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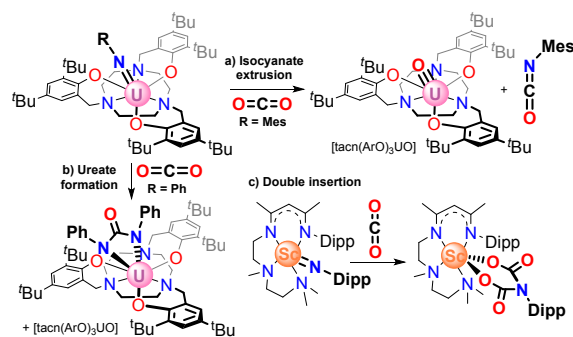
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ABSTRACT: The reactivity of alkali metal capped Ce(IV) imido compounds $[M(\text{DME})_2][\text{Ce}=\text{NAr}^{\text{F}}(\text{TriNOx})]$ (**1-M** with $M = \text{K, Rb, Cs}$ and $\text{Ar}^{\text{F}} = 3,5\text{-bis(trifluoromethyl)phenyl}$) with CO_2 and organic isocyanates has been evaluated. **1-Cs** reacted with CO_2 to yield an organocarbamate 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.^{1–4} Reactivity studies of uranium imidos with isocyanates and isothiocyanates,⁵ carbon disulfide,⁶ and carbon dioxide⁷ have been reported. Thorium terminal imido reactivity with various small molecules has also been described.^{8,9}

Examples of rare earth imido complexes are more limited.¹⁰ Capped lutetium and ytterbium imidos have been reported but, to date, their reactivity has not been explored.^{11,12} Isolation of a scandium terminal imido by the Chen group¹³ inspired multiple reactivity studies.^{14–16} 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,⁷ (b) the formation of metal-ureate and metal-oxo complexes¹⁷ or (c) the formation of metal-dicarbamate species (Scheme 1).¹⁴



Scheme 1. Selected examples of imido compounds reactivity with CO_2 .^{7,14} Mes = 2,4,6-trimethylphenyl, Dipp = 2,6-diisopropylphenyl.

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 $[2\pi+2\pi]$ -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.^{18,19}

An alternate strategy to isolating rare earth imido compounds in the +3 metal oxidation state is to exploit the relatively stabilizing +4 oxidation state of the element cerium. Recently, a series of alkali metal capped Ce(IV) imido compounds $[M(\text{DME})_2][\text{Ce}=\text{NAr}^{\text{F}}(\text{TriNOx})]$ (**1-M** with $M = \text{K, Rb, Cs}$, $\text{Ar}^{\text{F}} = 3,5\text{-bis(trifluoromethyl)phenyl}$, and $\text{TriNOx}^{3-} = [((2\text{-}^t\text{BuNO})\text{C}_6\text{H}_4\text{CH}_2)_3\text{N}]^{3-}$) was reported by our group.^{20–22} The absence of 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 was previously demonstrated to present a large nucleophilic and basic character, therefore promoting interaction with electrophilic moieties of substrates.^{20–22}

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Exposing a THF or a pyridine solution of the imido complex **1-Cs** to one atmosphere of CO₂ gas at room temperature resulted in an immediate color change from purple to brown-orange. The

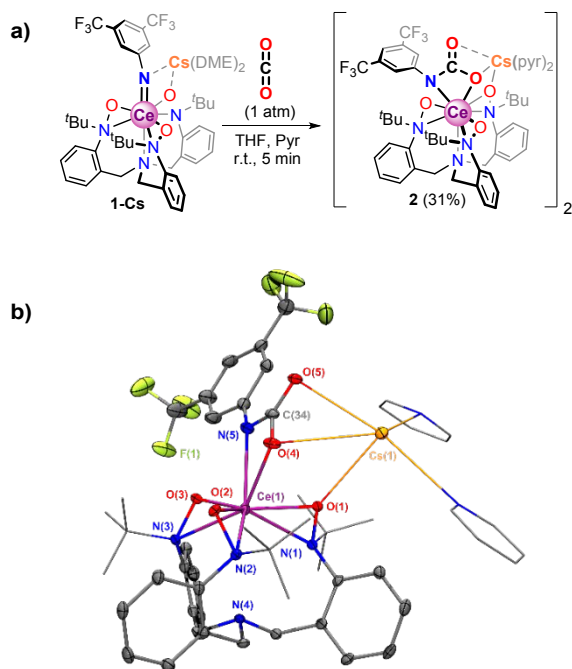


Figure 1. Synthesis of **2** from **1-Cs** and CO₂ (a) and thermal ellipsoid plot of the asymmetric unit of **2** (b). Hydrogen atoms are omitted for clarity; *tert*-butyl groups and pyridine molecules are depicted using a wireframe model.

recrystallized red-brown solid was analyzed with ¹H, ¹³C{¹H}, and ¹⁹F{¹H}, and ¹³³Cs NMR spectroscopy, indicating the formation of one main, diamagnetic, cerium-containing, C₃-symmetric reaction product characterized by a resonance at 170.1 ppm in its ¹³C NMR spectrum. Infrared spectroscopy exhibited a characteristic carbonyl stretch at 1646 cm⁻¹.^{23, 24} Recrystallization afforded the isolation of X-ray quality crystals in 31% yield (Figure 1a). An X-ray diffraction study revealed the structure of a dimeric organocarbamate (**2**) as suggested by the spectroscopic data. We were also interested in examining the role of the Cs⁺ in this reaction, if any, however, reactions of the uncapped imido complex: [Cs(2.2.2-cryptand)][Ce=NR^F(TriNOx)] with CO₂ have, as yet, 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 Cs⁺ cation is not expected to influence the reactivity of CO₂, comparing between **1-Cs** and [Cs(2.2.2-cryptand)][Ce=NR^F(TriNOx)].

The solid state structure of **2** (Figure 1b) featured an organocarbamate-dianion ligand bound in a κ² 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 TriNOx³⁻ ligand.²⁰ The structure also contained a Cs⁺ cation stabilized by the TriNOx³⁻ framework, the κ²-(O(4), O(5)) coordination of the carbamate fragment and two pyridine molecules. Compound **2** had an overall dimeric structure (Figure S1). 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 °C was sufficient to inhibit decomposition over the course of 1 week. Notably, no formation of the isocyanate Ar^F-NCO or the cerium-oxo cluster {Cs[Ce=O(TriNOx)]₄} were observed during this period.²⁰

Compound **2** is a rare example of a structurally characterized lanthanide organocarbamate.^{25,26} One previously example was reported from insertion of CO₂ into a lanthanide, 3-fold bridging imido compound.²⁷ Isolation of **2** is consistent with metal-terminal imido reactivity with CO₂, since formation of [2π+2π] cycloaddition (or insertion) products is the key step in all reported reactions of the metal-imidos with carbon dioxide.

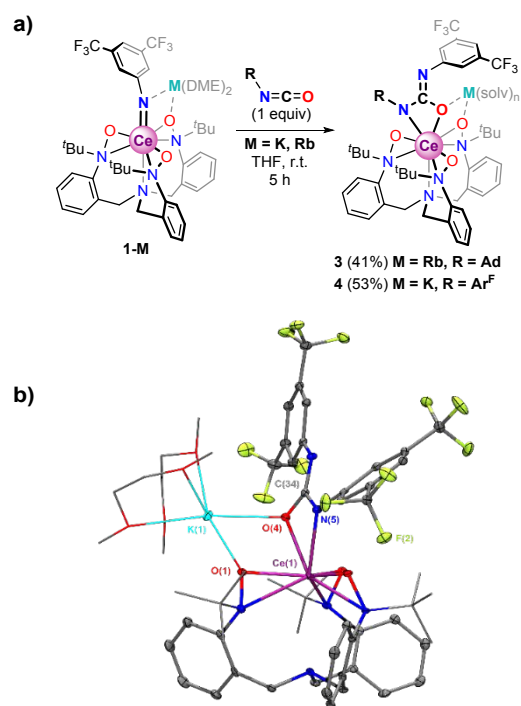


Figure 2. Synthesis of **3** and **4** (a) and thermal ellipsoid plot of **4** (b). Hydrogen atoms are omitted for clarity; *tert*-butyl groups and DME molecules are depicted using a wireframe model.

The 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).⁷ 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 CO₂ into the remaining metal-nitrogen bond, producing a dicarbamate species.²⁸ This type of reactivity was reported for Chen's scandium terminal imido compound, which yielded exclusively

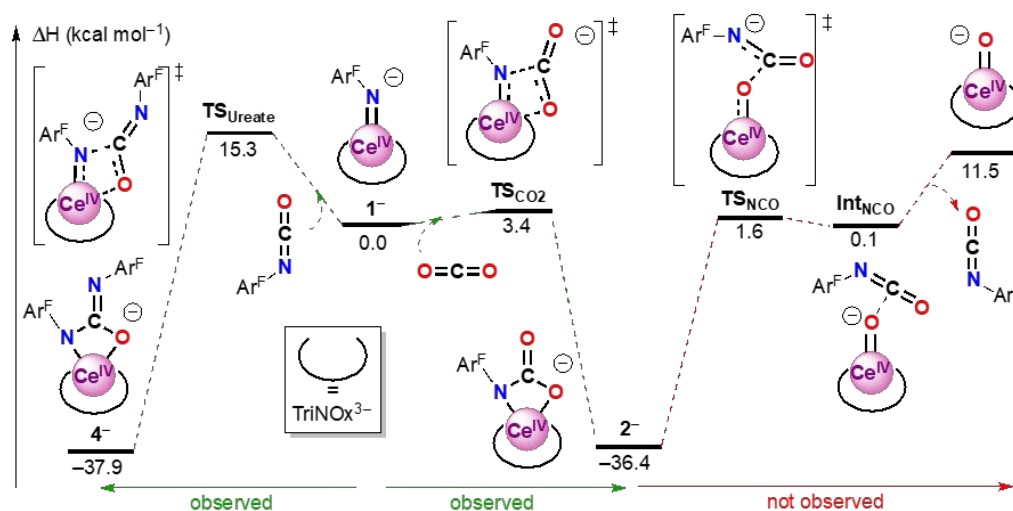


Figure 3. DFT-calculated reaction coordinates for the formation of **2**⁻ and **4**⁻ from **1**⁻ and the unobserved extrusion of isocyanate pathway

the dicarbamate product upon insertion of two equivalents of CO₂ (Scheme 1c).¹⁶ Dicarbamate products were also observed upon treating uranium nitride complexes with CO₂ as reported by Mazzanti.^{18, 29}

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 CO₂ depends on the nature of the imido substituent.²⁸ 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 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 Ar^F-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 CO₂ (Scheme 1b) and to investigate reactivity of **1-M** with organic isocyanate moieties, **1-K** was reacted with Ar^F-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 CO₂. In all cases, formation of C₃-symmetric Ce(IV) products were observed (Figure S11 and Figure S14). Recrystallization yielded X-ray quality crystals (Figure 2a).

Reaction of **1-Rb** with adamantyl isocyanate afforded the ureate complex {[Rb{Ce(OC(NAd)N-Ar^F)(TriNOx)}]}₂·DME (**3**) in 41% yield. The solid-state structure contained two [Ce(OC(NAd)N-Ar^F)(TriNOx)]⁻ fragments bridged by two inequivalent Rb cations (Figure S3). Each of these fragments featured a κ²-(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 Ar^F-NCO to yield the metalloureate [K(DME)₂][Ce(OC(NAr^F)N-Ar^F)(TriNOx)] (**4**) (Figure 2b). The ureate dianion is coordinated in an unsymmetrical κ²-(N,O) mode to the Ce cation (Figure 2b). Infrared and NMR spectroscopic data were in accord with the formation of the metalloureate and compare well with the relevant literature.^{5, 30-32}

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 CO₂ molecule led very easily to a transition state (TS_{CO2}, Figure 3) located 3.4 kcal mol⁻¹ above the reactants.

The imaginary frequency associated with this saddle point was in agreement with a [2π+2π] cycloaddition, resembling an insertion mechanism due to the large polarization of the cerium-nitrogen bond. From TS_{CO2}, 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 (Figure 3). The putative retrocycloaddition of **2**⁻ to yield the adduct Int_{NCO} was found to require 38 kcal mol⁻¹ through TS_{NCO} (Figure 3). Notably, the dissociation of Int_{NCO} to give the Ce-oxo anionic complex and the isocyanate Ar^F-NCO was computed to require an extra +11.5 kcal mol⁻¹, therefore supporting the unlikelihood to access the isocyanate extrusion pathway from **2** (Figure 3).

The formation of the ureate complex **4**⁻ by reaction of the imido complex **1**⁻ and Ar^F-NCO was found to proceed through TS_{Ureate}. This cycloaddition required 15.3 kcal mol⁻¹, in accord with a slower reaction than the CO₂ addition as observed experimentally. Overall, the formation of the ureate **4**⁻ by the reaction **1**⁻ with CO₂, extrusion of Ar^F-NCO, and reaction of Ar^F-NCO with a second equivalent of **1**⁻ is unlikely to occur (Figure 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 (Chart 1b).⁷ This possibility was examined but required more than 48 kcal mol⁻¹ from the carbamate **2**⁻ (Figure S19). In summary, both monometallic and bimetallic computed routes disagreed with the production of **4** from the reaction of **1-M** with CO₂, 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.¹⁴ Despite our efforts, every attempt to locate a second CO₂ insertion transition state were unsuccessful as it always led back to TS_{CO₂} with the second CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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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Conflicts of interest

There are no conflicts to declare.

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Cerium Imido Complexes Form Stable Intermediates with Heteroallenes:

