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Facile Construction of a Novel Aminoquinazolinate Anionic Ligand through Organolanthanide-Mediated Intermolecular Nucleophilic Addition/Cyclization of Anthranilonitrile

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Compounds $Cp_2Ln[\kappa^3\text{-}(4\text{-}NH(C_8N_2H_4)(2\text{-}NH_2C_6H_4)]$ [$Cp = C_5H_5$; Ln = Er (**1**), Y (**2**)] were synthesized by the reaction of $Cp_2LnN^iPr_2(THF)$ with anthranilonitrile, indicating a novel organolanthanide-mediated intermolecular nucleophilic addition/cyclization of anthranilonitrile. To trap the intermediate **I**, a probe reaction of $Cp_2ErN^iPr_2(THF)$ with anthranilonitrile and carbodiimide has also been investigated.

The activity of organolanthanide derivatives on unsaturated organic small molecules is one of the important fields of organolanthanide chemistry,[1–3] and insertion, one flourishing subdiscipline of this field, has been studied extensively in past decades.[4–8] This is a practical application to the synthesis of organolanthanide derivatives and a potential understanding of catalytic processes.[1c,3g] 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. Our recent interests are in the investigation of the substituent effects on the activity of organolanthanide derivatives containing bisfunctional group ligands such as *o*- or *p*-aminothiophenolate toward unsaturated organic small molecules. We found that the adjacent amino group of the *o*-aminothiophenolate ligand readily adds to the C═N bond of carbodiimide or isocyanate for construction of a novel guanidinate or thiazolate skeleton.[9]

Organic nitrile is one useful reagent in organic synthesis for the construction of many important N-heterocycle compounds, and its reactivity toward organometallic complexes is a fundamental interest in organometallic chemistry.[10] Upon comparison with the investigations on the reactivity of organolanthanide hydrides and alkyl complexes to nitriles, which provide many important organometallic reactions and

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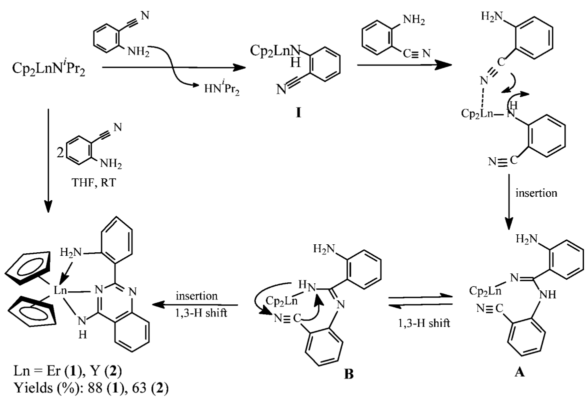
interesting structures,[11,12] examples of organolanthanide amide reactions with nitriles were scarcely reported.[12c,e,13] To further study the substituent effects on insertions and/or extend the scope of this NH_2 addition, we now investigate the reactivity of organolanthanide amides toward anthranilonitrile. Herein we report a new organolanthanide-mediated intermolecular nucleophilic addition/cyclization of anthranilonitrile to construct a novel 4-aminoquinazolinate anionic ligand.

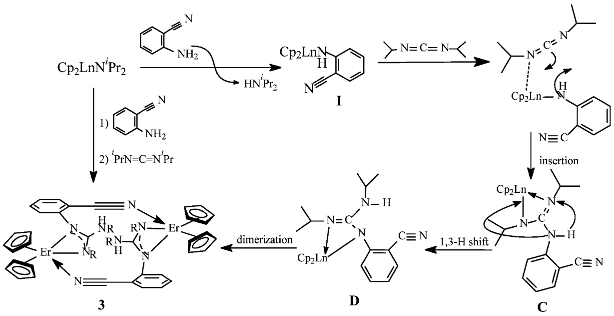
The reaction of $Cp_2LnN^iPr_2(THF)$ with 2 equiv of anthranilonitrile in THF at room temperature afforded the isolated and structurally characterized complexes $Cp_2Ln[\kappa^3\text{-}(4\text{-}NH(C_8N_2H_4)(2\text{-}NH_2C_6H_4)]$ [Ln = Er (**1**), Y (**2**)] in moderate or high yields. Structural analysis reveals that an intermolecular nucleophilic addition/cyclization of anthranilonitrile takes place accompanied with the elimination of HN^iPr_2 to form a novel $[(4\text{-}NH(C_8N_2H_4)(2\text{-}NH_2C_6H_4)]^-$ ligand. It should be noted that the compounds also can be obtained from the reaction of $Cp_2LnN^iPr_2(THF)$ with 1 equiv of anthranilonitrile under the same conditions in lower yields. As far as we are aware, the dimerization of anthranilonitrile usually occurs under the drastic conditions of a high temperature of about 190 °C or upon microwave irradiation in the presence of a strong base such as ^{t}BuOK.[14] In our systems, this reaction readily takes place under very mild conditions, attributed to the Lewis acid activity of the organolanthanide moiety toward anthranilonitrile molecules.

A proposed mechanism for the formation of **1** and **2** is illustrated in Scheme 1. The first step is protonolysis of the diisopropylamine ligand by an anthranilonitrile molecule to generate the intermediate **I**. A further nitrile group from another anthranilonitrile molecule inserts into the Ln−N bond of **I**, to give **A**, and then transforms into **B** through 1,3 hydrogen shift. The final products are formed by nitrile insertion and a 1,3 hydrogen shift again. Attempts to isolate the intermediate **B** were unsuccessful. It is possible that a more stable aromatic pyrimidine skeleton contributes to the occurrence of further nucleophilic addition/cyclization.

Scheme 1. Proposed Mechanism of the Formation of **1** and **2**



Scheme 2. Proposed Mechanism for the Formation of **3**



To obtain additional insight into the mechanism and scope of the reaction, we investigated the following two reactions: (1) the reaction of $Cp_2ErN^iPr_2$ with anthranilonitrile and benzonitrile; (2) the reaction of $Cp_2ErN^iPr_2$ with anthranilonitrile and $^iPrN{=}C{=}N^iPr$. Unfortunately, attempts to obtain pure products were unsuccessful; we only obtained oily mixtures in reaction 1. So, the mixtures were hydrolyzed and analyzed by gas chromatography/mass spectrometry to give two main products of dimerization of anthranilonitrile and cyclization of anthranilonitrile with benzonitrile in the mole ratio of 46:39. Reaction 2 can give two isolated compounds $[Cp_2Er(\mu\text{-}\kappa^1{:}\kappa^2\text{-}NCC_6H_4N(H)C(NH^iPr){=}N^iPr)]_2$ (**3**) and **1** in 47% and 9% yields, respectively. This result maybe indicates that nucleophilic additions of carbodiimide and anthranilonitrile with **I** are competitive. The proposed mechanism for the formation of **3** also is shown in Scheme 2, a typical process of the σ-bond metathesis and further insertion of carbodiimide molecules, accompanied with a 1,3 hydrogen shift.[4e] Indeed, we cannot exclude other possible progresses of these reactions such as the addition of N−H bonds to the C≡N triple bond of nitrile groups or the C=N double bond of carbodiimide molecules.

All of these 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 ^1H NMR spectra of **2**, in addition to multiplets for aromatic protons in the range 7.7−7.2 ppm, one doublet for the NH proton at about 2.7 ppm, one singlet for NH_2 protons at about 4.3 ppm, and multiplets for Cp ring protons in the range 6.9−6.6 ppm. Their solid-state structures of **1**−**3** were also determined by single-crystal X-ray diffraction analysis.[15]

1 and **2** crystallize from the solvent mixture of THF and toluene at −20 °C in the rhombohedral system, space group $R\bar{3}$. Structural determination results (Figure 1) show that **1**

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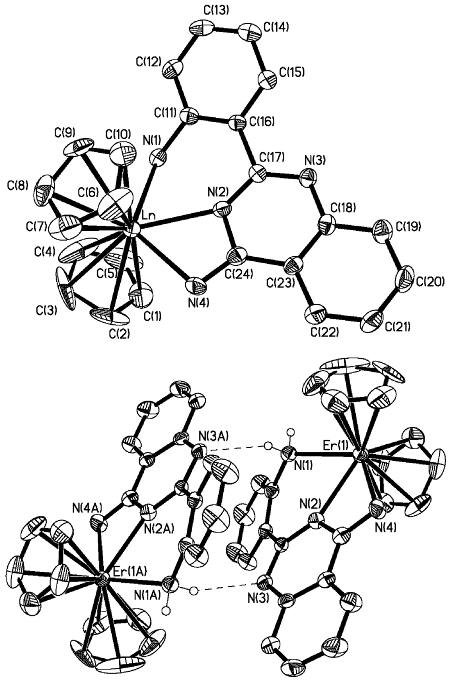

Figure 1. Molecular structures (30% thermal ellipsoids) of Cp$_2$Ln[κ^3-(4-NH(C$_8$N$_2$H$_4$)(2-NH$_2$C$_6$H$_4$)] [Ln = Er (**1**), Y (**2**)] (top). Hydrogen-bonded pairs of **1** (bottom).

and **2** are isostructural. Both are solvent-free monomers with the lanthanide atom bonded to two η^5-Cp rings and one κ^3-4-amino(2-aminobenzoyl)quinazolinate ligand to form a distorted bipyramidal geometry. A planar aromatic quinazoline skeleton has been constructed from the corresponding bond length and angle data. Interestingly, a dimer structure (Figure 1, bottom) is formed by a novel pair of intermolecular N−H···N hydrogen-bonding interactions from the N−H bond of the NH$_2$ group and one nitrogen atom of another quinazoline skeleton.[13]

As expected, the coordinated amidinate moiety forms essentially a planar four-membered ring with the lanthanide atom within experimental error (Ln−N2−C24−N4). The bond angles around C24 are consistent with sp^2 hybridization. In **1**, the C24−N2 [1.372(7) Å] and C24−N4 [1.291(7) Å] distances of the amidinate group are in intermediate values between the C−N single- and double-bond distances, indicating that the π electrons of the C═N double bond in the present structure are partially delocalized.[16] Consistent with this observation, the Er−N2 and Er−N4 distances, 2.384(5) and 2.388(5) Å, respectively, are approximately equivalent and are intermediate between the values observed for a Er−N single or donor bond.

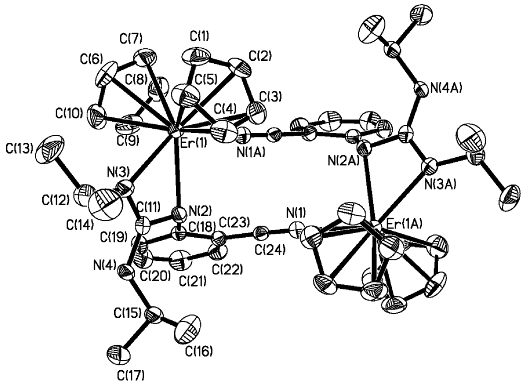

Figure 2. Molecular structure (30% thermal ellipsoids) of **3**. Hydrogen atoms have been removed for the sake of clarity.

In **3** (Figure 2), the adjacent amino group has combined with a carbodiimide unit, forming a novel guanidinate ligand [2-NCC$_6$H$_4$N═C(NH^{i}Pr)N^{i}Pr]$^-$, which connects with the center metal by a novel μ-κ^1:κ^2-bonding mode. The inert nitrile group is coordinated to another erbium atom, forming a dinuclear 12-membered ring. One hydrogen atom of the adjacent amino group shifts to the uncoordinated nitrogen atom, similar to that of the observed organolanthanide trisubstituted guanidinates.[4e,9b] The guanidinate ligand also exhibits delocalized bonding throughout the N3C guanidinate core. The planarity of the ErN2C ring and nearly equivalent C11−N2 and C11−N3 [1.366(7) and 1.306(7) Å, respectively] and Er1−N2 and Er1−N3 [2.452(4) Å and 2.385(5) Å, respectively] bond lengths suggests the existence of a resonance stabilization in the ErN2C ring and no hydrogen atom at the coordinated nitrogen atom. The distance between the central carbon and uncoordinated nitrogen [C11−N4 1.372(7) Å] is slightly shorter than that expected for C(sp^2)−N(sp^3) single bonds (C−N$_{av}$ 1.416 Å)[17] and indicates a partial p−π conjugation between the lone-pair electron on noncoordinated nitrogen and the N−C−N unit.[4e]

In summary, organolanthanide-mediated intermolecular nucleophilic addition/cyclization of anthranilonitrile was reported for the first time and offers a potential route for the construction of a coordinated pyrimidine ring skeleton.

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Supporting Information Available: Detailed experimental procedures, full characterization data, and X-ray data for **1**−**3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Crystallographic data for **1**: C$_{24}$H$_{21}$N$_4$Er, M = 532.71, $R\bar{3}$, a = 31.880(8) Å, c = 10.801(4) Å, γ = 120°, V = 9506(5) Å^3, T = 298(2) K, F(000) = 4698, μ(Mo Kα) = 3.989 mm^{-1}, 14 539 reflections, 4163 unique (R_{int} = 0.0693), R1 = 0.0325, and wR2 = 0.0633. Crystallographic data for **2**: C$_{24}$H$_{21}$N$_4$Y, M = 454.36, $R\bar{3}$, a = 31.866(8) Å, c = 10.778(4) Å, γ = 120°, V = 9478(5) Å^3, T = 293(2) K, F(000) = 4176, μ(Mo Kα) = 2.786 mm^{-1}, 13 397 reflections, 3714 unique (R_{int} = 0.1801), R1 = 0.0797, and wR2 = 0.1730. Crystallographic data for **4**: C$_{48}$H$_{58}$N$_8$Er$_2$, M = 1081.54, $C2/c$, a = 15.734(5) Å, b = 18.357(5) Å, c = 16.754(5) Å, β = 108.508(6)°, V = 4592(2) Å^3, T = 293(2) K, F(000) = 2152, μ(Mo Kα) = 3.672 mm^{-1}, 11 307 reflections, 5007 unique (R_{int} = 0.0586), R1 = 0.0413, and wR2 = 0.0797.

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