alcohol suggests that far higher reaction temperatures would be required to effect tertiary alcohol hydroalkoxylation on a reasonable time scale. Note also that literature reports of organolanthanide-mediated hydroalkoxylation[16,43] and group 4 metal and organo-f-element-catalyzed hydrothiolation[15c,18a,21g] do not include examples of tertiary alcohols or thiols. With few exceptions, secondary functionalities proceed at a slower rate than primary functionalities in each of these catalytic systems.

The Baldwin ring-closure rules state that five-membered rings close more rapidly than six-membered rings,[44] and this trend is ubiquitous in f-element-catalyzed intramolecular hydroelementations as in the present **8** → **9** vs **4** → **5** and **6** → **7** vs **10** → **11** transformations (Table 3).[15e,16b,18b,35b] Greatly enhanced reactivity is observed in the present study for substrates in which the alcohol and alkyne functionalities are linked by a relatively rigid *ortho*-disubstitued arene versus those with a flexible aliphatic linker as in conversions **8**→ **9** vs **6** → **7** and **4** → **5** vs **10** → **11** (Table 3). It is reasonable that the reduced degrees of freedom with the more rigid linkers poise the functionalities in a preorganized structure favorable to the cyclization transition state. In the case of substrate **6**, there is also likely transition state stabilization by the alkyne−arene conjugation. Evidence for such an electronic contribution is more explicitly isolated in the case of organothorium-catalyzed *intermolecular* hydrothiolation reactions, in which 1-ethynylcyclohexene is more reactive than cyclohexylacetylene toward insertion into L$_n$Th−SR bonds (eq 5).[21g]



Alkyne Substituent Effects. Substitution at the C≡C linkage increases the steric demands of the hydroalkoxylation transition state, strongly depressing the turnover frequency (**16** → **17** vs **8** → **9** in Table 3). Achieving the requisite four-center transition state for the insertion process (Scheme 2, step *ii*) is more energetically demanding when substituents are directly joined to the alkyne or the alcohol carbon atom. A result is that the products formed from the terminal alkyne substrates show exclusively *E*-selectivity at the C=C bond (Table 3, entries 7−10). As shown in Figure 6, the sterically congested coordination sphere likely repels the alkyne substituent and directs addition toward *E*-selectivity for double-bond formation.

While steric demands strongly influence the present cyclization rates, electronic contributions are in some cases important as well. The only alkyne substrate that fails to react cleanly to completion is 5-trimethylsilylpent-4-yn-1-ol, **18**. This

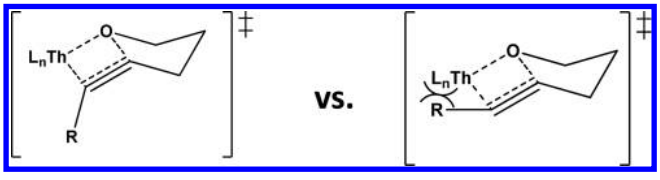


Figure 6. Two possible insertive transition states leading to double bonds with either *E*-orientation (left) or *Z*-orientation (right).

dx.doi.org/10.1021/om300881b | *Organometallics* 2013, 32, 2517−2528

substrate is proposed to undergo a process involving TMS group transfer to the alcohol oxygen, driven by the large Si−O bond enthalpy, generating a silyl ether. An analogous process was previously described in lanthanide-mediated silylalkyne chemistry[16b] (Scheme 3), and the key step, σ-bond metathesis involving an M−X bond and a TMS−acetylenyl bond, has been observed previously for organoactinides.[21f,37] While the alkynyl TMS substituent inhibits the present hydroalkoxylation/cyclization process, the electronics of the phenyl substituent (**16** → **17**) likely accelerate it. Figure 7 depicts a likely arene−

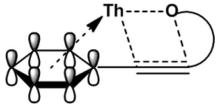
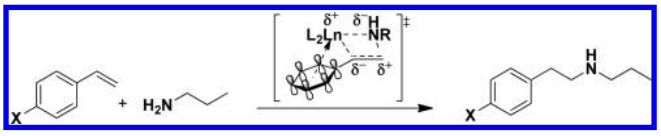


Figure 7. Interaction of an organothorium center with aryl substituents on the alkyne substrates.

electrophilic 5f center π-interaction, which serves to prearrange the substrate in an orientation favorable for cyclization. Note that a rate enhancement is also observed when aryl-substituted alkynes are compared to methyl-substituted alkynes in organolanthanide-catalyzed hydroalkoxylation.[16b,45] Studies of organolanthanide-catalyzed intermolecular hydroamination invoke a similar explanation for the inverted regioselectivity observed for styrenes versus aliphatic olefins (Scheme 5).[46]

Scheme 5. Proposed Origin of Inverted Regioselectivity in Organolanthanide-Catalyzed Styrene Hydroamination



This is attributed to the strong structural influence of Ln−arene interactions.[47] Additional stabilization can plausibly be attributed to stabilization of the δ^- charge by the electron-withdrawing phenyl group.[46a]

Comparison to Other f-Element-Catalyzed Hydroelementation Processes. While organo-f-element catalysts are known to be highly active for hydroelementation processes such as hydrosilylation,[20a,48] hydrophosphination,[49] and hydroamination,[15e,k,m,q,25,35] only recently has the utility of oxygen[16a,30,43c,50] and sulfur[15c,18a,21g,51] substrate functionalities been investigated. The bond enthalpies for a series of f-element M−X bonds are summarized in Figure 8 and illustrate the

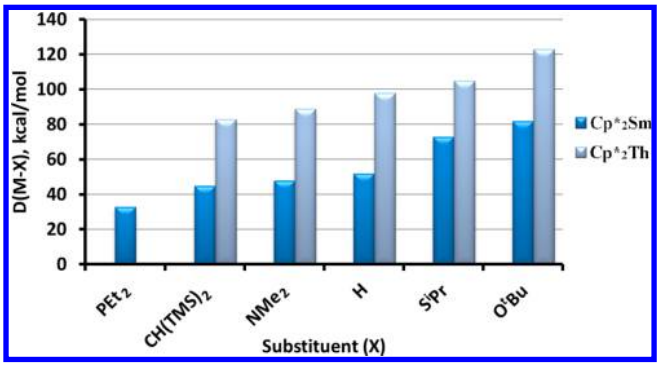


Figure 8. Selected organo-f-element metal−ligand bond disruption enthalpies.[33]

significant energetic challenge in translating known L_nM-N, L_nM-P, or L_nM-C bond insertive processes to those involving L_nM-O bonds. Traditionally, alkoxide and thiolate functionalities were sparsely investigated in organo-f-element catalytic processes such as hydroelementation because of the expected thermodynamic unfavorability.[52] Alcohols and thiols were assumed to form unreactive species due to the established stabilities of the L_nM-OR and L_nM-SR linkages.[19r,34,53] Recently it was observed that $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th{=}E$ (E = S or O) complexes undergo [2 + 2] cycloaddition reactions with $Ph_2C{=}O$ and $Ph_2C{=}S$, but are unreactive toward alkynes.[22a] Similarly, disruption of An−O σ-bonds is typically observed only with the concurrent formation of new An−O bonds, doubtless reflecting the large thermodynamic barrier.[21h,54] The present study represents the first report of insertion into an An−OR σ-bond by carbon−carbon unsaturation, driven by the exothermicity of additions to C≡C bonds, as illustrated in Scheme 2.[19d]

The representative transformation **8** → **9** was examined over a broad temperature range using catalyst **1**. From these data, activation parameters were derived by Eyring (Figure 4) and Arrhenius (Supporting Information) analysis.[36] The values $\Delta H^{\ddagger}$ = 27.9(0.4) kcal/mol, $\Delta S^{\ddagger}$ = −3.0(1.1) eu, and E_a = 28.6(0.4) kcal/mol are largely in accord with expectations based on values and trends observed in other f-element-catalyzed hydroelementation/cyclization processes (Table 4). The values of $\Delta H^{\ddagger}$ and E_a in alkyne hydroamination processes are known to be larger for An versus Ln centers in hydroamination (Table 4), and this trend holds for the present hydroalkoxylation/cyclization results as well. Additionally, $\Delta H^{\ddagger}$ and E_a values are greater for lanthanide-mediated hydroalkoxylation/cyclization versus hydroamination/cyclization processes. Again, the relatively large $\Delta H^{\ddagger}$ and E_a values for the present study follow a similar trend in being somewhat larger than the corresponding values for organoactinide-catalyzed hydroamination. Comparison of $\Delta S^{\ddagger}$ values indicates a less negative value for hydroalkoxylation versus hydroamination using the same metal center, following literature trends and likely indicating increased degrees of freedom on proceeding to the four-center transition state.[15m,16b] However, the $\Delta S^{\ddagger}$ for the present study is significantly less negative than for the analogous organolanthanide-catalyzed transformation. This trend parallels aminodiene cyclization, where An catalysts proceed with a $\Delta S^{\ddagger}$ value 17 eu less negative than analogous Ln catalysts.[35a,40a] A broader examination of the literature reveals a lack of consistent trends in $\Delta S^{\ddagger}$ values for An versus Ln catalysts employed for similar catalytic processes.[18c,40b,55] In terms of mechanism, this may reflect less change in the degrees of freedom as the insertive transition state is approached (or the transition state lies on a different place on the reaction coordinate) in the present hydroalkoxylation/cyclizations relative to hydroamination/cyclization processes.

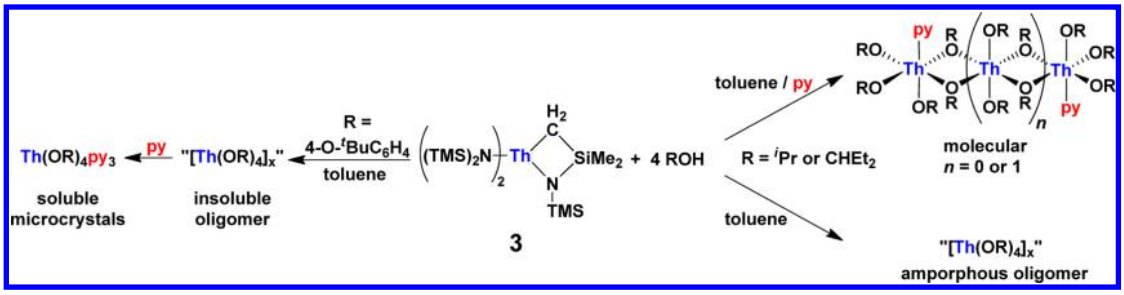
Ligation and Structure. The first report of organolanthanide-catalyzed hydroalkoxylation/cyclization used $Ln[N(TMS)_2]_3$ complexes as precatalysts.[16c] The labile proligands were intended to be rapidly protonolyzed by alcoholic substrates to afford catalytically active homoleptic metal−alkoxide species. To study organothorium-catalyzed hydroalkoxylation/cyclizations, a different ligand set is necessary due to the low solubility of homoleptic thorium alkoxides.[33,56] The literature reflects an infamous dearth of structural certainty, with the first crystallographic characterization of a homoleptic aliphatic thorium alkoxide remaining elusive until nearly four

dx.doi.org/10.1021/om300881b | Organometallics 2013, 32, 2517−2528

Table 4. Activation Parameters for Selected f-Element-Catalyzed Hydroelementation/Cyclization Processes Involving C≡C Bonds[15m,16b,35a]

Entry	Precatalyst	Substrate	Product	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)	E_a (kcal/mol)
1	(CGC)Th(NMe$_2$)$_2$ **1**			27.9(0.4)	-3.0(1.1)	28.6(0.4)
2[16b]	La[N(TMS)$_2$]$_3$			20.2(1.0)	-11.8(0.3)	20.9(0.3)
3[35a]	(CGC)Th(NMe$_2$)$_2$ **1**			14(2)	-27(5)	15(2)
4[15m]	Cp*$_2$SmCH(TMS)$_2$			11(8)	-27(6)	11(2)

Scheme 6. Moderation/Suppression of Thorium Alkoxide Oligomerization by Pyridine[59]



decades after Bradley and co-workers' initial reports of their syntheses.[57] Thorium alkoxides consist of varying degrees of alkoxide-bridged oligomeric species, with the degree of oligomerization heavily dependent on the nature of the alkyl group.[33,56,58] Therefore, it is plausible that the active catalytic species of the present study have oligomeric structures highly dependent on the specific substrate used. Nevertheless, the kinetic rate law is not consistent with rapid, reversible dissociation of oligomeric species prior to the turnover-limiting step.

The solubility of the active alkoxide species in the present work is maintained by using strongly binding/sterically demanding Cp* and CGC ligands.[18a,42c,d] While amide and alkyl proligands are instantly protonolyzed by alcohols, 5f Cp* derivatives are significantly more resistant to protonolysis. Each of the characteristic ^{1}H NMR spectroscopic resonances of the free H$_2$CGC ligand are absent in spectra during the course of these catalytic reactions. Rapid, reversible dissociation is unlikely, given the sluggish reaction rates for H$_2$CGC protonolytic reactivity in the synthesis of (CGC)Th(NMe$_2$)$_2$.[25] These factors argue for active catalytic species in which the CGC ligand remains bound in a normal η^1,η^5-Th fashion.

It has been reported that the formation of oligomeric thorium alkoxides can be moderated or significantly suppressed by the addition of strongly σ-binding ligands.[59] In these reports, pyridine serves to moderate oligomer size by cleaving and "capping" the thorium tetraalkoxides (Scheme 6).[59,60] The propensity of these complexes to undergo cleavage by a Lewis base, as well as the degree of oligomerization achievable, is strongly influenced by the nature of the alkoxide ligand. Thus, precatalyst **3**, which has no Cp*-type binding sites, undergoes significant precipitation during the course of the catalytic reaction. Nevertheless, alkynol hydroalkoxylation/cyclization catalyzed by **3** proceeds rapidly until no starting material is observable by ^{1}H NMR spectroscopy, arguing that while there may be varying degrees of oligomerization, some catalytically active species are present in the solutions. Using an internal ^{1}H NMR standard, it is determined that the reaction proceeds only to ~72% of the theoretical yield, at which point substrate is no longer detectible in the NMR spectrum, indicating that a significant portion of the substrate has been removed from the solution in the precipitation.

■ CONCLUSIONS

Several organothorium complexes are found to display high catalytic activity with respect to alkynyl alcohol hydroalkoxylation/cyclization. Of these, it is shown that the lack of strongly binding/sterically demanding (methylCp-based) ligation produces insoluble and marginally active catalysts. The scope of substrates includes primary and secondary alcohols, as well as terminal and internal alkynes. However, allenes and 1,3-dienes are found to be poor substrates that lead to precipitation upon heating with (CGC)Th(NMe$_2$)$_2$. For example, the rate of (CGC)Th-mediated allenyl alcohol hydroalkoxylation/cyclization slows with increasing catalyst precipitation. For alkynyl alcohols the catalytic cycle is proposed to involve turnover-limiting alkyne insertion into the Th−O bond, generating a transitory Th−C species. The ensuing and rapid protonolysis by alcohol substrate generates the cyclized product and regenerates the Th−O-bonded catalyst. The activation parameters $\Delta H^{\ddagger}$ = 27.9(0.4) kcal/mol, $\Delta S^{\ddagger}$ = −3.0(1.1) eu,

dx.doi.org/10.1021/om300881b | Organometallics 2013, 32, 2517−2528

and E_a = 28.6(0.4) kcal/mol largely follow the trends observed with related f-element insertive hydroelementation processes.

This work provides an enhanced understanding of the activity and selectivity of organoactinide catalysts and expands the frontier of known organoactinide reactivity. Although actinide−oxygen bonds were traditionally believed to be unreactive, this work and recent literature demonstrate the potential utility of such species. The rate-limiting step of this reaction (Scheme 2, step *ii*) is the first example of C≡C bond insertion into an actinide−oxygen bond. The demonstrated necessity of strongly binding/sterically encumbered ancillary ligands will likely provide groundwork for developing new organo-f-element-mediated reactions involving polar substrate functionalities.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: t-marks@northwestern.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank NSF (Grants CHE-0809589 and CHE-1213235) for financial support. We also thank Dr. M. Weberski and Dr. C. Weiss for helpful discussions, and Dr. B. Stubbert for samples of several catalysts.

■ REFERENCES

(1) (a) Munoz, M. P. *Org. Biomol. Chem.* **2012**, *10*, 3584−3594. (b) Alcaide, B.; Almendros, P.; Martínez del Campo, T.; Redondo, M. C.; Fernández, I. *Chem.—Eur. J.* **2011**, *17*, 15005−15013. (c) Behr, A.; Johnen, L.; Neubert, P. *Catal. Sci. Technol.* **2012**, *2*, 88−92. (d) Williams, D. B. G.; Sibiya, M. S.; van Heerden, P. S. *Fuel Process. Technol.* **2012**, *94*, 75−79. (e) Patil, N. T.; Kavthe, R. D.; Shinde, V. S. *Tetrahedron* **2012**, *68*, 8079−8146. (f) Blunt, J. W.; Copp, B. R.; Munro, M. H. G.; Northcote, P. T.; Prinsep, M. R. *Nat. Prod. Rep.* **2006**, *23*, 26−78. (g) Elliot, M. C.; Williams, E. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2303−2340. (h) Mitchinson, A.; Nadin, A. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2862−2892. (i) Elliot, M. C. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1291−1318. (j) Alali, F. Q.; Liu, X. X.; McLaughlin, J. L. *J. Nat. Prod.* **1999**, *62*, 504−540. (k) Boivin, T. L. B. *Tetrahedron* **1987**, *43*, 3309−3362.

(2) (a) Zhou, T.; Zhu, G.; Huang, X.; Liu, B. *Tetrahedron Lett.* **2012**, *53*, 4955−4958. (b) Guimares, A. D.; Dorneles, E. M. S.; Andrade, G. I.; Lage, A. P.; Miyoshi, A.; Azevedo, V.; Gouveia, A. M. G.; Heinemann, M. B. *Vet. Microbiol.* **2011**, *153*, 299−306. (c) Chandrasekhar, B.; Ryu, J.-S. *Tetrahedron* **2012**, *68*, 4805−4812. (d) Brown, T. J.; Weber, D.; Gagné, M. R.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2012**, *134*, 9134−9137. (e) Swamy, N. K.; Yazici, A.; Pyne, S. G. *J. Org. Chem.* **2010**, *75*, 3412−3419. (f) Zhang, Z.; Liu, C.; Kinder, R. E.; Han, X.; Qian, H.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2006**, *128*, 9066−9073. (g) Cox, E. D.; Cook, J. M. *Chem. Rev.* **1995**, *95*, 1797−1842. (h) Larcock, R. C.; Leong, W. W. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon: New York, 1991; Vol. *4*. (i) Bird, C. W.; Cheeseman, G. W. H. In *Comprehensive Heterocyclic Chemistry*; Katrinsky, A. R.; Rees, C. W., Eds.; Pergamon Press: Oxford, 1984; Vol. *4*, pp 89−154.

(3) (a) Krause, N.; Winter, C. *Chem. Rev.* **2011**, *111*, 1994−2009. (b) Wang, Z. J.; Brown, C. J.; Bergman, R. G.; Raymond, K. N.; Toste, F. D. *J. Am. Chem. Soc.* **2011**, *133*, 7358−7360. (c) Widenhoefer, R. A. *Chem.—Eur. J.* **2008**, *14*, 5382−5391. (d) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180−3211. (e) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079−3160.

(4) (a) Fjermestad, T.; Ho, J. H. H.; Macgregor, S. A.; Messerle, B. A.; Tuna, D. *Organometallics* **2011**, *30*, 618−626. (b) Genin, E.; Antoniotti, S.; Michelet, V.; Genêt, J.-P. *Angew. Chem., Int. Ed.* **2005**, *44*, 4949−4953.

(5) (a) Ho, J. H. H.; Choy, S. W. S.; Macgregor, S. A.; Messerle, B. A. *Organometallics* **2011**, *30*, 5978−5984. (b) Ho, J. H. H.; Hodgson, R.; Wagler, J.; Messerle, B. A. *Dalton Trans.* **2010**, *39*, 4062−4069. (c) Kondo, M.; Kochi, T.; Kakiuchi, F. *J. Am. Chem. Soc.* **2010**, *133*, 32−34.

(6) (a) Reddy, M. S.; Kumar, Y. K.; Thirupathi, N. *Org. Lett.* **2012**, *14*, 824−827. (b) Corma, A.; Leyva-Pérez, A.; Sabater, M. J. *Chem. Rev.* **2011**, *111*, 1657−1712. (c) Alcaide, B.; Almendros, P.; Alonso, J. M. *Org. Biomol. Chem.* **2011**, *9*, 4405−4416. (d) Ye, L.; Cui, L.; Zhang, G.; Zhang, L. *J. Am. Chem. Soc.* **2010**, *132*, 3258−3259. (e) Du, X.; Song, F.; Lu, Y.; Chen, H.; Liu, Y. *Tetrahedron* **2009**, *65*, 1839−1845. (f) Hamilton, G. L.; Kang, E. J.; Mba, M.; Toste, F. D. *Science* **2007**, *317*, 496−499.

(7) (a) Suzuki, M.; Yanagisawa, A.; Noyori, R. *Tetrahedron Lett.* **1983**, *24*, 1187−1188. (b) Riediker, M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 5842−5844.

(8) (a) Zeni, G.; Larock, R. C. *Chem. Rev.* **2004**, *104*, 2285−2310. (b) Compain, P.; Goré, J.; Vatèle, J. M. *Tetrahedron* **1996**, *52*, 10405−10416. (c) Utimoto, K. *Pure Appl. Chem.* **1983**, *55*, 1845−1852.

(9) (a) McDonald, F. E.; Gleason, M. M. *J. Am. Chem. Soc.* **1996**, *118*, 6648−6659. (b) McDonald, F. E.; Schultz, C. C. *J. Am. Chem. Soc.* **1994**, *116*, 9363−9364.

(10) (a) Liu, P. N.; Wen, T. B.; Ju, K. D.; Sung, H. H. Y.; Williams, I. D.; Jia, G. *Organometallics* **2011**, *30*, 2571−2580. (b) Liu, P. N.; Su, F. H.; Wen, T. B.; Sung, H. H. Y.; Williams, I. D.; Jia, G. *Chem.—Eur. J.* **2010**, *16*, 7889−7897. (c) Zacuto, M. J.; Tomita, D.; Pirzada, Z.; Xu, F. *Org. Lett.* **2010**, *12*, 684−687. (d) Varela-Fernández, A.; González-Rodríguez, C.; Varela, J. s. A.; Castedo, L.; Saá, C. *Org. Lett.* **2009**, *11*, 5350−5353. (e) Trost, B. M.; Rhee, Y. H. *J. Am. Chem. Soc.* **2002**, *124*, 2528−2533. (f) Trost, B. M.; Rhee, Y. H. *J. Am. Chem. Soc.* **1999**, *121*, 11680−11683.

(11) (a) Moilanen, S. B.; Tan, D. S. *Org. Biomol. Chem.* **2005**, *3*, 798−803. (b) Alcazar, E.; Pletcher, J. M.; McDonald, F. E. *Org. Lett.* **2004**, *6*, 3877−3880. (c) Wipf, P.; Graham, T. H. *J. Org. Chem.* **2003**, *68*, 8798−8807. (d) McDonald, F. E.; Reddy, K. S.; Diaz, Y. *J. Am. Chem. Soc.* **2000**, *122*, 4304−4309.

(12) Pale, P.; Chuche, J. *Eur. J. Org. Chem.* **2000**, 1019−1025.

(13) (a) Li, Y.; Liu, J. H.-C.; Witham, C. A.; Huang, W.; Marcus, M. A.; Fakra, S. C.; Alayoglu, P.; Zhu, Z.; Thompson, C. M.; Arjun, A.; Lee, K.; Gross, E.; Toste, F. D.; Somorjai, G. A. *J. Am. Chem. Soc.* **2011**, *133*, 13527−13533. (b) Witham, C. A.; Huang, W.; Tsung, C.-K.; Kuhn, J. N.; Somorjai, G. A.; Toste, F. D. *Nat. Chem.* **2010**, *2*, 36−41. (c) Huang, W. Y.; Liu, J. H. C.; Alayoglu, P.; Li, Y. M.; Witham, C. A.; Tsung, C. K.; Toste, F. D.; Somorjai, G. A. *J. Am. Chem. Soc.* **2010**, *132*, 16771−16773.

(14) (a) Varela-Fernandez, A.; Garcia-Yebra, C.; Varela, J. A.; Esteruelas, M. A.; Saa, C. *Angew. Chem., Int. Ed.* **2010**, *49*, 4278−4281. (b) Xu, X. B.; Liu, J.; Liang, L. F.; Li, H. F.; Li, Y. Z. *Adv. Synth. Catal.* **2009**, *351*, 2599−2604. (c) Nakamura, M.; Ilies, L.; Otsubo, S.; Nakamura, E. *Org. Lett.* **2006**, *8*, 2803−2805.

(15) (a) Trambitas, A. G.; Melcher, D.; Hartenstein, L.; Roesky, P. W.; Daniliuc, C.; Jones, P. G.; Tamm, M. *Inorg. Chem.* **2012**, *51*, 6753−6761. (b) Hild, F.; Dagorne, S. *Organometallics* **2012**, *31*, 1189−1194. (c) Weiss, C. J.; Marks, T. J. *Dalton Trans.* **2010**, *39*, 6576−6588. (d) Yu, X. H.; Marks, T. J. *Organometallics* **2007**, *26*, 365−376. (e) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673−686. (f) Ryu, J. S.; Marks, T. J.; McDonald, F. E. *J. Org. Chem.* **2004**, *69*, 1038−1052. (g) Hong, S.; Marks, T. J. *J. Am. Chem. Soc.* **2002**, *124*, 7886−7887. (h) Ryu, J. S.; Marks, T. J.; McDonald, F. E. *Org. Lett.* **2001**, *3*, 3091−3094. (i) Arredondo, V. M.; Tian, S.; McDonald, F. E.; Marks, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 3633−3639. (j) Arredondo, V. M.; McDonald, F. E.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 4871−

4872. (k) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 1757−1771. (l) Roesky, P. W.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 4705−4711. (m) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 9295−9306. (n) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 707−708. (o) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241−10254. (p) Giardello, M. A.; Conticello, V. P.; Brard, L.; Sabat, M.; Rheingold, A. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10212−10240. (q) Li, Y.; Fu, P.-F.; Marks, T. J. *Organometallics* **1994**, *13*, 439−440. (r) Gagné, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275−294. (s) Sun, Y.; Wu, G.; Cen, D.; Chen, Y.; Wang, L. *Dalton Trans.* **2012**, *41*, 9682−9688.

(16) (a) Seo, S.; Marks, T. J. *Chem.—Eur. J.* **2010**, *16*, 5148−5162. (b) Seo, S. Y.; Yu, X. H.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 263−276. (c) Yu, X. H.; Seo, S.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 7244−7245.

(17) Quantum chemical study: Motta, A.; Fragala, I. L.; Marks, T. J. *Organometallics* **2010**, *29*, 2004−2012.

(18) (a) Weiss, C. J.; Wobser, S. D.; Marks, T. J. *Organometallics* **2010**, *29*, 6308−6320. (b) Kawaoka, A. M.; Douglass, M. R.; Marks, T. J. *Organometallics* **2003**, *22*, 4630−4632. (c) Gagne, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108−4109. (d) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111−8118. (e) Jeske, G.; Schock, L. E.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103−8110. (f) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51−56.

(19) (a) Sharma, M.; Andrea, T.; Brookes, N. J.; Yates, B. F.; Eisen, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 1341−1356. (b) Broderick, E. M.; Gutzwiller, N. P.; Diaconescu, P. L. *Organometallics* **2010**, *29*, 3242−3251. (c) Barnea, E.; Eisen, M. S. *Coord. Chem. Rev.* **2006**, *250*, 855−899. (d) Burns, C. J.; Eisen, M. S. Homogeneous and Heterogeneous Catalytic Processes Promoted by Organoactinides. In *The Chemistry of the Actinide and Transactinide Elements*; Morss, L. R.; Edelstein, N. M.; Fuger, J., Eds.; Springer: Dordrecht, 2006; Vol. *5*, pp 2911−3012. (e) Barnea, E.; Andrea, T.; Kapon, M.; Berthet, J. C.; Ephritikhine, M.; Eisen, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 10860−10861. (f) Wang, J.; Dash, A. K.; Kapon, M.; Berthet, J. C.; Ephritikhine, M.; Eisen, M. S. *Chem.—Eur. J.* **2002**, *8*, 5384−5396. (g) Straub, T.; Haskel, A.; Neyroud, T. G.; Kapon, M.; Botoshansky, M.; Eisen, M. S. *Organometallics* **2001**, *20*, 5017−5035. (h) Dash, A. K.; Wang, J. X.; Berthet, J. C.; Ephritikhine, M.; Eisen, M. S. *J. Organomet. Chem.* **2000**, *604*, 83−98. (i) Wang, J. X.; Dash, A. K.; Berthet, J. C.; Ephritikhine, M.; Eisen, M. S. *J. Organomet. Chem.* **2000**, *610*, 49−57. (j) Wang, J. Q.; Dash, A. K.; Berthet, J. C.; Ephritikhine, M.; Eisen, M. S. *Organometallics* **1999**, *18*, 2407−2409. (k) Haskel, A.; Straub, T.; Dash, A. K.; Eisen, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 3014−3024. (l) Chen, Y. X.; Metz, M. V.; Li, L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 6287−6305. (m) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842−857. (n) Straub, T.; Frank, W.; Reiss, G. J.; Eisen, M. S. *Dalton Trans.* **1996**, 2541−2546. (o) Haskel, A.; Straub, T.; Eisen, M. S. *Organometallics* **1996**, *15*, 3773−3775. (p) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5515−5525. (q) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* **1988**, *7*, 1828−1838. (r) Bruno, J. W.; Stecher, H. A.; Morss, L. R.; Sonnenberger, D. C.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7275−7280. (s) Smith, G. M.; Carpenter, J. D.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 6805−6807. (t) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650−6667. (u) Broach, R. W.; Schultz, A. J.; Williams, J. M.; Brown, G. M.; Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Science* **1979**, *203*, 172−174.

(20) (a) Andrea, T.; Eisen, M. S. *Chem. Soc. Rev.* **2008**, *37*, 550−567. (b) Evans, W. J. *Inorg. Chem.* **2007**, *46*, 3435−3449. (c) Cotton, S. *Lanthanide and Actinide Chemistry*; John Wiley & Sons: Uppingham, Rutland, UK, 2006. (d) Aspinall, H. C. *Chemistry of the f-Block Elements*; Taylor & Francis: Washington, DC, 2001. (e) Marks, T. J. *Science* **1982**, *217*, 989−997.

(21) (a) Ren, W.; Song, H.; Zi, G.; Walter, M. D. *Dalton Trans.* **2012**, *41*, 5965−5973. (b) Lam, O. P.; Heinemann, F. W.; Meyer, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 5965−5968. (c) Siladke, N. A.; Ziller, J. W.; Evans, W. J. *J. Am. Chem. Soc.* **2011**, *133*, 3507−3516. (d) Matson, E. M.; Fanwick, P. E.; Bart, S. C. *Organometallics* **2011**, *30*, 5753−5762. (e) Matson, E. M.; Forrest, W. P.; Fanwick, P. E.; Bart, S. C. *J. Am. Chem. Soc.* **2011**, *133*, 4948−4954. (f) Andrea, T.; Barnea, E.; Wang, J. X.; Eisen, M. S. *IOP Conf. Ser.: Mater. Sci. Eng.* **2010**, *9*, 012027. (g) Weiss, C. J.; Wobser, S. D.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 2062−2063. (h) Andrea, T.; Barnea, E.; Eisen, M. S. *J. Am. Chem. Soc.* **2008**, *130*, 2454−2455.

(22) (a) Ren, W.; Zi, G.; Fang, D.-C.; Walter, M. D. *J. Am. Chem. Soc.* **2011**, *133*, 13183−13196. (b) Fortier, S.; Kaltsoyannis, N.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2011**, *133*, 14224−14227. (c) Thomson, R. K.; Graves, C. R.; Scott, B. L.; Kiplinger, J. L. *Inorg. Chim. Acta* **2011**, *369*, 270−273. (d) Arnold, P. L.; Pécharman, A.-F.; Love, J. B. *Angew. Chem., Int. Ed.* **2011**, *50*, 9456−9458. (e) Aitken, G.; Hazari, N.; Frey, A. S. P.; Cloke, F. G. N.; Summerscales, O.; Green, J. C. *Dalton Trans.* **2011**, *40*, 11080−11088. (f) Arnold, P. L.; Turner, Z. R.; Bellabarba, R. M.; Tooze, R. P. *Chem. Sci.* **2011**, *2*, 77−79. (g) Frey, A. S. P.; Cloke, F. G. N.; Coles, M. P.; Maron, L.; Davin, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 6881−6883. (h) Mansell, S. M.; Kaltsoyannis, N.; Arnold, P. L. *J. Am. Chem. Soc.* **2011**, *133*, 9036−9051. (i) Zuend, S. J.; Lam, O. P.; Heinemann, F. W.; Meyer, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 10626−10630. (j) Lam, O. P.; Bart, S. C.; Kameo, H.; Heinemann, F. W.; Meyer, K. *Chem. Commun.* **2010**, *46*, 3137−3139. (k) Lam, O. P.; Heinemann, F. W.; Meyer, K. *C. R. Chim.* **2010**, *13*, 803−811. (l) Castro, L.; Lam, O. P.; Bart, S. C.; Meyer, K.; Maron, L. *Organometallics* **2010**, *29*, 5504−5510.

(23) (a) Braunschweig, H.; Breitling, F. M. *Coord. Chem. Rev.* **2006**, *250*, 2691−2720. (b) Gromada, J.; Carpentier, J. F.; Mortreux, A. *Coord. Chem. Rev.* **2004**, *248*, 397−410. (c) Okuda, J. *Dalton Trans.* **2003**, 2367−2378. (d) Arndt, S.; Okuda, J. *Chem. Rev.* **2002**, *102*, 1953−1976. (e) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428−447.

(24) (a) Schuetz, S. A.; Day, V. W.; Sommer, R. D.; Rheingold, A. L.; Belot, J. A. *Inorg. Chem.* **2001**, *40*, 5292−5295. (b) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *Dalton Trans.* **1973**, 1021−1023. (c) Alyea, E. C.; Bradley, D. C.; Copperthwaite, R. G. *Dalton Trans.* **1972**, 1580−1584.

(25) Stubbert, B. D.; Stern, C. L.; Marks, T. J. *Organometallics* **2003**, *22*, 4836−4838.

(26) (a) Chang, S.; Lee, M.; Jung, D. Y.; Yoo, E. J.; Cho, S. H.; Han, S. K. *J. Am. Chem. Soc.* **2006**, *128*, 12366−12367. (b) Patil, N. T.; Lutete, L. M.; Wu, H.; Pahadi, N. K.; Gridnev, I. D.; Yamamoto, Y. *J. Org. Chem.* **2006**, *71*, 4270−4279.

(27) (a) Kamijo, S.; Dudley, G. B. *Tetrahedron Lett.* **2006**, *47*, 5629−5632. (b) Knoess, H. P.; Furlong, M. T.; Rozema, M. J.; Knochel, P. *J. Org. Chem.* **1991**, *56*, 5974−5978.

(28) Trost, B. M.; Pinkerton, A. B. *J. Am. Chem. Soc.* **2002**, *124*, 7376−7389.

(29) (a) Fischer, D.; Tomeba, H.; Pahadi, N. K.; Patil, N. T.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 4764−4766. (b) Sashida, H.; Ohyanagi, K.; Minoura, M.; Akiba, K. *J. Chem. Soc., Perkin Trans. 1* **2002**, 606−612. (c) Villemin, D.; Goussu, D. *Heterocycles* **1989**, *29*, 1255−1261.

(30) Seo, S.; Yu, X.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *131*, 263−276.

(31) Dormond, A.; Elbouadili, A.; Aaliti, A.; Moise, C. *J. Organomet. Chem.* **1985**, *288*, C1−C5.

(32) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751−767.

(33) (a) Bradley, D. C.; Chatterjee, A. K.; Wardlaw, W. *J. Chem. Soc.* **1956**, 2260−2264. (b) Bradley, D. C.; Saad, M. A.; Wardlaw, W. *J. Chem. Soc.* **1954**, 1091−1094.

(34) Nolan, S. P.; Stern, D.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7844−7853.

(35) (a) Stubbert, B. D.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 4253−4271. (b) Stubbert, B. D.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 6149−6167.
(36) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*, 2nd ed.; McGraw-Hill, Inc: New York, 1995.
(37) Wang, J.; Gurevich, Y.; Botoshansky, M.; Eisen, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 9350−9351.
(38) Kim, S.; Lee, P. H. *J. Org. Chem.* **2011**, *77*, 215−220.
(39) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; Wiley-Interscience: New York, 1984.
(40) (a) Hong, S.; Tian, S.; Metz, M. V.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 14768−14783. (b) Hong, S.; Kawaoka, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 15878−15892.
(41) Tobisch, S. *Chem.—Eur. J.* **2010**, *16*, 3441−3458.
(42) (a) Meskaldji, S.; Belkhiri, L.; Arliguie, T.; Fourmigué, M.; Ephritikhine, M.; Boucekkine, A. *Inorg. Chem.* **2010**, *49*, 3192−3200. (b) Belkhiri, L.; Arliguie, T.; Thuéry, P.; Fourmigué, M.; Boucekkine, A.; Ephritikhine, M. *Organometallics* **2006**, *25*, 2782−2795. (c) Bursten, B. E.; Strittmatter, R. J. *Angew. Chem., Int. Ed.* **1991**, *30*, 1069−1085. (d) Strittmatter, R. J.; Bursten, B. E. *J. Am. Chem. Soc.* **1991**, *113*, 552−559.
(43) (a) Dzudza, A.; Marks, T. J. *Chem.—Eur. J.* **2010**, *16*, 3403−3422. (b) Dzudza, A.; Marks, T. J. *Org. Lett.* **2009**, *11*, 1523−1526. (c) Janini, T. E.; Rakosi, R. I.; Durr, C. B.; Bertke, J. A.; Bunge, S. D. *Dalton Trans.* **2009**, 10601−10608.
(44) (a) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 4th ed.; John Wiley & Sons: New York, 1992. (b) Baldwin, J. E. *Chem. Commun.* **1976**, 734−735.
(45) Seo, S.; Marks, T. J. *Chem.—Eur. J.* **2010**, *16*, 5148−5162.
(46) (a) Ryu, J. S.; Li, G. Y.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 12584−12605. (b) Yuen, H. F.; Marks, T. J. *Organometallics* **2009**, *28*, 2423−2440.
(47) Bochkarev, M. N. *Chem. Rev.* **2002**, *102*, 2089−2118.
(48) (a) Voskoboynikov, A. Z.; Shestakova, A. K.; Beletskaya, I. P. *Organometallics* **2001**, *20*, 2794−2801. (b) Dash, A. K.; Wang, J. Q.; Eisen, M. S. *Organometallics* **1999**, *18*, 4724−4741. (c) Fu, P. F.; Brard, L.; Li, Y. W.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7157−7168.
(49) (a) Motta, A.; Fragalà, I. L.; Marks, T. J. *Organometallics* **2005**, *24*, 4995−5003. (b) Kawaoka, A. M.; Douglass, M. R.; Marks, T. J. *Organometallics* **2003**, *22*, 4630−4632. (c) Takaki, K.; Koshoji, G.; Komeyama, K.; Takeda, M.; Shishido, T.; Kitani, A.; Takehira, K. *J. Org. Chem.* **2003**, *68*, 6554−6565. (d) Douglass, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 10221−10238.
(50) Yu, X.; Seo, S.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 7244−7245.
(51) Weiss, C. J.; Marks, T. J. *J. Am. Chem. Soc.* **2010**, *132*, 10533−10546.
(52) Eisen, M. Catalytic C−N, C−O, and C−S Bond Formation Promoted by Organoactinide Complexes. In *C−X Bond Formation*; Vigalok, A., Ed.; Springer-Verlag: Berlin, 2010; Vol. *31*, pp 157−184.
(53) (a) Nolan, S. P.; Porchia, M.; Marks, T. J. *Organometallics* **1991**, *10*, 1450−1457. (b) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824−6832.
(54) (a) Baker, R. J.; Walshe, A. *Chem. Commun.* **2012**, *48*, 985−987. (b) Barnea, E.; Moradove, D.; Berthet, J. C.; Ephritikhine, M.; Eisen, M. S. *Organometallics* **2006**, *25*, 320−322. (c) Villiers, C.; Thuery, P.; Ephritikhine, M. *Eur. J. Inorg. Chem.* **2004**, 4624−4632.
(55) (a) Tian, S.; Arredondo, V. M.; Stern, C. L.; Marks, T. *Organometallics* **1999**, *18*, 2568−2570. (b) Li, Y.; Marks, T. *Organometallics* **1996**, *15*, 3770−3772.
(56) Bradley, D. C.; Chatterjee, A. K.; Wardlaw, W. *J. Chem. Soc.* **1956**, 3469−3472.
(57) Clark, D. L.; Huffman, J. C.; Watkin, J. G. *J. Chem. Soc., Chem. Commun.* **1992**, 266−268.
(58) (a) Van der Sluys, W. G.; Sattelberger, A. P. *Chem. Rev.* **1990**, *90*, 1027−1040. (b) Bradley, D. C.; Saad, M. A.; Wardlaw, W. *J. Chem. Soc.* **1954**, 3488−3490.
(59) (a) Barnhart, D. M.; Clark, D. L.; Gordon, J. C.; Huffman, J. C.; Watkin, J. G. *Inorg. Chem.* **1994**, *33*, 3939−3944. (b) Berg, J. M.; Clark, D. L.; Huffman, J. C.; Morris, D. E.; Sattelberger, A. P.; Streib, W. E.; Vandersluys, W. G.; Watkin, J. G. *J. Am. Chem. Soc.* **1992**, *114*, 10811−10821.
(60) (a) Clark, D. L.; Watkin, J. G. *Inorg. Chem.* **1993**, *32*, 1766−1772. (b) Clark, D. L.; Sattelberger, A. P.; Van der Sluys, W. G.; Watkin, J. G. *J. Alloys Compd.* **1992**, *180*, 303−315.