Synthesis and Catalytic Characteristics of Novel Constrained-Geometry Organoactinide Catalysts. The First Example of Actinide-Mediated Intramolecular Hydroamination

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*Summary: The synthesis, characterization, and reactivity of a series of organoactinide constrained-geometry complexes, (CGC)An(NRR′)$_2$ (CGC = Me$_2$Si(η^5-Me$_4$C$_5$)-(^{t}BuN); An = Th, **1**; An = U, **2**; R = R′ = Me, **a**; R = Et, R′ = Me, **b**; R = R′ = Et, **c**), are reported. These complexes are effective precatalysts for intramolecular catalytic hydroamination/cyclization of aminoalkenes and aminoalkynes. Comparisons of structure and reactivity are drawn with previously reported trivalent organolanthanide CGC catalytic systems.*

Hydroamination is a challenging, highly desirable, atom-economical transformation defined as the formal addition of an N−H bond across a unit of C−C unsaturation.[1] Current catalytic research activity in this area is widespread[2,3] and spans the entire Periodic Table.[1] Organolanthanide-catalyzed amino-olefin hydroamination has been extensively investigated,[1] typically displaying nearly quantitative yields[3] in addition to high regio- and diastereoselectivities (>95%), moderate enantioselectivities (as high as 74%),[4] and appreciable functional group tolerance[3h] in intramolecular hydroamination/cyclization reactions. The success and versatility of CGC ancillary ligation in lanthanide (Ln)[3b,d,5a−c] and early transition metal[5d,6] catalytic chemistry, as well as the pronounced structure, charge, covalency, and redox property differences between organolanthanides and organoactinides,[7] raise intriguing questions of what unusual properties actinide (An) CGC complexes might exhibit. This communication reports the synthesis of a new class of constrained-geometry organoactinide catalysts and compares their hydroamination/cyclization properties with those of analogous Ln complexes.[3d,8]

Amine/alkane elimination syntheses[9] using a protic ligand reagent and the corresponding homoleptic alkyl- or amidometal precursor are used extensively throughout the Periodic Table. From previous success with lanthanides[3d] and literature precedent for An(NR$_2$)$_4$-based amine elimination syntheses,[10] homoleptic amidoactinides and H$_2$CGC reagents were chosen for preparation of the target (CGC)An(NR$_2$)$_2$ complexes (Scheme 1). The equilibrium position of the elimination reaction is controlled in part by the dialkylamine concentration, making removal of this byproduct essential for driving the reaction to completion. A slight excess of H$_2$CGC (based on AnCl$_4$) and frequent removal of volatiles affords the desired products under mild conditions in up to 77% yield.[11] Where investigated, (CGC)An(NR$_2$)$_2$ syntheses from in situ generated or purified (e.g., sublimed) An(NR$_2$)$_4$ reagents yield essentially identical results. The new complexes were characterized by conventional spectroscopic and analytical techniques,[11] and in several cases by X-ray diffraction (vide infra).

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(11) See Supporting Information for complete details.

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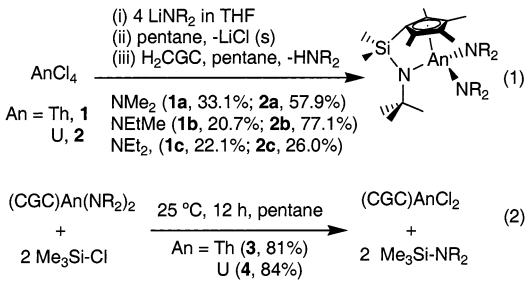
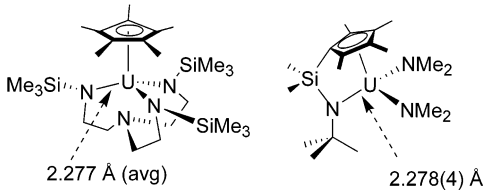
Scheme 1. Synthesis of Complexes 1−4[a]



[a] Yields for eq 1 based on $AnCl_4$. See Supporting Information for full details.

Dichloro complexes (CGC)$AnCl_2$ (An = Th, **3**; An = U, **4**) were prepared via reaction of bis-amides **1** and **2** with excess chlorotrimethylsilane (TMSCl) to afford dichlorides **3** and **4** in quantitative yield (by NMR spectrosopy) and excellent purity (Scheme 1).[11] The dichlorides are likely dimeric or trimeric in the solid state,[5a,b,12,13] and their extremely low solublity in suitable solvents precludes cryoscopic molecular weight measurements. Lewis basic solvents were not extensively explored in these syntheses in order to prevent formation of undesirable solvent adducts[3g] or anionic "ate" species.[5a,b] Attempts to prepare **3** and **4** by traditional salt elimination reactions in noncoordinating solvents gave complicated product mixtures. The TMSCl amide−halide transposition avoids adduct formation, shows no evidence for oligomeric byproducts, and proceeds cleanly under mild conditions.

Complexes **1a** and **2a**−**c** were characterized by single-crystal X-ray diffraction (Figure 1).[11] Trends in the Cp″(c)−An−N1 angle (Cp″(c) = Me_4C_5 centroid) indicate that steric openness in f-element CGC complexes increases in the order Yb < Sm < U < Th.[3d,11] In contrast, less constrained ligand systems, e.g., $Me_2SiCp''_2AnE_2$[14] and Cp'_2AnE_2[15] (Cp′ = Me_5C_5; E = CH_2(TMS), Cl), have Cp(c)−An−Cp(c) angles that are greater than the aforementioned Cp″(c)−An−N1 angles by ∼25° and 40°, respectively. The ^{t}BuN−U bond length in **2a** is nearly identical (<2σ difference) to the silyl-substituted amide bonds in $Cp'U(N[CH_2CH_2N(TMS)]_3)$:[16]



The ^{t}BuN−An bond in **1a** and **2a**−**c** is significantly longer (>3σ) than the An−NR_2 bonds, likely owing to steric constraints in addition to the decreased basicity[17] of the $(Me_2Si)^t$BuN moiety.

Examples of organoactinide-mediated hydroamination are rare.[18] The present studies focus on the competence of CGC organoactinides for catalytic *intramolecular*

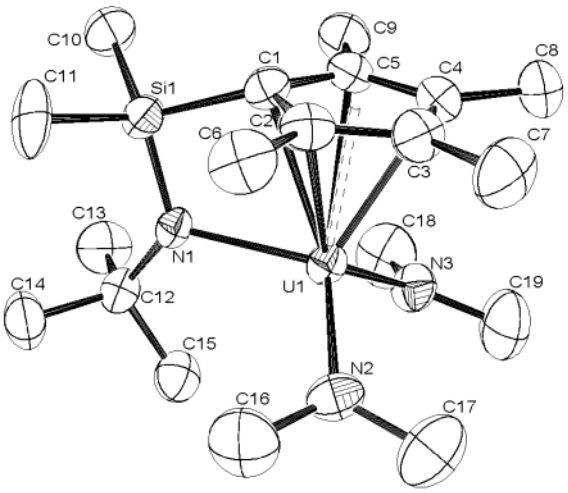


Figure 1. Molecular structure of $(CGC)U(NMe_2)_2$ complex **2a** with hydrogen atoms omitted for clarity. See Supporting Information for full details. Selected bond distances (Å) and angles (deg): U−N1, 2.278(4); U−N2, 2.207(4); U−N3, 2.212(4); U−C1, 2.638(5); U−C2, 2.708(5); U−C3, 2.771(5); U−C4, 2.763(5); U−C5, 2.676(5); Cp″(c)−U, 2.425; Cp″(c)−U−N1, 93.31; N2−U1−N3, 109.57(17); N1−Si1−C1, 96.3(2). [Cp″(c) = Me_4C_5 centroid of C1− C5.] Thermal ellipsoids are shown at 50% probability.

Table 1. Summary of Catalytic Hydroamination/ Cyclization with Organoactinide Catalysts

Entry	Subtsrate	Product	Precatalyst[a]	N_t, h^{-1} (°C)[b,c]
1.			(CGC)Th$(NR_2)_2$	15 (25)
2.	H_2N	N H	(CGC)U$(NR_2)_2$	2.5 (25)
3.	**5**	**7**	Cp'_2ThMe_2	0.4 (25)
4.			(CGC)Th$(NR_2)_2$	1460 (25)
5.	H_2N Ph Ph	Ph N H	(CGC)U$(NR_2)_2$	430 (25)
	6	**8**		
6.			(CGC)Th$(NR_2)_2$	82 (25)
7.	H_2N SiMe3	SiMe3 N	(CGC)U$(NR_2)_2$	>1600 (25)
	9	**12**		
9.			(CGC)Th$(NR_2)_2$	7.8 (25)
10.	H_2N H	H N	(CGC)U$(NR_2)_2$	1210 (25)
	10	**13**		
11.			Cp'_2UMe_2	26 (25)
12.			(CGC)Th$(NR_2)_2$	4.3 (25)
13.	H_2N Ph	Ph N	(CGC)U$(NR_2)_2$	51 (25)
14.	**11**	**14**	Cp'_2ThMe_2	0.8 (60)

[a] Precatalyst loading 0.3−7 mol %. Substrate solutions in C_6D_6 added to a frozen solution of precatalyst and internal standard in C_6D_6 and frozen without mixing. Samples were then thawed and shaken immediately prior to kinetic studies. See Supporting Information for details. [b] Turnover frequency; reaction progress monitored by ^{1}H NMR spectroscopy. [c] All product yields >90%.

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(13) Single crystals suitable for X-ray diffraction studies have not been obtained to date, although NMR spectroscopy, electron-impact mass spectrometry, and elemental analysis indicate clean formation of **3** and **4** by this method.

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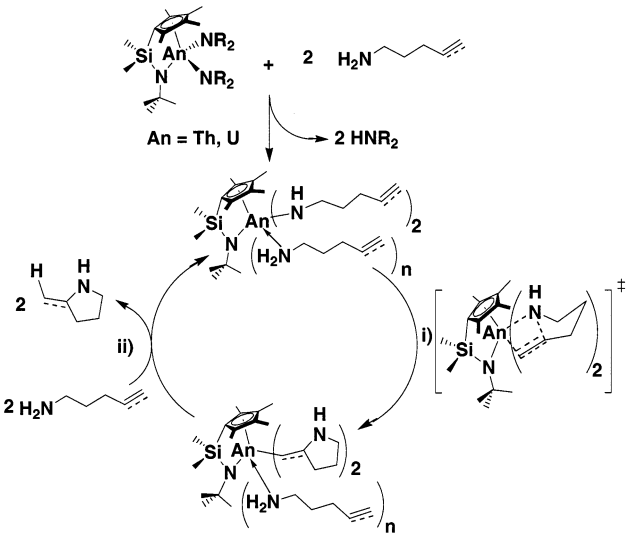
Scheme 2. Plausible Reaction Mechanism for (CGC)An-Mediated Intramolecular Hydroamination and Cyclization of Aminoalkenes and Aminoalkynes[a]



[a] For aminoalkynes, the product in step (ii) rapidly undergoes tautomerization after protonolysis from the metal to the products shown in Table 1.

hydroamination/cyclization of aminoalkenes **5** and **6** and of aminoalkynes **9**−**11**, as well as comparison to (CGC)LnE (E = $N(TMS)_2$, $CH(TMS)_2$)[3d] and Cp'_2AnMe_2 systems. It can be seen in Table 1 that complexes **1** and **2** are excellent precatalysts for the rapid, regioselective conversion of a representative series of substrates. Owing to rapid precatalyst protonolysis by incoming substrate, the nature of the departing amide group (H−NR_2, R = Et; R = Me; R = Et, R′ = Me) does not affect reaction rates. Kinetic results are consistent with observations made for similar transformations using organolanthanide precatalysts,[3] namely, rate ∝ [precatalyst]^1[substrate]^0, implying turnover-limiting C=C/C≡C insertion into the An−NHR bond.[3] Observed rate dependence on metal ionic radius is also reminiscent of organolanthanides in that larger ionic radius centers are more active for intramolecular aminoalkene cyclization,[3a−d,g−h] while smaller ionic radius centers more rapidly cyclize aminoalkynes.[3e,f] The sterically open coordination environment of the tetravalent (CGC)An$(NR_2)_2$ moiety effects rapid formation of cyclized product with rates comparable to those of the most active trivalent (CGC)LnE systems.[1,3]

A plausible organoactinide-mediated reaction pathway consistent with the present data is proposed in Scheme 2.[19] The unique availability of *two* actinide amido sites for incoming amino-olefin (versus one for trivalent (CGC)Ln catalysts) may conceivably allow dual, synchronized substrate cyclization. It can be seen that the more sterically open environment of the CGC ligand greatly enhances N_t for aminoalkene substrates by allowing greater access to the metal center without compromising the kinetic and electronic stability of the catalytically active species. Comparison to prior studies with lanthanocene and related catalysts[3] and results here with Cp'_2AnMe_2 complexes (An = Th, U; Table 1, entries 3, 11, 14) suggest that while steric effects are indeed a major factor modulating reactivity, the extent to which covalency and synchronicity are involved will require further investigation. The rate dependence on metal center openness is appreciable for aminoalkenes, where a nearly 40-fold rate enhancement is observed upon changing ancillary ligation from Cp'_2ThMe_2 to the sterically more accessible **1** (Table 1, entries 1, 3). Interestingly, sterically less open Cp'_2ThMe_2 effects rather sluggish cyclization of aminoalkyne **11** (R′ = Ph), even at 60 °C, whereas Cp'_2UMe_2 mediates the cyclization of aminoalkyne **10** (R′ = H) nearly 50 times less rapidly than does **2** at 25 °C (Table 1, entries 11, 14). Although it was observed previously that organolanthanide catalysts with smaller metal ion sites effect aminoalkyne cyclization at substantially greater rates,[3d,e] the influence of ligation environment on this transformation has not been investigated in detail using (CGC)Ln complexes.

In summary, the coordinatively open CGC actinide complexes described here exhibit excellent reactivity for the intramolecular catalytic hydroamination/cyclization of aminoalkenes and aminoalkynes. Future work will focus on optimizing catalyst structures for regio- and stereoselective transformations including tandem cyclizations and intermolecular additions.

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Supporting Information Available: Details describing synthesis and characterization of **1**−**4** and structure determinations for **1a** and **2a**−**c**, including listings of final coordinates, thermal parameters, bond distances, and bond angles, are provided. Kinetic details and a representative plot are included. Crystallographic data for **1a** and **2a**−**c** are also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) An alternative cycle proceeding through an An=NR species (see ref 18) as a catalytically inactive species or as the active catalyst species cannot be rigorously ruled out at this time. Imide formation as a reversible, turnover-limiting step seems unlikely given the observed independence of overall rate on [substrate].