

Ketimide Reactivity

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**, $BIPM^{TMS} = C(PPh_2NSiMe_3)_2$]. 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_2BIPM^{TMS} [$BIPM^{TMS} = C(PPh_2NSiMe_3)_2$] to form the thorium dichloride intermediate $[Th(BIPM^{TMS})(Cl)_2]$.^[17] This intermediate was not isolated and

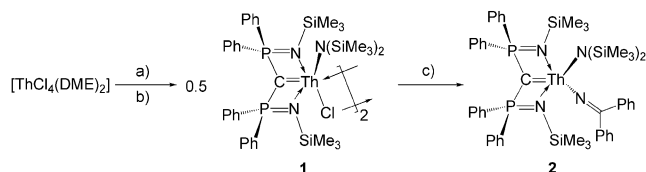
[*] Dr. E. Lu, Dr. W. Lewis, Prof. A. J. Blake, Prof. S. T. Liddle
School of Chemistry, University of Nottingham, University Park
Nottingham, NG7 2RD (UK)
E-mail: stephen.liddle@nottingham.ac.uk

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treated with one equivalent of $\text{KN}(\text{SiMe}_3)_2$ in situ. After work-up and recrystallization, the thorium carbene amide chloride $[\text{Th}(\text{BIPM}^{\text{TMS}})\{\text{N}(\text{SiMe}_3)_2\}(\mu\text{-Cl})_2]$ (**1**) was obtained in 85 % yield as a pale yellow solid (Scheme 1). Although



Scheme 1. Synthesis of **1** and **2**. Reagents and conditions:

- a) $\text{Li}_2\text{BIPM}^{\text{TMS}}$, THF, -78°C , -2 LiCl ; b) $\text{KN}(\text{SiMe}_3)_2$, C_6H_6 , RT, $-\text{KCl}$; c) $\text{LiN}=\text{CPh}_2$, C_6H_6 , RT, $-\text{LiCl}$.

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 $[\text{Li}(\text{N}=\text{CPh}_2)]$ 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 $[\text{Th}(\text{BIPM}^{\text{TMS}})\{\text{N}(\text{SiMe}_3)_2\}(\text{N}=\text{CPh}_2)]$ (**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 $p \perp (\text{N}) \rightarrow \pi^* (\text{N}=\text{C})$ 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 $\text{Th}-\text{N}$ linkage; the $\text{Th}-\text{N}_{\text{ketimide}}$ distance is significantly shorter than the $\text{Th}-\text{N}_{\text{amide}}$ bond ($\text{Th}-\text{N}_4$ 2.265(6) Å versus $\text{Th}-\text{N}_3$ 2.350(7) Å). The ketimide $\text{N}=\text{C}$ bond length is 1.279(10) Å, and $\text{Th}-\text{N}-\text{C}$ bond angle is $171.3(6)^\circ$. These parameters suggest that the $\text{Th}-\text{N}_{\text{ketimide}}$ interaction may be stronger than the $\text{Th}-\text{N}_{\text{amide}}$ interaction,^[11] and may feature some multiple bond character. The $\text{Th}=\text{C}_{\text{carbene}}$ 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 $\text{M}=\text{C}$ bond in An and rare-earth BIPM carbene complexes is polarized,^[14,18] a modest multiple bond character of the $\text{Th}=\text{C}_{\text{carbene}}$ bonds in **1** and **2** is suggested by comparison to the thorium alkyl complex $[\text{Th}(\text{CH}_2\text{CMe}_3)_5][\text{Li}(\text{THF})_4]$,^[20] in which the $\text{Th}-\text{C}$ single bond (2.50–2.56 Å) is longer than the $\text{Th}=\text{C}$ bonds in **1** or **2**.

The presence of $\text{Th}=\text{C}_{\text{carbene}}$, $\text{Th}-\text{N}_{\text{amide}}$, and $\text{Th}-\text{N}_{\text{ketimide}}$ bonds in **2** offers the opportunity to probe their competitive reactivity toward unsaturated organic molecules. For the $\text{M}=\text{C}$

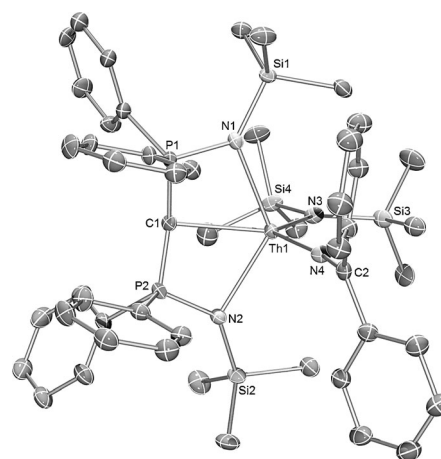
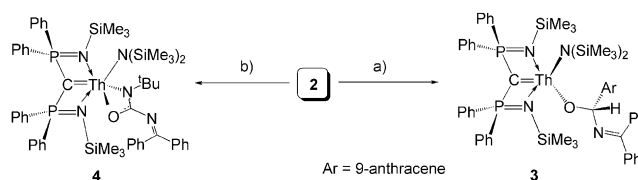


Figure 1. Molecular structure of $[\text{Th}(\text{BIPM}^{\text{TMS}})\{\text{N}(\text{SiMe}_3)_2\}(\text{N}=\text{CPh}_2)]$ (**2**). Displacement ellipsoids set at 40% probability. Hydrogen atoms and minor disorder components are omitted for clarity. Selected bond lengths [Å] and angles [$^\circ$]: $\text{Th}-\text{C}1$ 2.474(8), $\text{Th}-\text{N}3$ 2.350(7), $\text{Th}-\text{N}4$ 2.265(6), $\text{N}4-\text{C}2$ 1.279(10), $\text{Th}-\text{N}1$ 2.431(7), $\text{Th}-\text{N}2$ 2.429(6); $\text{Th}-\text{N}4-\text{C}2$ $171.3(6)$.

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 $\text{C}=\text{E}$ ($\text{E} = \text{O}, \text{N}$) bonds has been well-documented, even in complexes that can be considered as sterically saturated.^[14,15,18] On the other hand, $\text{M}-\text{N}_{\text{amide}}$ bonds ($\text{M} = d$ - 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 $\text{Th}=\text{C}_{\text{carbene}}$ and $\text{Th}-\text{N}_{\text{amide}}$ linkages, the $\text{Th}-\text{N}_{\text{ketimide}}$ 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 $\text{Th}-\text{N}_{\text{ketimide}}$ linkage (Scheme 2).



Scheme 2. Reactions of **2** with 9-anthracene carboxaldehyde or $t\text{BuNCO}$ to give **3** and **4**. Reagents and conditions: a) ArCHO , toluene, RT; b) $t\text{BuNCO}$, 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 $[\text{Th}(\text{BIPM}^{\text{TMS}})\{\text{N}(\text{SiMe}_3)_2\}\{\text{OC}(\text{H})(\text{NCPH}_2)(\text{C}_{14}\text{H}_9)\}]$ (**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 alkyloxide derivative (Figure 2) arising from the selective insertion of the C=O bond of 9-anthracene carboxaldehyde into the Th–N_{ketimide} bond.

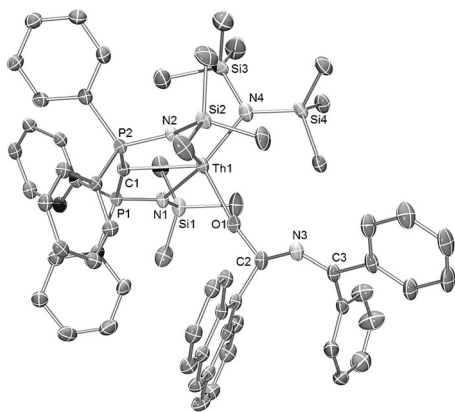


Figure 2. Molecular structure of [Th(BIPM^{TMS}){N(SiMe₃)₂}{OC(H)(NCPH₂)(C₁₄H₉)}] (**3**). Displacement ellipsoids set at 40% probability. Hydrogen atoms, minor disorder components, and toluene solvent molecule in lattice are omitted for clarity. Selected bond lengths [Å]: Th–C1 2.453(4), Th–O 2.166(3), 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).

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.^[14,15] 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(SiMe₃)₂}{OC(N*t*Bu)NCPH₂}] (**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 κ²-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 C₆D₆ solvent. In case of **3**, heating at 60°C leads to the slow formation of the alkene Wittig-product ArC(H)=C(PPh₂NSiMe₃)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

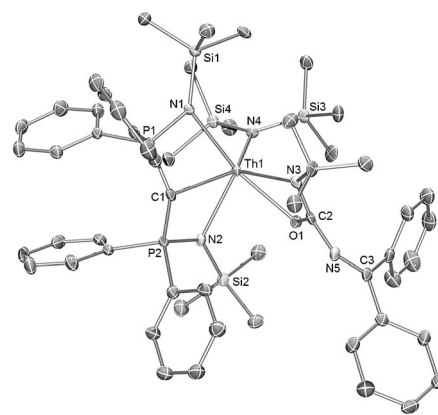


Figure 3. Molecular structure of [Th(BIPM^{TMS}){N(SiMe₃)₂}{OC(N*t*Bu)NCPH₂}] (**4**). Displacement ellipsoids set at 40% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Th–C1 2.463(5), Th–N1 2.531(4), Th–N2 2.483(5), Th–N3 2.491(5), Th–N4 2.344(4), Th–O 2.391(4), O–C2 1.304(7), C2–N3 1.316(8), C2–N5 1.392(8), N5–C3 1.288(8).

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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