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Addition of E−H (E = N, P, C, O, S) Bonds to Heterocumulenes Catalyzed by Benzimidazolin-2-iminato Actinide Complexes

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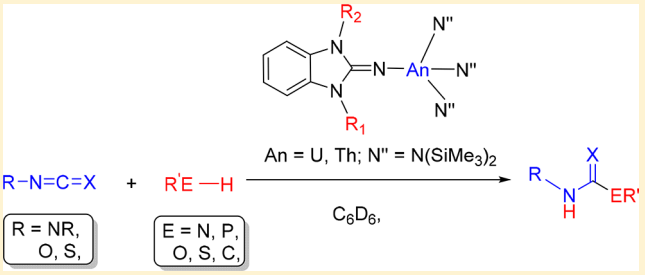
Supporting Information

ABSTRACT: The synthesis and characterization of benzimidazolin-2-iminato actinide(IV) complexes [(Bim$^{R1/R2}$N)An(N{SiMe$_3$}$_2$)$_3$] (An = U, Th) (**1−6**) is reported. All complexes were obtained in high yields, and their solid state structures were established through single-crystal X-ray diffraction analysis. Using **1−6** as precatalysts, the addition of mono- and bifunctional E−H (E = N, P, C, O, S) substrates to various heterocumulenes, including carbodiimides, isocyanates, and isothiocyanates, was investigated, affording the respective addition products in high yields under very mild reaction conditions. Various amines were applicable to this reaction, indicating a large scope capability of amine nucleophiles for the insertion process.



INTRODUCTION

Organoactinide complex-mediated hydroelementation processes, usually realized by the addition of E−H (E = N, S, P, Si, O) moieties to unsaturated bonds, have experienced a phenomenal acceleration in research activity over the past two decades. Some representative results that were made in this field comprise hydrosilylation,[1−4] hydroamination,[5−10] hydrothiolation[11−13] reactions, etc., revealing facile and atom-efficient approaches for the construction of carbon-heteroatom bonds. However, hydroelementation of heterocumulenes,[14−27] which straightforwardly affords guanidine-type compounds that have considerable application in coordination chemistry and biorelevant fields, has been scarcely investigated using actinide precursors. Compared with transition metals and lanthanide complexes, organoactinides exhibit metal centers bearing 5f valence orbitals and very sizable ionic radii, which in turn enable large coordination numbers and unusual coordination geometries of the corresponding complexes.[28−39] These properties usually allow them to display unique catalytic behaviors in organic transformations, such as enhanced catalytic activities as well as regio- and chemoselectivities.[1,5,40−42] These considerations prompted us to thoroughly investigate the aforementioned hydrofunctionalization of heterocumulenes with the aid of various organoactinide systems. In addition, previous reports on the hydrofunctionalization reactions by using transition metals and lanthanide complexes usually involve only one or two certain kinds of E−H nucleophiles or heterocumulene substrates, and thus provide only a small substrate scope. Therefore, scientifically, it is highly challenging and demanding to develop some catalytic systems that exhibit high tolerance toward heteroatoms and are able to catalyze diversified substrates. Previous studies had shown that actinide complexes displayed good tolerance toward nitrogen and silicon heteroatoms.[5,10,43−46] When it comes to oxygen-containing substrates, however, catalytic transformations are extremely challenging because of the formation of strong oxygen-actinide bonds due to the high oxophilicities of the metal centers (bond strength of 208.0 kcal mol^{-1} for Th−O and 181.0 kcal mol^{-1} for U−O). So far, only a very limited number of catalytic examples are available for organoactinide mediated reactions involving oxygen-containing substrates, such as the Tishchenko reaction,[47−49] hydroalkoxylation,[50,51] small molecule activation,[35,52] and polymerization of cyclic esters.[53−55] On the basis of this consideration, a series of oxygen-containing nucleophiles and heterocumulenes were also investigated in the present work. Moreover, it has been well-recognized that steric bulkiness and electronic properties are powerful methods to manipulate the reactivity of organoactinide catalysts. Previous studies in our group proved that the reactivity of coordinative unsaturated actinide complexes could be increased by regulating the electronic properties of the ancillary ligands.[54,56] Therefore, in the present work, we combine these steric and electronic factors together into a new family of actinide complexes, and investigate their impact on the hydroelementation process.

Our interest was focused on imidazolin-2-iminato-type ligands, due to their highly nucleophilic and strongly basic properties.[57−60] In addition, through efficient stabilization of a positive charge on the imidazolium ring, such ligands can be

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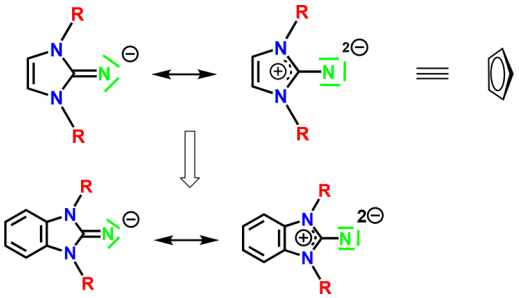
regarded as $2\sigma,4\pi$-electron donors and thus as cyclopentadienyl analogues. Previous work has shown that the nature of the backbone has a great influence on the zwitterion structure of the ligand and thereby on the properties of the $M-N_{(C=N)}$ bond.[61] Inspired by this, we decided to incorporate a phenyl ring in the backbone of the imidazolin-2-iminato ligand (Scheme 1), based on the consideration that the presence of

Scheme 1. Mesomeric Structures of Imidazolin-2-iminato (Top) and Benzimidazolin-2-iminato (Bottom) Ligands



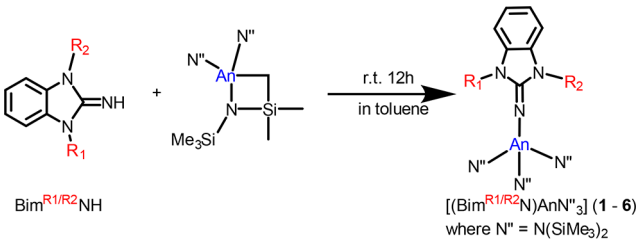
the phenyl ring will impact the nature of the C═N double bond and thus influence the bonding properties of An−N linkage (An = Th, U).[62] Moreover, asymmetric ligands with one small group on one side and a sterically demanding group on the other side are preferred here, which will potentially provide more space for the incoming substrates for accessing the actinide centers.

RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes. A series of asymmetric benzimidazolin-2-iminato ligands bearing substituents of different steric demand were prepared (see the Supporting Information). Subsequent treatment with 1 equiv of the actinide metallacycles $[(Me_3Si)_2N]_2An[\kappa^2\text{-}(N,C)\text{-}CH_2Si(CH_3)_2N(SiMe_3)]$ (An = Th, U) at room temperature for 12 h and recrystallization from toluene at −35 °C afforded the target mono(benzimidazolin-2-iminato) actinide(IV) complexes $[(Bim^{R1/R2}N)AnN''_3]$ (An = U, Th; N″ = $N(SiMe_3)_2$) (**1**−**6**) in high yields (Scheme 2).[63] Detailed crystallographic data and selected bond lengths and angles are presented in Table S1−S2 (Supporting Information).

X-ray analysis revealed that all six complexes are isostructural (Figures 1−2), displaying distorted tetrahedral geometries around the metal atoms. From the crystallographic data, a clear trend can be found, i.e., the An−N(1) bond distances are shorter, with values of 2.133(3), 2.200(4), 2.131(3), 2.155(5), 2.139(7) and 2.184(3) Å for **1**, **2**, **3**, **4**, **5** and **6**, respectively, compared to the $An-N_{amino}$ bond distances. The differences in the U−N(1) bond distances for the uranium complexes, **1**, **3**, **5**, or among the thorium complexes **2**, **4**, **6** are neglectable. Moreover, the An−N(1)−C(1) angles, with values of 161.0(2), 159.6(3), 166.0(2), 164.6(4), 176.0(5) and 175.2(3)° for **1**, **2**, **3**, **4**, **5** and **6**, respectively, are more or less close to linearity. These data indicate a substantial π-character and thus a higher bond order of the An−N(1) bonds. Similar results were also observed in other imidazolin-2-iminato-supported transition metal, lanthanide and actinide complexes.[57,59,64−66] In order to make clear whether the presence of the benzene ring on the imidazolin-2-imine backbone will influence the electronic structure of the resulting complexes, a comparison between the present six complexes and previously reported imidazolin-2-

Scheme 2. Synthetic Procedures for Benzimidazolin-2-iminato Actinide Complexes $[(Bim^{R}{}_1{}^{/R}{}_2N)AnN''_3]$ (An = U, Th; N″ = $N(SiMe_3)_2$)



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

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

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

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

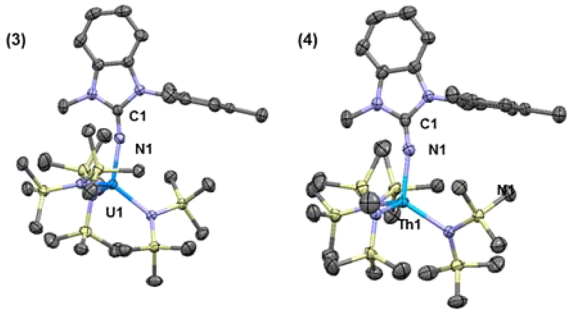


Figure 1. Solid state structures of complexes **3** and **4** (thermal ellipsoids are drawn at 50% probability). Hydrogen atoms are omitted for clarity. (C1−N1:1.283(4) Å (**3**), 1.248(7) Å (**4**); N1−An1:2.131(3) Å (**3**), 2.155(5) Å (**4**); C1−N1−An1:166.0(2)° (**3**), 164.6(4)° (**4**)).

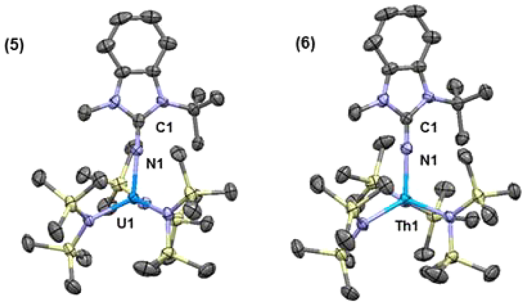


Figure 2. Solid state structures of complexes **5** and **6** (thermal ellipsoids are drawn at 50% probability). Hydrogen atoms are omitted for clarity. (C1−N1:1.302(10) Å (**5**), 1.280(5) Å (**6**); N1−An1:2.139(7) Å (**5**), 2.184(3) Å (**6**); C1−N1−An1:176.0(5)° (**5**), 175.2(3)° (**6**)).

iminato actinide $[(Im^{R}N)AnN''_3]$ counterparts was performed.[67] Unexpectedly, no obvious changes of the structural parameters were observed. For instance, for the $[Bim^{Me/Mes}N]$ ligated U (**3**) and Th (**4**) complexes, the An−N(1) bond distances are 2.131(3) Å (**3**) and 2.155(5) Å (**4**), which are quite similar to the reported $[Im^{Mes}N)AnN''_3]$ counterparts with values of 2.143(4) Å (U) and 2.189(7) Å (Th), respectively. Similar phenomena were also observed for the

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[Bim$^{Me/tBu}$N] ligated U and Th complexes, displaying values of 2.139(7) Å (**5**) and 2.184(3) Å (**6**), vs 2.118(8) Å (U) and 2.176(8) Å (Th) in [Im^{tBu}N)AnN″$_3$] analogues. From these results, it can be seen that the incorporation of the benzene ring in the ligand backbone shows little influence on the electronic properties of the corresponding complexes.

In contrast to the little changes in the electronic properties, the steric properties differ significantly as indicated by comparison of the cone angles, which are defined as the angle between the metal at the vertex of the cone, formed by the coordinating ligands and the metal center, and the hydrogen atoms at its perimeter. The present six complexes display cone angles of 138° (**1**), 140° (**2**), 114° (**3**), 111° (**4**), 99° (**5**), 98° (**6**) respectively, which are much smaller as compared to the corresponding values in all imidazolin-2-iminato actinide [(Im^{R}N)AnN″$_3$] systems (with cone angles of 204° (R = Dipp, An = Th), 205° (R = Dipp, An = U), 139° (R = Mes, An = Th), 138° (R = Mes, An = U), 117°(R = *t*Bu, An = Th), 118°(R = *t*Bu, An = U) respectively), implying that the new actinide complexes exhibit much more open space around the metal for the incoming substrates. Besides, for the present six complexes, changing the substituents from Dipp, Mes, ^{t}Bu affords a decrease of the cone angle, suggesting that catalytically active species generated from **1** and **2** can be expected to be the most sterically encumbered.

Catalytic Addition Reactions. The results of the catalytic addition reactions of a series of REH (E = N, P, C, O, S) moieties to *N*,*N*′-diisopropylcarbodiimide (DIC), *N*,*N*′-dicyclohexylcarbodiimide (DCC), 1,3-di-*p*-tolylcarbodiimide (DTC), phenylisocyanate (PhNCO), and phenylisothiocyanate (PhNSC) are presented below. The reaction of aniline PhNH$_2$ with DIC was first investigated by using the different precatalysts (**1**−**6**). As a control experiment, a blank reaction, i.e., only DIC and PhNH$_2$, was carried out at 75 °C for 24h, and no formation of product was observed. In contrast, with the aid of a catalytic amount (2 mol %) of the benzimidazolin-2-iminato actinide complexes **1**−**6**, fast guanylation reactions took place, affording **7af** in high yields, which then underwent a 1,3-hydride shift and gave the final product **8af** (Table 1, runs 1−6). A representative preparative scale-up reaction using complex **2** was performed, giving **8af** in high yield (97.8%). Additionally, no significant differences were observed when varying the steric structure of the ligand and the type of actinide center, indicating the high efficiency of all six complexes. Compared to previous guanylation processes promoted by [Im^{Dipp}N)ThN″$_3$],[45] higher conversions, even in a shorter amount of time, were observed herein, suggesting a higher reactivity of the [(Bim$^{R}{}_1{}^{/R}{}_2$N)AnN″$_3$] complexes. These superior results can be explained by the decreased cone angles around the catalytically active actinide species, which provides better accessibility of substrate to the metal center and thus results in higher catalytic activities.

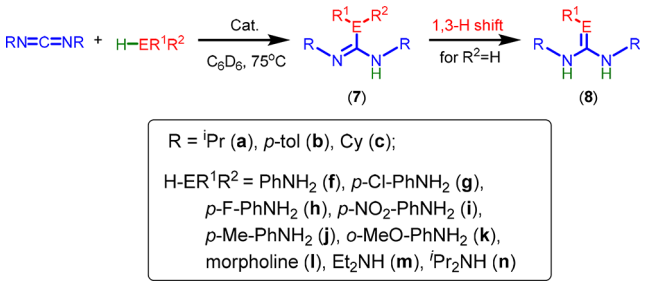
The uranium (**1**) and thorium (**2**) complexes were then chosen as precatalysts for the addition of various amines to carbodiimides (Scheme 3). Representative results are summarized in Table 1. It can be observed that a wide range of primary and secondary amines can be used for this reaction. C−X (X = Cl, F, O, NO$_2$) bonds survived during the reaction, indicating a good functional group tolerance of the active species. The presence of either electron-withdrawing or electron-donating substituents on the aniline showed big impact on the reactivity of the starting materials in the allotted time. For instance, reacting aniline with electron-donating groups (*o*-MeO-PhNH$_2$, runs 15−16, Table 1) allows the reaction to go to completion in 6 h. However, using *p*-nitroaniline (*p*-NO$_2$−PhNH$_2$, runs 11−12, Table 1), a much longer reaction time (24 h) was needed in order to achieve full consumption of the starting materials, indicating the decreased nucleophilicity due to the presence of the strong electron-withdrawing nitro group. Besides varying electronic effects, substituted anilines with bulkier groups in the *ortho*-position, e.g., 2,6-Me$_2$PhNH$_2$, 2,6-^{i}Pr$_2$PhNH$_2$, etc., were also tried for this reaction, unfortunately, no reactions were observed, suggesting the inaccessibility of the actinide center for sterically encumbered anilines.

Table 1. Catalytic Reaction of Carbodiimide with N−H Species Mediated by Complexes 1−6[a]

run	cat.	RNCNR[b]	HER^{1}R^2 /HER^3	time (h)	conv. (%)[c]	prod.
1	**1**	DIC	PhNH$_2$	6	96	**8af**
2	**2**			6	>99	
3	**3**			6	98	
4	**4**			6	>99	
5	**5**			6	95	
6	**6**			6	96	
7	**1**	DIC	*p*Cl-PhNH$_2$	6	97	**8ag**
8	**2**			6	97	
9	**1**	DIC	*p*F-PhNH$_2$	6	96	**8ah**
10	**2**			6	98	
11	**1**	DIC	*p*NO$_2$−PhNH$_2$	24	>99	**8ai**
12	**2**			24	95	
13	**1**	DIC	*p*Me-PhNH$_2$	6	>99	**8aj**
14	**2**			6	96	
15	**1**	DIC	*o*MeO-PhNH$_2$	6	96	**8ak**
16	**2**			6	>99	
17	**1**	DIC	Morpholine	12	36	**7al**
18	**2**			12	39	
19	**1**	DTC	PhNH$_2$	4	>99	**8bf**
20	**2**			3	>99	
21	**1**	DTC	Morpholine	12	>99	**7bl**
22	**2**			12	>99	
23	**1**	DTC	Et$_2$NH	12	>99	**7bm**
24	**2**			12	>99	
25	**1**	DTC	^{i}Pr$_2$NH	24	77	**7bn**
26	**2**			24	69	
27	**1**	DCC	PhNH$_2$	6	>99	**8cf**
28	**2**			6	>99	

[a]Reaction conditions: 2 mol % (7 μmol) precatalyst, 50 equiv of substrates, 600 μL C_6D_6, 75 °C. [b]DIC: *i*PrNCN*i*Pr; DTC: (*p*-tol)NCN(*p*-tol); DCC: *Cy*NCN*Cy*. [c]Determined by ^{1}H NMR of the crude reaction mixture.

Scheme 3. Catalytic Insertion of Amines N−H into Carbodiimide



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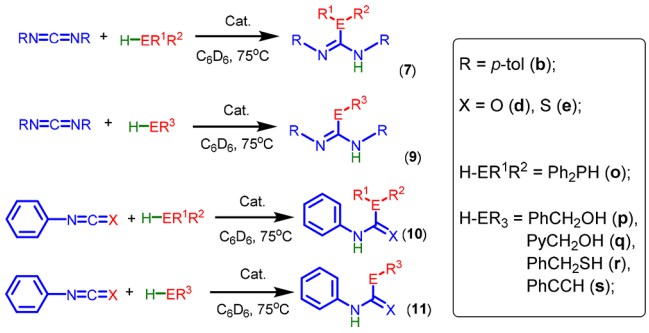
Similar reactions were performed using DTC and DCC as the heterocumulenes (runs 19−20, 27−28, Table 1), from which, in comparison with DIC, no different catalytic behavior was revealed for the substrate DCC; in contrast, it took only half of the reaction time for the full consumption of DTC, implying an accelerated reaction rate for this substrate. This superior reactivity is an expected corollary of the increased electrophilic property of the NCN moiety, due to the presence of the phenyl ring in DTC, which resulted in a rapid insertion reaction and more labile An−N bonds afterward. Moreover, it should be noted that DTC can react with the aliphatic secondary amines morpholine, Et_2NH, and $^iPr_2NH$, albeit in longer times, affording the target products **7bl**, **7bm**, **7bm**, in high yields, whereas similar reactions proved to be inaccessible for DIC (for Et_2NH, $^iPr_2NH$) or led to much lower yields of the corresponding products (for morpholine), which reflects once again the higher reactivity of DTC.

Encouraged by the extraordinarily high catalytic activities and the unusual functional group tolerance in the aforementioned guanylation reactions, our attention was turned to the possibility of addition of other E−H moieties (PH, CH, OH, SH) to carbodiimides (Scheme 4, Table 2). DTC was selected

Scheme 4. Catalytic Insertion of E−H into Different Heterocumulenes



here due to its higher reactivity as revealed above. Reactions between diphenylphosphine (Ph_2PH) and DTC were first carried out by using complexes **1**−**6** as catalyst precursors, and quantitative conversions to phosphaguanidine (**7bo**) were observed. Subsequent experiments using phenylacetylene (PhCCH) as the nucleophile for the addition to DTC, and the thorium precatalyst **2** was found to be more active than its uranium congener **1** in these reactions, in which product yields of 99% and 69% were furnished, respectively. The superior activity of complex **2** can probably be ascribed to different electronic properties of the actinide centers. In contrast to the catalytic addition of phosphine and terminal alkynes to carbodiimides, which have been studied using organolanthanide precursors, alcohol and thiol moieties containing substrates have long been neglected. This is due to the catalyst poisoning, emanating from the strong oxygen and sulfur bonds with the actinide metals (Th−S 145.2, and U−S 121.9 kcal mol^{-1}).[68]

Pioneering work was accomplished recently by our group when using sterically less congested actinide amido complexes. An unprecedented actinide-catalyzed addition of alcohols to carbodiimides was achieved,[51] implying an unusually high activity of An−O bonds toward carbodiimides. Therefore, the use of OH and SH containing nucleophiles was also attempted herein, and it was exciting to find that complexes **1** and **2** are also capable of serving as highly efficient catalysts for the

Table 2. Catalytic Reaction of Carbodiimide, Phenylisocyanate and Phenylisothiocyanate with E−H Species Mediated by Complexes 1−6[a]

run	cat.	RNCNR/ PhNCX[b]	HER^1R^2 /HER^3	time (h)	conv. (%)[c]	prod.
1	**1**	DTC	Ph_2PH	6	>99	**7bo**
2	**2**			9	>99	
3	**3**			9	>99	
4	**4**			9	>99	
5	**5**			9	>99	
6	**6**			9	>99	
7	**1**	DTC	PhCCH	6	69	**9bs**
8	**2**			6	>99	
9	**1**	DTC	$PhCH_2OH$	1	>99	**9bp**
10	**2**			1	>99	
11	**1**	DTC	$PyCH_2OH$	1	>99	**9bq**
12	**2**			1	>99	
13	**1**	DTC	$PhCH_2SH$	6	>99	**9br**
14	**2**			6	>99	
15	**1**	PhNCO	$PhCH_2SH$	12	69	**11dr**
16	**2**			12	91	
17	**1**		Ph_2PH	12	58	**10do**
18	**2**			12	32	
19	**1**	PhNCS	$PhCH_2SH$	12	73	**11er**
20	**2**			12	58	
21	**1**		Ph_2PH	12	70	**10eo**
22	**2**			12	63	

[a]Reaction conditions: 2 mol % (7 μmol) precatalyst, 50 equiv of substrates, 600 μL C_6D_6, 75 °C, runs 5−10 were studied at room temperature. [b]DTC: (*p*-tol)NCN(*p*-tol). [c]Determined by ^1H NMR of the crude reaction mixture.

insertion of DTC into the E−H bonds of $PhCH_2OH$, $PyCH_2OH$, $PhCH_2SH$, affording the corresponding isourea and isothiourea products quantitatively at room temperature. The presence of a coordinating pyridyl group showed negligible influence on the activity, pointing at a potentially good tolerance of heterocyclic functionalities. The substrate scope of the insertion reaction was further expanded to isocyanates and isothiocyanates. Using phenylisocyanate and phenylisothiocyanate, as the heterocumulene source, the addition of Ph_2PH and $PhCH_2SH$ was studied, affording products **10** and **11** in moderate to high yields. These results demonstrate the generation of a quite robust catalytically active species from complexes **1** and **2**, which paves the way for further transformation of oxygen- and sulfur-containing substrates by employing organoactinide precursors.

To further increase the scope of the precatalysts and to achieve the synthesis of bis(guanidine) compounds, that potentially serve as templates for the constructing of larger molecules, bifunctional substrates were also applied in this catalytic addition reaction (Scheme 5, Table 3). With 2 mol % loadings of the precatalysts **1** and **2**, the reaction between homobifunctional compounds, the diamines (*m*-NH_2PhNH_2, *p*-NH_2PhNH_2) and the diol (*p*-$HOCH_2$−$PhCH_2OH$), with DTC in a 1:2 molar ratio produced the bis(guanidine) **13at**, **13au** and the bis(isourea) **12bv** in almost quantitative yields. Reacting the heterobifunctional substrate 2-propyn-1-ol, which contains hydroxyl (OH) and terminal alkyne (C≡CH) as different nucleophiles, with an equimolar amount of DTC afforded compound **14bw** with an isourea structure in high yields, indicating the superior reactivity of the hydroxyl group as compared to the terminal alkyne toward the metal

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Scheme 5. Catalytic Insertion of Bifunctional Substrates into Carbodiimide

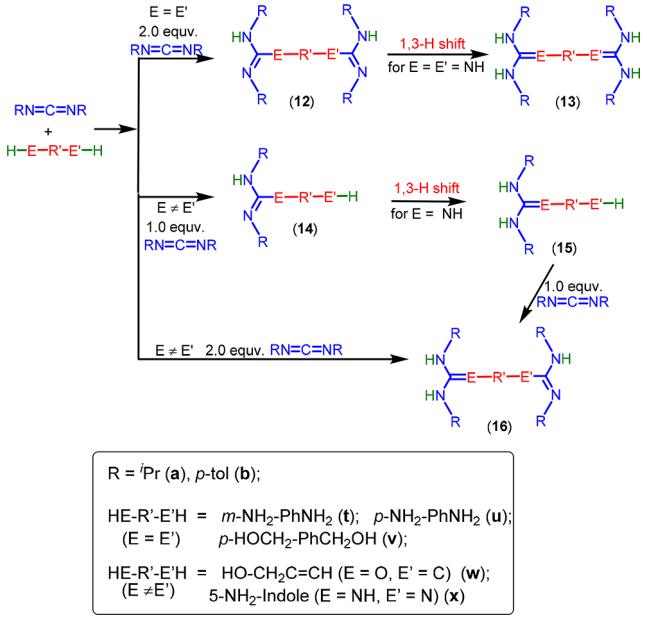


Table 3. Catalytic Reaction of Carbodiimide and Bifunctional Substrates HE−R′−E′H by Complexes 1−2[a]

run	cat.		HE−R′−E′H	time (h)	conv. (%)[b]	prod.
1	**1**	E = E′	*m*-NH_2−$PhNH_2$	6	>99	**13at**
2	**2**			6	>99	
3	**1**		*p*-NH_2−$PhNH_2$	6	>99	**13au**
4	**2**			6	>99	
5	**1**		*p*-$HOCH_2$−$PhCH_2OH$	12	>99	**12bv**
6	**2**			12	>99	
7	**1**	E ≠ E′	HO−$CH_2C{\equiv}CH$ (E = O, E′ = C)	3	>99	**14bw**
8	**2**			3	>99	
9[d]	**1**		5-NH_2−Indole (E = NH, E′ = N)	24	>99	**15ax**
10[c,d]	**1**			24	>99	**16ax**

[a]Reaction conditions: 2 mol % (7 μmol) precatalyst, 50 equiv of substrates, 600 μL C_6D_6, 75 °C. [b]Determined by ^{1}H NMR of the crude reaction mixture. [c]Another 1.0 equiv of DTC was added. [d]110 °C in toluene-*d* was applied; molar ratio of [DIC]/[5-NH_2−Indole] = 1/1 and 2/1 was used for runs 9 and 10, respectively.

atom. Further addition of 1 equiv of DTC to this reaction mixture led to unidentifiable polymeric products, which could not be isolated. The reaction of 5-aminoindole with 1.0 equiv of DIC proceeded selectively at the primary amino group to afford the monoguanidine compound **15ax**, demonstrating that primary amino groups can be distinguished from secondary amino groups under the present reaction conditions. Heating this reaction mixture with one more equivalent of DIC gave rise to the bis(guanidine) **16ax** in an almost quantitative yield. Compound **16ax** can be also obtained by reaction of 5-amidoindole with 2.0 equiv of DIC in a one-pot reaction.

To shed light on the active catalyst species, stoichiometric experiments using the system composed of DIC, $PhNH_2$ and catalyst **2** were performed. The initial reaction between catalyst **2** and 3 equiv of DIC was studied by in situ NMR spectroscopy in C_6D_6; unfortunately, no reaction was observed even after heating at 50 °C for 24 h (specific NMR spectra are presented in the Supporting Information), indicating that the sterically encumbered bis(trimethylsilyl)amido moieties, $N(SiMe_3)_2$, cannot add to the carbodiimide. In contrast, reactions between catalyst **2** and 3 equiv of $PhNH_2$ gave instantly the corresponding thorium anilide compounds, and the concomitant appearance of the peak of free amine $HN(SiMe_3)_2$. After heating at 50 °C for 24 h, all Th−$N(SiMe_3)_2$ moieties were replaced by Th-NHPh, with simultaneous release of 3 equiv of $HN(SiMe_3)_2$. To this reaction mixture another 3 equiv of DIC were added and immediate NMR spectroscopic changes were observed for the *i*Pr group (from DIC), indicating an effective insertion of the carbodiimide into the thorium-anilide bonds. On the basis of these results, it can be concluded that the Th-NHPh moiety, originating from reaction between catalyst **2** and aniline, is the operative active species during this catalytic cycle.

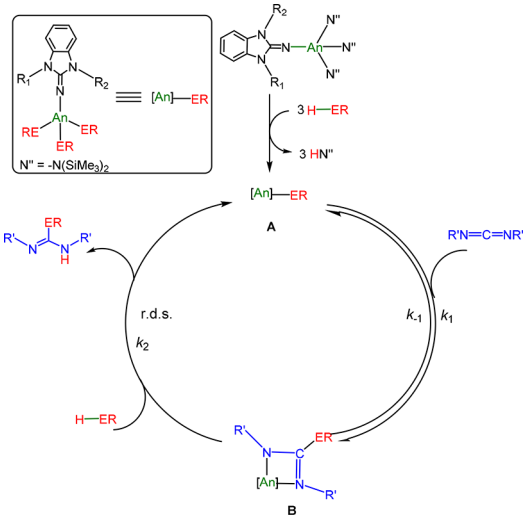
Kinetic studies of catalytic addition of $PhNH_2$ to DIC by using precatalyst **2** revealed a first-order dependence on DIC, $PhNH_2$ and **2**, giving rise to the rate eq 1:[69]

$$\frac{\partial p}{\partial t} = k_{obs}\cdot[\mathbf{2}][\mathrm{DIC}][\mathrm{PhNH_2}] \quad (1)$$

Deuterium labeling studies with aniline-*N*,*N*-d_2 afforded a kinetic isotopic effect (KIE) of K_H/K_D = 1.37, corroborating that the rate-determining step (r.d.s.) of the catalytic cycle is the protonolysis of the guanidinate. The thermodynamic activation parameters were experimentally calculated from the Erying and Arrhenius plots (Supporting Information), affording a rather low activation barrier (E_a) of 11.3(6) kcal mol^{-1}, and the enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation of 10.7(3) kcal mol^{-1} and −45.0(6) e.u. respectively. The latter value indicates as expected for actinides, a four-centered ordered transition state.

On the basis of the above analysis, a plausible catalytic mechanism for the addition of RE−H moieties into carbodiimides could be proposed as shown in Scheme 6. In the initial step, the actinide amido compound An−$N(SiMe_3)_2$ undergoes protonolysis with protonated RE−H, affording the active species **A**, which then undergoes a rapid equilibrium for the nucleophilic addition reaction to carbodiimide, giving rise to the actinide guanidinate species **B**. A subsequent slow

Scheme 6. Plausible Mechanism for Catalytic Insertion of REH into Carbodiimide



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protonolytic cleavage by an additional molecule of RE−H completes the catalytic cycle with the concomitant releasing of the target product and the regeneration of the active species **A**.

CONCLUSION

The synthesis of mono(benzimidazolin-2-iminato) actinide(IV) complexes $[(Bim^{R}{}_{1}{}^{/R}{}_{2}N)An(N\{SiMe_3\}_2)_3]$ was performed by treating actinide metallacycles with benzimidazolin-2-imine ligands to afford **1**−**6** in high yields. These catalysts were found to be highly active in catalyzing the addition of E−H (E = N, P, C, O, S) moieties to different heterocumulenes, including carbodiimides, isocyanates and thioisocyanates, affording the corresponding products in high yields under mild reaction conditions. Bifunctional substrates were found to be suitable substrates, and a series of bis(guanidine) and bis(isourea) compounds were obtained. For the present system, diversified substrates bearing various functionalities can be employed, indicating a high tolerance of the catalytically active species toward heteroatoms. It can be deduced from the kinetic studies that the insertion reactions follow first order dependence on both of the two substrates and the precatalyst, and deuterium-labeling studies showed that the protonolytic cleavage of the product is the rate-determining step of the catalytic cycle.

EXPERIMENTAL SECTION

General Considerations. All manipulations of air sensitive materials were performed with rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a high vacuum line (10^{-5} Torr), or in nitrogen filled MBraun and Vacuum Atmospheres gloveboxes with a medium capacity recirculator (1−2 ppm oxygen). Argon and nitrogen were purified by passage through an MnO oxygen removal column and a Davison 4 Å molecular sieve column. Analytically pure solvents were dried and stored with Na/K alloy and degassed by three freeze−pump−thaw cycles prior to use (hexane, toluene, benzene-d_6). Aniline was refluxed over stannous chloride and distilled under vacuum, followed by refluxing in calcium hydride under nitrogenous atmosphere and distilling under vacuum. 1,3-diisopropylcarbodiimide (DIC), phenylisocyanate, phenylisothiocyanate, *ortho*-anisidine, 4-fluoroaniline, diethylamine, benzyl alcohol, 2-pyridinemethanol and benzylmercaptan were distilled from sodium bicarbonate or CaH_2 under nitrogen atmosphere. 1,3-Di-*p*-tolylcarbodiimide (DTC), 4-chloroaniline, 4-nitroanline, 4-methylaniline were dried under vacuum (10^{-6} atm) for 12 h on a high vacuum line. Phenylacetylene (ABCR) was distilled under vacuum and degassed by three freeze−pump−thaw cycles. Diphenylphosphine (Sigma-Aldrich) was used as received and stored in the glovebox. All the aforementioned reagents were stored in an inert atmosphere glovebox prior to use. The benzimidazolin-2-imine ligand $Bim^{Dipp/Me}NH$ was prepared according to previous reports,[62] and the other two ligands $Bim^{Mes/Me}NH$ and $Bim^{tBu/Me}NH$ were prepared using similar methods, which can be found in the Supporting Information. The actinide metallacycles were prepared according to previous reports.[70] Benzimidazolin-2-iminato actinide complexes **1** and **2** were prepared according to our previous work.[62] $PhND_2$ was synthesized according to previous reports.[46] NMR spectra were recorded on Bruker Avance 300 and Avance 400 Bruker spectrometers. Chemical shifts for ^1H NMR and ^{13}C NMR measurements are reported in ppm and referenced using residual proton or carbon signals of the deuterated solvent relative to tetramethylsilane. (Warning: uranium (primarily isotope ^{238}U) and natural thorium (^{232}Th) are weakly radioactive with a half-life of 4.47×10^9 years and 1.41×10^{10} years, respectively).

Synthesis of Complex ***3***. Complex **3** was prepared using a similar method as our previous work.[62] A solution of uranium metallacycle (0.11g, 0.15 mmol) in 2 mL toluene was treated with 1.0 equiv of benzimdiazol-2-imine ligand (0.040 g, 0.15 mmol) in 3 mL toluene. The reaction mixture was stirred at room temperature for 12 h, and the solvent was removed partially, recrystallization from concentrated toluene solution afforded the target complex in high yield. Yield: 0.13 g, (0.14 mmol, 93%). ^1H NMR (300 MHz, C_6D_6) δ 96.84 (s, 3H, CH_3), 26.33 (d, J = 7.8 Hz, 1H, H_{Ar}), 14.88 (d, J = 7.8 Hz, 1H, H_{Ar}), 11.80 (d, J = 7.1 Hz, 1H, H_{Ar}), 8.12 (d, J = 7.1 Hz, 1H, H_{Ar}), 0.24 (s, 1H, H_{Ar}), 0.06 (br, 3H, CH_3), −4.33 (s, 1H, H_{Ar}), −5.07 (s, 3H, CH_3), −5.61 (s, 3H, CH_3), −8.26 (s, 9H, $Si(CH_3)_3$), −11.47 to −12.19 (br, 45H, $Si(CH_3)_3$). ^{13}C NMR (75 MHz, C_6D_6) δ 173.29 (C═N), 170.16 (C_{Ar}), 157.21(C_{Ar}), 132.37(C_{Ar}), 129.24(C_{Ar}), 128.44(C_{Ar}), 125.56-(C_{Ar}), 124.67(C_{Ar}), 124.17(C_{Ar}), 115.93(C_{Ar}), 113.52(C_{Ar}), 112.78-(C_{Ar}), 31.64(CH_3), 22.49(CH_3), 19.99(CH_3), 5.88($Si(CH_3)_3$). Anal. Calcd For $C_{35}H_{72}N_6Si_6U$: C, 42.74; H, 7.38; N, 8.54. Found: C, 42.89; H, 7.30; N, 8.67.

Synthesis of Complex ***4***. Preparation of complex **4** was carried out using similar method as (**3**) using thorium metallacycle (0.11 g, 0.15 mmol) and benzimidazolin-2-imine ligand $Bim^{Mes/Me}NH$ (0.04 g, 0.15 mmol). Yield: 0.14 g, (0.14 mmol, 97%). ^1H NMR (300 MHz, C_6D_6) δ 6.93−6.84 (m, 1H, H_{Ar}), 6.82−6.73 (m, 1H, H_{Ar}), 6.72 (s, 2H, H_{Ar}), 6.63−6.53 (m, 1H, H_{Ar}), 6.19 (d, J = 7.7 Hz, 1H, H_{Ar}), 3.34 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 1.98 (s, 6H, CH_3), 0.36 (s, 54H, $Si(CH_3)_3$). ^{13}C NMR (75 MHz, C_6D_6) δ 143.73(C═N), 138.38(C_{Ar}), 137.10-(C_{Ar}), 131.24(C_{Ar}), 130.73(C_{Ar}), 130.32(C_{Ar}), 129.33(C_{Ar}), 128.85-(C_{Ar}), 121.20(C_{Ar}), 121.09(C_{Ar}), 107.40(C_{Ar}), 106.49(C_{Ar}), 28.54-(CH_3), 20.64(CH_3), 17.90(CH_3), 4.37($Si(CH_3)_3$). Anal. Calcd For $C_{35}H_{72}N_6Si_6Th$: C, 43.00; H, 7.42; N, 8.60. Found: C, 43.12; H, 7.48; N, 8.69.

Synthesis of Complex ***5***. Preparation of complex **5** was carried out using similar method as (**3**) using uranium metallacycle (0.11 g, 0.15 mmol) and benzimidazolin-2-imine ligand $Bim^{tBu/Me}NH$ (0.03 g, 0.15 mmol). Yield: 0.12g, (0.13 mmol, 89%). ^1H NMR (300 MHz, C_6D_6) δ 44.50−40.37 (b, 3H, CH_3), 18.16 (b, 9H, $C(CH_3)_3$), 17.12 (m, 1H, H_{Ar}), 13.49 (m, 1H, H_{Ar}), 13.30 (m, 1H, H_{Ar}), 0.27 to −0.22 (m, 1H, H_{Ar}), −11.10 (b, 54H, $Si(CH_3)_3$). ^{13}C NMR (75 MHz, C_6D_6) δ 166.75(C═N), 161.14(C_{Ar}), 130.94(C_{Ar}), 129.28(C_{Ar}), 128.84(C_{Ar}), 125.26(C_{Ar}), 120.98(C_{Ar}), 81.82($C(CH_3)_3$), 39.23(CH_3), 2.14(Si-(CH_3)$_3$). Anal. Calcd For $C_{30}H_{70}N_6Si_6U$: C, 39.10; H, 7.66; N, 9.12. Found: C, 39.00; H, 7.57; N, 9.03.

Synthesis of Complex ***6***. Preparation of complex **6** was carried out using similar method as (**3**) using thorium metallacycle (0.11 g, 0.15 mmol) and benzimidazolin-2-imine ligand $Bim^{tBu/Me}NH$ (0.03 g, 0.15 mmol). Yield: 0.11 g, (0.12 mmol, 82%). ^1H NMR (300 MHz, C_6D_6) δ 7.31−6.76 (m, 3H, H_{Ar}), 6.67−6.37 (m, 1H, H_{Ar}), 3.30 (s, 3H, CH_3), 1.87 (s, 9H, $C(CH_3)_3$), 0.68−0.48 (br, 54H, $Si(CH_3)_3$). ^{13}C NMR (75 MHz, C_6D_6) δ 144.48(C═N), 131.68(C_{Ar}), 129.80(C_{Ar}), 125.43(C_{Ar}), 120.60(C_{Ar}), 112.45(C_{Ar}), 106.87(C_{Ar}), 57.54($C(CH_3)_3$), 30.39(CH_3), 28.20(CH_3), 4.92($Si(CH_3)_3$), 3.77($Si(CH_3)_3$). Anal. Calcd For $C_{30}H_{70}N_6Si_6Th$: C, 39.36; H, 7.71; N, 9.18. Found: C, 39.45; H, 7.88; N, 9.25.

General Procedure for the Catalytic Addition of Nucleophiles into Heterocumulenes. A sealable J. Young NMR tube was loaded with approximate 5 mg of the desired catalyst from a stock solution in C_6D_6 inside the glovebox, followed by the addition of heterocumulenes (50 equiv) and nucleophiles (50 equiv), and the reaction was immediately diluted to 600 μL with C_6D_6. Samples were taken out of the glovebox and the reaction progress was monitored by ^1H NMR spectroscopy. The crude mixtures were analyzed using ^1H NMR, ^{13}C NMR and mass spectrometry, the values were compared to previous literature.

Kinetic Studies of $PhNH_2$ *into DIC Using Complex* ***2***. All the kinetic experiments were done in a similar method. In a J. Young NMR tube, typical amount of precatalyst **2**, DIC, aniline and C_6D_6 was added in the glovebox and then the tube was sealed. Take the tube out of the glovebox and freeze it in ice bath until the ^1H NMR experiment began. All the experiments were done by changing one substrate or catalyst while keeping the other reagents constant and the data was collected every 2 min up to one and a half hours. The product concentrations were measured by the area ratio of methyl group at 0.99 and 0.84 ppm, which were assigned to the starting material and product respectively normalized with an internal standard. Initial reaction rates were determined by least-squares fit of product

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concentration versus time, and the plots were shown in Figures S1–S6.

Activation parameters including enthalpy ($\Delta H^{\ddagger}$), entropy ($\Delta S^{\ddagger}$) and activation energy (E_a) were calculated from kinetic data using Eyring and Arrhenius plots. In a typical sample, the J. Young tube was loaded with desired amount of catalyst **2**, DIC, aniline and sealed. Then the sample was inserted into Bruker Avance 300 spectrometer, which had been previously set to the desired temperature. The data was collected every 1 min up to one and a half hours. Initial reaction rates were determined by the least-square fit of product concentration versus time, and Eyring and Arrhenius plots were shown in Figures S7–S9. Enthalpy ($\Delta H^{\ddagger}$), entropy ($\Delta S^{\ddagger}$) and activation energy (E_a) were calculated from the slope and intercept of the least-squares fit.

The Rate Kinetic Law. According to the proposed mechanism (Scheme 6), the protonation step is the rate-determining step (k_2), based on the kinetic isotope effect, which is well-known to be in this order of magnitude for RDS in four centered transition states with actinides and lanthanides complexes.[71] Therefore, we can assume a steady-state approximation giving the following rate equations:

$$\frac{\partial p}{\partial t} = k_2 \cdot [\mathrm{HER}] \cdot [\mathbf{B}] \tag{2}$$

$$k_1 \cdot [\mathbf{A}][\mathrm{NCN}] - k_{-1}[\mathbf{B}] = 0 \tag{3}$$

where p is the concentration of final insertion product, and t is reaction time.

By substitution of eq 3 into eq 2, we can see the kinetic rate law for this reaction:

$$\frac{\partial p}{\partial t} = \frac{k_2 k_1}{k_{-1}} \cdot [\mathrm{HER}] \cdot [\mathbf{A}] \cdot [\mathrm{NCN}]$$

The concentration of **A** equals the concentration of the precatalysts as the protonolysis step is a rapid reaction. Therefore, when we used the thorium complex **2**, aniline, and DIC to study the reaction rate laws, the following equation can be obtained.

$$\frac{\partial p}{\partial t} = k_{\mathrm{obs}} \cdot [\mathbf{2}][\mathrm{DIC}][\mathrm{PhNH_2}]$$

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00502.

NMR spectra, kinetic and stoichiometric experiments, deuterium-labeling studies; Crystallographic data for complexes **3**–**6** (PDF)

Accession Codes

CCDC 1559912–1559915 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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