Actinide Catalysis

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Actinide-Mediated Catalytic Addition of E–H Bonds (E = N, P, S) to Carbodiimides, Isocyanates, and Isothiocyanates**

Isabell S. R. Karmel, Matthias Tamm, and Moris S. Eisen**

Abstract: *Unprecedented catalytic reactivity of actinide coordination complexes toward heterocumulenes, such as carbodiimides, isocyanates, and isothiocyanates is reported. The mono(imidazolin-2-iminato) thorium(IV) complex [Th(Im^{Dipp}N){N(SiMe$_3$)$_2$}$_3$] (**1**) was applied as a precatalyst for the addition of E–H (E = N, P, S) bonds to the Y=C=X core (Y = R$_2$N; X = NR$_2$, O, S) of carbodiimides, isocyanates, and isothiocyanates. The respective insertion products were obtained in high yields under mild reaction conditions, with complex **1** displaying high tolerance toward functional groups and heteroatoms.*

Metal-mediated catalytic hydroelementation reactions of C–C multiple bonds, which are known as the addition of an E–H (E = N, S, P, Si, O) bond across an unsaturated C–C bond, have gained popularity in the scientific community over the past decade, because they represent an atom-economical route for the synthesis of various families of organic molecules.[1] Hydroelementation reactions comprising the hydroamination,[2,3] hydrosilylation,[4,5,2f] hydrophosphination,[6,7] hydroalkoxylation,[8] and hydrothiolation[9,2f,8b] of alkenes and alkynes have been studied with a wide range of transition metal, lanthanide, and actinide catalysts, in which actinide coordination complexes often displayed a complementary reactivity to their transition-metal and lanthanide congeners.[10] In addition to hydroelementation reactions, lanthanide complexes have been applied as catalysts for the addition of E–H bonds (E = N, P) to carbodiimides, isocyanates, and isothiocyanates, yielding the respective guanidine, phosphaguanidine, and thiourea derivatives, respectively,[11] which have found wide application as ligands for coordination compounds,[12] in the field of medicinal[13] and materials chemistry,[14] as well as synthons in organic chemistry.[15] Hence, developing atom-efficient, versatile catalytic systems for their preparation represents a major challenge in the field of homogeneous catalysis, especially because the respective metal catalyst is required to display a tolerance toward functional groups and heteroatoms. Previous studies by Evans et al. have shown that carbodiimides can effectively insert into the An–C (An = Th, U) bond of Cp*$_2$An(CH$_3$)$_2$, yielding mixed cyclopentadienyl actinide amidinate complexes in high yield.[16] Similarly, the synthesis of actinide complexes with various phosphido,[17] sulfido[18] and dithiolene[19] ligands was reported, and the reactivity of selected examples toward stoichiometric amounts of carbon dioxide and carbon disulfide was studied.[20] It should be noted, however, that these actinide species have not been investigated as part of a catalytic process.

We have recently shown that the mono(imidazolin-2-iminato) thorium(IV) complex [Th(Im^{Dipp}N){N(SiMe$_3$)$_2$}$_3$] (**1**), which can be obtained selectively in high yield by a protonolysis reaction of the thorium metallacycle [{(Me$_3$Si)N}$_2$Th{κ^2-*C*,*N*-CH$_2$SiMe$_2$N(SiMe$_3$)}] with the neutral imidazolin-2-imine ligand Im^{Dipp}NH [Eq. (1)], can be used as an active catalyst for the dimerization of aldehydes, displaying high catalytic activity and selectivity toward the formation of asymmetrically substituted esters.[21] Thus, we decided to investigate the substantial question whether the stoichiometric reactivity toward carbodiimides displayed by organometallic actinide complexes[16,20] can be incorporated into a catalytic cycle by the protonolytic cleavage of the An–N bond, formed by the insertion of the carbodiimide, with different families of R–E–H (E = N, P, S; R = alkyl, aryl, H) moieties, yielding actinide amido, phosphido, and sulfide intermediates. Therefore, we set out to study the catalytic activity of actinide coordination complexes toward different families of heterocumulene systems and REH moieties, in which E is a nucleophilic element, expanding the scope of accessible products. Owing to the high activity, selectivity, and tolerance toward functional groups displayed by **1** in the Tishchenko reaction,[21] the thorium compound **1** was applied for all further catalytic studies with heterocumulenes presented herein. In general, imidazolin-2-iminato ligands are considered as monodentate N-donor ligands, which can act as 2σ,4π-electron donors to a metal atom,[22] especially when coordinated to early transition metals in high oxidation states[23] and lanthanides,[24] thus forming strong M–N bonds with a potentially higher bond order. Due to the high nucleophilicity and strong basicity of imidazolin-2-iminato ligands, the electron density of highly electrophilic metal centers, such as actinides and lanthanides, is slightly increased, which in turn reduces their electrophilicity and often enhances their catalytic activity toward highly nucleophilic substrates.[25] Thus, on the one hand, the open coordination sphere of the mono(imidazolin-2-iminato) thorium(IV) complex **1** should allow for a rapid insertion of the heterocumulenes into the Th–N$_{amido}$ bond. On the other hand,

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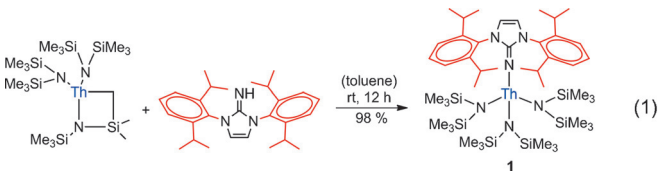
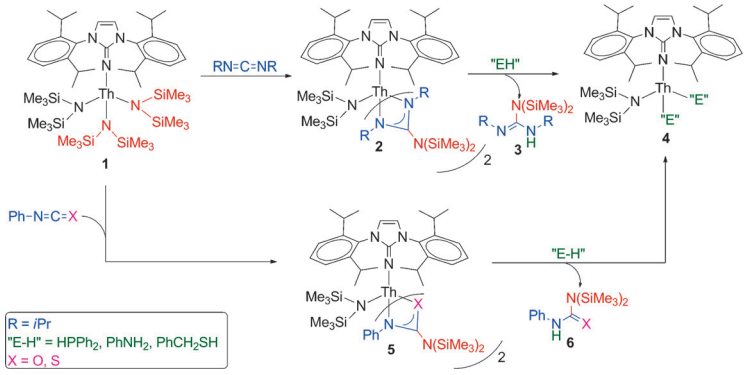
the increased electron density of **1** should lead to an increased catalytic activity in the presence of amines, phosphines, and thiols, as the formation of thermodynamically stable, catalytically inactive An–E species is avoided.

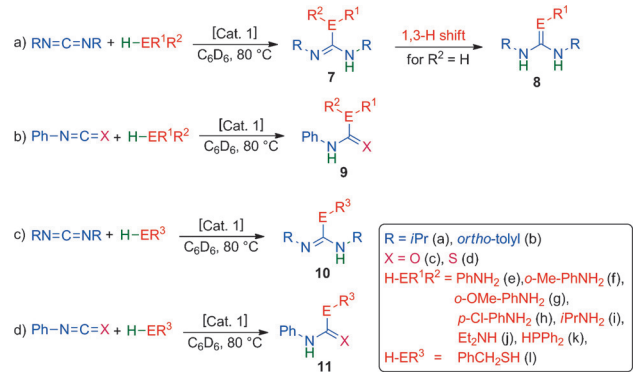


(1)

To study the reactivity of $[Th(Im^{Dipp}N)\{N(SiMe_3)_2\}_3]$ (**1**) toward heterocumulenes, experiments with stoichiometric amounts of carbodiimide, phenyl isocyanate, and phenyl isothiocyanate were carried out, and the reactions were monitored by ^1H NMR spectroscopy, showing for all cases an insertion of two equivalents of the heterocumulene into two $Th–N_{amido}$ bonds of complex **1**. After the addition of two equivalents of the REH moieties, the respective insertion products **2** and **5** were obtained (Scheme 1), as well as the thorium amide, phosphide, and sulfide species **4**. Catalytic experiments were performed using 1 mol% of $[Th(Im^{Dipp}N)\{N(SiMe_3)_2\}_3]$ (**1**) and equimolar amounts of the heterocumulenes and inserting-moieties REH, which were added to a stock solution of the catalyst inside a glove box



Scheme 1. Reactions of $[Th(Im^{Dipp}N)\{N(SiMe_3)_2\}_3]$ (**1**) with stoichiometric amounts of heterocumulenes.



Scheme 2. Catalytic additions of E–H moieties to carbodiimides, isocyanates, and isothiocyanates mediated by complex **1**.

Table 1: Catalytic reactions of carbodiimides with E–H moieties mediated by complex **1**.[a]

Entry	RNCNR	HER^1R^2/HER^3	Yield [%] (**7**, **8**, and **10**)
1	*i*PrNCN*i*Pr	$PhNH_2$	92
2	*i*PrNCN*i*Pr	*o*-OMe-$C_6H_4NH_2$	90
3	*i*PrNCN*i*Pr	*o*-Me-$C_6H_4NH_2$	54
4	*i*PrNCN*i*Pr	*p*-Cl-$C_6H_4NH_2$	90
5	*i*PrNCN*i*Pr	$HN(C_2H_5)_2$	79
6	*i*PrNCN*i*Pr	*i*PrNH$_2$	97
7	*i*PrNCN*i*Pr	$HPPh_2$	99
8	*i*PrNCN*i*Pr	$HSCH_2Ph$	88
9	(*o*-tol)NCN(*o*-tol)	$PhNH_2$	96
10	(*o*-tol)NCN(*o*-tol)	$HN(C_2H_5)_2$	95
11	(*o*-tol)NCN(*o*-tol)	$HPPh_2$	97
12	(*o*-tol)NCN(*o*-tol)	$HSCH_2Ph$	95

[a] Reaction conditions: 4.48 μmol of catalyst **1**; cat./RNCNR: 1/50; cat./HER^1R^2: 1/50; 750 μL C_6D_6; 80 °C; yield was determined by ^1H NMR spectroscopy of the crude reaction mixture after 12 h.

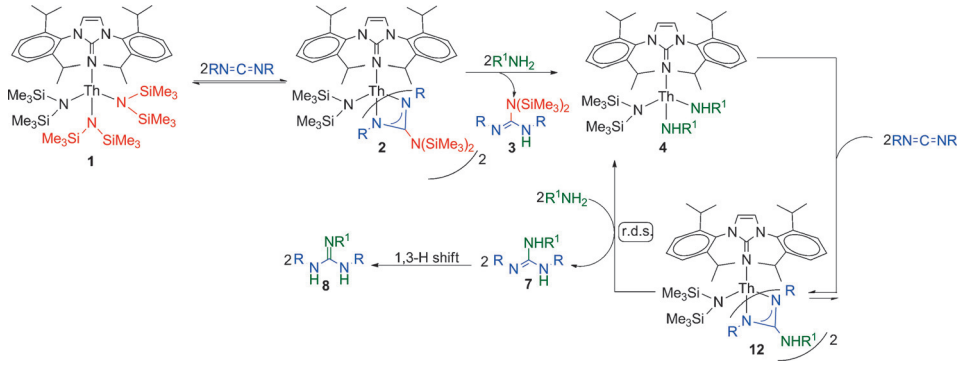
(Scheme 2). The reaction mixture was then heated to 80 °C and monitored by ^1H NMR spectroscopy until full conversion of the starting materials was observed (Tables 1 and 2). The reaction of primary and secondary amines with carbodiimides selectively afforded the guanidines **7** in moderate to high yields, which underwent a 1,3-hydride shift when using primary amines to yield the symmetric guanidines **8** (Table 1). Similarly, the addition of phosphines and thiols to the NCN moiety of carbodiimides was catalyzed by thorium complex **1**, yielding phosphaguanidines and thioureas **7** and **10**, respectively (Table 1). Furthermore, the addition of amines, phosphines, and thiols to isocyanates and isothiocyanates was studied, affording the insertion products **9** and **11** in high yields (Table 2). Hence, the mono(imidazolin-2-iminato) thorium(IV) complex **1** displays an unusual tolerance toward several heteroatoms, such as oxygen, phosphorus, sulfur, and nitrogen, as well as toward several functional groups, for example, OMe and Cl, allowing for a large scope of products to be accessed.

To determine the percentage of active precatalyst in the catalytic transformations, poisoning experiments were per-

Table 2: Catalytic reactions of isocyanates and thioisocyanates with E–H moieties mediated by complex **1**.[a]

Entry	PhNCX	HER^1R^2/HER^3	Yield [%] (**9** and **11**)
1	PhNCO	$PhNH_2$	76
2	PhNCO	$HPPh_2$	78
3	PhNCO	$HSCH_2Ph$	89
4	PhNCO	$HN(C_2H_5)_2$	83
5	PhNCS	$PhNH_2$	82
6	PhNCS	$HPPh_2$	78
7	PhNCS	$HSCH_2Ph$	88
8	PhNCS	$HN(C_2H_5)_2$	87

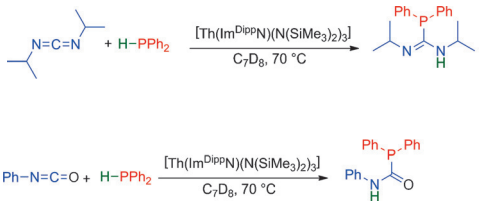
[a] Reaction conditions: 4.48 μmol of catalyst **1**; cat./PhNCX: 1/50; cat./HER^1R^2: 1/50; 750 μL C_6D_6; 80 °C; yield was determined by ^1H NMR spectroscopy of the crude reaction mixture after 12 h.



Scheme 3. Proposed mechanism for the thorium-mediated addition of E–H moieties to carbodiimides.

formed with isopropanol. When the reactions were carried out with a catalyst/isopropanol ratio of 1:0.25, a decrease in the catalytic activity of 12.5% was observed. When a catalyst/isopropanol ratio of 1:2 was used, no catalytic activity was found, indicating that all catalyst **1** is active. Moreover, experiments with stoichiometric amounts of carbodiimides (Scheme 3) showed that two of the three amido groups in complex **1** are activated, leading to the formation of a bis(guanidinate) intermediate (**2**), which after the addition of two further equivalents of the nucleophilic moiety, for example, aniline, gave the thorium amido species **4**. However, when complex **1** was reacted with a stoichiometric amount of aniline, intermediate **4** was not obtained, even upon heating to 80 °C for prolonged periods of time. Therefore, the first step in the catalytic cycle is the insertion of two equivalents of carbodiimide into the Th–N_{amido} bonds of complex **1**, forming the bis(guanidinate) thorium species **2**. Subsequent insertion of two equivalents amine affords the active catalyst **4** under elimination of two equivalents of $N(SiMe_3)_2$-substituted guanidine **3**. An additional insertion of two equivalents of carbodiimide into the Th–N bonds of compound **4** yields the bis(guanidinate) thorium complex **12**, which upon protonolysis with two equivalents of amine gives two equivalents of guanidine **7** and regenerates the active catalyst **4**. Guanidine **7** undergoes a subsequent 1,3-hydride shift forming the symmetric guanidine **8**.

To shed light on the mechanism, kinetic experiments were performed. Hence, in situ NMR experiments were carried out for the addition of diphenyl phosphine to 1,3-diisopropylcarbodiimide (DIC) [Eq. (2)] or phenyl isocyanate [Eq. (3)], revealing that the reactions display a first-order dependence on 1,3-diisopropylcarbodiimide or phenyl isocyanate as well as on diphenylphosphine and complex **1**, giving rise to the kinetic rate Equations (4) or (5). In addition, performing the kinetic experiments with the deuterated phosphine $DPPh_2$ afforded a kinetic isotopic effect of $K_H/K_D = 1.98$, corroborating that the rate determining step (r.d.s.) of the mechanism (Scheme 3) is the protonolysis of the phosphaguanidine.



(2)

(3)

$$\frac{\partial p}{\partial t} = k_{obs} \cdot [i\text{PrNCN}i\text{Pr}]^1 \cdot [HPPh_2]^1 \cdot [Th(Im^{Dipp}N)(N(Si(CH_3)_3)_2)_3]^1 \quad (4)$$

$$\frac{\partial p}{\partial t} = k_{obs} \cdot [PhNCO]^1 \cdot [HPPh_2]^1 \cdot [Th(Im^{Dipp}N)(N(Si(CH_3)_3)_2)_3]^1 \quad (5)$$

The thermodynamic activation parameters (Figure 1) were determined from the Eyring and Arrhenius plots

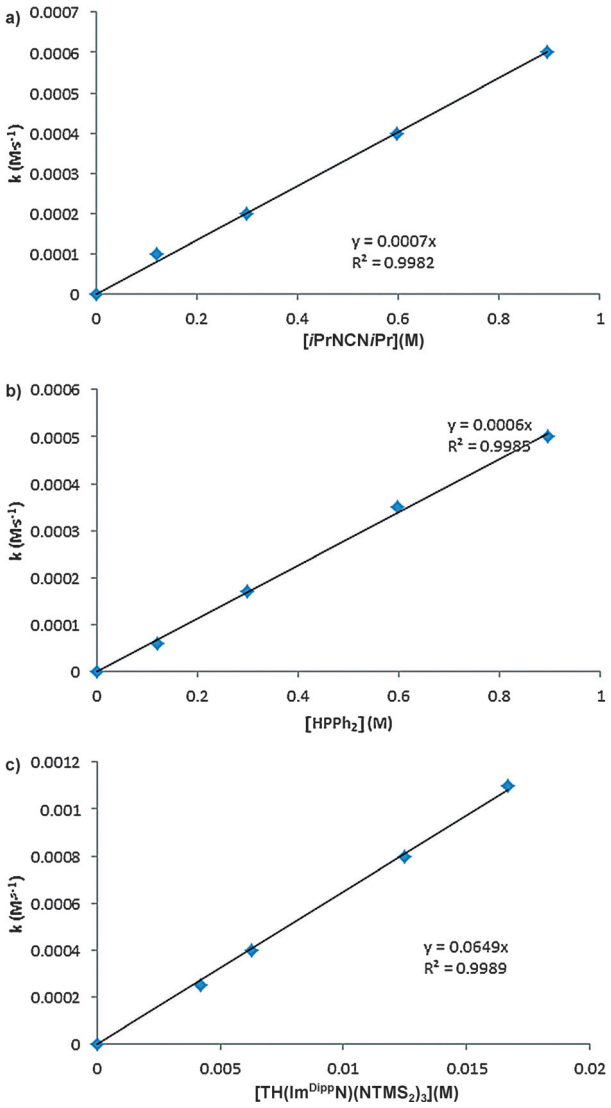


Figure 1. Plot of reaction rate $\partial p/\partial t$ against the concentration of a) DIC for the reaction of DIC and $HPPh_2$; b) $HPPh_2$ for the reaction of DIC and $HPPh_2$; c) of complex **1**.

displaying a higher activation barrier (E_a) for the reaction of 1,3-diisopropylcarbodiimide with diphenylphosphine [Eq. (2)] than for the analogous reaction with phenyl isocyanate [Eq. (3)], with values of $E_a = 20.7(2)$ kcal mol^{-1} ($\Delta H^{\neq} = 19.9(2)$ kcal mol^{-1}) and $E_a = 17.6(2)$ kcal mol^{-1} ($\Delta H^{\neq} = 16.9(2)$ kcal mol^{-1}), respectively. The entropy of activation, determined from the Eyring plots, displays negative values of $\Delta S^{\neq} = -20.7(4)$ cal mol^{-1} K^{-1} and $\Delta S^{\neq} = -25.8(4)$ cal mol^{-1} K^{-1}, for the reaction of 1,3-diisopropylcarbodiimide with diphenylphosphine [Eq. (2)] and phenylisocyanate with diphenylphosphine [Eq. (3)], respectively, corroborating an ordered four-centered transition state for both reactions.[26]

In summary, this work introduces new reactivity for actinide coordination complexes, exemplified by the mono(imidazolin-2-iminato) thorium(IV) complex [Th(Im^{Dipp}N){N(SiMe$_3$)$_2$}$_3$] (**1**). The reactivity of complex **1** was studied for the catalytic addition of primary and secondary amines, phosphines, and thiols to the central Y=C=X linkage of various heterocumulenes, for example, carbodiimides, isocyanates, and isothiocyanates. The thorium compound **1** displayed an unusual tolerance toward heteroatoms and functional groups, giving the respective insertion products in high yields and selectivity. Kinetic studies together with kinetic experiments using the deuterated substrate DPPh$_2$ indicate that the protonolysis is the most plausible rate-determining step of the reaction.

Keywords: actinide catalysis · carbodiimides · nucleophilic insertion · isocyanates · thioisocyanates

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