Ketimide Reactivity

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The Ketimide Ligand is Not Just an Inert Spectator: Heteroallene Insertion Reactivity of an Actinide–Ketimide Linkage in a Thorium Carbene Amide Ketimide Complex**

*Erli Lu, William Lewis, Alexander J. Blake, and Stephen T. Liddle**

Abstract: *The ketimide anion $R_2C{=}N^-$ is an important class of chemically robust ligand that binds strongly to metal ions and is considered ideal for supporting reactive metal fragments due to its inert spectator nature; this contrasts with R_2N^- amides that exhibit a wide range of reactivities. Here, we report the synthesis and characterization of a rare example of an actinide ketimide complex [Th(BIPM^{TMS}){N(SiMe$_3$)$_2$}(N=CPh$_2$)] [**2**, BIPM^{TMS} = C(PPh$_2$NSiMe$_3$)$_2$]. Complex **2** contains Th=C$_{carbene}$, Th–N$_{amide}$ and Th–N$_{ketimide}$ linkages, thereby presenting the opportunity to probe the preferential reactivity of these linkages. Importantly, reactivity studies of **2** with unsaturated substrates shows that insertion reactions occur preferentially at the Th–N$_{ketimide}$ bond rather than at the Th=C$_{carbene}$ or Th–N$_{amide}$ bonds. This overturns the established view that metal-ketimide linkages are purely inert spectators.*

Amide (R_2N^-) and ketimide ($R_2C{=}N^-$) (R = alkyl, aryl, or silyl groups) monoanions are two important classes of monodentate nitrogen-donor ligands in coordination and organometallic chemistry. The negative charge of both these types of ligand is N-centered and can form a covalent M–N bond in metal complex derivatives. However, there is a crucial difference between amides and ketimides: in the former the nitrogen hybridization is sp^2 or sp^3 and it bears two N–C/Si singly bonded groups, whereas in the latter the nitrogen hybridization is sp or sp^2 and it is bonded to only one carbon atom with a N=C double bond. These differences in structure and bonding lead to a significantly different reactivity of these two types of M–N bond. The M–N$_{amide}$ bond is reactive, and readily engages in protonolysis and insertion of unsaturated organic substrates; this has been extensively studied for decades and these reactions play a vital role in very important catalytic processes such as hydroamination, hydroalkoxylation, and ring-opening polymerization of lactones.[1] In sharp contrast, the M–N$_{ketimide}$ bond is chemically inert, and resistant to insertion and electrophilic attack.[2] In fact, the chemically inert nature of M–N$_{ketimide}$ bonds renders ketimides the ligand of choice when spectator ligands are required to stabilize highly reactive species in a broad range of applications including strongly oxidizing high-valent uranium and Group 7–9 complexes,[3] diuranium inverted-sandwich arene complexes,[4] and olefin polymerization catalysts.[5] To the best of our knowledge, the only reported reactivity of any metal–ketimide, in the absence of acidic hydrogens, involves β-R-group eliminations and free-radical redox C–C bond homolysis degradation reactions of the ketimide rather than M–N$_{ketimide}$ insertion chemistry.[6]

Nonaqueous actinide chemistry has received burgeoning interest in the past decade.[7] Although actinide amides are less well-developed than their transition metal counterparts, they have been known for decades and their reactivity is extensively investigated.[8–10] In contrast, actinide ketimides were unknown until 2002. After the first example of a uranium ketimide,[11] a relatively small number of actinide ketimides have been synthesized and characterized.[12] Studies of the An–N$_{ketimide}$ (An = U, Th) bond have shed light on the important question of the amount of 5f orbital participation in bonding.[13] However, from a reactivity perspective, and as compared to their transition metal counterparts, the An–N$_{ketimide}$ bond is generally considered to be chemically inert,[11] and considerably stronger than analogous An–N$_{amide}$ bonds. Indeed, no insertion reactivity of the An–N$_{ketimide}$ spectator ligand linkage with a wide range of substrates has ever been observed,[11,12] despite the fact that the An–N$_{ketimide}$ linkage is usually the least sterically hindered linkage in An-complexes. Furthermore, from a general perspective, a direct comparison of bonding character and reactivity of M–N$_{amide}$/M–N$_{ketimide}$ linkages in one molecule is desirable but still absent. Such studies may provide information on potential catalytic mechanisms and/or deactivation pathways of such complexes, and open new horizons for M–N linkage reactivity.

As part of our investigations of An-ligand multiple bond chemistry,[14] we describe here the synthesis of a thorium carbene amide ketimide that features Th=C$_{carbene}$, Th–N$_{amide}$, and Th–N$_{ketimide}$ bonds in one molecule. Preliminary reactivity studies unexpectedly revealed that insertion reactions occur at the traditionally inert M–N$_{ketimide}$ site, rather than at the M=C$_{carbene}$[15] or M–N$_{amide}$ bonds. This observation overturns the view that ketimides are purely inert spectator ligands.

To begin with, [ThCl$_4$(DME)$_2$][16] was treated with one equivalent of Li$_2$BIPM^{TMS} [BIPM^{TMS} = C(PPh$_2$NSiMe$_3$)$_2$] to form the thorium dichloride intermediate [Th(BIPM^{TMS})(Cl)$_2$].[17] This intermediate was not isolated and treated with one equivalent of KN(SiMe$_3$)$_2$ in situ. After work-up and recrystallization, the thorium carbene amide chloride [Th(BIPM^{TMS}){N(SiMe$_3$)$_2$}(μ-Cl)]$_2$ (**1**) was obtained in 85% yield as a pale yellow solid (Scheme 1). Although

[*] Dr. E. Lu, Dr. W. Lewis, Prof. A. J. Blake, Prof. S. T. Liddle
School of Chemistry, University of Nottingham, University Park
Nottingham, NG7 2RD (UK)
E-mail: stephen.liddle@nottingham.ac.uk

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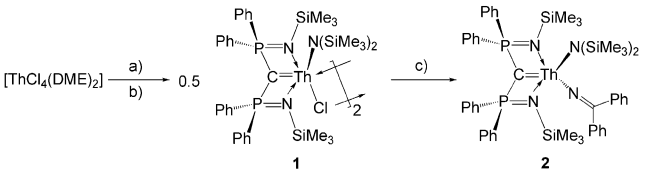


Scheme 1. Synthesis of **1** and **2**. Reagents and conditions: a) Li_2BIPM^{TMS}, THF, −78 °C, −2 LiCl; b) $KN(SiMe_3)_2$, C_6H_6, RT, −KCl; c) $LiN{=}CPh_2$, C_6H_6, RT, −LiCl.

a number of covalent uranium carbenes have been reported in recent years,[14,18] thorium analogues remain exceptionally rare.[19] Treatment of **1** with two equivalents of $[Li(N{=}CPh_2)]$ in benzene at room temperature results in a color change from pale yellow to intense orange. Because of the $6d^05f^0$ metal ion configuration, Th^{IV} complexes have usually been reported as essentially colorless. After the work-up, the thorium carbene amide ketimide $[Th(BIPM^{TMS})\{N(SiMe_3)_2\}(N{=}CPh_2)]$ (**2**) was isolated as orange crystals in 91 % yield (Scheme 1).

The characterization data for **1** and **2** are consistent with their formulations.[17] The vivid orange color of **2** (both in the solid-state and in solution) is noteworthy for a $6d^05f^0$ metal complex. The electronic absorption spectra of **2** exhibits a broad, intense electronic absorption band from the UV to visible wavelength range, and a strong absorption between 450 and 550 nm. Since **1** is pale yellow and the $6d^05f^0$ electronic configuration of Th^{IV} precludes metal-localized f–f, d–f, and d–d transitions, and on the basis of definitive prior work,[12c] we conclude this transition is due to a spin-allowed but orbital-forbidden $p\perp(N)\rightarrow\pi^*$ (N=C) and ligand-to-metal charge transfer (LMCT).

The solid-state structures of **1** and **2** were confirmed by X-ray crystallography (**1**, Figure S1; **2**, Figure 1). The salient structural feature of **2** is the two types of Th–N linkage; the Th–$N_{ketimide}$ distance is significantly shorter than the Th–N_{amide} bond (Th–N4 2.265(6) Å versus Th–N3 2.350(7) Å). The ketimide N=C bond length is 1.279(10) Å, and Th-N-C bond angle is 171.3(6)°. These parameters suggest that the Th–$N_{ketimide}$ interaction may be stronger than the Th–N_{amide} interaction,[11] and may feature some multiple bond character. The Th=$C_{carbene}$ bond lengths in **1** and **2** are 2.410(8) Å and 2.474(8) Å, respectively, which is similar to other thorium BIPM carbene complexes (2.43–2.50 Å).[19] Although the M=C bond in An and rare-earth BIPM carbene complexes is polarized,[14,18] a modest multiple bond character of the Th=$C_{carbene}$ bonds in **1** and **2** is suggested by comparison to the thorium alkyl complex $[Th(CH_2CMe_3)_5][Li(THF)_4]$,[20] in which the Th–C single bond (2.50–2.56 Å) is longer than the Th=C bonds in **1** or **2**.

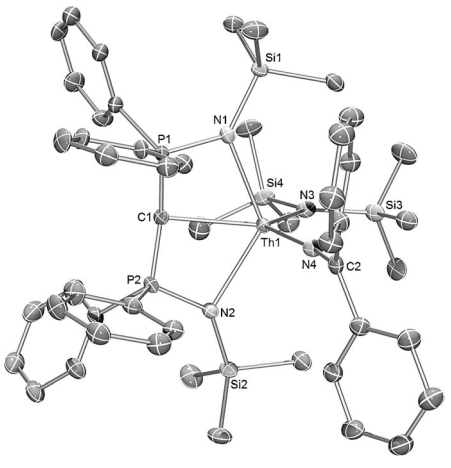
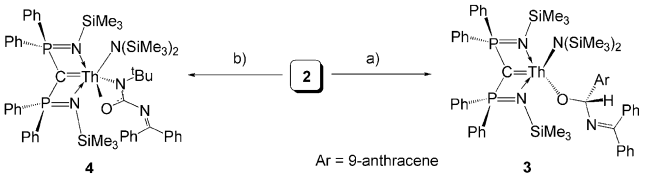


Figure 1. Molecular structure of $[Th(BIPM^{TMS})\{N(SiMe_3)_2\}(N{=}CPh_2)]$ (**2**). Displacement ellipsoids set at 40% probability. Hydrogen atoms and minor disorder components are omitted for clarity. Selected bond lengths [Å] and angles [°]: Th–C1 2.474(8), Th–N3 2.350(7), Th–N4 2.265(6), N4–C2 1.279(10), Th–N1 2.431(7), Th–N2 2.429(6); Th-N4-C2 171.3(6).

The presence of Th=$C_{carbene}$, Th–N_{amide}, and Th–$N_{ketimide}$ bonds in **2** offers the opportunity to probe their competitive reactivity toward unsaturated organic molecules. For the M=C bond in An and rare-earth metal carbene complexes with BIPM ligands, the cycloaddition and Wittig-type group transfer reaction towards unsaturated organic substrates containing C=E (E = O, N) bonds has been well-documented, even in complexes that can be considered as sterically saturated.[14,15,18] On the other hand, M–N_{amide} bonds (M = d- or f-block metal) are also known to undergo a wide range of reactions with unsaturated substrates. Moreover, irrespective of the predicted reactivity of the Th=$C_{carbene}$ and Th–N_{amide} linkages, the Th–$N_{ketimide}$ bond would be anticipated to be inert. However, we find that when **2** is reacted with one equivalent of aldehyde or isocyanate, insertion reactions occur at the Th–$N_{ketimide}$ linkage (Scheme 2).



Scheme 2. Reactions of **2** with 9-anthracene carboxaldehyde or *t*BuNCO to give **3** and **4**. Reagents and conditions: a) ArCHO, toluene, RT; b) *t*BuNCO, toluene, RT.

When **2** was treated with one equivalent of 9-anthracene carboxaldehyde in C_6D_6 at room temperature, the orange color of **2** faded into pale yellow within 12 h. ^1H and ^{31}P NMR spectroscopic monitoring of the reaction showed that **2** was completely converted into the new complex $[Th(BIPM^{TMS})\{N(SiMe_3)_2\}\{OC(H)(NCPh_2)(C_{14}H_9)\}]$ (**3**) within 12 h. The reaction was scaled up with toluene as solvent, providing **3** as yellow crystals in 61 % yield (Scheme 2);[17] this moderate crystalline yield is due to the high solubility of **3** in toluene and not the production of other side-products in the reaction. Unlike **2**, **3** is pale-colored and has no significant absorptions in its electronic absorption spectrum in the UV/Vis range, which is consistent with the loss of the Th–$N_{ketimide}$ bond. Single-crystals suitable for X-ray crystallographic study were obtained from a toluene/hexane mixture, and X-ray analysis confirmed that **3** is a thorium carbene amide

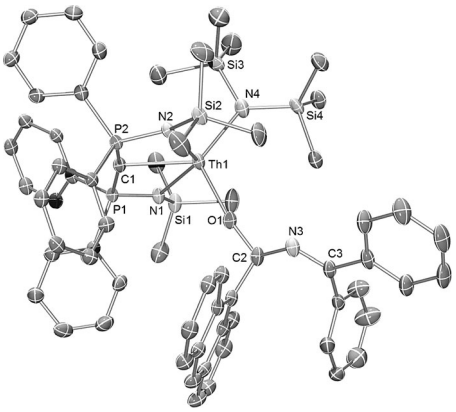


Figure 2. Molecular structure of [Th(BIPM^{TMS}){N(SiMe$_3$)$_2$}{OC(H)-(NCPh$_2$)(C$_{14}$H$_9$)}] (**3**). Displacement ellipsoids set at 40% probability. Hydrogen atoms, minor disorder components, and toluene solvent molecule in lattice are omitted for clarity. Selected bond lengths [Å]: Th–C1 2.453(4), Th–O 2.166(3), Th–N1 2.453(4), Th–N2 2.460(4), Th–N4 2.359(4), O–C2 1.392(6), C2–N3 1.471(6), N3–C3 1.290(7).

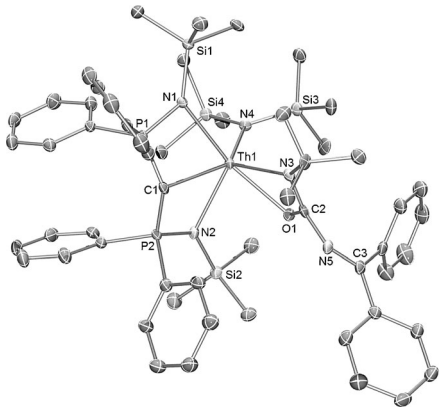


Figure 3. Molecular structure of [Th(BIPM^{TMS}){N(SiMe$_3$)$_2$}{OC-(N*t*Bu)NCPh$_2$}] (**4**). Displacement ellipsoids set at 40% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Th–C1 2.463(5), Th–N1 2.531(4), Th–N2 2.483(5), Th–N3 2.491(5), Th–N4 2.344(4), Th–O 2.391(4), O–C2 1.304(7), C2–N3 1.316(8), C2–N5 1.392(8), N5–C3 1.288(8).

alkyloxide derivative (Figure 2) arising from the selective insertion of the C=O bond of 9-anthracene carboxaldehyde into the Th–N$_{ketimide}$ bond.

Isocyanate is an important heteroallene with versatile reactivity in organic and polymer synthesis and insertions of isocyanates into M–N$_{amide}$ bonds in the d-block are widely reported.[21] We have previously shown that the M=C bonds (M = lanthanide or uranium) in BIPM derivatives readily undergo [2+2] cycloaddition reactions with the C=O bond.[14l,15] When **2** was treated with one equivalent of *tert*-butyl isocyanate (*t*BuN=C=O) in toluene at room temperature, pale-yellow crystals of [Th(BIPM^{TMS}){N(SiMe$_3$)$_2$}{OC-(N*t*Bu)NCPh$_2$}] (**4**) were obtained in 49% yield (Scheme 2). The moderate crystalline yield is due to the high solubility of **4** in toluene, and **4** was confirmed to be the single product by an NMR-scale reaction with > 95% conversion. The structure of complex **4** was confirmed by X-ray crystallography as a thorium carbene amide ureate (Figure 3). In this instance, the Th–N$_{ketimide}$ bond was again shown to be active in insertion chemistry. The ureate ligand, which is formed by the selective insertion of C=O into the Th–N$_{ketimide}$ bond, is coordinated to the thorium center in a κ^2-O, N manner.

To address the issue of whether **3** or **4** can react further we treated them with one more equivalent of 9-anthracene carboxaldehyde (for **3**) or *t*BuNCO (for **4**) in C$_6$D$_6$ solvent. In case of **3**, heating at 60 °C leads to the slow formation of the alkene Wittig-product ArC(H)=C(PPh$_2$NSiMe$_3$)$_2$.[14b] In case of **4**, heating to 60 °C resulted in an intractable mixture and decomposition. These results indicate that the Th–N$_{amide}$ and Th=C$_{carbene}$ bonds in **2** are more resistant towards chemical transformations than the Th–N$_{ketimide}$, which is the opposite of what would be expected.

To conclude, a thorium carbene amide ketimide bearing Th=C$_{carbene}$, Th–N$_{amide}$, and Th–N$_{ketimide}$ linkages has been synthesized and fully characterized. A comparative study of these linkages has shown that, in contrast to the established view, the Th–N$_{ketimide}$ bond is not an inert spectator and can in fact engage in insertion reactivity. These results open a new horizon of reactivity for M–N$_{ketimide}$ linkages, and suggest that in a wider context the role of the ketimide ligand in coordination and organometallic chemistry as a reactive functional group, instead of just being an inert supporting ligand, deserves consideration. Further studies toward using this methodology to incorporate the ketimide group into organic molecules are underway.

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