

Lanthanide(III) nosylates as new nitration catalysts

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Abstract—Lanthanide(III) nosylates are novel, recyclable catalysts prepared from the noncorrosive and inexpensive *p*-nitrotoluenesulfonic acid and the corresponding lanthanide(III) oxide. With 5–10% catalyst loading, atom economic nitration of simple aromatic compounds was achieved in good to high yields.

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Lanthanide compounds are an important class of reagents in modern organic synthesis. The unique electronic properties of the lanthanides offer new structural and reactivity patterns not present in main group and d-transition metal chemistry. In addition, the low toxicity and availability at moderate price make the lanthanides even more attractive to organic chemists. Various aspects of lanthanide mediated organic reactions have been described in several excellent reviews.¹ Among the many useful lanthanide reagents, lanthanide(III) triflates have been especially recognised as catalyst for various reactions such as Diels–Alder cycloadditions, Friedel–Crafts acylations and alkylations, Michael, and Mukaiyama reactions among others.² The lanthanide(III) triflates are expected to be strong Lewis acids due to the electron-withdrawing trifluoromethanesulfonate group. Indeed, triflic acid is one of the strongest acids known till date, and its pK_a value has been estimated to be lower than -12 .³

The unique property of lanthanide(III) triflates to act as water tolerant Lewis acids was subsequently used for the nitration of a range of simple aromatic compounds in good to excellent yields using a stoichiometric amount of nitric acid.⁴ Since the only by-product of the nitration reaction was water, this procedure is advantageous compared to the commonly used nitration procedure that requires use of potent mixtures of concentrated nitric and sulfuric acids, leading to excessive acid waste streams, which are environmentally unfriendly and

expensive to treat. The extreme acidity of triflic acid is thought to be necessary to increase the polarising power of the metal ion, which plays a crucial role in the formation of the de facto nitrating agent NO_2^+ .⁵ On the other hand, the strong acidity and corrosivity of the triflic acid used for the preparation of the lanthanide(III) triflate catalysts often poses problems in practical handling.

Another nitration procedure with the use of lanthanide(III) reagents employed lanthanide salts of perfluorooctanesulfonic acid as catalysts in various fluorinated solvents.⁶ Although that procedure required a very small catalyst loading for achieving moderate to good yields (40–60%) of nitrotoluene, the method is still unlikely to be utilised on a large industrial scale since the fluorinated solvents are much more expensive than most of the conventional solvents, and in addition, their large global warming potential could pose serious environmental problems.⁷

In a search for lanthanide(III) catalysts, which do not require the use of hazardous or costly fluorinated compounds we first examined lanthanide(III) salts of aromatic sulfonic acids, such as *p*-toluenesulfonic acid. The reaction we chose for testing these catalysts was nitration of toluene, because it requires catalysts that are water compatible but that are at the same time also strong Lewis acids. However, the aromatic sulfonic acids are much weaker acids than the triflic acid, (the acidity of *p*-toluenesulfonic acid is e.g., about six orders of magnitude less than that of triflic acid), and therefore their lanthanide complexes are expected to be much weaker Lewis acids than $\text{Ln}(\text{OTf})_3$. We first tested lanthanide(III) nosylates as nitration catalysts, and surprisingly, these complexes efficiently catalysed

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conversion of toluene to nitrotoluene, but they were not very effective in the nitration of benzene or aromatic compounds with electron-withdrawing groups.

In an attempt to improve the activity of the catalyst we decided to explore lanthanide(III) salts of *p*-nitrobenzenesulfonic acid.⁸ Ln(Nos)₃, also called lanthanide nosylates. The p*K*_a value of the *p*-nitrobenzenesulfonic acid is -7.23,⁹ which implies that lanthanide(III) nosylates should be stronger Lewis acids than the lanthanide(III) tosylates. However, the lanthanide nosylates are virtually unexplored compounds and to the best of our knowledge, no literature data on their chemical and structural properties are available. The crystal structure of scandium(III) salt of *m*-nitrobenzenesulfonic acid has been reported,¹⁰ as well as some solubility studies of lanthanide(III) *m*-nitrobenzenesulfonate salts¹¹ (Fig. 1).

We prepared a series of lanthanide(III) nosylates by reaction between *p*-nitrobenzenesulfonic acid and the corresponding lanthanide(III) oxide.¹² After an initial screening, lanthanum(III) nosylate was selected as the most promising candidate for the nitration of a range of simple aromatic compounds using a stoichiometric amount of 67% nitric acid and 5–10% catalyst loading.¹³ The results of reactions performed in refluxing 1,2 dichloroethane for 16 h are shown in Table 1. The nitration of some substrates was completed within a shorter period of time, for example, quantitative nitration of naphthalene required less than 2 h, while toluene was nitrated within 4 h.

Besides lanthanum(III) nosylate, we tested other lanthanide(III) nosylates for their catalytic activity, and to our surprise, the observed trend was exactly the opposite than the trend reported for lanthanide(III) triflates.^{4,5} While the catalytic activity of triflate salts increases with decreasing ionic radius of the lanthanide(III) ion, the catalytic activity of lanthanide(III) nosylate salts decreases with the decrease of the ionic radius of the

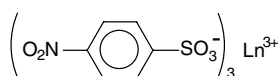


Figure 1. Formula of Ln(Nos)₃ complexes.

Table 1. Nitration of arenes in the presence of lanthanum(III) nosylate^a

| Arene | Conversion (%) ^b | Product distribution (%) ^b | | |
|------------------|-----------------------------|---------------------------------------|-------------|-----------------------|
| | | <i>ortho</i> | <i>meta</i> | <i>para</i> |
| Benzene | 81 | — | — | — |
| Toluene | >98 | 54 | 6 | 40 |
| Bromobenzene | 74 | 42 | — | 58 |
| <i>m</i> -Xylene | >98 | 4-NO ₂ :86 | — | 2-NO ₂ :14 |
| <i>p</i> -Xylene | 84 | — | — | — |
| Naphthalene | >98 | 1-NO ₂ :92 | — | 2-NO ₂ :8 |

^a 2 mmol of the substrate with 10 mol% of La(Nos)₃ and 1 equiv of 67% HNO₃ in refluxing 1,2-dichloroethane for 16 h.

^b GC/¹H NMR analysis.

Table 2. Effect of lanthanide(III) nosylate on the nitration of *p*-xylene^a

| Ln(Nos) ₃ | Conversion (%) ^b |
|----------------------|-----------------------------|
| La | 81 |
| Nd | 42 |
| Sm | 33 |
| Gd | 27 |
| Dy | 21 |
| Yb | 19 |

^a 2 mmol of the substrate with 10 mol% of Ln(Nos)₃ and 1 equiv of 67% HNO₃ in refluxing 1,2-dichloroethane for 16 h.

^b ¹H NMR analysis.

lanthanide(III) ion. As Table 2 shows, lanthanum(III) nosylate is a more efficient catalyst for the nitration of *p*-xylene than nosylate salts of the heavier lanthanides.

The different rates with various lanthanide nosylates indicate the involvement of the metal center in the nitration mechanism. However, the different trend in catalytic activity observed for lanthanide triflates and nosylates indicates that the counter ion also plays a significant role in the reaction. The single crystal structure of ytterbium(III) triflate shows that eight or nine water molecules occupy the first coordination sphere, while the triflate counter ions are not involved in the binding to the lanthanide(III) ion.¹⁴ In contrary, the single crystal structure of ytterbium(III) nitrobenzenesulfonate shows six water molecules in the first coordination sphere, and two counter ions directly coordinated to the metal centrum via oxygen atom, while the third counter ion is found in the second coordination sphere.¹⁵ ¹H NMR measurements in weakly coordinating solvents (e.g., acetone-*d*₆) containing 5 vol% of D₂O confirmed that this structure is preserved in such solution, in which the water content is comparable to that in our catalytic system.¹⁶ As it has been suggested that the key step in the nitration reaction is interaction of the nitric acid molecule with the metal centre,^{4,5} it is likely that bulky aromatic ligands around the ytterbium(III) ion could impose steric problems for this interactions. Unfortunately, we were not able to obtain crystals of good quality of lanthanum(III) nosylate, but the single crystal X-ray structures of analogous lanthanide(III) tosylates showed that in the lanthanum(III) complex tosylate ions are not present in the first coordination sphere, while in the complexes of smaller lanthanides, including ytterbium, two tosylate ligands are directly coordinated to the metal centre.¹⁷ This is consistent with our finding that La(Tos)₃ is more effective for the nitration of toluene than Yb(Tos)₃. In the lanthanide triflate catalysed reactions the tuning of the activity via steric effects is not present and the only factor, which determines the reactivity is the polarising power of the lanthanide ion. However, relative ratios of the various isomers produced in the lanthanide(III) nosylate catalysed nitrations are consistent with the nitration mechanism proposed for the lanthanide(III) triflate catalyst in which NO₂⁺ is the de facto nitrating agent.^{4,5}

The catalysts could be easily recovered and their ¹H NMR spectra were identical to the spectra of freshly prepared catalysts. The recovered catalysts were shown

Table 3. Recovery of lanthanum(III) nosylate after nitration of toluene^a

| Run | Conversion (%) ^b | Mass of catalyst/mg ^c |
|-----|-----------------------------|----------------------------------|
| 1 | >98 | 158 (96) |
| 2 | >98 | 146 (89) |
| 3 | 91 | 125 (76) |
| 4 | 82 | 102 (62) |

^a 2 mmol of toluene, 164 mg of La(Nos)₃ (10 mol%) and 1 equiv of 67% HNO₃ in refluxing 1,2-dichloroethane for 4 h.

^b ¹H NMR analysis.

^c Mass of recovered catalyst after each run. The values in parenthesis indicate the percentage recovery.

to be active for further nitrations with no change in selectivity and activity (Table 3).

In conclusion, we have demonstrated that novel lanthanide(III) catalysts can be prepared from *p*-nitrobenzenesulfonic acid. The latter has some major advantages compared to triflic acid: it is noncorrosive and it is much cheaper to attain. The catalytic efficiency of lanthanum(III) nosylate for the atom economic nitrations is comparable to the catalytic efficiency of ytterbium(III) triflate. We are currently exploring lanthanide(III) nosylates as catalysts for other types of organic reactions.

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- In a typical procedure, 67% nitric acid (2 mmol, 135 μ l) was added to a stirred suspension of La(Nos)₃ (0.2 mmol, 164 mg) in 1,2-dichloroethane (5 ml). *p*-Xylene (2 mmol, 245 μ l) was added and the mixture was heated at reflux for 16 h. After the solution was left to cool, water was added, and organic phase was dried (MgSO₄) and evaporated to give the nitrated product. The aqueous phase was evaporated to yield La(Nos)₃ (156 mg, 95%).
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