



Investigation and mechanistic study into intramolecular hydroalkoxylation of unactivated alkenols catalyzed by cationic lanthanide complexes

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ABSTRACT

Cationic lanthanide complexes of the type $[\text{Ln}(\text{CH}_3\text{CN})_9]^{3+}[(\text{AlCl}_4)_3]^{3-} \cdot \text{CH}_3\text{CN}$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Er}, \text{Yb}, \text{Y}$) served as effective catalysts for the intramolecular hydroalkoxylation/cyclization of unactivated alkenols to yield the cyclic ethers with Markovnikov regioselectivity under mild conditions. Novel cationic complexes, $[\text{AlCl}(\text{CH}_3\text{CN})_5]^{2+}[(\text{AlCl}_4)_2]^{2-} \cdot \text{CH}_3\text{CN}$ and $[\text{Nd}(\text{CH}_3\text{CN})_9]^{3+}[(\text{FeCl}_4)_3]^{3-} \cdot \text{CH}_3\text{CN}$, were synthesized and evaluated for the intramolecular hydroalkoxylation/cyclization of unactivated alkenols for comparison. The active sequence of $[\text{Nd}(\text{CH}_3\text{CN})_9]^{3+}[(\text{FeCl}_4)_3]^{3-} \cdot \text{CH}_3\text{CN} < [\text{AlCl}(\text{CH}_3\text{CN})_5]^{2+}[(\text{AlCl}_4)_2]^{2-} \cdot \text{CH}_3\text{CN} < [\text{Nd}(\text{CH}_3\text{CN})_9]^{3+}[(\text{AlCl}_4)_3]^{3-} \cdot \text{CH}_3\text{CN}$ observed indicated that both the cation and anion have great influence on the activity. Comparative study on the activity of AlCl_3 and its cationic complex $[\text{AlCl}(\text{CH}_3\text{CN})_5]^{2+}[(\text{AlCl}_4)_2]^{2-} \cdot \text{CH}_3\text{CN}$ revealed the formation of the cationic Al center enhanced the activity greatly. The ^1H NMR studies indicated the activation of hydroxyl and olefin by the cationic Ln^{3+} center were involved in the reaction pathways.

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1. Introduction

Saturated oxygen heterocycles are recognized as important structural moieties that are found in a wide range of naturally occurring and biologically active molecules, such as polyethers, antibiotics, acetogenins and prostaglandins.¹ Intramolecular addition of an O–H bond across an unsaturated C–C bond of a pendant olefin (intramolecular hydroalkoxylation) is an atom-economical, and therefore particularly attractive, approach for preparing saturated oxygen heterocycles. The hydroalkoxylation of alkenols traditionally involves reaction with a stoichiometric amount of a toxic metal ion, followed by reduction.² Catalytic processes for such transformations are limited, particularly for unactivated alkenols. Brønsted acids,³ transition metals salts⁴ such as those of gold,^{4a} tin,^{4b} ruthenium,^{4c,4d,4h} and platinum,^{4e} and some metal triflates⁵ have been reported as effective catalysts for intramolecular and intermolecular hydroalkoxylation of olefins. However, these transition metal catalysts are either toxic or relatively expensive.

Therefore, the development of new, efficient and cheaper methods for intramolecular and intermolecular hydroalkoxylation of olefins has attracted great attention.⁶ Recently, Marks et al. reported that homoleptic lanthanide amido complexes ($\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$) are effective and selective precatalysts for the intramolecular hydroalkoxylation/cyclization of alkynyl and allenyl alcohols providing exocyclic enol ethers.⁷ Lanthanide triflates ($\text{Ln}(\text{OTf})_3$) also serve as efficient catalysts for the intramolecular hydroalkoxylation/cyclization of primary or secondary, and aliphatic or aromatic hydroxyalkenes at room temperature in ionic liquids, affording five- and six-membered oxygen heterocycles with Markovnikov-type selectivity.⁸

Cationic metal species are generally more electrophilic than their neutral forms, and thus are more active homogeneous catalysts. Cationic lanthanide alkyl complexes are well known to be more active and selective in catalyzing olefin polymerization and copolymerization with respect to their neutral analogs.⁹ However, the use of cationic lanthanide complexes in organic transformations remains limited, and examples include intramolecular hydroamination,¹⁰ dimerization of phenylacetylene¹¹ and hetero-Diels-Alder reaction.¹²

We previously reported that anhydrous lanthanide trichlorides

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(LnCl₃) react easily with anhydrous AlCl₃ in acetonitrile (CH₃CN), affording disconnected ion-pair Ln/Al complexes, [Ln(CH₃CN)₉]³⁺[(AlCl₄)₃]³⁻·CH₃CN, in almost quantitative yields.¹³ The lanthanide ions in these cationic complexes exhibit high electrophilicity and therefore can act as catalysts for styrene polymerization without the need for a co-catalyst.¹⁴ These studies led us to investigate the intramolecular hydroalkoxylation of unactivated alkenols using these complexes as catalysts, with the aim of expanding the scope of cationic lanthanide complexes in organic synthesis. It was found that these complexes show good activity for a wide range of substrates, and we now disclose these results. The syntheses and molecular structures of novel cationic complexes, [AlCl(CH₃CN)₅]²⁺[(AlCl₄)₂]²⁻·CH₃CN and [Nd(CH₃CN)₉]³⁺[(FeCl₄)₃]³⁻·CH₃CN, and investigation of their catalytic activity in the intramolecular hydroalkoxylation of alkenols were studied to assess the influence of both the cation and the counteranion on the activity of this type of complex.

2. Results and discussion

2.1. Optimization of the intramolecular hydroalkoxylation

2.1.1. Syntheses of [Ln(CH₃CN)₉]³⁺[(AlCl₄)₃]³⁻·CH₃CN (Ln = Pr **I**, Nd **II**, Sm **III**, Gd **IV**, Er **V**, Yb **VI** and Y **VII**) and the molecular structures of the Nd and Y complexes

A series of cationic complexes, [Ln(CH₃CN)₉]³⁺[(AlCl₄)₃]³⁻·CH₃CN, containing the early to later lanthanide metals were synthesized by the reaction of LnCl₃ and AlCl₃ in CH₃CN according to a reported procedure (Scheme 1).¹³

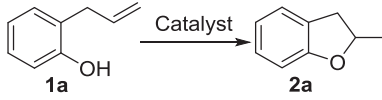
The solid state structures of the [Nd(CH₃CN)₉]³⁺[(AlCl₄)₃]³⁻·CH₃CN **II** and [Y(CH₃CN)₉]³⁺[(AlCl₄)₃]³⁻·CH₃CN **VII** complexes were determined by X-ray crystal structural analysis,¹⁵ as they were unknown in the literature. They are isostructural and isomorphous, and their molecular structures are similar to that of the analogous Sm complex reported previously.¹³ Both have an ion-pair structure consisting of one cation [Ln(CH₃CN)₉]³⁺ and three anions of (AlCl₄)⁻ (See Supplementary data).

2.1.2. Solvent effects on the catalytic intramolecular hydroalkoxylation/cyclization of alkenols

The intramolecular hydroalkoxylation/cyclizations of aromatic alkenol **1a** and aliphatic alkenol **1b** were investigated as model reactions, using 5 mol% of **II** in CHCl₃ at 65 °C for **1a**, and in DCE at 83 °C for **1b**. We were pleased to observe that the [Nd(CH₃CN)₉]³⁺[(AlCl₄)₃]³⁻·CH₃CN complex exhibited high catalytic activity in both reactions, affording 95% conversion of **1a** to cyclic ether **2a** (Table 1, entry 1), and 93% yield of cyclic ether **2b** (Table 2, entry 1) after 24 h. These encouraging results led us to examine the reactions further in various solvents. Thus, DCE, CHCl₃ and CH₃CN for the reaction of **1a**, and CHCl₃, DCE, CH₃NO₂ and toluene for the reaction of **1b** were investigated with a 5 mol% catalyst loading at different temperatures. The choice of solvent appeared to have a noticeable effect on both reactions. The hydroalkoxylation/cyclization reactions of **1a** in CHCl₃ at 65 °C and in DCE at 83 °C were almost complete after 24 h, affording **2a** in 95% and 90% yield, respectively (Table 1, entries 1 and 2). However, only a trace of **2a** was obtained when the reaction was carried out in CH₃CN (Table 1, entry 3). Moreover, whereas reaction of

Table 1

Screening of [Ln(CH₃CN)₉]³⁺[(AlCl₄)₃]³⁻·CH₃CN complexes and solvents for intramolecular hydroalkoxylation/cyclization of **1a**.



Entry	Ln catalyst (loading, mol%)	Solvent	GC yield (%)
1	II (5.0)	CHCl ₃	95
2 ^b	II (5.0)	DCE	90
3 ^b	II (5.0)	CH ₃ CN	8
4 ^c	II (5.0)	CHCl ₃	80
5 ^d	II (5.0)	CHCl ₃	73
6 ^e	II (5.0)	—	49
7	I (2.5)	CHCl ₃	81
8	II (2.5)	CHCl ₃	82
9	III (2.5)	CHCl ₃	87
10	IV (2.5)	CHCl ₃	88
11	VII (2.5)	CHCl ₃	95
12	VI (2.5)	CHCl ₃	>99
13	VI (1.0)	CHCl ₃	>99
14	VI (1.0)	CHCl ₃	93 ^f
15	VI (0.5)	CHCl ₃	81

^a Reactions were conducted with 1 mmol of substrate in 2 mL of solvent at 65 °C for 24 h.

^b At 83 °C.

^c The concentration of substrate was 1 mol/L.

^d The concentration of substrate was 2 mol/L.

^e Solvent free.

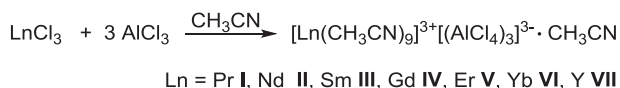
^f 18 h.

unsaturated alcohol **1b** gave an almost quantitative yield of cyclic ether **2b** in DCE at 83 °C (93% yield, Table 2, entry 1), only 88% and 80% conversion of **1b** to **2b** was achieved when using toluene at 110 °C and CH₃NO₂ at 100 °C, respectively (Table 2, entries 2 and 4). Only a 50% yield of **2b** was obtained in CHCl₃ at 65 °C (Table 2, entry 3). Thus, the optimal solvent for this system is CHCl₃ for aromatic hydroxyalkenes, and DCE for aliphatic hydroxyalkenes.

The reaction concentration also affects the yield of the reaction. As illustrated in Table 1, the yield of **2a** decreased with an increase in the concentration of **1a** in a range from 0.5 to 2.0 mol/L (Table 1, entries 1, 4 and 5). The lowest-yielding reaction of **2a** was under solvent-free conditions (49%, Table 1, entry 6). This may be attributed to the poor solubility of the catalyst both in the substrate and the resulting product.

2.1.3. Lanthanide metal effects on catalytic intramolecular hydroalkoxylation/cyclization of alkenols

The influence of the lanthanide metal (Ln) on the model reactions of **1a** and **1b** was then screened in CHCl₃ at 65 °C for the former (Table 1), and in DCE at 83 °C for the latter (Table 2). As shown in Table 1, the activity of the complexes [Ln(CH₃CN)₉]³⁺[(AlCl₄)₃]³⁻·CH₃CN increases substantially with a decrease in the Ln ionic radius. The reaction using the smallest ionic radius catalyst (Yb) afforded a quantitative yield of **2a**, medium-sized Ln catalysts (Sm and Gd) afforded 87–88% yields of **2a**, and 81–82% yields were achieved for the larger Nd and Pr metal catalysts (Table 1, entries 7–10 and 12). The activity of the Y complex is somewhat lower than that of the Yb complex (Table 1, entry 11). The sequence of Pr ~ Nd < Sm ~ Gd < Y < Yb observed here is consistent with an increasing trend of Lewis acidity of the Ln ions. This pattern parallels that of organolanthanide-catalyzed aminoalkyne hydroamination/cyclizations,¹⁶ and Ln(OTf)₃-catalyzed hydroxyalkene hydroalkoxylation/cyclizations,⁸ but not that of organolanthanide-catalyzed aminoalkene hydroamination/cyclizations,¹⁷ or organolanthanide-catalyzed hydroxyalkyne and



Scheme 1. Syntheses of [Ln(CH₃CN)₉]³⁺[(AlCl₄)₃]³⁻·CH₃CN.

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