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COMMUNICATION

Rare-earth metal-mediated addition/cyclization of the 2-cyanobenzoamino anion†

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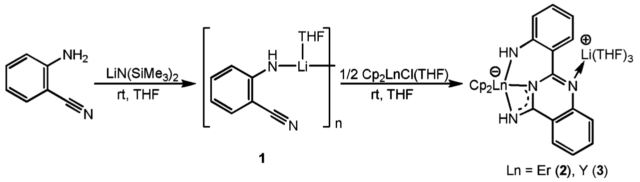
Reaction of two equiv of $[2\text{-NCC}_6\text{H}_4\text{HNLi(THF)}]_n$ (1) with $\text{Cp}_2\text{LnCl(THF)}$ yields the heterobimetallic complexes $\text{Cp}_2\text{Ln}[\kappa^3\text{-(4-NH}{=}(\text{C}_8\text{N}_2\text{H}_4)(2\text{-NHC}_6\text{H}_4)]\text{Li(THF)}_3$ (Cp = C_5H_5; Ln = Er (2), Y(3)), indicating an organolanthanide-mediated nucleophilic addition/cyclization of the 2-cyanobenzoamino anion to construct the 4-iminoquinazolinate dianionic ligand.

There is fundamental interest in the reactivity of organolanthanide complexes with unsaturated organic small molecules, because this is the source for developing new catalytic reactions and catalysts.[1–3] Many efforts have focused on a detailed understanding of the insertion of these organic small molecules into lanthanide–ligand bonds over the last decade.[4–8] However, little is known about the functional substituent participation reaction, when insertion occurs on the lanthanide–ligand bonds of organolanthanide complexes containing the functional substituent ligands. Recently, our interest has been focused on the investigation of the addition of the N–H bonds of organolanthanide derivatives to some unsaturated organic small molecules to construct a novel neutral or anionic ligand or an *N*-heterocyclic skeleton.[9,10] As part of this program, we investigated the reaction of $\text{Cp}_2\text{LnN}^i\text{Pr}_2$ with anthranilonitrile, and found an organolanthanide-mediated intermolecular nucleophilic addition/cyclization of anthranilonitrile to construct the 4-aminoquinazolinate anionic ligand $[\kappa^3\text{-(4-NH(C}_8\text{N}_2\text{H}_4)(2\text{-NH}_2\text{C}_6\text{H}_4)]^-$.[10] In this reaction, we suggested that the intermediate $\text{Cp}_2\text{LnN(H)C}_6\text{H}_4\text{CN-2}$ (**I**) is formed by the protonolysis of the diisopropylamine ligand by one anthranilonitrile molecule. To obtain this intermediate, we synthesized $2\text{-NCC}_6\text{H}_4\text{HNLi}$ by the reaction of $\text{LiN(SiMe}_3)_2$ with anthranilonitrile, and investigated its reactivity with $\text{Cp}_2\text{LnCl(THF)}$ (Ln = Er, Y). A novel rare-earth metal-mediated nucleophilic addition/cyclization of 2-cyanobenzoamino anion has been observed for the construction of the 4-iminoquinazolinate dianionic ligand $[\kappa^3\text{-(4-NH}{=}(\text{C}_8\text{N}_2\text{H}_4)(2\text{-NHC}_6\text{H}_4)]^{2-}$. This reaction process is different from the aforementioned reaction.[10] Herein we wish to report these results.

Treatment of $\text{LiN(SiMe}_3)_2$ with one equiv of anthranilonitrile in THF at room temperature gave the expected lithium amide $[2\text{-NCC}_6\text{H}_4\text{HNLi(THF)}]_n$ (**1**) in almost quantitative yield, as shown in Scheme 1. The reactions of **1** with another equiv of $\text{LiN(SiMe}_3)_2$ or excess of $\text{LiN(SiMe}_3)_2$ with anthranilonitrile only afforded **1**. No further insertion of $\text{LiN(SiMe}_3)_2$ into the C≡N triple bond of the residual cyano group of **1** was observed during these reactions. This is significantly different from those found in the reaction of $\text{LiN(SiMe}_3)_2$ with benzonitrile, where $\text{LiN(SiMe}_3)_2$ insertion into the N≡C triple bond of the nitrile group accompanies a 1,3 silyl shift to yield the corresponding amidinate lithium,[11] an important precursor for preparation of organometallic amidinate complexes. This might be attributed to the different reactivity of benzonitrile and anthranilonitrile.[11c,d] It should be noted that the reaction of *n*-butyllithium with anthranilonitrile under the similar conditions was complicated, no pure compound **1** was isolated.



Scheme 1 Synthesis of complexes **1–3**.

With **1** in hand, we decided to explore its reactivity toward lanthanocene chlorides. Reaction of $\text{Cp}_2\text{LnCl(THF)}$ with two equiv of **1** in THF at room temperature afforded the isolated and structural characterized complexes $\text{Cp}_2\text{Ln}[\kappa^3\text{-(4-NH}{=}(\text{C}_8\text{N}_2\text{H}_4)(2\text{-NHC}_6\text{H}_4)]\text{Li(THF)}_3$ (Ln = Er (**2**), Y(**3**)) in 76% and 81% isolated yield, respectively, as shown in Scheme 1. Structural analysis results revealed that a novel 4-iminoquinazolinate dianionic ligand $[\kappa^3\text{-(4-NH}{=}(\text{C}_8\text{N}_2\text{H}_4)(2\text{-NHC}_6\text{H}_4)]^{2-}$ is formed. We also investigated the reaction of $\text{Cp}_2\text{LnCl(THF)}$ with one equiv of **1** under the same conditions, and could not obtain the intermediate **I** or lanthanide benzopyrazolate complexes $\text{Cp}_2\text{Ln}[\text{C}_7\text{H}_5\text{N}_2]$, an intramolecular addition/cyclization product, but only isolated **2** and **3** in lower yields. These results indicated that the cyano group of **I** favours further nucleophilic addition with another molecule of **1**.

A proposed process for the formation of **2–3** is illustrated in Scheme 2. The first step is a salt-metathesis of Cp_2LnCl with **1** to generate the intermediate **I**. Further the adjacent nitrile group of **I** inserts into the Li–N bond of another molecule of **1**, to give **A**,

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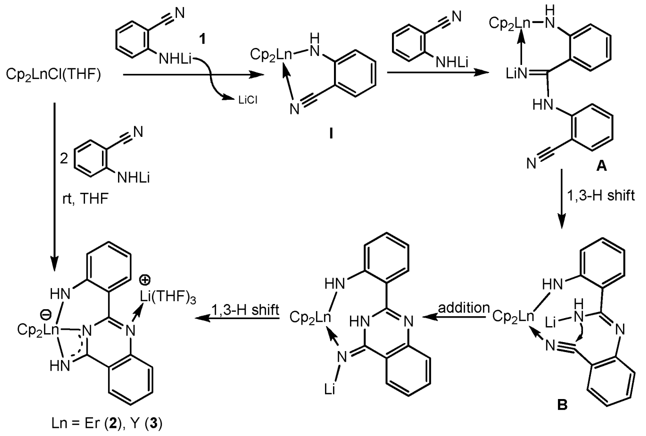

Scheme 2 Plausible mechanism of the formation of **2** and **3**.

and then transforms into **B** through a 1,3 hydrogen shift. The final products are formed by nitrile insertion into the Li–N bond, a 1,3 hydrogen shift and a 1,5 lithium cation shift. Two nitrile insertions into Li–N bonds are vital for the formation of **2** and **3**, which is different from those found in Cp$_2$Ln[κ^3-(4-NH(C$_8$N$_2$H$_4$)(2-NH$_2$C$_6$H$_4$)] (Ln = Er, Y),[10] in which the quinazoline skeleton was constructed through two nitrile insertions into Ln–N bonds. Consideration of the fact that the dimerization/cyclization of **1** cannot occur in the preparation of **1** leads us to suggest that the activation of the adjacent nitrile group *via* the coordination interaction with the Ln^{3+} ions in the intermediates **I** and **B** plays a key role to this nucleophilic addition/cyclization.

All of these new complexes are air- and moisture-sensitive, and soluble in THF and toluene. They were fully characterized by elemental analysis and spectroscopic properties, which are in good agreement with the proposed structures. In the IR spectra, **1** exhibits one absorption at 3274 cm^{-1} attributable to the N–H bond, one absorption at 2206 cm–1 attributable to the C≡N triple bond, and two well-defined bands at 1078 and 910 cm^{-1} for the coordinated THF. In the ^{1}H NMR spectrum of **3**, in addition to four multiplets for aromatic protons at 7.06, 7.02, 6.83, 6.13 ppm, one broad singlet for NH protons at about 4.86 ppm, and one singlet for the Cp ring protons at about 6.33 ppm, and two multiplets for three coordinated THF molecules at 3.54 and 1.45 ppm were obtained. The solid-state structures of **1–2** were also determined by X-ray single-crystal diffraction analysis.

Compound **1** crystalizes from the solvent mixture of THF and *n*-hexane at −20 °C in the monoclinic system, space group $P2_1/c$. Structural determination results (Fig. 1) show that **1** is two-dimension polymer, in which the 2-cyanobenzoamino anionic ligand displays a μ$_3$-bridge bonding mode with three lithium ions. Each of lithium atoms is coordinated to one oxygen atom form THF molecule and three nitrogen atoms from three different 2-cyanobenzoamino ligands to form distorted tetrahedron geometry. The N2–C1 distance of the nitrile group (1.129(4) Å) is comparable to the observed value for a coordinated η^1-N≡C triple bond of organonitriles (1.10–1.20 Å).[11a,b] The Li–N bond distances (Li1–N1 2.067(5) Å, Li1–N1A 2.038(5) Å, Li1–N2B 2.035(6) Å) are almost equivalent, and between in the range of Li–N single and donor bond distance.[11a,b]

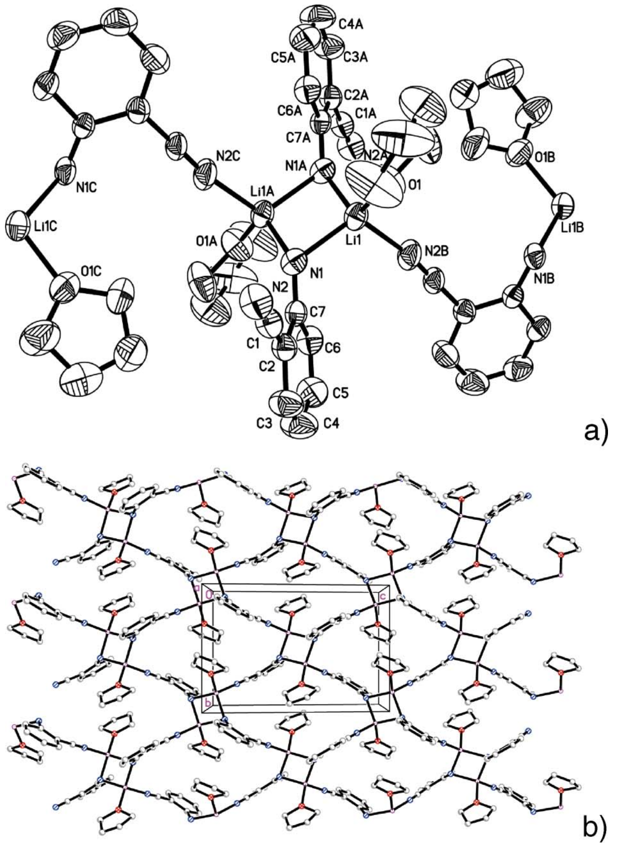

Fig. 1 Molecular structure (30% thermal ellipsoids) and packing diagram of [2-NCC$_6$H$_4$NHLi(THF)]$_n$, **1**. Hydrogen atoms have been removed for the sake of clarity. Selected bond lengths (Å) and angles (°): Li1–N1 2.067(5), Li1–N1A 2.038(5), Li1–N2B 2.035(6), Li1–O1 1.936(6); O1–Li1–N1 108.2(2), O1–Li1–N2B 110.1(3), O1–Li1–N1A 116.6(3), N1–Li1–N1A 102.1(2), N1–Li1–N2B 114.1(3), N1A–Li1–N2B 105.8(2).

Fig. 2 shows the molecular structure of **2** and selected bond distances and angles. X-Ray analysis shows that **2** is a heterobimetallic complex. The erbium atom carries two η^5-Cp rings and one κ^3-4-amino(2-imidobenzoyl)quinazolinate ligand to form a distorted bipyramid geometry. The coordination number of Er^{3+} is nine. The lithium ion Li$^+$ is coordinated by one κ^1-4-amino(2-amidobenzoyl)quinazolinate ligand and three THF molecules. The coordination number of Li$^+$ is four. A planar aromatic quinazoline skeleton has been constructed from the corresponding bond lengths and angles data.

The coordinated amidinate moiety forms essentially a planar four-membered ring with the lanthanide atom and the bond angles around C1 (sum = 360°) are consistent with sp^2 hybridization. The C1–N1 distance of [1.291(7) Å] is slightly longer than the accepted value for the C(sp^2)═N(sp^2) double-bond (1.28 Å).[12] Consistent with this observation, the Er1–N1 and Er1–N2 distances, 2.345(4) Å and 2.405(5) Å, are in the range of Er–N donor bond, and significantly longer than that of the corresponding Er–N bond of amidine anionic compound Cp$_2$Er[(^{t}BuN)$_2$C(^{n}Bu)] (Er–N$_{av}$ 2.281(5) Å).[13] The C1–N2 [1.369(6) Å], C8–N2 [1.346(6) Å], and C8–N3 [1.334(6) Å] distances are in intermediate values between the C–N single- and double-bond distances,[14] indicating that the π-electrons of the C═N double bond in the present structure are delocalized over the N1–C1–N2–C8–N3 unit. The distance of Er1–N4 is 2.288(6) Å, and in the range of an Er–N single

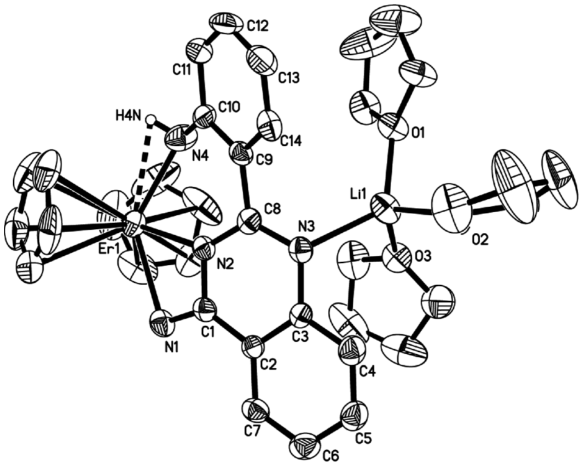

Fig. 2 Molecular structures (30% thermal ellipsoids) of Cp$_2$Er[κ3-(4-NH(C$_8$N$_2$H$_4$)(2-NH$_2$C$_6$H$_4$)], **2**. Hydrogen atoms have been removed for the sake of clarity. Selected bond lengths (Å) and angles (°): Er1–N4 2.288(6), Er1–N2 2.345(4), Er1–N1 2.406(5), Er1–H4N 2.40(6), Li1–N3 2.121(10), N1–C1 1.291(7), N2–C1 1.369(6), N2–C8 1.346(6), N3–C8 1.334(6), N3–C3 1.392(6), C1–C2 1.454(7), C2–C3 1.402(6); N1–C1–N2 100.8(6), N1–C1–C2 131.8(6), N2–C1–C2 117.4(5), C8–N2–C1 120.6(5), C8–N3–C3 115.4(5), C3–C2–C1 117.1(5), N3–C3–C2 123.0(5), N3–C8–N2 125.8(5).

bond.[15] Interestingly, the residual hydrogen atom of the amido group contacts with the erbium ion through an agnostic hydrogen bond interaction (Er1–H4N 2.40(6) Å).[16]

In summary, a rare-earth metal-mediated intermolecular nucleophilic addition/cyclization of 2-cyanobenzoamino anion was reported to construct a 4-iminoquinazolinate dianionic ligand [κ^3-(4-NH=(C$_8$N$_2$H$_4$)(2-NHC$_6$H$_4$)]$^{2-}$ for the first time, which provided a potential strategy for introducing a substituent at the N3 atom of the pyrimidine ring skeleton.

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