



Lu, Erli and Lewis, William and Blake, Alexander J. and Liddle, Stephen T. (2014) The ketimide ligand is not just an inert spectator: heteroallene insertion reactivity of an actinide-ketimide linkage in a thorium carbene amide ketimide complex. *Angewandte Chemie International Edition*, 53 (35). pp. 9356-9359. ISSN 1521-3773

Access from the University of Nottingham repository:

http://eprints.nottingham.ac.uk/46640/1/Lu_et_al-2014-Angewandte_Chemie_International_Edition%20%281%29.pdf

Copyright and reuse:

The Nottingham ePrints service makes this work by researchers of the University of Nottingham available open access under the following conditions.

This article is made available under the Creative Commons Attribution licence and may be reused according to the conditions of the licence. For more details see: <http://creativecommons.org/licenses/by/2.5/>

A note on versions:

The version presented here may differ from the published version or from the version of record. If you wish to cite this item you are advised to consult the publisher's version. Please see the repository url above for details on accessing the published version and note that access may require a subscription.

For more information, please contact eprints@nottingham.ac.uk

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

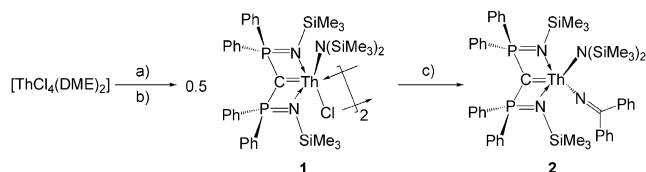
[*] Dr. E. Lu, Dr. W. Lewis, Prof. A. J. Blake, Prof. S. T. Liddle
School of Chemistry, University of Nottingham, University Park
Nottingham, NG7 2RD (UK)
E-mail: stephen.liddle@nottingham.ac.uk

[**] We thank the Royal Society, the Marie Curie International Incoming Fellowship (E.L.), the Engineering and Physical Sciences Research Council, and the University of Nottingham for generously supporting this work.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201404898>.

© 2014 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

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 ($\text{Th}-\text{N4}$ 2.265(6) Å versus $\text{Th}-\text{N3}$ 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 $\text{M}=\text{C}$

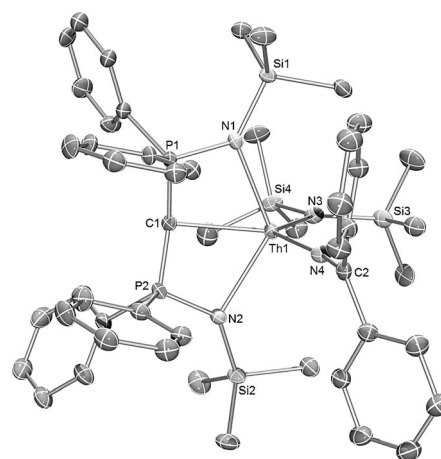
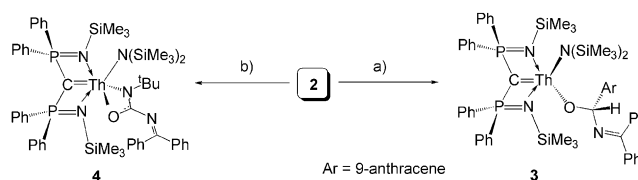


Figure 1. Molecular structure of $[\text{Th}(\text{BIPM}^{\text{TMS}})\{\text{N}(\text{SiMe}_3)_2\}(\text{N}=\text{CPh}_2)]$ (**2**). Displacement ellipsoids set at 40% probability. Hydrogen atoms and minor disorder components are omitted for clarity. Selected bond lengths [Å] and angles [$^\circ$]: $\text{Th}-\text{C1}$ 2.474(8), $\text{Th}-\text{N3}$ 2.350(7), $\text{Th}-\text{N4}$ 2.265(6), $\text{N4}-\text{C2}$ 1.279(10), $\text{Th}-\text{N1}$ 2.431(7), $\text{Th}-\text{N2}$ 2.429(6); $\text{Th}-\text{N4}-\text{C2}$ $171.3(6)$.

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.

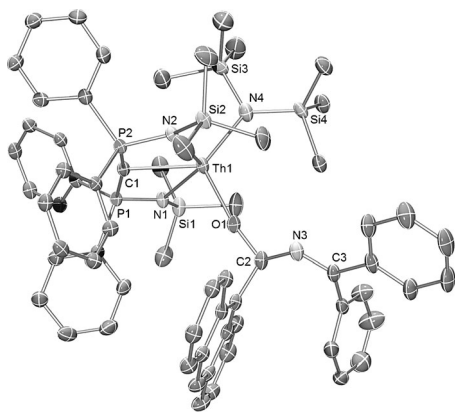


Figure 2. Molecular structure of [Th(BIPM^{TMS}){N(SiMe₃)₂}{OC(H)(NCPH₂)(C₁₄H₉)}] (**3**). Displacement ellipsoids set at 40% probability. Hydrogen atoms, minor disorder components, and toluene solvent molecule in lattice are omitted for clarity. Selected bond lengths [Å]: Th–C1 2.453(4), Th–O 2.166(3),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

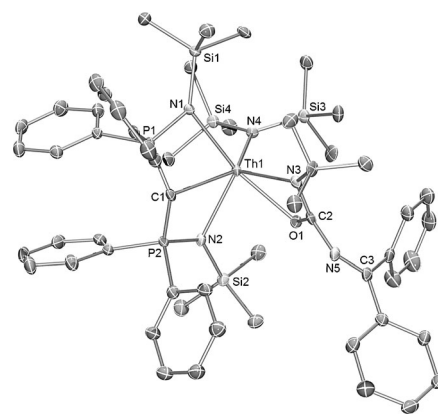


Figure 3. Molecular structure of [Th(BIPM^{TMS}){N(SiMe₃)₂}{OC(N*t*Bu)NCPH₂}] (**4**). Displacement ellipsoids set at 40% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Th–C1 2.463(5), Th–N1 2.531(4), Th–N2 2.483(5), Th–N3 2.491(5), Th–N4 2.344(4), Th–O 2.391(4), O–C2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

Received: May 2, 2014

Revised: June 2, 2014

Published online: July 7, 2014

Keywords: amides · carbenes · ketimides · N ligands · thorium

- [1] a) M. F. Lappert, A. Protchenko, P. Power, A. Seeber, *Metal Amide Chemistry*, Wiley, Hoboken, **2009**; b) J. F. Hartwig in *Organotransition Metal Chemistry. From Bonding to Catalysis*, University Science Books, Sausalito, **2010**, chap. 4.
- [2] For representative works concerning early-transition-metal ketimides, see: a) M. J. Ferreira, A. M. Martins, *Coord. Chem. Rev.* **2006**, *250*, 118, and references therein; b) W. J. Zhang, K. Nomura, *Inorg. Chem.* **2008**, *47*, 6482; c) R. A. D. Soriaga, J. M. Nguyen, T. A. Albright, D. M. Hoffman, *J. Am. Chem. Soc.* **2010**, *132*, 18014.
- [3] a) R. A. Lewis, G. Wu, T. W. Hayton, *J. Am. Chem. Soc.* **2010**, *132*, 12814; b) R. A. Lewis, S. Morochnik, A. Chapovetsky, G. Wu, T. W. Hayton, *Angew. Chem.* **2012**, *124*, 12944; *Angew. Chem. Int. Ed.* **2012**, *51*, 12272; c) L. A. Seaman, G. Wu, N. Edelstein, W. W. Lukens, N. Magnani, T. W. Hayton, *J. Am. Chem. Soc.* **2012**, *134*, 4931; d) R. A. Lewis, S. P. George, A.

- Chapovetsky, G. Wu, J. S. Figueroa, T. W. Hayton, *Chem. Commun.* **2013**, 49, 2888.
- [4] P. L. Diaconescu, C. C. Cummins, *J. Am. Chem. Soc.* **2002**, *124*, 7660.
- [5] a) S. Zhang, W. E. Piers, X. Gao, M. Parvez, *J. Am. Chem. Soc.* **2000**, *122*, 5499; b) D. R. Armstrong, K. W. Henderson, I. Little, C. Jenny, A. R. Kennedy, A. E. McKeown, R. E. Mulvey, *Organometallics* **2000**, *19*, 4369; c) S. Zhang, W. E. Piers, *Organometallics* **2001**, *20*, 2088; d) V. Taberner, T. Guenca, E. Herdtweck, *J. Organomet. Chem.* **2002**, *663*, 173; e) J. Liu, K. Nomura, *Adv. Synth. Catal.* **2007**, *349*, 2235; f) K. Itagaki, K. Nomura, *Macromolecules* **2009**, *42*, 5097; g) K. Nomura, *Dalton Trans.* **2009**, 8811, and references therein.
- [6] a) P. Zhao, J. F. Hartwig, *J. Am. Chem. Soc.* **2005**, *127*, 11618; b) P. Zhao, J. F. Hartwig, *Organometallics* **2008**, *27*, 4749; c) R. A. Lewis, G. Wu, T. W. Hayton, *Inorg. Chem.* **2011**, *50*, 4660; d) R. A. Lewis, D. E. Smiles, J. M. Darmon, C. E. Stieber, G. Wu, T. W. Hayton, *Inorg. Chem.* **2013**, *52*, 8218.
- [7] M. B. Jones, A. J. Gaunt, *Chem. Rev.* **2013**, *113*, 1137.
- [8] For reviews see: Chapter 5 of Ref. [1a], and J. C. Berthet, M. Ephritikhine, *Coord. Chem. Rev.* **1998**, *178–180*, 83.
- [9] The first uranium amide: R. G. Jones, G. Karmas, G. A. Martin, H. Gilman, *J. Am. Chem. Soc.* **1956**, *78*, 4285. The first thorium amide: D. C. Bradley, M. H. Gitlitz, *J. Chem. Soc. A* **1969**, 980.
- [10] Representative examples of actinide amides and their application in catalysis after 2010, see: a) O. Bénard, J. C. Berthet, P. Thuéry, M. Ephritikhine, *Chem. Commun.* **2011**, 47, 9057; b) P. L. Arnold, Z. R. Turner, R. M. Bellabarba, R. P. Tooze, *Chem. Sci.* **2011**, *2*, 77; c) L. A. Seaman, S. Fortier, G. Wu, T. W. Hayton, *Inorg. Chem.* **2011**, *50*, 636; d) B. M. Gardner, W. Lewis, A. J. Blake, S. T. Liddle, *Inorg. Chem.* **2011**, *50*, 9631; e) R. K. Thomson, C. R. Graves, B. L. Scott, J. L. Kiplinger, *Inorg. Chem. Commun.* **2011**, *14*, 1742; f) S. Fortier, J. R. Walensky, G. Wu, T. W. Hayton, *J. Am. Chem. Soc.* **2011**, *133*, 6894; g) E. L. Matson, P. E. Fanwick, S. C. Bart, *Organometallics* **2011**, *30*, 5753; h) B. M. Gardner, J. C. Stewart, A. L. Davis, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 9265; i) H. Yin, A. J. Lewis, U. J. Williams, P. J. Carroll, E. J. Schelter, *Chem. Sci.* **2013**, *4*, 798; j) A. J. Lewis, U. J. Williams, P. J. Carroll, E. J. Schelter, *Inorg. Chem.* **2013**, *52*, 7326; k) S. D. Wöbser, T. J. Marks, *Organometallics* **2013**, *32*, 2517.
- [11] J. L. Kiplinger, D. E. Morris, B. L. Scott, C. J. Burns, *Organometallics* **2002**, *21*, 3073.
- [12] a) K. C. Jantunen, C. J. Burns, I. Csatro-Rodriguez, R. E. Da Re, J. T. Golden, D. E. Morris, B. L. Scott, S. F. L. Taw, J. L. Kiplinger, *Organometallics* **2004**, *23*, 4682; b) M. Silva, M. A. Antunes, M. Dias, Â. Domingos, I. C. dos Santos, J. Marçalo, N. Marques, *Dalton Trans.* **2005**, 3353; c) R. E. Da Re, K. C. Jantunen, J. T. Golden, J. L. Kiplinger, D. E. Morris, *J. Am. Chem. Soc.* **2005**, *127*, 682; d) E. J. Schelter, D. E. Morris, B. L. Scott, J. L. Kiplinger, *Chem. Commun.* **2007**, 1029; e) E. J. Schelter, P. Yang, B. L. Scott, J. D. Thompson, R. L. Martin, P. J. Hay, D. E. Morris, J. L. Kiplinger, *Inorg. Chem.* **2007**, *46*, 7477; f) E. J. Schelter, P. Yang, B. L. Scott, R. E. Da Re, K. C. Jantunen, R. L. Martin, P. J. Hay, D. E. Morris, J. L. Kiplinger, *J. Am. Chem. Soc.* **2007**, *129*, 5139; g) E. J. Schelter, J. M. Veauthier, C. R. Graves, K. D. John, B. L. Scott, J. D. Thompson, J. A. Pool-Davis-Tournear, D. E. Morris, J. L. Kiplinger, *Chem. Eur. J.* **2008**, *14*, 7782; h) C. R. Graves, A. E. Vaughn, E. J. Schelter, B. L. Scott, J. D. Thompson, D. E. Morris, J. L. Kiplinger, *Inorg. Chem.* **2008**, *47*, 11879; i) W. J. Evans, N. A. Siladke, J. W. Ziller, *C. R. Chim.* **2010**, *13*, 775; j) B. L. Scott, J. L. Kiplinger, *J. Chem. Crystallogr.* **2011**, *41*, 1301.
- [13] a) A. E. Clark, R. L. Martin, P. J. Hay, J. C. Green, K. C. Jantunen, J. L. Kiplinger, *J. Phys. Chem. A* **2005**, *109*, 5481; b) D. J. Hilton, R. P. Prasadkumar, E. J. Schelter, V. K. Thorsmølle, S. A. Trugman, A. P. Shreve, J. L. Kiplinger, D. E. Morris, A. J. Taylor, *J. Phys. Chem. A* **2008**, *112*, 7840.
- [14] a) O. J. Cooper, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Dalton Trans.* **2010**, 39, 5074; b) O. J. Cooper, D. P. Mills, J. McMaster, F. Moro, E. S. Davies, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem.* **2011**, *123*, 2431; *Angew. Chem. Int. Ed.* **2011**, *50*, 2383; c) D. P. Mills, F. Moro, J. McMaster, J. van Slageren, W. Lewis, A. J. Blake, S. T. Liddle, *Nat. Chem.* **2011**, *3*, 454; d) D. P. Mills, O. J. Cooper, F. Tuna, E. J. L. McInnes, E. S. Davies, J. McMaster, F. Moro, W. Lewis, A. J. Blake, S. T. Liddle, *J. Am. Chem. Soc.* **2012**, *134*, 10047; e) D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Science* **2012**, *337*, 717; f) D. M. King, F. Tuna, J. McMaster, W. Lewis, A. J. Blake, E. J. L. McInnes, S. T. Liddle, *Angew. Chem.* **2013**, *125*, 5021; *Angew. Chem. Int. Ed.* **2013**, *52*, 4921; g) O. J. Cooper, D. P. Mills, J. McMaster, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake, S. T. Liddle, *Chem. Eur. J.* **2013**, *19*, 7071; h) D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Nat. Chem.* **2013**, *5*, 482; i) M. Gregson, E. Lu, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem.* **2013**, *125*, 13254; *Angew. Chem. Int. Ed.* **2013**, *52*, 13016; j) D. M. King, J. McMaster, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake, S. T. Liddle, *J. Am. Chem. Soc.* **2014**, *136*, 5619; k) B. M. Gardner, G. Balázs, M. Scheer, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem.* **2014**, *126*, 4573; *Angew. Chem. Int. Ed.* **2014**, *53*, 4484; l) O. J. Cooper, D. P. Mills, W. Lewis, A. J. Blake, S. T. Liddle, *Dalton Trans.* **2014**, DOI: 10.1039/c4dt00909f; m) E. Lu, O. J. Cooper, J. McMaster, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem.* **2014**, *126*, 6814; *Angew. Chem. Int. Ed.* **2014**, *53*, 6696.
- [15] The M=C bond in lanthanide and actinide metal carbene complexes bearing bis(iminophosphoran)methane (BIPM) ligands has versatile reactivity, including Wittig-type reactions, C–X (X = H, F, O) bond activation, and cycloadditions, see Ref. [14] and: a) D. P. Mills, L. Soutar, W. Lewis, A. J. Blake, S. T. Liddle, *J. Am. Chem. Soc.* **2010**, *132*, 14379; b) D. P. Mills, W. Lewis, A. J. Blake, S. T. Liddle, *Organometallics* **2013**, *32*, 1239; c) D. P. Mills, L. Soutar, O. J. Cooper, W. Lewis, A. J. Blake, S. T. Liddle, *Organometallics* **2013**, *32*, 1251.
- [16] T. Cantat, B. L. Scott, J. L. Kiplinger, *Chem. Commun.* **2010**, 46, 919.
- [17] See the Supporting Information for details.
- [18] a) T. Cantat, T. Arliguie, A. Noël, P. Thuéry, M. Ephritikhine, P. Le Floch, N. Mézailles, *J. Am. Chem. Soc.* **2009**, *131*, 963; b) J. C. Tourneux, J. C. Berthet, P. Thuéry, N. Mézailles, P. Le Floch, M. Ephritikhine, *Dalton Trans.* **2010**, 39, 2494; c) J. C. Tourneux, J. C. Berthet, T. Cantat, P. Thuéry, N. Mézailles, P. Le Floch, M. Ephritikhine, *Organometallics* **2011**, *30*, 2957; d) J. C. Tourneux, J. C. Berthet, T. Cantat, P. Thuéry, N. Mézailles, M. Ephritikhine, *J. Am. Chem. Soc.* **2011**, *133*, 6162; e) M. Ephritikhine, *C. R. Chim.* **2013**, *16*, 391.
- [19] a) G. Ma, M. J. Ferguson, R. McDonald, R. G. Cavell, *Inorg. Chem.* **2011**, *50*, 6500; b) W. S. Ren, X. B. Deng, G. F. Zi, D. C. Fang, *Dalton Trans.* **2011**, 40, 9662.
- [20] L. A. Seaman, J. R. Walensky, G. Wu, T. W. Hayton, *Inorg. Chem.* **2013**, *52*, 3556.
- [21] a) G. Chandra, A. D. Jenkins, M. F. Lappert, R. C. Srivastava, *J. Chem. Soc. A* **1970**, 2550; b) P. Braunstein, D. Nobel, *Chem. Rev.* **1989**, *89*, 1927; c) D. A. Gatley, J. R. Norton, P. A. Goodson, *J. Am. Chem. Soc.* **1995**, *117*, 986; d) H. P. Wang, H. W. Li, Z. W. Xie, *Organometallics* **2003**, *22*, 4522; e) K. C. Hsieh, W. Y. Lee, C. L. Lai, C. H. Hu, H. M. Lee, J. H. Huang, S. M. Peng, G. H. Lee, *J. Organomet. Chem.* **2004**, *689*, 3362; f) B. D. Ward, G. Orde, E. Clot, A. R. Cowley, L. H. Gade, P. Mountford, *Organometallics* **2005**, *24*, 2368; g) L. G. Alves, A. M. Martins, *Inorg. Chem.* **2012**, *51*, 10.