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Catalytic Addition of Alcohols into Carbodiimides Promoted by Organoactinide Complexes

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Supporting Information

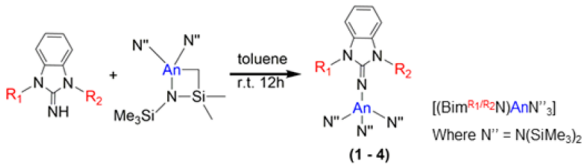
ABSTRACT: The insertion of alcohols into carbodiimides mediated by benzimidazolin-2-iminato actinide complexes $[(Bim^{R_1/R_2}N)AnN''_3]$ [N″ = $N(SiMe_3)_2$] is presented herein. Analysis of single-crystal data revealed that steric hindrance, rather than electronic properties, plays an important role in determining the accessibility for this insertion process. All actinide complexes showed excellent activities under very mild conditions. Stoichiometric reactions in combination with kinetic and thermodynamic studies allow us to propose a plausible active species and a mechanism for the catalytic cycle.

Early-actinide (An) uranium- and thorium-complex-mediated carbon-heteroatom bond formations are at the scientific forefront because of their unique catalyst structure−reactivity relationships, as well as their high atom efficiency.[1−12] However, because of the formation of strong oxygen−actinide bonds due to their oxophilicities,[8,13,14] catalytic organic transformations with oxygen-containing substrates have been extremely challenging. In contrast to some recent progress in lanthanide-mediated reactions of oxygen-containing substrates,[8,15,16] only a very limited number of catalytic examples are available so far for organoactinides.[17−26]

Catalytic insertions of E−H (NH, PH, SH, ≡CH, etc.) bonds into carbodiimides has attracted considerable attention in recent years.[27−39] On the basis of the observation in Tishchenko and hydroalkoxylation reactions that An−O can be an active moiety in catalytic processes,[21−26] uranium and thorium-based complexes were used for the intermolecular addition of alcohols to heterocumulenes. Exploratory investigations with mono(imidazolin-2-iminato)thorium(IV) and -uranium(IV) complexes $[(Im^RN)AnN''_3]$ [An = Th, U; R = Dipp; N″ = $-N(SiMe_3)_2$] indicated, in spite of their high activities in the hydroelementation of nonoxygenated substrates, that the insertion of alcohols into carbodiimides was unfeasible.[40,41] Recent attempts using sterically less demanding amido actinide metallacycles allowed us to achieve the unprecedented actinide-catalyzed addition of alcohols to carbodiimides; however, attempts to elucidate the structure of the active species were challenging because of the formation of a mixture of actinide alkoxides upon protonolysis of the amido moieties by the alcohols.[42] The difference of the two aforementioned systems is the presence of a sterically highly encumbered imidazolin-2-iminato ligand in the former one, which might keep the expected active species, mono(imidazolin-2-iminato)thorium(IV) trialkoxides, from attacking the carbodiimides, thus leading to no activity. These considerations raised our curiosity toward developing a new family of complexes that contain, on the one hand, a less sterically demanding ligand (i.e., a smaller cone angle vide infra), which might allow the insertion of alcohols into carbodiimides to occur, and that exhibit, on the other hand, good solubility upon protonolysis with alcohols to clearly characterize the structure of potential intermediates. The monoanionic imidazolin-2-iminato ligand is of great interest owing to its ability to act as a $2\sigma,4\pi$-electron donor, which renders this system isolobal with the widely used cyclopentadienides.[19,43−45] Herein, we borrowed the concept of η^5-indenyl, when compared with the cyclopentadienyl group, by incorporating a phenyl ring into the backbone of the imidazolin-2-iminato moiety to change its electronic properties and synthesized a series of benzimidazolin-2-iminato ligands. Moreover, to create more accessible, sterically less encumbered metal atoms, smaller N-substituents (Me, ^{i}Pr) were introduced into the ligands. Treating these new ligand precursors with 1 equiv of the corresponding actinide metallacycle in toluene afforded the corresponding benzimidazolin-2-iminato actinide complexes **1**−**4** in high yields (Scheme 1).

The solid-state structures of all of the complexes were confirmed by X-ray crystallography (Figure 1). Resembling previous lanthanide and actinide counterparts,[19,20,46,47] all four complexes displayed shorter $An-N_{C=N}$ bonds compared to the corresponding $An-N_{amido}$ bonds, as well as approximate linearity for An−N−C angles, corroborating a higher bond order of An−

Scheme 1. Synthesis of Benzimidazolin-2-iminato Actinide Complexes $[(Bim^{R_1/R_2}N)AnN''_3]$



(**1**) $[(Bim^{Me/Dipp}N)UN''_3]$, R_1= Me, R_2= Dipp, An = U;

(**2**) $[(Bim^{Me/Dipp}N)ThN''_3]$, R_1= Me, R_2= Dipp, An = Th;

(**3**) $[(Bim^{^iPr/^iPr}N)UN''_3]$, R_1= R_2= ^{i}Pr, An = U;

(**4**) $[(Bim^{^iPr/^iPr}N)ThN''_3]$, R_1= R_2= ^{i}Pr, An = Th;

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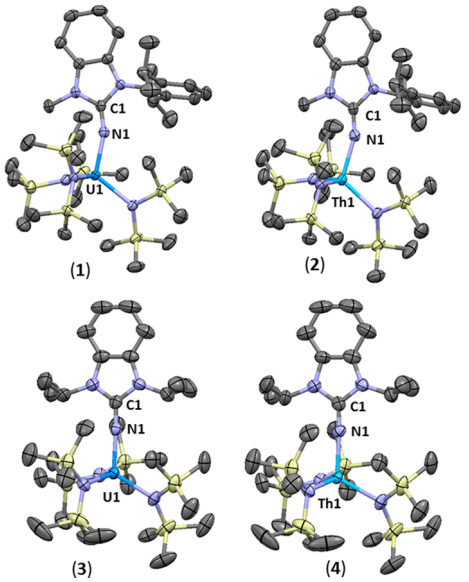


Figure 1. Solid-state structures of complexes **1**−**4** (thermal ellipsoids are drawn at 50% probability). Hydrogen atoms are omitted for clarity.

$N_{C=N}$ bonds. The geometric parameters of complexes **1**−**4** are very much alike as to the corresponding imidazolin-2-iminato complexes.[19,20,43] These similarities among the complexes lead to the conclusion that the presence of the phenyl ring on the backbone has little influence on the electronic structure of the ligand attached to the metal. Despite the smal changes in the electronic structures, when it comes to the cone angle, which is an important parameter to evaluate the proximity of the ligand substituents to the metal center,[48,49] compared to the ca. 204° in $[(Im^{Dipp}N)ThN''_3]$, much smaller cone-angle values were displayed for the benzimidazolin-2-iminato actinide complexes (138°, 140°, 122°, and 119° for **1**−**4**, respectively), indicating that these new actinide complexes exhibited much more open spaces available to the metal toward the incoming substrates.

On the basis of these observations, we attempted to investigate the intermolecular insertion of methanol (MeOH) into diisopropylcarbodiimide (DIC) and 1,3-di-*p*-tolylcarbodiimide (DTC) (Table 1). To our pleasure, all new complexes are active in the intermolecular addition reaction, affording the corresponding isourea products with moderate-to-high yields, whereas no reaction was observed in the absence of actinide complexes. It is important to point out that the ligand itself does not induce the addition reaction, and freshly recrystallized complexes are used in the catalytic reactions. Table 1 shows a clear trend in the activity of the complexes for alcohol insertion when different carbodiimides were employed. Higher conversions, even in a short amount of time, were obtained for the more electrophilic substrate DTC, suggesting that the addition of the alkoxo moiety to the carbodiimide sp carbon is easier because of the presence of the *p*-tolyl group compared to the electron-releasing ^{i}Pr group. The scope of the reaction with regard to the alcohol substrate was studied by varying the steric bulkiness and acidity of the alcohols. The catalytic addition of the less sterically encumbered alcohols, i.e., MeOH and ethanol (EtOH), to DIC by precatalysts **1** and **2** led to moderate yields; however, no turnovers were observed when using larger alcohols [isopropyl alcohol (^{i}PrOH) and *tert*-butyl alcohol (^{t}BuOH)]. Similar trends were revealed when DTC was used, which required longer reaction times to fully consume the bulkier ^{i}PrOH and ^{t}BuOH. Like the aliphatic alcohols, changing the size of the phenol substrates has an important impact on this intermolecular addition reaction. Hence, using the sterically hindered 2,4-$^{t}Bu_2C_6H_3OH$ resulted in lower activities compared to using 2,6-$Me_2C_6H_3OH$. Moreover, the diol (1,3-propanediol) and triol (triethanolamine) were employed in this catalytic reaction to show the scope capabilities for these organoactinides (Scheme 2).

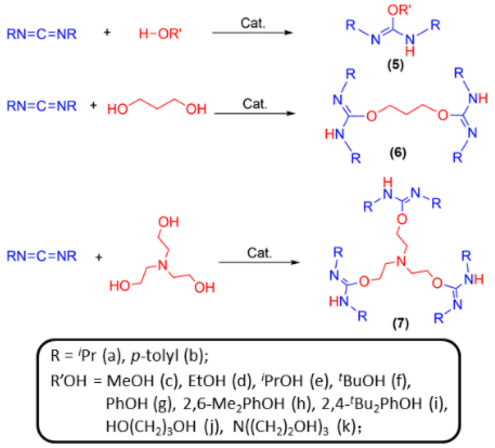
Combining these catalytic results with the bond properties shown in the single-crystal X-ray structures, as well as the different catalytic behaviors revealed for $[(Bim^{R_1/R_2}N)AnN''_3]$ compared to the $[(Im^{Dipp}N)ThN''_3]$ systems, we can conclude

Table 1. Catalytic Insertion of Alcohols into Carbodiimides

run[a]	Cat.	RNCNR	R′OH[b]	time (h)	conv (%)[c]	product
1	**1**	DIC	MeOH	24	28	**5ac**
2	**2**	DIC		24	12	
3	**3**	DIC		24	56	
4	**4**	DIC		24	26	
5	**1**	DTC		1	>99	**5bc**
6	**2**	DTC		1	>99	
7	**3**	DTC		1	>99	
8	**4**	DTC		1	>99	
9	**1**	DTC	EtOH	24	20	**5ad**
10	**2**			24	20	
11	**1**	DTC		1	96	**5bd**
12	**2**			1	>99	
13	**1**	DTC	^{i}PrOH	3	98	**5be**
14	**2**			5	>99	
15	**1**	DTC	^{t}BuOH	5	>99	**5bf**
16	**2**			5	94	
17	**1**	DTC	PhOH	2	>99	**5bg**
18	**2**			2	94	
19	**1**	DTC	2,6-$Me_2C_6H_3OH$	2	93	**5bh**
20	**2**			2	95	
21	**1**	DTC	2,4-$^{t}Bu_2C_6H_3OH$	12	94	**5bi**
22	**2**			12	92	
23	**1**	DTC	PDO	2	>99	**6bj**
24	**2**			2	>99	
25	**1**	DTC	TEOA	3	>99	**7bk**
26	**2**			6	94	

[a]Reaction conditions: 7 μmol of catalysts, [Cat.]/[RNCNR]/[OH] = 1/50/50, 500 μL of C_6D_6, room temperature. [b]PDO = propane-1,3-diol [$HO(CH_2)_3OH$]; TEOA = triethanolamine ($N[(CH_2)_2OH]_3$). [c]The yield was determined by ^{1}H NMR spectroscopy of the crude reaction mixture.

Scheme 2. Catalytic Insertion of Alcohols into Carbodiimides



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that the steric hindrances play a more important role in catalyzing the intermolecular addition of alcohols to carbodiimides.

To shed some light on the mechanism, stoichiometric reactions of the precatalyst **2** with 3 and 10 equiv of DTC were first carried out in situ in benzene-d_6, showing no reactivity. This result indicates that the amido moieties do not insert into DTC, forming a guanidinate ligand. In contrast, reactions between the catalyst **2** and 3 equiv of 2,4-^{t}Bu$_2$C$_6$H$_3$OH took place rapidly to afford 3 equiv of hexamethyldisilazane and the corresponding mono(benzimidazolin-2-iminato)thorium(IV) trialkoxide [(Bim$^{Me/Dipp}$N)Th(O-2,4-^{t}Bu$_2$Ph)$_3$] complex, whose structure was determined by ^{1}H NMR spectroscopy. It is important to note that the resulting [(Bim$^{Me/Dipp}$N)Th(O-2,4-^{t}Bu$_2$Ph)$_3$] complex was completely dissolved in the nonpolar solvent benzene at room temperature and led to a clearly transparent solution. Further, reacting the precatalyst **2** with 10 equiv of 2,4-^{t}Bu$_2$C$_6$H$_3$OH generated a mixture of [(Bim$^{Me/Dipp}$N)Th(O-2,4-^{t}Bu$_2$C$_6$H$_3$)$_3$] and 7 equiv of unreacted phenol, to which 10 equiv of DTC was added, and a rapid consumption of ca. 70% of DTC was observed, implying that [(Bim$^{Me/Dipp}$N)Th(O-2,4-^{t}Bu$_2$C$_6$H$_3$)$_3$] is an active species for the addition of an alcohol to a carbodiimide. During these stoichiometric studies, the freshly formed intermediate [(Bim$^{Me/Dipp}$N)Th(O-2,4-^{t}Bu$_2$Ph)$_3$] was stable at room temperature for at least 24 h. However, exposing it to higher temperatures (50 °C) in the presence of excessive 2,4-^{t}Bu$_2$C$_6$H$_3$OH resulted in protonation of the ligand, forming the intermediate **C** [(Bim$^{Me/Dipp}$NH)$_2$Th(O-2,4-^{t}Bu$_2$C$_6$H$_3$)$_4$], whose structure had been confirmed by single-crystal spectroscopy (Figure 2). It is interesting to note that this intermediate

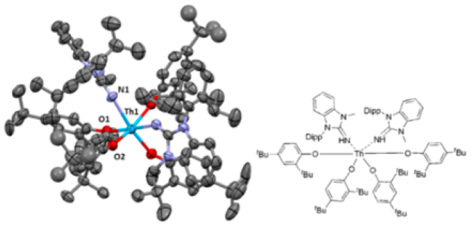


Figure 2. Single crystal and structure of the reaction intermediate [(Bim$^{Me/Dipp}$NH)$_2$Th(O-2,4-^{t}Bu$_2$Ph)$_4$].

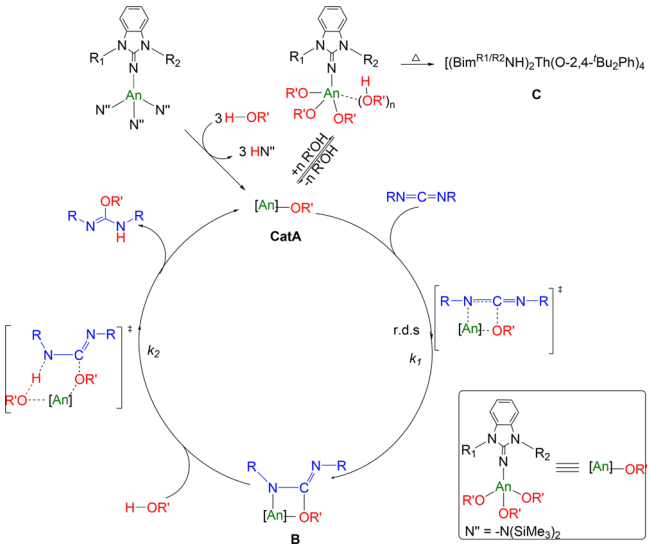
was also found to be active for the intermolecular addition of 2,4-^{t}Bu$_2$C$_6$H$_3$OH to DTC (with slightly lower reactivity compared to complex **2**), corroborating again the reactivity of the An−O moieties.

Kinetic studies of the catalytic addition of 2,4-^{t}Bu$_2$C$_6$H$_3$OH to DTC using complex **2** gives rise to the rate equation (1).

$$\frac{\partial p}{\partial t} = K_{obs}[\mathbf{2}]^1[\mathrm{DTC}]^1[2,4\text{-}^t\mathrm{Bu_2PhOH}]^{-1} \quad (1)$$

Thermodynamic parameters for the same system were calculated from the Erying and Arrhenius plot, displaying an activation barrier (E_a) of 16.2(9) kcal mol^{-1} and the enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation of 15.6(7) kcal mol^{-1} and −27.0(3) eu, respectively, indicating an organized transition state at the rate-determining step. A plausible mechanism for the intermolecular addition of alcohols is presented in Scheme 3. The reaction of the precatalyst [(Bim$^{R_1/R_2}$N)AnN″$_3$] with the alcohol gave the active intermediate [(Bim$^{R_1/R_2}$N)AnOR$_3$] (**Cat-A**) through an acid−base protonolysis reaction. The insertion of the alkoxide into a carbodiimide produces the actinide isourea

Scheme 3. Proposed Mechanism for the Intermolecular Addition of Alcohols to Carbodiimides Promoted by Actinide Complexes



species **B**. Protonation of **B** by another alcohol molecule releases the product with concomitant regeneration of the active species **Cat-A**. Deuterium-labeling studies using 2,4-^{t}Bu$_2$C$_6$H$_3$OD, DTC, and the catalyst **2** afforded a KIE value of k_H/k_D = 1.02 ± 0.04, indicating that the protonolysis of **B** is not the turnover limiting step of the catalytic cycle.

In summary, this present work showed our approach to preparing isourea products through the intermolecular addition of alcohols to carbodiimides promoted by the precatalysts [(Bim$^{R_1/R_2}$N)AnN″$_3$].

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b00357.

NMR spectra, kinetic and stoichiometric experiments, and deuterium-labeling studies (PDF)

Crystallographic data for complexes **1**−**4**, intermediate **C** (CIF)

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Notes

The authors declare no competing financial interest.

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