

Lanthanide iodides as promoters of acetonitrile amination. Molecular structure of MeC(=NH)NHPr^t , MeC(=NH)NHBu^t and $\{\text{Dy}[\text{MeC(=NH)NEt}_2]_6\}\text{I}_3$

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Abstract

Amination of acetonitrile by the amines MeNH_2 , Pr^nNH_2 , Pr^tNH_2 , Bu^tNH_2 , and Et_2NH is efficiently promoted by the lanthanide iodides LnI_2 ($\text{Ln} = \text{Nd, Dy, Tm}$), LnI_3 ($\text{Ln} = \text{Pr, Nd, Dy}$) and $\text{LnI}_3(\text{THF})_3$ ($\text{Ln} = \text{Pr, Nd, Dy}$). The formed mono- and N,N' -disubstituted amidines MeC(=NH)NHR ($\text{R} = \text{Pr}^t, \text{Bu}^t$), MeC(=NH)NEt_2 , MeC(=NR)NHR ($\text{R} = \text{Me, Pr}^n$) were isolated mainly as the complexes with starting iodide of general composition $\text{LnI}_2(\text{amidine})_x$ (**1**) or $\text{LnI}_3(\text{amidine})_x$ (**2**) ($x = 3-8$). In the products **1**, which evidently are the mixtures of LnI_2^{2+} , LnI_2^+ and LnI_3 derivatives, the metal exists in trivalent state but one of the ligands actually is amidinate anion. A part of the generated amidines remains in the reaction solutions in free form. Heating of the **1** and **2** in vacuum at 150–200 °C affords corresponding amidine and the complexes with reduced amount of the amidine ligands $\text{LnI}_2(\text{amidine})_y$ (**3**) or $\text{LnI}_3(\text{amidine})_y$ (**4**) ($y = 2-3$). The products **3** and **4** displayed the same catalytic activity in the acetonitrile-amine cross-coupling as the initial iodides. SmI_2 and especially YbI_2 revealed lower activity. The structure of isopropylacetamide (**5**), *tert*-butylacetamide (**6**) and $\{\text{Dy}[\text{MeC(=NH)NEt}_2]_6\}\text{I}_3(\text{MeCN})$ (**7**) were determined by X-ray diffraction analysis.

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1. Introduction

The amidines are well studied and broadly used class of compounds, which find application as antibiotics, drugs and as synthons for the preparation of other biologically active organic compounds [1]. Besides, they are attractive as specific versatile ligands in coordination chemistry. Among the preparative routes to N-substituted amidines the cross-coupling of amines and nitriles is one of the most applicable method developed over 50 years ago [1,2]. The addition is promoted by Lewis acids such as SbCl_6 , FeCl_3 , AlCl_3 , SnCl_4 or complexes of d-transition metals [3]. The

reactions usually are carried out with stoichiometric amount of the reagents and can be used for the synthesis of mono-, di- and trisubstituted amidines. Later it was found that the lanthanide(III) perchlorate [4] and triflates [5] catalyze amination of nitriles upon heating at 100 °C to give N,N' -disubstituted amidines with high conversion of the reagents for *n*-propyl-, *i*-propyl-, *n*-butyl-, phenylamines but not for the bulkier *t*-butylamine, which affords monosubstituted amidine in low yield. In the reactions with the other amines the monosubstituted amidines were not isolated, however their generation was proposed on the first stage of the processes. Formation of essential amount of symmetrically substituted triazines as by-products was observed in some cases. Lanthanide nitrates and chlorides revealed no activity in these syntheses [5]. More recently, chemists in China have established that SmI_2 also catalyzes

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the formation of *N,N'*-disubstituted amidines from nitriles and amines at 55–80 °C [6] while at room temperature, as it was pointed out previously [7], these reactions do not occur. The yield of acetamidines with SmI₂ varies from 35% to 80% for *n*-propyl- and *n*-butylamines but 0% for isopropylamine. Like the reactions with triflates these syntheses are accompanied by the formation of triazines, the yield of which reaches 22%. On the grounds of color change of reaction mixtures from dark blue to light brown the authors suggested that the real active species in these reactions are Sm³⁺ ions although the mechanism of their formation and arrangement of the samarium intermediates were not discussed.

Studying reactivity of LnI₂ (Ln = Nd, Dy, Tm) we have found that these salts, unlike SmI₂, easily reduce acetonitrile and benzonitrile to give various products of C–C and C–N coupling [8,9]. In the case of MeCN the processes resulted in formation of new type complexes containing novel tridentate bis(ethylimine)ethylamine ligand $\{[(\text{MeC}=\text{NH})_2\text{CMeNH}_2]\text{Dy}(\text{MeCN})_6\}_3\text{I}_3$ (Ln = Dy, Tm [8], Nd [10]). On the other hand, it has been established recently [11] that the diiodides of Sm, Eu, Tm, and Yb are soluble in isopropylamine. NdI₂ and DyI₂ also are dissolved in PrⁱNH₂ but slowly react with it. Other primary amines do not dissolve all LnI₂ but energetically react with NdI₂ and DyI₂. These data prompted us to investigate the ability of lanthanide diiodides to promote the acetonitrile-amine condensation. In course of the study we have found that not only most of LnI₂ but as well as the lanthanide triiodides LnI₃ are active in the acetamidines formation from MeCN and amines. In this paper we report on the obtained results and discuss presumable schemes of amidines formation. Several alkyl amines (MeNH₂, PrⁿNH₂, PrⁱNH₂, BuⁿNH₂, and Et₂NH) were used in the study, however the main test reactions have been performed with PrⁱNH₂ since this amine revealed lowest activity in the above mentioned syntheses activated by SmI₂.

2. Results and discussion

2.1. Reactions with LnI₂

The reactions of equimolar mixture of acetonitrile and isopropylamine in the presence of 1–1.5% mol of NdI₂, DyI₂ or TmI₂ proceed alike: in a few minutes after stirring of the mixtures at room temperature they are decolorized and grayish precipitate of **1** is formed. The precipitates are insoluble not only in acetonitrile and isopropylamine but also in other organic solvents what hampers their detailed characterization. Content of metal and iodine in the products **1** isolated in 89–91% yield responds to a formula LnI₂[MeC(=NH)NHPrⁱ]₅, which agrees with IR spectra displaying the absorption bands of C≡N (1581 cm⁻¹) and N–H (3261, 3208, 3111, 1561 cm⁻¹) groups. Since color of the precipitates, which is not characteristic for Ln²⁺ compounds, their low reactivity as well as the μ_{eff} value 3.5 μ_{B} for neodymium and 7.2 μ_{B} for thulium

complexes clearly indicate trivalent state of the metal, the compounds actually are amidine-amidinate complexes of the type LnI₂[MeC(=NH)NHPrⁱ]⁻[MeC(=NH)NHPrⁱ]₄. Considering extremely high predisposition of NdI₂ and DyI₂ to disproportionation [12], the arrangement of the precipitates could be alternatively interpreted as mixtures of the triiodide LnI₃[MeC(=NH)NHPrⁱ]₅ and the monoiodide LnI[MeC(=N)NHPrⁱ]₂⁻[MeC(=NH)NHPrⁱ]₃ complexes. In the reaction solutions only negligible amounts of free isopropylacetamidine (**5**) were found by means of chromatography and NMR analysis. Heating of the products **1** to 180 °C in dynamic vacuum leads to separation of three of the five amidine **5** molecules. Total yield of **5** (calculated for LnI₂)¹ including free amidine in the solutions reached 183%, 202% and 270% for NdI₂, DyI₂ and TmI₂, respectively (Table 1). Increase reaction time from 8 to 50 h practically did not influence on the amidine yields, however increase of the reaction temperature to 70 °C in the case of DyI₂ resulted in enhancing the yield of **5** to 360%. The solid substances **3**, which remained after partial removing of amidine **5**, mimic the products **1** by color, solubility and IR spectra but have another ratio of metal, iodine and MeC(=NH)NHPrⁱ (or [MeC(=N)NHPrⁱ]⁻) ligands: 1:2:2. Upon heating of **3** above 180–220 °C, the substances undergo deep decomposition to give dark gray unidentified solids.

Since the formation of complexes **1** and consequently amidine **5** under given conditions proceeds readily but as it was found only in minor amount in the solution free amidine we assumed that the amidine generation is dramatically detained after the products **1** formation because of blocking of Ln³⁺ ions by amidinate [MeC(=N)NHPrⁱ]⁻ groups and coordinately bonded amidine **3** molecules. Partial removing of the amidine ligands would deliver the coordination sphere of Ln³⁺ ions regenerating their catalytic activity. In agreement with this assumption we have found that the treatment of **3** (Nd, Dy, Tm) by MeCN/PrⁱNH₂ mixture gives again the products **1**. For neodymium complex the procedure was repeated thrice to give each time the amidine **5** in 180–200% yield calculated for **3**.² Thus, the synthesis of amidine **5** from acetonitrile and isopropylamine in the attendance of LnI₂ (Nd, Dy, Tm) can be represented by Scheme 1. Because we were unable to separate the insoluble complexes formed in these reactions the real catalytic species responsible for the amination of C≡N groups remain unclear. We believe that all probable products generated in the first stage (each of which contains Ln³⁺ cation but one, two or three I⁻ anions) are able to promote this process. The data quoted below confirm such a supposition.

¹ The terms conversion or turnover number normally using for catalytic reactions in the considered processes are no indicative because pseudo catalytic character of the transformations in some cases.

² Note, the gray precipitate formed after decomposition of **1**(Nd, Dy, Tm) at 220 °C displayed only weak catalytic activity in the acetonitrile-isopropylamine coupling.

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