Lanthanide(III) Nitrobenzenesulfonates as New Nitration Catalysts: The Role of the Metal and of the Counterion in the Catalytic Efficiency

Tatjana N. Parac-Vogt,[a] Sophia Pachini,[b] Peter Nockemann,[a] Kristof Van Hecke,[a] Luc Van Meervelt,[a] and Koen Binnemans*[a]

Keywords: Homogeneous catalysis / Lanthanides / Lewis acids / Electrophilic substitution / Nitration / Rare earths

Lanthanide(III) complexes of *p*-nitrobenzenesulfonic acid, Ln(*p*-NBSA)$_3$, *m*-nitrobenzenesulfonic acid, Ln(*m*-NBSA)$_3$, and 2,4-nitrobenzenesulfonic acid, Ln(2,4-NBSA)$_3$, were prepared, characterized and examined as catalyst for the nitration of benzene, toluene, xylenes, naphthalene, bromobenzene and chlorobenzene. The initial screening of the catalysts showed that lanthanum(III) complexes were more effective than the corresponding ytterbium(III) complexes, and that catalysts containing the bulky 2,4-NBSA ligand were less effective than the catalyst containing *p*-NBSA (nosylate) or *m*-NBSA ligands. Examination of a series of Ln(*p*-NBSA)$_3$ and Ln(*m*-NBSA)$_3$ catalysts revealed that there is a clear correlation between the ionic radii of the lanthanide(III) ions and the yields of nitration, with the lighter lanthanides being more effective. The X-ray single crystal structure of Yb(*m*-NBSA)$_3$·6H$_2$O shows that two *m*-NBSA ligands are directly bound to the metal centre while the third ligand is not located in the first coordination sphere, but it is hydrogen bonded to one of the water molecules which is coordinated to ytterbium(III). NMR studies suggest that this structure is preserved under the conditions used in the nitration reaction. The structure of Yb(*m*-NBSA)$_3$ is markedly different from the structure of the well-known ytterbium(III) triflate catalyst. The coordination of the nitrobenzenesulfonate counterion to the lanthanide(III) ion suggests that steric effects might play an important role in determining the efficiency of these novel nitration catalysts.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

In the past decade, a great number of organic synthetic reactions involving lanthanide reagents have been explored.[1] Due to their unique electronic properties, the lanthanides offer new structural and reactivity patterns not present in main group and d-transition metal chemistry. Many important reactions such as carbon−carbon bond-forming reactions, asymmetric catalysis, polymer synthesis, etc., could be promoted by using various lanthanide catalysts. Some of those procedures, which have been summarized in several excellent reviews, play an important role in modern organic synthesis.[2] Among the many useful lanthanide reagents, lanthanide(III) triflates have been recognized as unique Lewis acids and they are currently of great research interest. Unlike classic Lewis acids such as AlCl$_3$, BF$_3$, TiCl$_4$, SnCl$_4$, etc., which decompose readily in the presence of water, lanthanide triflates are stable and can function as Lewis acids in aqueous media.[3] They are able to catalyse numerous reactions in aqueous solutions, such as Diels−Alder reactions,[4] aldol reactions,[5] Michael addition [6] and allylation of carbonyl and imine compounds.[7]

The use of lanthanide reagents for the aromatic nitration has been already demonstrated more than twenty years ago by Ouertani et al., but this procedure required stoichiometric quantities of lanthanide(III) nitrates for the selective nitration of phenols.[8] On the other hand, Waller et al. have shown that only catalytic amounts of scandium(III) or lanthanide(III) triflates were needed for the successful nitration of a range of simple aromatic compounds.[9,10] Unlike the commonly used industrial procedure, that requires use of potent mixtures of concentrated nitric and sulfuric acids, this procedure uses catalytic quantities of lanthanide(III) triflates as replacement for sulfuric acid and only one equivalent of nitric acid. In this way, excessive acid waste streams that are environmentally unfriendly and expensive to treat are avoided, and the only by-product of the nitration reaction is water. However, use of the lanthanide triflate catalysts on a very large scale is unlikely due to their relatively high cost and due to the fact that one needs to handle the strongly corrosive triflic acid for their preparation.

Nitration of aromatic compounds by the use of lanthanide reagents could also be achieved in fluorous solvents

---

[a] Katholieke Universiteit Leuven, Department of Chemistry,
Celestijnenlaan 200F, 3001 Leuven, Belgium
Fax: (internat.) +32-16-327992
E-mail: Koen.Binnemans@chem.kuleuven.ac.be
[b] Laboratory of Inorganic and General Chemistry, Faculty of Chemistry, Aristotle University of Thessaloniki,
Thessaloniki 54124, Greece

DOI: 10.1002/ejoc.200400475

using lanthanide salts of perfluorooctanesulfonic acid as catalysts.[11] Although very small catalyst loading were sufficient for achieving moderate to good yields (40−60%) of nitrotoluene, this method is also unlikely to be utilized on a large scale due to the high costs of fluorinated solvents and their large global warming potential that could pose serious environmental problems.[12]

We recently reported that lanthanide(III) salts of *p*-toluenesulfonic acid efficiently catalysed the conversion of toluene to nitrotoluene, but they were not very effective in the nitration of aromatic compounds with electron-withdrawing groups.[13] In an attempt to increase the activity of the catalyst we also explored lanthanide(III) salts of *p*-nitrobenzenesulfonic acid, which are also called lanthanide(III) nosylates.[14] Both *p*-toluenesulfonic and *p*-nitrobenzenesulfonic acids have some major advantages compared to triflic acid, because they are non-corrosive and much cheaper to obtain. Although the acidity of *p*-nitrobenzenesulfonic acid is at least five orders of magnitude weaker than that of triflic acid,[15] its lanthanide(III) salts seem to be sufficiently strong Lewis acids to catalyse efficiently the nitration of electron rich and mildly electron poor arenes. However, contrary to nitrations catalysed by lanthanide(III) triflates, in which the catalytic activity of triflate salts increases with decreasing ionic radius of the lanthanide(III) ion,[9−10] the catalytic activity of lanthanide(III) nosylate salts decreases with the decrease of the ionic radius of the lanthanide(III) ion. This intriguing difference prompted us to examine the role that both metal center and the counterion play in the reaction mechanism. We also characterized these novel lanthanide(III) catalysts, which are virtually unexplored compounds. To the best of our knowledge, no literature data about chemical and structural properties of these reagents are available up to now.

Results and Discussion

Synthesis and Characterization of the Catalysts

Lanthanide(III) complexes of three different nitrobenzenesulfonic acids: *p*-Nitrobenzenesulfonic (*p*-HNBSA), *m*-nitrobenzenesulfonic (*m*-HNBSA), and 2,4-nitrobenzenesulfonic (2,4-HNBSA) acids, were synthesized (Figure 1).

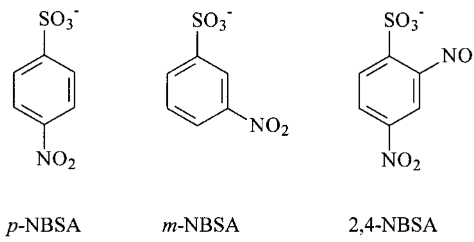


Figure 1. Sulfonates used as counterions for lanthanide(III) catalysts: *p*-NBSA = *para*-nitrobenzenesulfonate; *m*-NBSA = *meta*-nitrobenzenesulfonate; 2,4-NBSA = 2,4-dinitrobenzenesulfonate

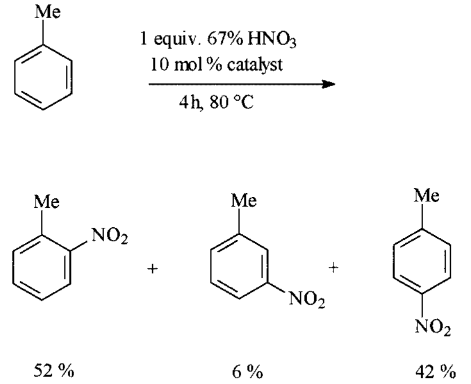
Single crystal and thermal analytical studies of related lanthanide complexes with *p*-toluenesulfonic acid, the so-called lanthanide tosylates, showed that this type of complexes initially crystallize with nine water molecules in the first coordination sphere, and that seven water molecules are lost upon heating at ca. 55 °C.[16] As the coordination number of the lanthanides is always high (commonly 8 or 9), it has been proposed that upon removal of hydrated water molecules from the crystal, the sulfonate anions move and act as multidentate ligands forming more metal-oxygen bonds in place of the removed water oxygen atoms. The elemental analysis results of lanthanide(III) complexes with nitrosulfonic acids (Exp. Sect.) indicated that upon drying the crystalline solid at 40 °C in vacuo, some water of crystallization is lost, but the complexes still contain two to six molecules of water. Consequently, infrared spectroscopic data of the complexes showed strong and broad absorption in the region 3200−3600 cm^{-1}, corresponding to the −OH stretching frequency of water molecules.

Since it has been known that some sulfonic acids are capable of promoting nitration reactions[17] it is important to demonstrate the absence of trace amounts of free nitrobenzenesulfonic acid in the lanthanide(III) catalyst. The infrared spectra of lanthanide(III) complexes showed that the broad absorption between 2400 and 3000 cm^{-1}, typical for the OH stretching mode of protonated nitrobenzenesulfonic acid,[18] was absent in all cases. Furthermore, the aqueous solution of lanthanide(III) complexes always had a close-to-neutral pH, which further confirms the absence of free nitrobenzenesulfonic acid in the isolated catalysts.

Screening of the Lanthanide(III) Catalysts

Previous studies involving various reactions catalysed by lanthanide(III) triflates have shown that ytterbium(III) triflate is the most effective catalyst among all the lantha-

Table 1. Nitration of toluene in the presence of ytterbium(III) and lanthanum(III) catalysts containing different counterions



Counterion	Conversion (%)[a] Yb^{III}	La^{III}
p-NBSA	61%	> 98%
m-NBSA	58%	> 98%
2,4-NBSA	41%	83%

[a] ^1H NMR analysis, the product distribution of different nitrotoluene isomers was in each reaction the same.

© 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

nides(III) triflates.[3] A screening of the entire series of lanthanide(III) triflates for their catalytic activity in nitration also revealed a clear inverse correlation between the extent of nitration reaction and the ionic radius of the trivalent lanthanide ion.[10] The reaction we chose for the initial screening of the catalytic activity of Ln(*p*-NBSA)$_3$, Ln(*m*-NBSA)$_3$, and Ln(2,4-NBSA)$_3$ catalysts was the nitration of toluene. We first examined catalysts containing either ytterbium(III) or lanthanum(III) ions, as these two ions represent two extreme examples of the lanthanide(III) series in terms of ionic radius. To our surprise, when the nitration reaction was quenched after four hours, the lanthanum(III) catalysts gave in all the cases much higher yields than the corresponding ytterbium(III) catalysts (Table 1).

Further experiments also showed that the lanthanum(III) catalysts were consistently more efficient in the nitration reaction of other aromatic compounds than the ytterbium(III) catalysts, so we focused our attention on the former system.

Nitration of Arenes with La(*p*-NBSA)$_3$, La(*m*-NBSA)$_3$ and La(2,4-NBSA)$_3$ Catalysts

All nitration reactions were performed in 1,2-dichloroethane at reflux temperature in the presence of a stoichiometric amount of 67% nitric acid and 10 mol % of the catalysts. In the control experiments with no catalyst, only slow reaction occurred and only a small amount of nitrated products were observed. We initially anticipated that due to the stronger electron-withdrawing ability of the 2,4-NBSA group, La(2,4-NBSA)$_3$ would have a stronger Lewis acidity than La(*p*-NBSA)$_3$ and La(*m*-NBSA)$_3$. Therefore, La(2,4-NBSA)$_3$ was expected to be a more efficient catalyst than La(*p*-NBSA)$_3$ and La(*m*-NBSA)$_3$. However, as Table 2 shows, in all reactions La(*p*-NBSA)$_3$ and La(*m*-NBSA)$_3$ were superior nitration catalysts compared to the La(2,4-NBSA)$_3$ compounds. In all the cases no dinitrated products were observed, and in accordance with this, none of the catalysts was effective for the nitration of nitrobenzene.

Table 2. Nitration of aromatics in the presence of different lanthanum(III) catalysts

Arene	Conversion (%)[a][b] La(*p*-NBSA)$_3$	La(*m*-NBSA)$_3$	La(2,4-NBSA)$_3$
toluene[c]	> 98	> 98	> 98
naphthalene[d]	> 98	> 98	> 98
benzene	82	77	58
m-xylene[e]	> 98	> 98	74
p-xylene	78	80	32
bromobenzene[f]	74	69	18
chlorobenzene[g]	76	70	19

[a] 3 mmol of the substrate with 10 mol % of the catalyst and 1 equiv. of 67% HNO$_3$ in refluxing 1,2-dichloroethane for 16 h. [b] GC/^{1}H NMR analysis; the product distribution of nitro isomers was independent on the catalyst. [c] Isomer distributions (%): *ortho*: 52; *meta*: 6; *para*: 42. [d] Isomer distributions (%): 1-NO$_2$: 91; 2-NO$_2$: 9. [e] Isomer distributions (%): 4-NO$_2$: 87; 2-NO$_2$: 13. [f] Isomer distributions (%): *ortho*: 42; *para*: 58. [g] Isomer distributions (%): *ortho*: 44; *para*: 56.

The effect of catalyst concentration on the reaction yields was examined for the nitration of naphthalene. Within 30 minutes, one equivalent of nitric acid and only 5 mol % of the La(*p*-NBSA)$_3$ catalyst were sufficient for the quantitative conversion of naphthalene to 1-mononitronaphthalene and 2-mononitronaphthalene, while 2 mol % of the catalysts yielded 87% of the same products. (Table 3).

Table 3. Effect of the La(*p*-NBSA)$_3$ catalyst loading on the extent of naphthalene nitration

Catalyst load(%)[a] [b]	Reaction yield
10%	100
5%	100
2%	87
1%	72

[a] 3 mmol of the substrate and 1 equiv. of 67% HNO$_3$ in refluxing 1,2-dichloroethane for 30 min. [b] GC analysis; the product distribution of 1-NO$_2$ and 2-NO$_2$ isomers was in each reaction 92:8.

Effect of the Lanthanide(III) Ion on the Nitration Reaction

As already mentioned, the initial screening of the catalytic activity showed that lanthanum(III) catalysts were superior to ytterbium(III) catalysts. In order to elucidate the role of the metal center in the nitration reaction, a series of Ln(*p*-NBSA)$_3$ and Ln(*m*-NBSA)$_3$ catalysts with different lanthanide(III) ions was examined as potential catalysts. Although all complexes were found to exhibit catalytic properties, marked differences were apparent. There is a clear correlation between the ionic radii of the lanthanide(III) ions and the yields of the nitration, with the lighter lanthanides being the more effective ones. As a result, among Ln(*m*-NBSA)$_3$ catalysts, lanthanum(III) (atomic number 57) gave 80% conversion of *p*-xylene to nitro-*p*-xylene over 16 h, whereas the ytterbium(III) (atomic number 70) catalyst yielded only 20% of the nitrated product over the same period (Figure 2). A similar trend was observed for the nitration of naphthalene catalysed by Ln(*p*-NBSA)$_3$ (Table 4), although the relative differences in catalytic activities between lighter and heavier lanthanides were smaller (Table 3).

This trend is opposite to the trend observed in lanthanide(III) triflate catalysts in which there is an inverse correlation between the catalytic activity and the ionic radii of the lanthanide(III) ion.[10] It has been reasoned that the electrostatic interaction between the lanthanide ion and nitric acid, which is crucial for the formation of the nitronium ion (NO_2^+) as the de facto nitrating agent, increases as the polarising power (i.e. charge-to size-ratio) of lanthanide ion increases. However, it is obvious that in the case of lanthanide(III) nitrobenzosulfonate catalysts the electrostatic interactions do not play the decisive role in the extent of nitration, since the complex with the least polarizing lanthanide (i.e. the lanthanum ion) is the most effective. The isomer distributions for the nitration of arenes are nevertheless consistent with the distribution expected for the direct elec-

© 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

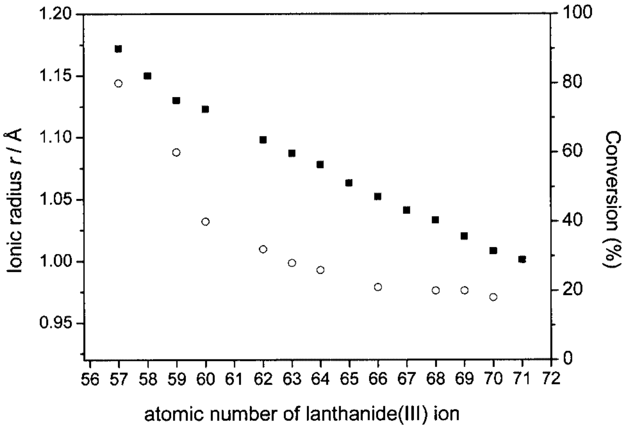


Figure 2. Effect of the lanthanide(III) ion in Ln(m-NBSA)$_3$ on the conversion of p-xylene to nitro-p-xylene. The ionic radii of the lanthanide(III) ions are shown for the sake of comparison

Table 4. Effect of various Ln(p-NBSA)$_3$ for the nitration of naphthalene

Ln^{III}(%)[a] [b]	Conversion
La	100
Nd	97.1
Sm	88.6
Eu	93.9
Gd	83.4
Dy	82.4
Tm	82.1
Yb	72.5

[a] 3 mmol of the substrate with 10 mol % of the catalyst and 1 equiv. of 67% HNO_3 in refluxing 1,2-dichloroethane for 30 min. [b] GC analysis; the product distribution of 1-NO_2 and 2-NO_2 isomers was in each reaction 92:8.

trophilic attack by the nitronium ion. The mechanism by which the nitronium ion is formed presumably involves the binding of nitric acid to the lanthanide(III) ion, resulting in proton liberation due to the strong polarization by the metal. The liberated proton reacts further with another molecule of nitric acid yielding a nitronium ion in the classical manner.[19] It is at this point important to note that the identity of the counterion is crucial for the catalytic activity. It has been shown that simple lanthanide salts such as lanthanide(III) chlorides or nitrates are poor nitration catalysts.[10] The counterion needs to be the conjugate base of a sufficiently strong acid so that nitric acid is preferentially protonated, producing a nitronium ion.

Role of the Counterions in the Nitration Reaction

How can we explain that the extent of nitration is the smallest in the case of strongly polarizing lanthanide ions? Since lanthanide(III) nitrobenzenesulfonates and lanthanide(III) triflate catalysts differ only in the nature of the counterion, it is likely that the anions play the decisive role in catalytic reaction. Therefore, it is helpful to consider the interactions of these anions with the lanthanide(III) catalysts. In lanthanide(III) triflates, the triflate counterions are outer sphere and are merely spectator ions. X-ray crystal structures of hydrated lanthanides(III) triflates have been reported for the entire lanthanide series, and they all show that nine water molecules occupy the first coordination sphere and that triflate counterions are in the outer sphere.[20] The solution studies on lanthanides(III) triflates suggest that this structure is preserved in solution and that the triflates are essentially spectator ions.[21] We were able to determine the X-ray single crystal structure of Yb(m-NBSA)$_3$·6H_2O, and this structure shows that the coordination environment around the ytterbium(III) is occupied by two oxygen atoms from the sulfonate group of m-NBSA and six oxygen atoms from water molecules (Figure 3, Table 5, Table 6). The coordination polyhedron around ytterbium(III) can be described as a slightly distorted quadratic antiprism. The third m-NBSA anion is not located in the first coordination sphere, but forms hydrogen bonds with two of the coordinated water molecules. The dihedral angle between the nitro group and the plane of the phenyl ring of the non-coordinating 3-nitrobenzenesulfonate molecule is with 20.1(10)° noticeable greater than the angle for the two coordinating molecules with 2.5(11)° and 6.1(9)°, respectively.

This difference in structure compared to ytterbium(III) triflate may explain the significant differences in the efficiency of these two catalysts. In order for the interaction between lanthanide(III) ion and the nitric acid to occur, displacement of one of the ligands in the first coordination sphere is necessary. While in the case of Yb(OTf)$_3$ there is no steric hindrance for this interaction, it is conceivable that in the case of Yb(m-NBSA)$_3$, the bulky m-NBSA ligands present in the first coordination sphere may hinder this interaction. This may also explain why Ln(*2,4*-NBSA)$_3$ catalysts with bulky counterions are inferior compared to Ln(p-NBSA)$_3$ and Ln(m-NBSA)$_3$.

Unfortunately, we were not able to isolate crystals of lanthanum(III) catalysts of a quality good enough for the single-crystal X-ray analysis, so it is not possible to tell if in these complexes counterions are directly bound to the lanthanide(III) centre or if they are merely spectator ions. Even if the counterions are located in the first coordination sphere, the steric hindrance around larger lanthanum(III)ion should be lesser than the smaller ytterbium(III) ion. However, it is possible that lanthanum(III) complexes of nitrobenzenesulfonic acids follow the same structural pattern as analogous lanthanum(III) tosylate complexes, in which there are nine water molecules occupying the first coordination sphere while the counterions are not interacting with the metal centre.[22] This type of structure would be consistent with the high activity of the lanthanum(III) catalyst, since the absence of bulky counterions in the first coordination sphere poses no steric hindrance for the interaction between the lanthanum(III) and nitric acid. In contrary, the ytterbium(III) tosylate complex has a structure very similar to the structure of Yb(m-NBSA)$_3$ in which two ligands are directly bound to ytterbium(III).[16] The analogy between the structures of the lanthanide(III) nitrobenzenesulfonate

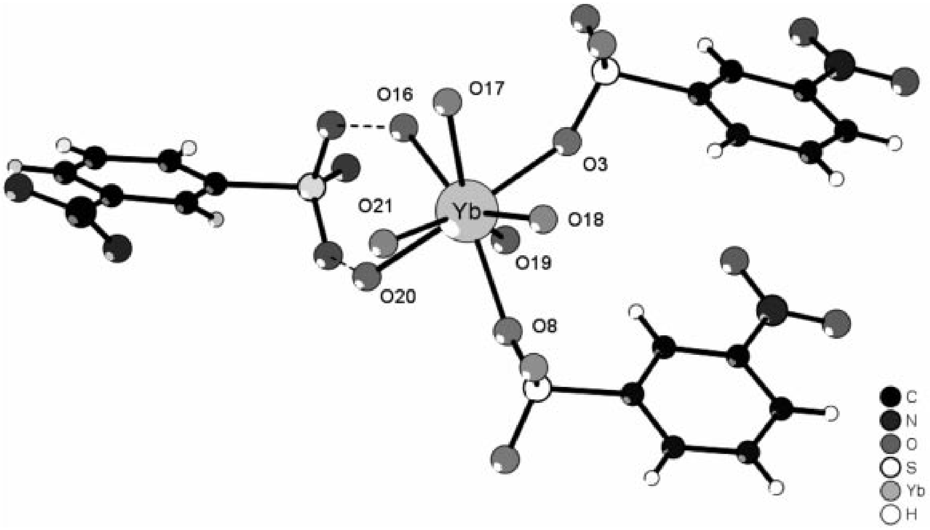


Figure 3. Molecular structure of Yb(*m*-NBSA)$_3$·6H$_2$O

Table 5. Crystallographic data for the compound Yb(*m*-NBSA)$_3$·6H$_2$O

Formula	$C_{18}H_{12}N_3O_{22}S_3Yb$
Formula mass	891.56
Dimensions (mm)	0.2 × 0.2 × 0.1
Color	colorless
Crystal system	monoclinic
Space group	*C*2/*c*
a (Å)	56.55(3)
b (Å)	7.624(4)
c (Å)	14.158(8)
β (°)	93.28(3)
V (Å^3)	6094(6)
Z	8
$D_{\text{calcd.}}$ (g·cm^{-3})	1.944
$\theta_{\text{max.}}$ (°)	70.72
$\mu_{\text{Cu-}K\alpha}$ (mm^{-1})	8.499
F(000)	3480
Measured reflections	23853
Unique reflections	5725
Observed reflections [$F_o > 4\sigma(F_o)$]	4578
Parameters refined	424
R_1	0.0815
ωR_2	0.2240
R_1 (all data)	0.0972
ωR_2 (all data)	0.2388
GooF	1.068

Table 6. Yb−O distances for Yb(*m*-NBSA)$_3$·6H$_2$O

Atoms	Distance (Å)
Yb1−O3	2.276(5)
Yb1−O16	2.311(5)
Yb1−O21	2.319(5)
Yb1−O8	2.330(4)
Yb1−O19	2.346(5)
Yb1−O17	2.374(5)
Yb1−O18	2.394(5)
Yb1−O20	2.416(5)

and lanthanide(III) tosylate complexes is not surprising, if one takes into account the similarities of the nitrobenzenesulfonate and tosylate structures and their similar pK_a values.

Solution Studies of Ln(*p*-NBSA)$_3$ and Ln(*m*-NBSA)$_3$ Catalysts

^{1}H NMR spectra of Ln(*p*-NBSA)$_3$ and Ln(*m*-NBSA)$_3$ complexes were measured in order to gain more information about the structure of these complexes in solution. In aqueous solutions, proton resonances of the ligand showed the same chemical shifts as in the fully dissociated nitrobenzenesulfonic acids, implying that there was no binding of the nitrobenzenesulfonate ligand to the lanthanide(III) ion, so that complexes existed as purely lanthanide(III) aqua ions. The concentration of water in the NMR measurements was about five orders of magnitude greater than the concentration of the catalyst. Since the lanthanide(III) ions have a high affinity toward water molecules, it is not surprising that under the condition in which there is a huge excess of water they tend to exist as aqua complexes. However, the water solution clearly does not represent the experimental conditions applied in the nitration reaction. The nitration reactions were performed in 1,2-dichloroethane, and the only source of water comes from the 67% solution of the nitric acid. A simple calculation indicates that under reaction conditions the catalyst and the water were present in approximately equimolar amounts. Attempts to record proton NMR spectra under conditions which exactly mimic the nitration reaction conditions were unsuccessful, due to the low solubility of lanthanide(III) catalysts in chlorinated solvents. As an alternative, acetone was used as solvent and the proton NMR spectra of Eu(*m*-NBSA)$_3$ complexes were recorded in different [D$_6$]acetone/D$_2$O ratio. As Figure 4a shows, in the presence of a small amount of D$_2$O (less than 5 volume%) two sets of peaks with the intensity ratio of 2:1 were observed. The larger set of peaks which appeared in the region between $\delta = 0$ and 2 ppm could be assigned to *m*-NBSA ligands which are bound to europium(III). Due to this interaction *m*-NBSA protons experience a large paramagnetic shift. The smaller set of peaks appeared in the region between 7.5 and 9 ppm and was assigned to one *m*-NBSA ligand which is not directly bound to europium(III). Upon addition of D$_2$O (ca. 40 volume%), the larger set of peaks disappeared and all *m*-NBSA resonances appeared in the region between 7.5 and 9 ppm (Figure 4, b).

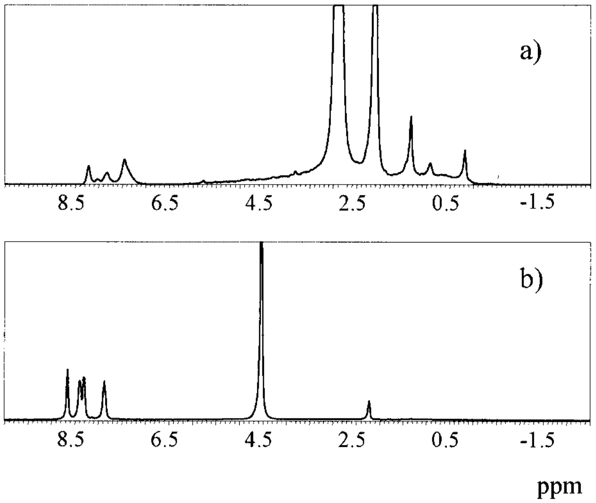


Figure 4. Proton NMR spectra of Eu(*m*-NBSA)$_3$ in [D$_6$]acetone containing (a) 5 vol% D$_2$O, and (b) 40 vol% D$_2$O. The large peaks at ca. 2.2, 3.0 and 4.6 ppm belong to the solvents

These experiments suggest that under condition in which the amount of water is limited, the solid-state structure is preserved in the solution, and that two *m*-NBSA ligands bind to the lanthanide(III) ion. Only upon adding large amount of water, these ligands become spectator ions.

Conclusions

In summary, we have demonstrated that efficient lanthanide(III) nitration catalysts can be prepared from *para*- and *meta*-nitrobenzenesulfonic acids. These acids have some major advantages compared to triflic acid as they are noncorrosive and cheaper to obtain. The catalytic efficiency of their lanthanum(III) complexes for the atom economic nitration of arenes is comparable to the catalytic efficiency of ytterbium(III) triflate. We have shown that contrary to triflate salts, a simple charge-to-size ratio of a lanthanide(III) ion cannot be used for the relative reactivity of the lanthanide nitrobenzenesulfonate salts as nitration catalysts. The evidence from the solid state and solution studies suggest that under the reaction conditions, the nitrobenzenesulfonate ions are likely to be bound to the lanthanide(III) ion, which could cause a steric hindrance for the interaction between a molecule of nitric acid and the lanthanide(III) ion. Because of the steric effects, the catalysts with the small-sized ytterbium(III) ion are inferior to the catalysts with the larger lanthanum(III) ion. Similarly, the steric reasons may explain why lanthanide(III) catalysts with the bulkier 2,4-nitrobenzenesulfonate ligand are less efficient than the corresponding *meta*- and *para*-nitrobenzenesulfonate lanthanide(III) catalysts.

Experimental Section

Materials and Methods: Reagents were obtained from Aldrich Chemical Co. Inc., Acros Organics or Rhodia Electronics and Catalysis, and used without further purification. The *p*-nitrobenzenesulfonic acid is commercially available, but it can be also obtained very cheaply, in a one-step procedure starting from sulfanilic acid.[23] ^{1}H NMR spectra were run with a Bruker Avance 300, operating at 300 MHz. GC analyses were performed at ThermoFinnigan Trace GC. Elemental analysis was performed on a CE Instruments EA-1110 elemental analyser.

General Procedure for the Synthesis of Ln(*p*-NBSA)$_3$, Ln(*m*-NBSA)$_3$ and Ln(2,4-NBSA)$_3$

The compounds were synthesized by the reaction of 1.1 equivalent of the corresponding lanthanide(III) oxide, and six equivalents of the sulfonic acid in aqueous solution. After stirring the solution in boiling water for 30 minutes, the excess of oxide was removed by filtration. The filtered solution was either left to crystallize or was evaporated to dryness and the resulting solid was dried in a vacuum oven at 50 °C overnight.

Results for Ln(*p*-NBSA)$_3$·*x*H$_2$O: La(*p*-NBSA)$_3$·2H$_2$O ($C_{18}H_{16}LaN_3O_{17}S_3$): calcd. C 27.66, H 2.06, N 5.37; found C 27.37, H 1.97, N 5.15. Nd(*p*-NBSA)$_3$·3H$_2$O ($C_{18}H_{18}N_3NdO_{18}S_3$): calcd. C 26.86, H 2.26, N 5.22; found C 26.42, H 2.27, N 4.98. Sm(*p*-NBSA)$_3$·2H$_2$O ($C_{18}H_{16}N_3O_{17}S_3Sm$): calcd. C 27.26, H 2.03, N 5.29; found C 27.16, H 1.97, N 5.29. Eu (*p*-NBSA)$_3$·5H$_2$O ($C_{18}H_{22}EuN_3O_{20}S_3$): calcd. C 25.47, H 2.61, N 4.95; found C 25.16, H2.64, N 4.65. Gd(*p*-NBSA)$_3$·5H$_2$O ($C_{18}H_{22}GdN_3O_{20}S_3$): calcd. C 25.32, H 2.59, N 4.92; found C 24.84, H 2.53, N 4.63. Dy(*p*-NBSA)$_3$·3H$_2$O ($C_{18}H_{18}DyN_3O_{18}S_3$): calcd. C 26.27, H 2.21, N 5.09; found C 26.34, H 2.31, N 4.91. Er(*p*-NBSA)$_3$·2H$_2$O ($C_{18}H_{16}ErN_3O_{17}S_3$): calcd. C 26.70, H 2.00, N 5.20; found C 27.20, H 2.01, N 5.22. Tm(*p*-NBSA)$_3$·5H$_2$O ($C_{18}H_{22}N_3O_{20}S_3Tm$): calcd. C 24.979, H 2.56, N 4.85; found C 24.75, H 2.56, N 4.68. Yb(*p*-NBSA)$_3$·5H$_2$O, ($C_{18}H_{22}N_3O_{20}S_3Yb$): calcd. C 24.86, H 2.55, N 4.83; found C 24.10, H 2.67, N 4.45.

Elemental Analysis Results for Ln(*m*-NBSA)$_3$·*x*H$_2$O: La(*m*-NBSA)$_3$·4H$_2$O ($C_{18}H_{20}N_3O_{19}S_3La$): calcd. C 26.45, H 2.46, N 5.14; found C 26.48, H 2.34, N 4.89. Pr(*m*-NBSA)$_3$·2H$_2$O ($C_{18}H_{16}N_3O_{17}PrS_3$): calcd. C 27.60, H 2.06, N 5.37; found C 27.68, H 2.33, N 5.45. Nd(*m*-NBSA)$_3$·4H$_2$O ($C_{18}H_{20}N_3NdO_{19}S_3$): calcd. C 26.27, H 2.45, N 5.10; found C 26.20, H 2.43, N 4.68. Sm(*m*-NBSA)$_3$·4H$_2$O ($C_{18}H_{20}N_3O_{19}S_3Sm$): calcd. C 26.08, H 2.43, N 5.06; found C 25.98, H 2.37, N 4.60. Eu (*m*-NBSA)$_3$·4H$_2$O ($C_{18}H_{20}EuN_3O_{19}S_3$): calcd. C 26.03, H 2.42, N 5.06; found C 25.95, H 2.38, N 4.70. Gd(*m*-NBSA)$_3$·4H$_2$O ($C_{18}H_{20}N_3O_{19}S_3Gd$): calcd. C 25.86, H 2.41, N 5.02; found C 25.70, H 2.35, N 4.61. Dy(*m*-NBSA)$_3$·4H$_2$O ($C_{18}H_{20}DyN_3O_{19}S_3$): calcd. C 25.70, H 2.39, N 4.99; found C 25.69, H 2.36, N 4.56. Er(*p*-NBSA)$_3$·H$_2$O ($C_{18}H_{14}N_3O_{16}S_3Er$): calcd. C 27.30, H 1.79, N 5.30; found C 27.20, H 2.01, N 5.22. Tm(*p*-NBSA)$_3$·5H$_2$O,($C_{18}H_{22}N_3O_{20}S_3Tm$): calcd. C 24.98, H 2.56, N 4.85; found C 24.75, H 2.56, N 4.68. Yb(*p*-NBSA)$_3$·4H$_2$O ($C_{18}H_{20}N_3O_{19}S_3Yb$): calcd. C 25.38, H 2.37, N 4.93; found C 25.76, H 2.51, N 5.04.

© 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Elemental Analysis Results for Ln(2,4-NBSA)$_3$·xH$_2$O: La(2,4-NBSA)$_3$·6H$_2$O ($C_{18}H_{21}LaN_6O_{27}S_3$): calcd. C 21.87, H 2.14, N 8.50; found C 21.43, H 2.24, N 7.91. Yb(2,4-NBSA)$_3$·6H$_2$O ($C_{18}H_{21}N_6O_{27}S_3Yb$): calcd. C 21.14, H 2.07, N 8.21; found C 20.76, H 2.17, N 7.69.

Single Crystal X-ray Data for Yb(*m*-NBSA)$_3$·6H$_2$O: A single crystal was obtained by slow evaporation of an aqueous solution of the ytterbium(III) complex. A crystal of dimensions 0.2 × 0.2 × 0.1 mm was mounted in a nylon loop for data collection at 110 K with a SMART 6000 diffractometer equipped with CCD detector using Cu-K$_\alpha$ radiation (λ = 1.54178 Å). The images were interpreted and integrated with the program SAINT from Bruker. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.[24] Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors. The refinement was complicated by the high crystal mosaicity. CCDC-246951 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336033; or deposit@ccdc.cam.uk).

General Procedure for the Lanthanide(III) Nitrobenzenesulfonate-Catalysed Nitration of Arenes: To a solution of the respective lanthanide(III) catalyst (5 mol %, 0.3 mmol) in nitric acid (67%, d = 1.41, 0.200 mL, 3.0 mmol) was added a solution of the aromatic compound (3 mmol) in 4 mL of 1,2-dichloroethane. The mixture was stirred and heated at reflux. After a given period of time the solution was cooled and diluted with water. The yellow organic phase was dried with MgSO$_4$, the solvent was evaporated and the residue was analysed by ^{1}H NMR or gas chromatography.

Acknowledgments

T. N. P. V. and K. B. are Postdoctoral Fellows of the FWO-Flanders (Belgium). Financial support has been provided by the K. U. Leuven (VIS/01/006.01/2002/-06/2004 and GOA 03/03) and by the FWO-Flanders (Krediet aan Navorsers to K. B.). The authors thank Rhodia electronics and Catalysis for a gift of rare-earth oxides.

---

[1] "*Lanthanides: Chemistry and Use in Organic Synthesis*" (S. Kobayashi, Ed.), Springer, Berlin, **1999**.

[2] [2a] H. B. Kagan, J. L. Namy, *Tetrahedron* **1986**, *42*, 6573−6614. [2b] G. A. Molander, *Chem. Rev.* **1992**, *92*, 29−68. [2c] G. A. Molander, C. R. Harris, *Chem. Rev.* **1996**, *96*, 307−338. [2d] G. A. Molander, C. R. Harris, *Tetrahedron* **1998**, *54*, 3321−3354. [2e] A. Krief, A. M. Laval, *Chem. Rev.* **1999**, *99*, 745−777. [2f] H. J. Liu, K. S. Shia, X. Shang, B. Y. Zhu, *Tetrahedron* **1999**, *55*, 3803−3830. [2g] P. G. Steel, *J. Chem. Soc., Perkin Trans. 1* **2001**, 2727−2751. [2h] J. Inanaga, H. Furuno, T. Hayano, *Chem. Rev.* **2002**, *102*, 2211−2225.

[3] S. Kobayashi, M. Sugiura, H. Kitagawa, W.W. L. Lam, *Chem. Rev.* **2002**, *6*, 2227−2302.

[4] S. Kobayashi, I. Hachiya, M. Araki, H. Ishitani, *Tetrahedron Lett.* **1993**, *34*, 3755−3758.

[5] [5a] S. Kobayashi, *Chem. Lett.* **1991**, 2187−2190. [5b] S. Arseniyadis, Q. Wang, D. Yashunsky, T. Kaoudi, A. R. Brondu, R. Potier, *Tetrahedron Lett.* **1995**, *36*, 1633−1636. [5c] S. Kobayashi, I. Hachiya, *J. Org. Chem.* **1994**, *59*, 3590−3596. [5d] S. Kobayashi, I. Hachiya, *Tetrahedron Lett.* **1992**, *33*, 1625−1628. [5e] S. Kobayashi, T. Wakabayashi, S. Nagayama, H. Oyamada, *Tetrahedron Lett.* **1997**, *38*, 4559−4562. [5f] S. Kobayashi, T. Busujima, S. Nagayama, *Chem. Commun.* **1998**, 19−20.

[6] E. Keller, B. L. Feringa, *Synlett* **1997**, 842−842.

[7] [7a] I. Hachiya, S. Kobayashi, *J. Org. Chem.* **1993**, *58*, 6958−6960. [7b] T. Akiyama, J. Iwai, *Tetrahedron Lett.* **1997**, *38*, 853−856.

[8] M. Ouertani, P. Girard, H. B. Kagan, *Tetrahedron Lett.* **1982**, *23*, 4315−4318.

[9] F. J. Waller, A. G. M. Barrett, D. C. Braddock, D. Ramprasad, *Chem. Commun.* **1997**, 613−614.

[10] F. J. Waller, A. G. M. Barrett, D. C. Braddock, R. M. McKinnell, D. Ramprasad, *J. Chem. Soc., Perkin Trans. 1* **1999**, 867−871.

[11] M. Shi, S-C. Cui, *Chem. Commun.* **2002**, 994−995.

[12] S. K. Fischer, M. McFarland, "*Alternatives to CFCs and Global warming: A systems approach to evaluating net contributions*", Materials Research Society, **1992**, vol. 17, p. 39.

[13] T. N. Parac-Vogt, K. Deleersnyder, K. Binnemans, *J. Alloy. Comp.* **2004**, *374*, 46−49.

[14] T. N. Parac-Vogt, K. Binnemans, *Tetrahedron Lett.* **2004**, *45*, 3137−3139.

[15] D. C. French, D. S. Crumrine, *J. Org. Chem.* **1990**, *55*, 5494−5496.

[16] Y. Ohki, Y. Suzuki, T. Takeuchi, A. Ouchi, *Bull. Chem. Soc., Jpn.* **1988**, *61*, 393.

[17] C. L. Coon, W. G. Blucher, M. E. Hill, *J. Org. Chem.* **1973**, *38*, 4243−4248.

[18] E. Pretsch, T. Clerc, J. Seibl, W. Simon in *Tabellen zur Strukturaufklärung organischer Verbindungen mit spektroskopischen Methoden*, Springer, Berlin, **1976**.

[19] [19a] G. A. Olah, R. Malhotra, S. C. Narang, *Nitration: Methods and Mechanisms*; VCH Publishers, New York, **1989**. [19b] K. Schofield, *Aromatic Nitration*; Cambridge University Press, Cambridge, **1980**.

[20] [20a] J. M. Harrowfield, D. L. Kepert, J. M. Patrick, A. H. White, *Aust. J. Chem.* **1983**, *36*, 483−492. [20b] A. Chatterjee, E. N. Maslen, K. J. Watson, *Acta Crystallogr., Sect. B* **1988**, *44*, 381−386.

[21] B. P. Hay, *Inorg. Chem.* **1991**, *30*, 2876−2884.

[22] D. L. Faithfull, J. M. Harrowfield, M. I. Ogden, B. W. Skelton, K. Third, A. H. White, *Aust. J. Chem.* **1992**, *45*, 583−594.

[23] M. Vincent, J. Maillard, M. Benard, *Bull. Soc. Chim. Fr.* **1962**, 158.

[24] SAINT, Manual Version 5/6.0, Bruker Analytical X-ray Systems Inc.: Madison, Wisconsin, **1997**. SHELXTL-NT, Manual Version 5.1, Bruker Analytical X-ray Systems Inc.: Madison, Wisconsin, **1997**.

Received July 5, 2004