Cyclotrimerization

Lanthanide–Imido Complexes and Their Reactions with Benzonitrile**

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Transition-metal–imido complexes have received much current interest because of the ability of the M=N group to undergo a wide range of reactions[1] such as metathesis of imines, aldehydes, and carbodiimides,[2] metallacycle formation with alkenes and alkynes,[3] hydroamination of alkynes and allenes,[4] and C–H bond activation.[5] In contrast to the extensive studies on the rich chemistry of transition-metal–imido complexes, reports on well-defined lanthanide–imido complexes are scarce[6] and the reactions of lanthanide–imido complexes have remained almost unexplored to date. This is mainly due to the lack of suitable complexes for reactivity studies.[7]

During our recent studies on lanthanide–polyhydrido complexes,[8] we found that reactions of the tetranuclear lanthanide polyhydrido complexes $[\{Cp'Ln(\mu\text{-}H)_2\}_4(thf)]$

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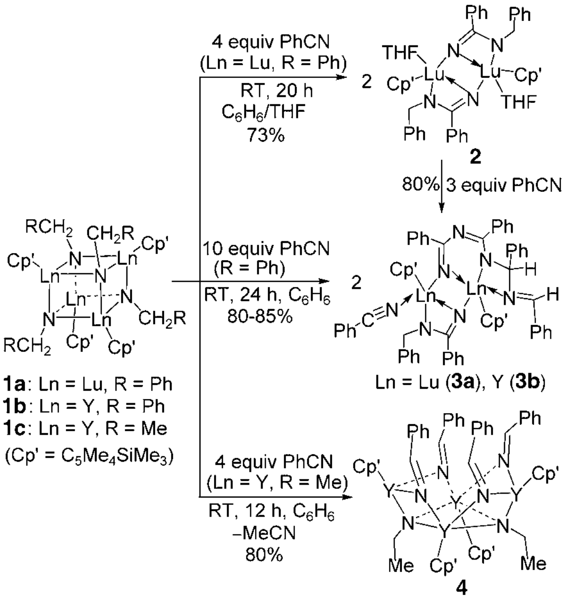
[**] This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 14078224, "Reaction Control of Dynamic Complexes") from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. We are also grateful to the Japan Society for the Promotion of Science (JSPS) for a Postdoctoral Fellowship for D.C.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200461939

($Cp' = \eta^5$-$C_5Me_4SiMe_3$; Ln = Lu, Y) with nitriles RCN can offer a convenient route to the corresponding imido complexes [{Cp′Ln(μ_3-NCH_2R)}$_4$] by double addition of the Ln–H units across the C≡N bond.[8a] The imido species formed in this way have a methylene substituent at the N atom and adopt a novel Ln_4N_4 cubane core structure with μ_3-N-Ln bridges, a structural feature that has not been observed previously. Here we report that this new class of imido complexes can show unprecedented reactivity. They not only exhibit strong nucleophilicity but can also transfer α-hydrogen atoms.

Reaction of benzylimido–lutetium complex [{Cp′Lu(μ_3-NCH_2Ph)}$_4$] (**1a**) with 4 equivalents of benzonitrile at room temperature in toluene gave the benzamidinate dianion complex **2** in 73% yield after recrystallization from THF (Scheme 1).[9] X-ray analysis showed that **2** has a dimeric structure (Figure 1) in which the two Lu atoms are bridged by the ketimido nitrogen atom (Lu–N 2.149(4), 2.326(4) Å), and the amido nitrogen atom is bonded terminally to one Lu atom (Lu–N 2.352(4) Å). The formation of **2** apparently proceeded by nucleophilic addition of the imido unit to the C≡N group of benzonitrile, which demonstrates that a lanthanide–imido bond, even in a bridging form, is very reactive. This is in contrast with what was observed previously for bonds between transition metals and bridging imido ligands, which are usually robust and unreactive.[1–5] Moreover, the resultant product **2** represents the first metal complex of an amidinate dianion, in contrast to the well-known complexes of various metals with amidinate monoanions $[RNC(R')NR]^-$ as ligands.[10]



Scheme 1. Nucleophilic addition and hydrogen transfer of lanthanide–imido complexes to benzonitrile.

Interestingly, the reaction of the ethylimido complex [{Cp′Y(μ_3-NCH_2CH_3)}$_4$] (**1c**) with benzonitrile did not afford an insertion product, but instead gave the mixed benzaldiminato/ethylimido complex **4** (Scheme 1). X-ray analysis established that **4** adopts a tetranuclear crownlike core structure, in which the four Y atoms are unsymmetrically bridged by four μ_2-benzaldiminato and two μ_3-ethylimido ligands (Y–N(μ_2-iminato) 2.298(7)–2.532(7) Å, Y–N(μ_3-imido) 2.116(6)–2.418(6) Å, mean C–N(iminato) 1.248(10) Å, mean C–N(imido) 1.473(7) Å; Figure 1). In this reaction, four molecules of benzonitrile were hydrogenated to give four benzaldiminato species by abstraction of four methylene hydrogen atoms from two of the four ethylimido units in **1c** with the release of two molecules of acetonitrile, while the other two ethylimido units remained unchanged. Such formation of an iminato species through hydrogen transfer from an imido species to a nitrile is, as far as we are aware, unprecedented.

When 10 equivalents of benzonitrile were allowed to react with the benzylimido complexes **1a** and **1b**, the benzonitrile tetramerization products **3a** and **3b** were obtained, respectively (Scheme 1). The reaction of the benzamidinate dianion complex **2** with 3 equivalents of benzonitrile also afforded **3a** in high yield, and this suggests that **2** is an intermediate in the formation of **3a** from **1a**. The structures of **3a** and **3b** were confirmed by X-ray analysis (Figure 1).

Although the formation of **2** from **1a** is straightforward, the formation of **3a** from **2** apparently requires both the insertion of two molecules of benzonitrile into a Lu–amido bond in **2** and hydrogen transfer from the methylene group to the two incoming benzonitrile molecules. The formation of **3a**

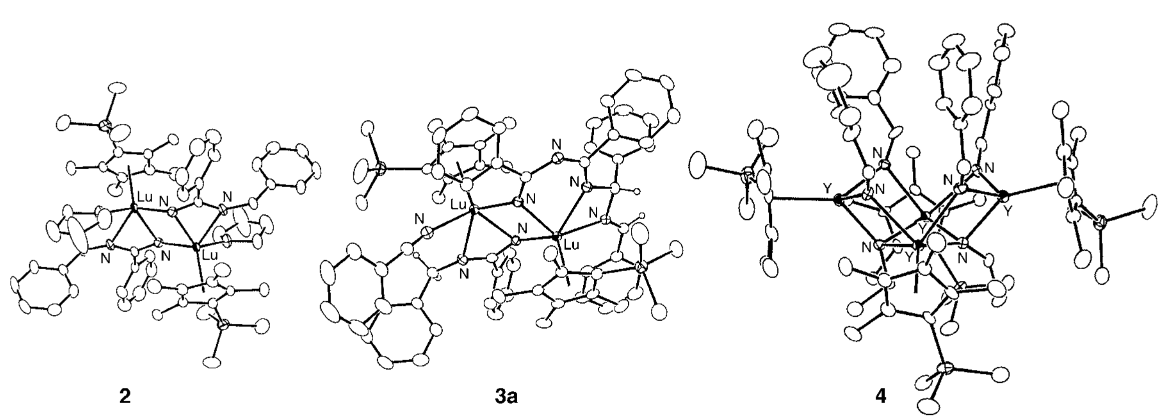
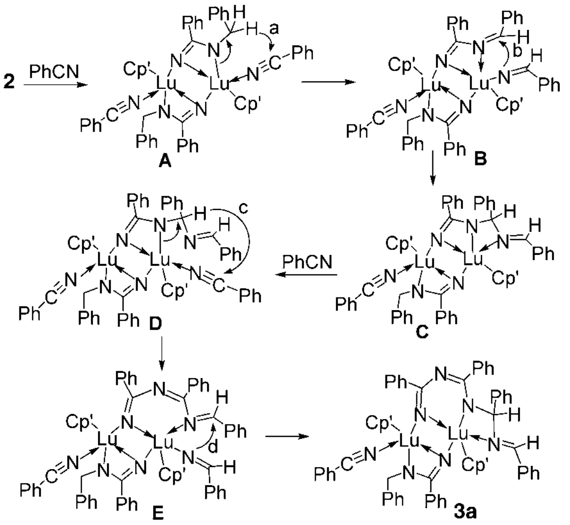


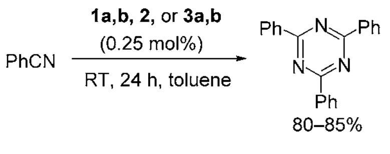
Figure 1. X-ray crystal structures of **2**, **3a**, and **4** with 30% probability ellipsoids. Hydrogen atoms and lattice solvent molecules are omitted for clarity.

from **2** could be explained by the reaction steps shown in Scheme 2. The coordination of one molecule of benzonitrile to each Lu atom in **2** should yield **A**. Hydrogen transfer from a methylene group to coordinated PhCN in **A** (step a)[11] should afford **B**. Nucleophilic addition of the newly formed benzaldiminato unit to the aldimine group (step b) could yield **C**, which on coordination of one molecule of PhCN gives **D**. Migration of the methine hydrogen atom to the PhCN unit in **D** (step c) followed by addition of the resulting aldiminato unit to the aldimine group in **E** (step d) should give **3a**.



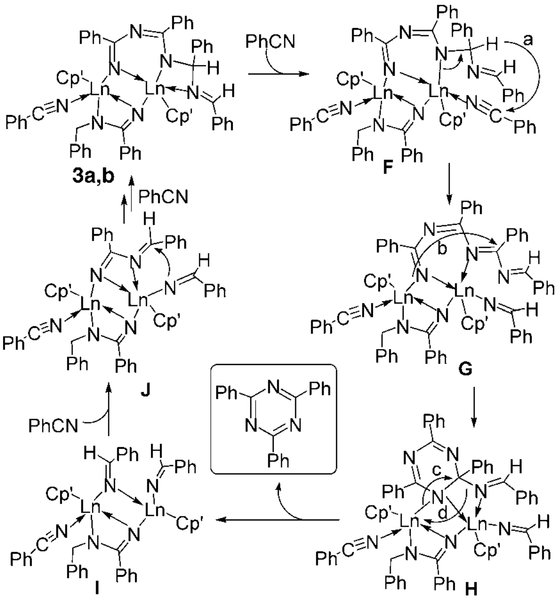
Scheme 2. Possible mechanism for the formation of **3a**.

It is also noteworthy that only one of the two benzamidinate dianion units in **2** formally participated in the reaction with benzonitrile. No reaction was observed between the remaining benzamidinate dianion unit and the benzonitrile ligand in **3a** or **3b** even at elevated temperatures (80 °C). Surprisingly to us, when an excess of benzonitrile was added to a solution of **3a** or **3b** in toluene, the benzonitrile cyclotrimerization product 2,4,6-triphenyl-1,3,5-triazine was formed selectively, while **3a** (or **3b**) was recovered. The polyhydrido complexes [{Cp'Ln(μ-H)$_2$}$_4$(thf)] **1a** and **1b** and benzamidinate dianion complex **2** also showed similar catalytic activity for the cyclotrimerization of benzonitrile (Scheme 3). Here, the formation of **3a** (or **3b**) was also observed after completion of the reaction which strongly suggests that **3a** (or **3b**) is the true catalytic species. The formation of 2,4,6-triphenyl-1,3,5-triazine, a cyclic benzonitrile trimer, from **3a** or **3b** (containing a linear benzonitrile tetramer as a ligand) clearly must involve both cyclization (intramolecular C–N bond formation) and C–N bond cleavage.



Scheme 3. Catalytic cyclotrimerization of benzonitrile.

A possible mechanism for the catalytic cyclotrimerization of benzonitrile by **3a** or **3b** is shown in Scheme 4. The coordination of one molecule of benzonitrile to a metal center in **3a** or **3b** could give **F**. Methine hydrogen transfer (step a) to coordinated benzonitrile would afford **G**. Intramolecular nucleophilic addition of the amido unit to the newly formed imine moiety (step b) could yield **H**. Aromatization of the resultant six-membered ring in **H** through step c (Ln–N bond cleavage and C=N bond formation) and step d (C–N bond cleavage and Ln–N bond formation) should release the triazine and generate **I**. An insertion of benzonitrile into **I** would give **J**, which resembles intermediate **B** in Scheme 2, and could regenerate **3a** or **3b** as described above.



Scheme 4. Possible mechanism for the catalytic cyclotrimerization of benzonitrile.

In summary, tetranuclear μ$_3$-N-bridged lanthanide–imido complexes **1a–c** undergo not only nucleophilic addition but also hydrogen-transfer reactions with benzonitrile to afford a new series of structurally characterizable multinuclear lanthanide complexes **2–4** that have novel structures. The combination of C–N bond-formation, hydrogen-transfer, and C–N bond-cleavage steps constitutes a unique catalytic cycle for the cyclotrimerization of benzonitrile.[12] This work demonstrates for the first time that lanthanide–imido complexes can show rich and unique chemistry that differs from that of d-block transition metal analogues.

Received: September 10, 2004

Keywords: cyclotrimerization · hydrogen transfer · lanthanides · N ligands · nitriles

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[7] The deprotonation approaches used successfully for the generation of transition-metal–imido species[1–5] did not seem to work well for the analogous lanthanide–imido complexes.[6] When main group metal–alkyl compounds, such as RLi or AlR_3, were used as a base to deprotonate primary amido–lanthanide complexes, the main group metal ions were often incorporated into the resultant imido products.[6c,d]

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