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Donor–Acceptor Systems

Experimental and Computational Studies on the Formation of Thorium–Copper Heterobimetallics

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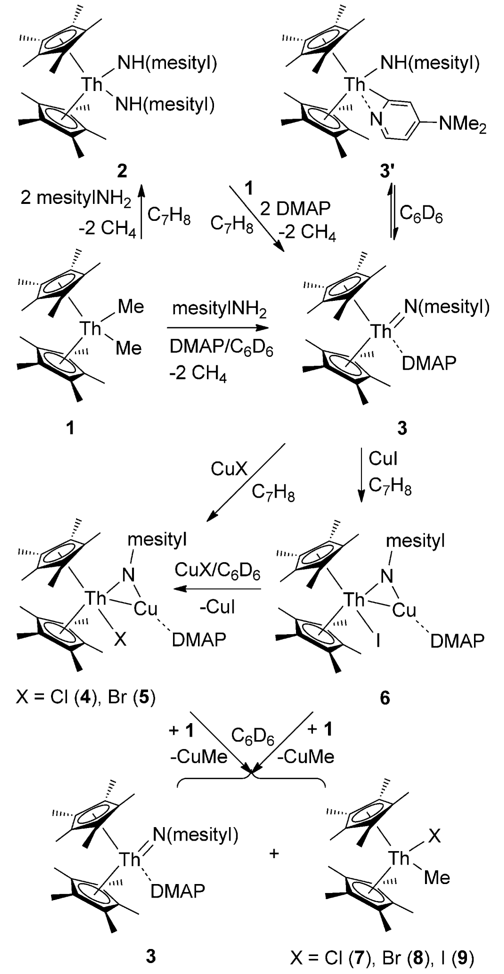
Abstract: The formation of actinide–transition metal heterobimetallics mediated by a terminal actinide imido complex was comprehensively studied. The reaction of the thorium imido complex [(η^5-C_5Me_5)$_2$Th=N(mesityl)(DMAP)] (**3**), prepared from [(η^5-C_5Me_5)$_2$ThMe$_2$] (**1**) and mesitylNH$_2$ or [(η^5-C_5Me_5)$_2$Th(NHmesityl)$_2$] (**2**) in the presence of 4-(dimethylamino)pyridine (DMAP), with copper(I) halides gave the first thorium–copper heterobimetallic compounds [(η^5-C_5Me_5)$_2$Th(X){N(mesityl)Cu(DMAP)}] (X = Cl (**4**), Br (**5**), I (**6**)). Complexes **4**–**6** feature an unusual geometry with a short Th–Cu distance, which DFT studies attribute to a weak donor–acceptor bond from the Cu^+ atom to the electropositive Th^{4+} atom. They are reactive species, as was shown by their reaction with the dimethyl complex [(η^5-C_5Me_5)$_2$ThMe$_2$] (**1**). Furthermore, a comparison between Th and early transition metals confirmed that Th^{4+} exhibits distinctively different reactivity from d-transition metals.

Uranium imido compounds are well studied,[1–3] whereas the related thorium species are still an area in its infancy, and only a few examples of structurally well-characterized representatives are known.[3j,4] The electronic ground state of Th is [Rn] $6d^27s^2$, which resembles those observed for early transition metals, such as Sc, Ti, Zr, and Hf for which several complexes with M=N bonds are known.[5,6] Because of their similar electronic ground state comparable reactivity to those of early transition metals might be envisioned, which also addresses the question whether 5f orbitals actively participate in the bonding of organothorium compounds.[7] To answer this question, a base-free terminal thorium imido complex [η^5-1,2,4-$(Me_3C)_3C_5H_2$]$_2$Th = N(*p*-tolyl) was prepared that readily reacted with various small molecules ranging from elemental sulfur (S_8) and selenium (Se), silanes, borane, internal acetylenes, nitriles, ketones, CS_2, isothiocyanates, carbodiimides, to organic azides and diazoalkane derivatives.[8] Encouraged by this broad spectrum of different substrates, we have set out to probe the reactivity of actinide imido species in the construction of actinide–transition metal bonds. Herein, we detail the preparation of the thorium imido species [(η^5-C_5Me_5)$_2$Th = N(mesityl)(DMAP)] (**3**) and its reactivity toward copper(I) halides to form heterobimetallic thorium–copper compounds.

Reaction of [(η^5-C_5Me_5)$_2$ThMe$_2$] (**1**) with two equivalents of mesitylNH$_2$ in toluene gave the bis(anilido) metallocene [(η^5-C_5Me_5)$_2$Th(NHmesityl)$_2$] (**2**) in good yield (Scheme 1). Its molec-



Scheme 1. Synthesis of complexes **2**–**9**.

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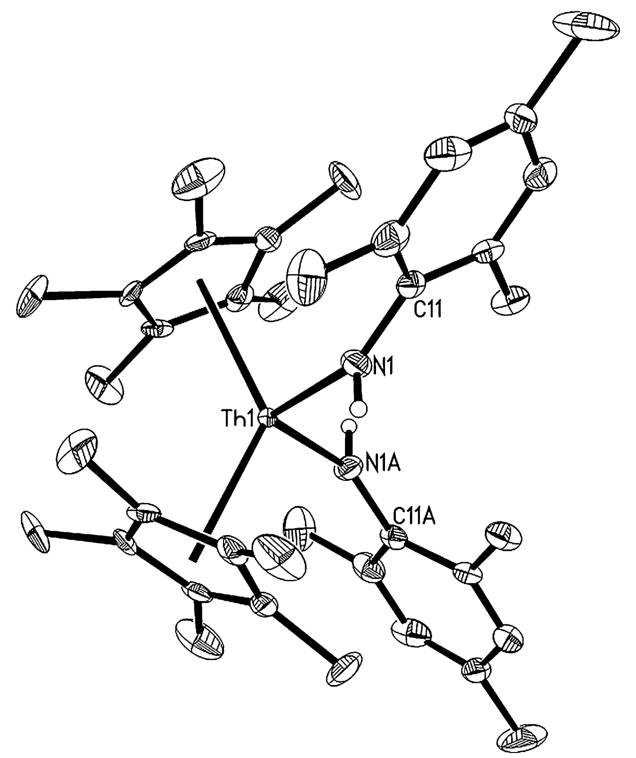

Figure 1. Molecular structure of **2** (thermal ellipsoids are drawn at the 35 % probability level).

ular structure is shown in Figure 1. The Th^{4+} ion is η^5-bound to two C_5Me_5 ligands and σ-coordinates to the nitrogen atoms of the two anilido groups mesitylNH in a distorted-tetrahedral geometry with an average Th–C(ring) distance of 2.825(13) Å and the Cp(cent)-Th-Cp(cent) angle of 130.9(6)° and the N(1)-Th-N(2) angle of 115.3(6)°. The average Th–N distance of 2.344(12) Å is significantly longer than that found in $[(\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2)_2Th(HNMe)_2]$ (2.241(4) Å), but comparable to that observed in $[(\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2)_2Th(HN\text{-}p\text{-tolyl})_2]$ (2.283(3) Å),[8b] which presumably reflects the increased steric hindrance of the $mesitylNH^-$ group. Therefore, complex **2** should also be more reactive than the less sterically encumbered bis(amido) compound $[(\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2)_2Th(HNMe)_2]$,[8b] which was confirmed by the thermal decomposition of **2** at approximately 150 °C (see the Supporting Information for details). Furthermore, in contrast to the reaction of $[(\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2)_2Th(HNMe)_2]$ with $[(\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2)_2ThMe_2]$,[8b] treatment of **2** with one equivalent of $[(\eta^5\text{-}C_5Me_5)_2ThMe_2]$ (**1**) at 50 °C in the presence of 4-(dimethylamino)pyridine (DMAP) gave the thorium imido $[(\eta^5\text{-}C_5Me_5)_2Th{=}N(mesityl)(DMAP)]$ (**3**; Scheme 1) for which an equilibrium between imido **3** and the amido pyridyl complex $[(\eta^5\text{-}C_5Me_5)_2ThNH(mesityl)(\eta^2\text{-}C,N\text{-}4\text{-}Me_2NC_5H_3N)]$ (**3′**) exists in C_6D_6 solution at ambient temperature. The equilibrium constant (K_{eq}) at 298 K between **3** and **3′** determined by ^1H NMR spectroscopy is 1.0. Alternatively, **3** is also accessible from the reaction of $[(\eta^5\text{-}C_5Me_5)_2ThMe_2]$ (**1**) with one equivalent of mesitylNH$_2$ in the presence of DMAP (Scheme 1).

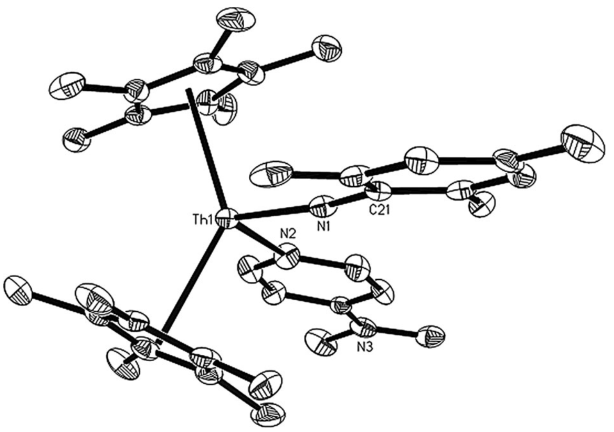

Figure 2. Molecular structure of **3** (thermal ellipsoids are drawn at the 35 % probability level).

The solid-state crystal structure of **3** is presented in Figure 2. The short Th–N(1) distance of 2.091(7) Å and the approximately linear Th-*N*-C angle (167.2(6)°) are consistent with a Th=N double bond.[9] These values agree favorably with those found in the related $[(\eta^5\text{-}C_5Me_5)_2Th{=}N(2,6\text{-}Me_2C_6H_3)(THF)]$ (d(Th–N) = 2.045(8) Å, $\sphericalangle$(Th-*N*-C) = 171.5(7)°)[4a] and with those observed for $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th{=}N(p\text{-tolyl})$ (d(Th–N) = 2.038(3) Å, $\sphericalangle$(Th-*N*-C) = 172.8(3)°).[8b] The relatively long Th–N(2) distance of 2.554(7) Å is consistent with a datively coordinated nitrogen atom, and it can be compared to that observed in $[(\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2)_2Th(O)(DMAP)]$ (2.587(5) Å).[8a] A DFT study reveals that the thorium–nitrogen double bond (Th=N) in **3** is strongly polarized and more adequately described as $Th^+–N^-$ (see the Supporting Information for details).

Based on the electronic structure of the moiety Th=N(mesityl) (for details, see the Supporting Information), significant reactivity toward electrophiles or Lewis acids can be expected. But although the reaction of the related uranium(IV) imido complexes with copper(I) halides induces an one-electron oxidation to U^V,[3o,p] addition of one equivalent of copper(I) halides (CuX) to the thorium imido moiety of **3** gave the thorium–copper heterobimetallic compounds $[(\eta^5\text{-}C_5Me_5)_2Th(X)\{N(mesityl)Cu(DMAP)\}]$ (X = Cl (**4**), Br (**5**), I (**6**)) in quantitative conversions (Scheme 1). DFT investigations suggest that the DMAP initially dissociates from **3** to give the imido intermediate **INTa** (Figure 3). In a next step, the Th=N functionality coordinates to the Cu atom of CuI, forming the intermediate **INTb**. Finally, an intermolecular nucleophilic attack between **INTb** and DMAP occurs to give the product **6** via the transition state **TS**, in which N(DMAP)–Cu and Cu–I distances are 3.559 and 2.489 Å, respectively. The N–Cu bond is formed, whereas the Cu–I bond is simultaneously broken, and the resulting I^- anion migrates to the Th atom to create a Th–I bond. Although the formation of the intermediate **INTb** is exergonic with ΔG(298 K) = −151.3 kJ mol^{-1}, the final product **6** is thermodynamically much more stable (ΔG(298 K) = −191.0 kJ mol^{-1}). In addition, the activation barrier to form **6** from intermediate **INTb** is only 12.9 kJ mol^{-1}, which accounts for the short lifetime of the non-isolable intermediate **INTb**,

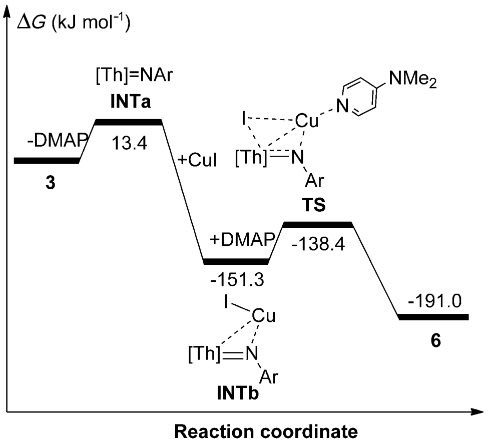

Figure 3. Free-energy profile [kJ mol^{-1}] for the reaction of **3** + CuI ([Th] = (η^5-C_5Me_5)Th; and Ar = 2,4,6-$Me_3C_6H_2$).

and only the final product **6** was detected by NMR spectroscopy. Reaction of CuI was also observed for scandium imido complexes, in which the Sc=N functionality coordinates to the Cu atom of CuI, forming scandium-copper-iodide (Sc-Cu-I) heterobimetallics.[5e] However, in contrast to the imido scandium compounds,[5e] the reaction of **3** with CuI yields a heterobimetallic iodo-thorium-copper (I-Th-Cu) complex **6** along with a complete cleavage of the Cu–I bond, as a consequence of the polarized Th^+–N^- bond. Moreover, halogen-atom exchange can be achieved upon addition of CuCl or CuBr to **6** to give compounds **4** and **5**, respectively, in quantitative conversions (Scheme 1).

The solid-state crystal structure of **6** is shown in Figure 4, whereas the molecular structures of **4** and **5** are provided in the Supporting Information. To the best of our knowledge, complexes **4**–**6** represent the first structurally characterized thorium–copper heterobimetallics, and the related uranium–copper species, [(Ph_3P)Cu(μ-SPh)$_3$U(μ-SPh)$_3$Cu(PPh_3)],[10b] is the only other reported heterobimetallic actinide–copper representative. The Th–N(1) distances (2.168(5)–2.178(9) Å) are slightly longer than the Th=N double bond in the imido complex **3** (2.091(7) Å), but much shorter than the Th–N single bond in the bis(anilido) complex **2** (2.344(12) Å). The Th-*N*-C angles of 143.9(4)-145.3(4)° significantly deviate from linearity in comparison to the Th-*N*-C angle observed in **3** (167.2(6)°), and are close to the Th-*N*-C angle in **2** (144.4(9)°). The Th–X distances of 2.727(1) Å (for Cl), 2.885(2) Å (for Br), and 3.120(1) Å (for I) are slightly longer than the average Th–X distances found in the related bis-halido complexes [(η^5-1,3-(Me_3C)$_2C_5H_3$)$_2ThCl_2$] (2.632(1) Å),[8b] [(η^5-1,2,4-(Me_3C)$_3C_5H_2$)$_2ThCl_2$] (2.621(1) Å),[8b] [(η^5-C_5Me_5)$_2ThBr_2$] (2.800(2) Å),[11] [(η^5-1,3-(Me_3C)$_2C_5H_3$)$_2ThBr_2$] (2.794(1) Å),[12] [(η^5-1,2,4-(Me_3C)$_3C_5H_2$)$_2ThBr_2$] (2.785(1) Å),[8c] [(η^5-C_5Me_5)$_2ThI_2$] (2.986(2) Å)[13] and [(η^5-1,3-(Me_3C)$_2C_5H_3$)$_2ThI_2$] (3.035(1) Å),[12] presumably due to the steric demand of the chelating imido ligand. In contrast, the Cu–N(1) distances of 1.874(4)–1.889(5) Å are virtually identical within the statistical uncertainties to the Cu–N(2) distances of 1.889(10)-1.894(5) Å, whereas the N(1)-Cu-N(2) angles of 172.9(2)-175.2(2)° deviate slightly from linearity. Furthermore, the Th–Cu distances of 3.140(1)–3.171(1) Å are significantly shorter than the sum of their covalent radii (3.38 Å; the covalent radii of Th 2.06 Å, Cu 1.32 Å),[14] but they are longer than the U–Cu distance (3.05(1) Å) in the related uranium–copper compound [(Ph_3P)Cu(μ-SPh)$_3$U(μ-SPh)$_3$Cu(PPh_3)][10b] attributed to the larger covalent radius of the Th atom (the covalent radii of Th 2.06 Å, U 1.96 Å).[14] Short thorium–transition metal bond lengths are also observed in other examples, such as [(η^5-C_5H_5)$_3$ThFe(η^5-C_5H_5)(CO)$_2$] (Th–Fe 2.940(5) Å),[10a] [(η^5-C_5Me_5)$_2$Th(μ-PPh_2)$_2$Pt(PMe_3)] (Th–Pt 2.984(1) Å),[10n] [(η^5-C_5Me_5)$_2$Th(μ-PPh_2)$_2$Ni(CO)$_2$] (Th–Ni 3.206(2) Å),[10m] [(η^5-C_5Me_5)$_2$Th(I)Ru(η^5-C_5H_5)(CO)$_2$] (Th–Ru 3.0277(6) Å)[10] and [(N(*o*-(NCH_2P*i*Pr_2)C_6H_4)$_3$)ThCo(CO)$_3$] (Th–Co 3.0771(5) Å).[10h] DFT studies revealed that the Wiberg bond order of Th–N in **6** (1.08) is smaller than that in **3** (1.24), and the Wiberg bond order of Cu–N(1) is 0.28, indicating that the Cu^+ atom moderates the donation of electron density from the imido ligand to the Th^{4+} atom. These computations also showed some overlap between an empty Th^{IV} orbital and the filled Cu^I 3d orbitals (see the Supporting Information for details), resulting in a computed Th–Cu Wiberg bond order of 0.30. Therefore, electron density of the Cu^I atom is partially donated to the electropositive Th^{IV} atom, and therefore, the interaction between thorium and copper is best described as a weak donor–acceptor bond $Cu^I \rightarrow Th^{IV}$. Nevertheless, no bond critical point (BCP) was traced between the Cu and Th atoms by a Bader analysis (see the Supporting Information for details), as a consequence only a weak interaction between Th^{IV} and Cu^I atoms can be assumed. Initial reactivity studies also confirmed this proposition, since degradation is observed when complexes **4**–**6** are treated with [(η^5-C_5Me_5)$_2ThMe_2$] (**1**), forming the thorium imido **3** and thorium methyl halido (η^5-C_5Me_5)$_2$Th(Me)X (X = Cl (**7**), Br (**8**), I (**9**)) accompanied by the loss of methyl copper (CuMe) (Scheme 1). The latter decomposes to copper metal (Cu) and ethane (CH_3CH_3) (for details, see the Supporting Information).

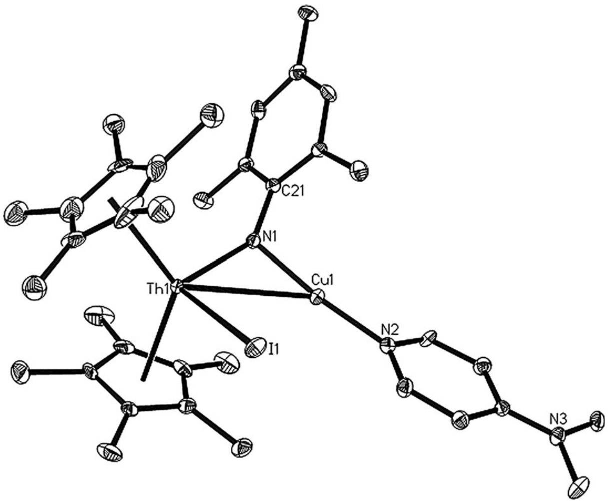

Figure 4. Molecular structure of **6** (thermal ellipsoids are drawn at the 35 % probability level).

In conclusion, in contrast to the reactivity of the uranium[3o,p] and scandium[5e] imides, addition of CuX to the thorium imido

[(η^5-C_5Me_5)$_2$Th=N(mesityl)(DMAP)] (**3**) cleaves the Cu–X bond and forms the heterobimetallic thorium–copper compounds [(η^5-C_5Me_5)$_2$Th(X){N(mesityl)Cu(DMAP)}] (X = Cl (**4**), Br (**5**), I (**6**)). For the reaction of uranium(IV) imido complexes with copper halides, oxidation of U^{IV} to U^{V} was observed,[3o,p] but this change in oxidation states is not possible for Th^{IV}. Nevertheless, the reactivity difference to early transition metals can be rationalized by a more polarized Th^{+}–N^{-} bond, supporting the notion that Th^{4+} belongs to the actinide metals rather than the d transition metals.[7c] Furthermore, DFT studies attributed the short Th–Cu bond lengths in the thorium–copper complexes to a weak donor–acceptor interaction between the electron-rich Cu^{I} and the electropositive Th^{IV} atoms, and therefore, the thorium–copper bimetallics are reactive compounds, as was illustrated by their reaction with the thorium dimethyl compound [(η^5-C_5Me_5)$_2$ThMe$_2$] (**1**). The preparation of new actinide imido complexes and the exploration of the intrinsic reactivity of heterobimetallic thorium–transition metal compounds are ongoing projects in our laboratories.

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Keywords: copper · heterometallic complexes · imido complexes · thorium · thorium–copper bond

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COMMUNICATION

Donor–Acceptor Systems

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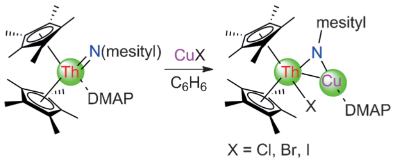
Experimental and Computational Studies on the Formation of Thorium–Copper Heterobimetallics



Time for thorium! Experimental and computational studies revealed that the thorium–copper bond is best described as a weak donor–acceptor interaction between the electron-rich Cu^{I} and the electropositive Th^{IV} atoms (see scheme).