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Reactivity of Ce(IV) imido compounds with heteroallenes†

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The reactivity of alkali metal capped Ce(IV) imido compounds [M(DME)₂][Ce=NR^F(TriNOx)] (1-M with M = K, Rb, Cs and Ar^F = 3,5-bis(trifluoromethyl)phenyl) with CO₂ and organic isocyanates has been evaluated. 1-Cs reacted with CO₂ to yield an organo-carbamate complex. Reaction of 1-K and 1-Rb with organic isocyanates yielded organoureate Ce(IV) complexes.

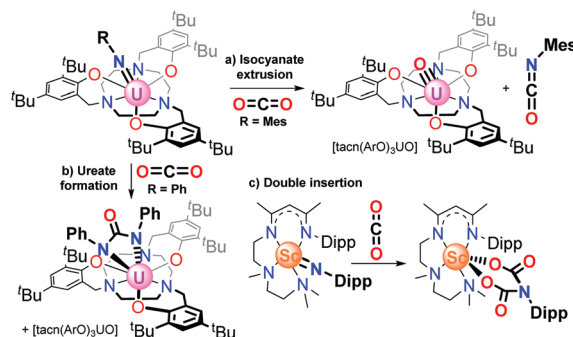
Lanthanide compounds with multiply bonded ligands, including the terminal imido moiety, are rare because the highly contracted lanthanide 4f orbitals are not energetically or spatially favorable for multiple bonding. The high degree of bond polarization renders such species extremely reactive. Reported examples of f-element imido compounds largely include uranium and thorium species.^{1–5} Reactivity studies of uranium imidos with isocyanates and isothiocyanates,⁶ carbon disulfide,⁷ and carbon dioxide⁸ have been reported. Thorium terminal imido reactivity with various small molecules has also been described.^{9,10}

Examples of rare earth imido complexes are more limited.¹¹ Bridging ytterbium imidos,¹² and terminal yttrium and lutetium imidos are known¹³ but, to date, their reactivities have not been explored. Isolation of a scandium terminal imido by the Chen group¹⁴ inspired multiple reactivity studies.^{15–17} Among small molecule substrates, carbon dioxide is privileged due to its abundance and significance. Multiple studies have revealed several (non-redox) activation pathways for titanium-, scandium-, and uranium-imido complexes. These routes include (a) the formation of metal-oxo complexes with the side-production of organic isocyanates,⁸ (b) the formation of metal-ureate and

metal-oxo complexes^{8,18} or (c) the formation of metal-dicarbamate species (Scheme 1).¹⁵

Importantly, all these pathways are proposed to proceed by the initial formation of a metal-coordinated *N*-substituted organocarbamate-dianion (or carbamate), which is typically considered to form by [2π+2π]-cycloaddition between the carbon dioxide molecule and the metal-nitrogen double bond. Despite being extensively proposed, characterized examples of carbamate intermediates have remained sparse in rare earth and actinide chemistry.^{19,20}

Contrary to other rare earth imido compounds found in the +3 metal oxidation state, cerium offers the opportunity to exploit the relatively stabilizing +4 metal oxidation state. Recently, a series of alkali metal capped Ce(IV) imido compounds [M(DME)₂][Ce=NR^F(TriNOx)] (1-M with M = K, Rb, Cs, Ar^F = 3,5-bis(trifluoromethyl)phenyl, and TriNOx^{3–} = [(2-^tBuNO)C₆H₄CH₂)₃N]^{3–}) was reported by our group.^{21–23} The limited data on lanthanide imido performance in small molecule activation led us to explore the reactivity of 1-M with heteroallenes. We hypothesized that the imido compounds would react readily with small molecules with polar bonds (carbon dioxide and organic isocyanates) due to the presence of the highly polarized imido moiety. The imido nitrogen atom



Scheme 1 Selected examples of imido compounds reactivity with CO₂.^{8,15} Mes = 2,4,6-trimethylphenyl, Dipp = 2,6-diisopropylphenyl.

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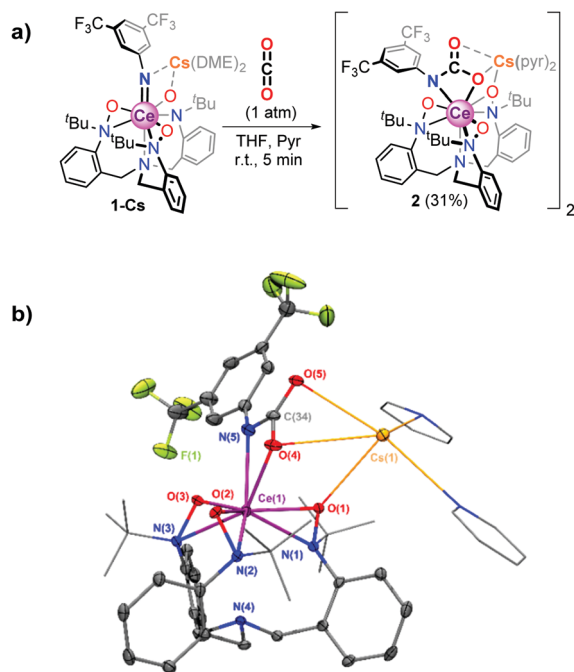


Fig. 1 Synthesis of **2** from **1-Cs** and CO_2 (a) and thermal ellipsoid plot of the asymmetric unit of **2** (b). Hydrogen atoms are omitted for clarity; *tert*-butyl groups and pyridine molecules are depicted using a wireframe model.

was previously demonstrated to present a large nucleophilic and basic character, (conjugate anilide $\text{pK}_a \approx 25$),⁵ therefore promoting interaction with electrophilic moieties of substrates.^{21–23}

Exposing a THF or a pyridine solution of the imido complex **1-Cs** to one atmosphere of CO_2 gas at room temperature resulted in an immediate color change from purple to brown-orange. The recrystallized red-brown solid was analyzed with ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{19}\text{F}\{^1\text{H}\}$, and ^{133}Cs NMR spectroscopy, indicating the formation of one main, diamagnetic, cerium-containing, C_3 -symmetric reaction product characterized by a resonance at 170.1 ppm in its ^{13}C NMR spectrum. Infrared spectroscopy exhibited a characteristic carbonyl stretch at 1646 cm^{-1} .^{24,25} Recrystallization afforded the isolation of X-ray quality crystals in 31% yield (Fig. 1a). An X-ray diffraction study revealed the structure of a dimeric organocarbamate (**2**) as suggested by the spectroscopic data. The role, if any, of the labile Cs^+ cation was examined by reaction of the uncapped imido complex $[\text{Cs}(2.2.2\text{-cryptand})][\text{Ce}=\text{NAr}^{\text{F}}(\text{TriNOx})]$ with CO_2 . However, as yet, the resulting reaction mixtures for the latter have not been tractable. However, our computational results indicate the association of the Cs^+ cation in **1-Cs** provides only marginal stabilization, compared to the energies of the other species along the reaction coordinate (*vide infra*). As such, the presence of labile Cs^+ cation is not expected to influence the reactivity with CO_2 , comparing between **1-Cs** and $[\text{Cs}(2.2.2\text{-cryptand})][\text{Ce}=\text{NAr}^{\text{F}}(\text{TriNOx})]$.

The solid state structure of **2** (Fig. 1b) featured an organocarbamate-dianion ligand bound in a κ^2 mode to the Ce(1) cation through the N(5) and O(4) atoms, forming a four-membered metallacycle. The bond lengths around Ce(1) were typical of a Ce(IV) cation in the TriNOx^{3-} ligand.²¹ The structure

also contained a Cs^+ cation stabilized by the TriNOx^{3-} framework, the $\kappa^2\text{-(O(4),O(5))}$ coordination of the carbamate fragment and two pyridine molecules. Compound **2** had an overall dimeric structure (Fig. S1, ESI[†]). Pyridine and THF solutions of **2** were unstable at room temperature, ^1H NMR monitoring of solutions of **2** showed its gradual degradation into yet unidentified paramagnetic species. However, storing a THF solution of **2** at $-5\text{ }^\circ\text{C}$ was sufficient to inhibit decomposition over the course of 1 week. Notably, no formation of the isocyanate $\text{Ar}^{\text{F}}\text{-NCO}$ or the previously identified cerium-oxo cluster $\{\text{Cs}[\text{Ce}=\text{O}(\text{TriNOx})]\}_4$ were observed during this period.²¹

Compound **2** is a rare example of a structurally characterized lanthanide organocarbamate.^{26,27} One previous example was reported from insertion of CO_2 into a lanthanide, 3-fold bridging imido compound.²⁸ Isolation of **2** is consistent with metal-imido reactivity with CO_2 , since formation of $[2\pi+2\pi]$ cycloaddition (or insertion) products is the key step in all reported reactions of the metal-imidos with carbon dioxide.

The stability of both d-block and f-block metallocarbamates determines the ultimate outcome of the reaction. Unstable metallocarbamates typically decompose to yield oxo-complexes with extrusion of isocyanate. For example, that type of reactivity was reported by Meyer and coworkers for a uranium(V) imido complex stabilized by a tripodal ligand framework (Scheme 1a).⁸ By decreasing the steric profile of the imido moieties, those authors demonstrated the formation of a mixture of oxo- and ureate-complexes proposed to be formed by the reaction of the intermediate metallocarbamate with a second equivalent of imido complex (Scheme 1b). In contrast to these pathways, the metallocarbamate intermediate may be stable enough to undergo a second insertion of CO_2 into the remaining metal-nitrogen bond, producing a dicarbamate species.²⁹ This type of reactivity was reported for Chen's scandium terminal imido compound, which yielded exclusively the dicarbamate product upon insertion of two equivalents of CO_2 (Scheme 1c).¹⁷ Dicarbamate products were also observed upon treating uranium nitride complexes with CO_2 as reported by Mazzanti.^{19,30}

Notably, the cerium metallocarbamate **2** reactivity did not adhere to either of those three reaction pathways. Previously, Mountford and coworkers found that the fate of titanium metallocarbamates formed in the reaction of titanium imido with CO_2 depends on the nature of the imido substituent.²⁹ Electron withdrawing aryl substituents promoted the double insertion while alkyl moieties directed the reaction towards isocyanate extrusion and formation of oxo complexes. These considerations did not seem to apply to the cerium metallocarbamate **2**. Namely, the 3,5-bis(trifluoromethyl)phenyl imido substituent of **1-Cs** did not promote the formation of a double insertion product. On the other hand, no formation of Ce(IV)-oxo complex, isocyanate $\text{Ar}^{\text{F}}\text{-NCO}$, or Ce(IV)-ureate complex (*vide infra*) was observed. This observation suggests the fundamental difference of the nature of the alkali-capped metal-nitrogen imido bond of **1-Cs** compared to d-block or f-block metal terminal imido bonds.

In order to demonstrate the absence of ureate complex during the reaction of **1-M** and CO_2 (Scheme 1b) and to investigate

reactivity of **1-M** with organic isocyanate moieties, **1-K** was reacted with $\text{Ar}^{\text{F}}\text{-NCO}$ and **1-Rb** was reacted with adamantyl isocyanate. Notably, isocyanate activation by the imido complexes **1-M** was relatively slow compared to the instantaneous reaction of **1-Cs** with CO_2 . In all cases, formation of C_3 -symmetric Ce(IV) products were observed (Fig. S11 and S14, ESI†). Recrystallization yielded X-ray quality crystals (Fig. 2a).

Reaction of **1-Rb** with adamantyl isocyanate afforded the ureate complex $[\text{Rb}[\text{Ce}(\text{OC}(\text{NAd})\text{N-Ar}^{\text{F}})(\text{TriNOx})]]_2\cdot\text{DME}$ (**3**) in 41% yield. The solid-state structure contained two $[\text{Ce}(\text{OC}(\text{NAd})\text{N-Ar}^{\text{F}})(\text{TriNOx})]^-$ fragments bridged by two inequivalent Rb cations (Fig. S3, ESI†). Each of these fragments featured a cerium-bonded, $\kappa^2\text{-(N,O)}$ ureate dianion ligands. Bond distances were consistent with Ce(IV) oxidation state. Similarly to the reaction of **1-Rb**, **1-K** reacted with $\text{Ar}^{\text{F}}\text{-NCO}$ to yield the metalloureate $[\text{K}(\text{DME})_2][\text{Ce}(\text{OC}(\text{NAr}^{\text{F}})\text{N-Ar}^{\text{F}})(\text{TriNOx})]$ (**4**) (Fig. 2b). The ureate dianion is coordinated in an unsymmetrical $\kappa^2\text{-(N,O)}$ mode to the Ce cation (Fig. 2b). Infrared and NMR spectroscopic data were in accord with the formation of the metalloureate and compare well with the relevant literature.^{6,31–33}

Next, we turned to computation to explore the mechanism of formation for the carbamate complex **2** and its relative stability toward the three classical pathways of decomposition described in Scheme 1. The formation of uncapped imido complex (**1**[−]) from **1-Cs** was computed to be marginally endothermic by 6.7 kcal mol^{−1}, so that the presence of Cs⁺ cation is not expected to influence the reactivity. Starting from the optimized structure of **1**[−], the approach of a CO_2 molecule led very easily to a transition state (TS_{CO_2} , Fig. 3) located 3.4 kcal mol^{−1} above the reactants.

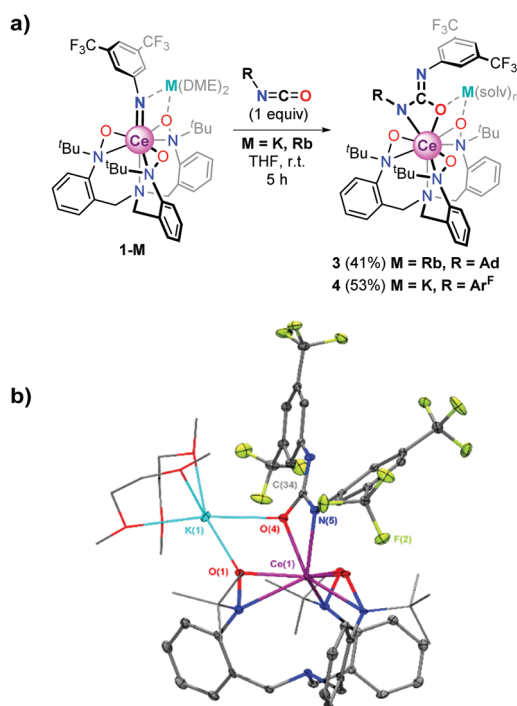


Fig. 2 Synthesis of **3** and **4** (a) and thermal ellipsoid plot of **4** (b). Hydrogen atoms are omitted for clarity; *tert*-butyl groups and DME molecules are depicted using a wireframe model.

The imaginary frequency associated with this saddle point was in agreement with a $[2\pi+2\pi]$ cycloaddition, resembling an insertion mechanism due to the large polarization of the cerium-nitrogen bond. From TS_{CO_2} , the metallocarbamate complex **2**[−] was located 36.4 kcal mol^{−1} below the reactants. These data agreed with our experimental evidence of an irreversible and fast reaction (Fig. 3). The putative retrocycloaddition of **2**[−] to yield the adduct Int_{NCO} was found to require 38 kcal mol^{−1} through TS_{NCO} (Fig. 3). Notably, the dissociation of Int_{NCO} to give the Ce-oxo anionic complex and the isocyanate $\text{Ar}^{\text{F}}\text{-NCO}$ was computed to require an extra +11.5 kcal mol^{−1}, therefore supporting the unlikelihood to access the isocyanate extrusion pathway from **2** (Fig. 3).

The formation of the ureate complex **4**[−] by reaction of the imido complex **1**[−] and $\text{Ar}^{\text{F}}\text{-NCO}$ was found to proceed through $\text{TS}_{\text{Ureate}}$. This cycloaddition required 15.3 kcal mol^{−1}, in accord with a slower reaction than the CO_2 addition as observed experimentally. Overall, the formation of the ureate **4**[−] by the reaction of **1**[−] with CO_2 , extrusion of $\text{Ar}^{\text{F}}\text{-NCO}$, and reaction of $\text{Ar}^{\text{F}}\text{-NCO}$ with a second equivalent of **1**[−] is unlikely to occur (Fig. 3, right). Meyer and Bart proposed that uranium-ureate complex could be formed by reaction of a carbamate- and imido-complexes by a bimetallic pathway (Scheme 1b).⁸ This possibility was examined but required more than 48 kcal mol^{−1} from the carbamate **2**[−] (Fig. S19, ESI†). In summary, both monometallic and bimetallic computed routes disagreed with the production of **4** from the reaction of **1-M** with CO_2 , in agreement with the experimental observations. Finally, the possibility of a double insertion mechanism was investigated (Scheme 1c) as observed for Chen's Sc-imido complex.¹⁵ Despite our efforts, every attempt to locate a second CO_2 insertion transition state was unsuccessful as it always led back to TS_{CO_2} with the second CO_2 molecule being released. Therefore, this route seems to be unlikely, an outcome also supported by experimental observation.

In summary, we report a reactivity study of alkali metal capped Ce(IV) imido compounds with CO_2 and organic isocyanates. The cycloaddition pathways described for d-block and actinide metal imido species apply to **1-M** Ce(IV) imido compounds. However, in contrast to precedent, metallocarbamate **2** obtained in the reaction of **1-Cs** with CO_2 did not undergo isocyanate extrusion with formation of a Ce(IV)-oxo or a Ce(IV)-ureate complex, nor did **1-Cs** show the insertion of a second equivalent of CO_2 to form a dicarbamate. Reactions of **1-Rb** and **1-K** with isocyanates produced stable ureates **3** and **4**, respectively. Further reactivity studies with other unsaturated organic substrates are underway and will be reported in due course.

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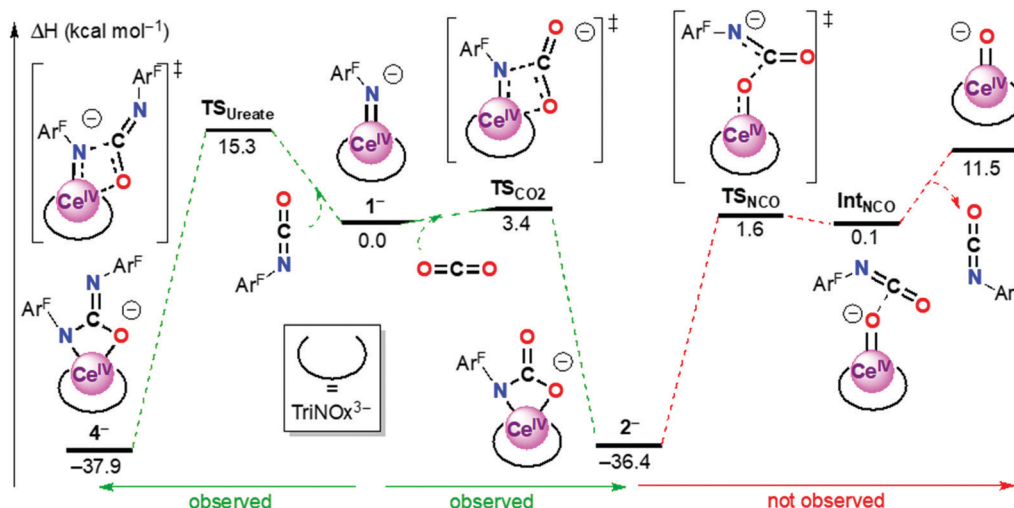


Fig. 3 DFT-calculated reaction coordinates for the formation of 2^- and 4^- from 1^- and the unobserved extrusion of isocyanate pathway.

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Conflicts of interest

There are no conflicts to declare.

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