

Lanthanide(III) and Group IV metal triflate catalysed electrophilic nitration: 'nitrate capture' and the rôle of the metal centre †

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The lanthanide(III) triflate, $[\text{Ln}(\text{OH}_2)_9](\text{OTf})_3$ ($\text{Ln} = \text{La-Lu}$), catalysed nitration of a representative arene, *viz.* bromobenzene, is reported. The extent of nitration is found to be dependent on the charge-to-size ratio of the tripositive metal centre. A mechanistic scenario involving 'nitrate capture' in the auto-ionisation of nitric acid is presented where triflic acid plays a key role in the generation of the *de facto* nitration agent: the nitronium ion. Preparation of the putative intermediates, $[(\text{H}_2\text{O})_x\text{Ln}(\text{NO}_3)](\text{OTf})_2$ ($\text{Ln} = \text{La-Lu}$), and characterisation by IR spectroscopy shows the nitrate anion is inner sphere and the triflate anions are outer sphere. Additionally, these salts show a steady increase in nitrate stretching IR frequencies as the charge-to-size ratio of the tripositive lanthanide increases, providing strong evidence for the nitrate capture model. Extrapolation to higher charge-to-size ratio predicts $[\text{Hf}(\text{OH}_2)_x](\text{OTf})_4$ to be a superior nitration catalyst. Experimental confirmation of theory is obtained by the application of $[\text{Hf}(\text{OH}_2)_x](\text{OTf})_4$ to the successful nitration of the strongly electron deficient arene *o*-nitrotoluene.

Introduction

Since Forsberg's initial contribution¹ in 1987, the lanthanide(III) triflates have become the focus of much current research.²⁻¹⁰ Subsequently pioneered by Kobayashi as recyclable water-tolerant Lewis acids, their potential to replace traditional Lewis acids has been much vaunted. This hope has been borne out by their successful application to bond-forming reactions traditionally mediated by strong Lewis acids: Diels-Alder cycloadditions,³ Friedel-Crafts acylations,⁴ Mukaiyama aldol additions,⁵ allylation reactions,⁶ alcohol esterifications,⁷ conjugate addition reactions,⁸ ring opening of oxiranes with amines,⁹ methanolysis of methoxyacetates,^{10a} in conjunction with indium for the reduction of ethyl 4-bromocrotonate with aldehydes^{10b} and in the addition reaction of trimethylsilyl cyanide to imines.^{10c} In addition, the catalyst can usually be recycled and re-used with little or no detriment to selectivity, activity or yield. Furthermore, and to our minds most critically, many of these lanthanide catalysed reactions can be run in and/or *perform optimally* in aqueous or protic media.^{5,6a,8c,d,10} This paradoxical state of affairs [the ability of the lanthanide(III) triflates to function as apparent strong Lewis acids in aqueous media] attracted us to consider the possibility of their use as a replacement for sulfuric acid in the electrophilic nitration of arenes with nitric acid. Indeed, we have recently reported the use of catalytic quantities of lanthanide(III) triflates for such a purpose.¹¹ Kagan and co-workers previously reported the use of stoichiometric quantities of lanthanide(III) nitrates for the nitration of phenols.¹² In our system using a catalytic quantity of lanthanide(III) triflate¹¹ only a single equivalent of 69% nitric acid is required, the only side product is water and the catalyst is readily recycled: an atom economic process.¹³ This led us to develop the superior Group IV metal triflates (Hf^{4+} , Zr^{4+}) for the catalytic nitration of the substantially electron deficient arene *o*-nitrotoluene.^{11b,14} During the course of these studies

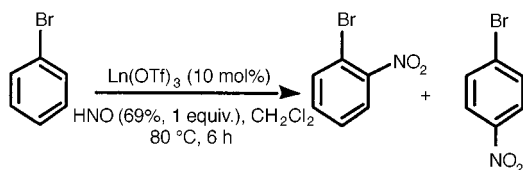
we had cause to delineate the rôle of the metal center in the nitration *milieu* and full experimental details of these findings are presented herein.

Results and discussion

As previously described,¹¹ a catalytic quantity of ytterbium(III) triflate (*ca.* 10 mol%) mediated the nitration of simple arenes with a single equivalent of 69% nitric acid in a two-phase solvent system. Ready recycling and the repeated catalytic competence of these metal salts was demonstrated by simple phase partition and evaporation of the aqueous phase at the completion of any particular nitration run followed by subsequent repeat nitration. Although efficient nitration of electron rich and mildly electron poor arenes was demonstrated, the system failed to mediate the nitration of strongly electron poor species such as benzoic acid, acetophenone and nitrobenzene. In accord with this no dinitrated adducts were observed in any case.

It is germane to note that the isomer distribution of the various nitroaromatics so-produced for a given arene were fully consistent with nitronium ion, or a nitronium 'carrier' of some description, acting as the *de facto* electrophilic nitrating agent.¹⁵ For instance, in the nitration of naphthalene the α - and β - mononitrated adducts were produced in 91:9 ratio; toluene gave a 52:7:41 distribution of the *ortho*, *meta* and *para* isomers respectively. Additionally we reported¹¹ that other lanthanide(III) triflates were also catalytically competent for nitration, but none so good as ytterbium. We have now screened the entire series of lanthanide(III) triflates for catalytic activity in nitration using a representative arene (*viz.* bromobenzene) within a given time period (Table 1 and Fig. 1). Aside from some scattered data points inspection of the data reveals a clear inverse correlation between the extent of nitration and the ionic radius of the tripositive lanthanide ion. This manifestation of the lanthanide contraction [the inverse correlation of ionic radii (which may be more usefully expressed as charge-to-size ratio Z/r — *vide infra*) and catalytic competence] is

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Table 1 Ln(OTf)₃ catalysed nitration of bromobenzene

Ln	Ionic radius ^a	Conversion (%) ^b
La	1.172	34
Ce ^c	1.15	21
Pr	1.13	30
Nd	1.123	39
Sm	1.098	49
Eu	1.087	57
Gd	1.078	54
Tb	1.063	62
Dy	1.052	49
Ho	1.041	57
Er	1.033	25
Tm	1.020	61
Yb	1.008	62
Lu	1.001	68

^a The tripositive ions. Values taken from the *Handbook of Chemistry and Physics*, 66th Edition, ed. R. C. Weast, CRC Press, 1985–1986.

^b As determined by GC-MS analysis. ¹H NMR analysis of the crude products showed a 2:3 ratio of 2-nitro-:4-nitrobromobenzene in all cases. ^c Ce(OTf)₄.

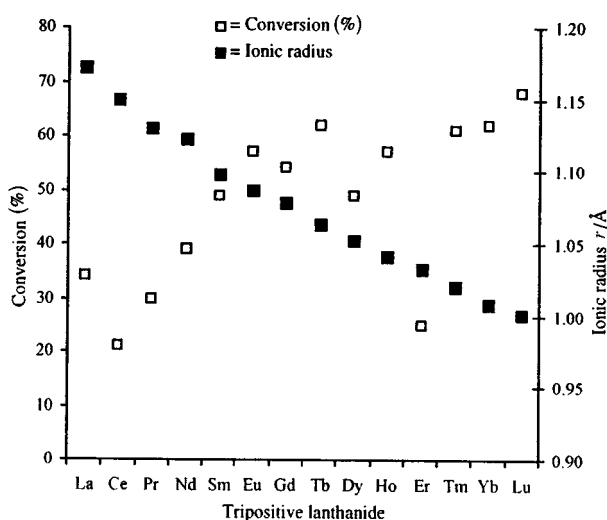


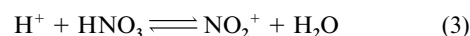
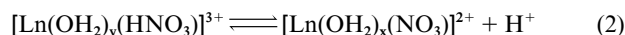
Fig. 1 Plot showing the conversion in the lanthanide(III) triflate catalysed nitration of bromobenzene, and also the ionic radii of the tripositive lanthanides.

indicative of interplay between the lanthanide ion and nitric acid where evidently an increasing electrostatic interaction between the two leads to greater reactivity. Taking this together with the observed isomer distributions indicative of nitronium ion as the *de facto* nitrating agent we propose the following mode of action for the lanthanide(III) triflate catalysed nitration of arenes with nitric acid.

X-Ray crystal structures of hydrated Ln(OTf)₃ have been reported for the entire lanthanide series and all show nine water molecules occupying the first coordination sphere in a tri-capped trigonal prism arrangement with outer sphere triflate counterions.¹⁶ It seems reasonable that this translates also to aqueous solution¹⁷ with only minor modifications to the gross structure: a tripositive lanthanide aqua ion and counteranionic triflates which are essentially spectator ions. The identity of the counterion for catalytic activity is, however, critical. For instance, we have shown that lanthanide(III) chlorides, toluene-

p-sulfonates and trifluoroacetates are poor nitration catalysts. Further aspects of the effects of the counterion will be reported in due course.

The interaction between hydrated tripositive lanthanide and nitrate anions in aqueous solution has been studied by a number of techniques and has yielded some interesting information. Abrahamer and Marcus¹⁸ demonstrated that nitrate can enter the inner coordination sphere of lanthanides at high nitrate concentration using ¹⁷O-enriched water (Er³⁺) and luminescence excitation spectroscopy unambiguously confirming the inner sphere binding capability of nitrate (Eu³⁺).¹⁹ Low temperature ¹⁵N NMR experiments in H₂O-acetone-Freon employing ¹⁵N labelled nitrate revealed the presence of Ln(NO₃)₂⁺ and Ln(NO₃)₂⁺ and other higher species with the 1:1 complex dominating (Eu³⁺, Sm³⁺, Nd³⁺ and Lu³⁺).²⁰ A recent microcalorimetry study estimated the equilibrium constant $K = 4.0 \pm 0.1 \text{ M}^{-1}$ for the first nitrate binding (Nd³⁺).²¹ Additionally, the use of large angle X-ray scattering has demonstrated that such coordinated nitrate anions act as bidentate ligands (Er³⁺).²² Further, Piriou and Svoronos demonstrated, *via* fluorescence spectroscopy, that the action of concentrated nitric acid (>4 M) on the *neutral* tris(nitrato)aqua europium(III) complex led to the formation of a higher order nitrate complex.²³ Thus it seems reasonable to consider that in our system association of nitric acid to the *tripositive* lanthanide center [eqn. (1)] could result in reversible



collapse to a bound bidentate nitrate species with concomitant liberation of an active proton [eqn. (2)].[‡] Such a proton could then go on to generate the requisite nitronium ion by protonation of nitric acid [eqn. (3)].¹⁵ Ultimately this can be viewed as the accentuation of the Brønsted acidity of nitric acid *via* a Lewis acid-Lewis base interaction between the tripositive lanthanide cation and nitrate anion. The ability of (1,1'-binaphthalene)-2,2'-diol (BINOL) to act as a proton source when used in conjunction with the Lewis acid tin(IV) chloride has previously been described by Yamamoto for which he coined the term 'Lewis-assisted Brønsted acidity' (LBA).²⁴ From a classical standpoint the above equates to 'nitrate capture' by the lanthanide ion in the auto-ionisation process of nitric acid [eqn. (4)] thus increasing the equilibrium concentration of nitronium ion. Since the smaller lanthanide ions would be expected to bind nitrate more strongly than the larger lanthanide ions, this model allows for a qualitative explanation of the observed reactivity of these metal triflates as the rare earth period is traversed.

At first sight there are at least two other possible mechanistic alternatives which bear consideration. A unidentate-bound nitrate could conceivably undergo heterolytic N-O bond cleavage to generate the nitronium ion as postulated for traditional Lewis acids.²⁵ Secondly, the arene may directly attack the lanthanide bound nitrate anion where literature precedent exists for titanium nitrates²⁶ and ceric ammonium nitrate.²⁷ However both these possibilities may be discounted since they fail to account for the role of the counterion.

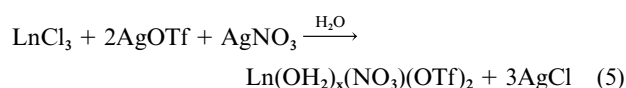
[‡] Formally the 'active proton' is triflic acid. Hence when it protonates nitric acid to produce the nitronium ion, it seems reasonable that the triflate group acts as the counterion, *i.e.* nitronium triflate is the *de facto* nitrating agent.

Table 2 Charge-to-size ratios (Z/r) and IR data for $[(\text{H}_2\text{O})_x\text{Ln}(\text{NO}_3)](\text{OTf})_2$

Ln	Z/r	$\nu_{\text{max}}/\text{cm}^{-1}$ (nitrate)	$\nu_{\text{max}}/\text{cm}^{-1}$ (triflate)
La	2.56	1459	1248, 1187, 1032, 641, 582, 524
Ce	2.61	1461	1243, 1188, 1031, 640, 580, 521
Pr	2.65	1469	1246, 1187, 1031, 638, 581, 524
Nd	2.67	1477	1246, 1188, 1031, 639, 582, 524
Pm	(2.70)	Radioactive	Radioactive
Sm	2.73	1478	1244, 1187, 1030, 637, 581, 523
Eu	2.76	1482	1247, 1187, 1030, 639, 581, 523
Gd	2.78	1484	1247, 1187, 1031, 638, 582, 525
Tb	2.82	1480	1247, 1185, 1031, 638, 582, 523
Dy	2.85	1490	1246, 1185, 1030, 637, 581, 522
Ho	2.88	1489	1247, 1185, 1030, 636, 580, 522
Er	2.90	1492	1245, 1183, 1030, 637, 579, 525
Tm	2.94	1496	1247, 1183, 1029, 636, 581, 523
Yb	2.98	1492	1246, 1182, 1029, 637, 580, 523
Lu	3.00	1497	1246, 1182, 1029, 638, 581, 524
Hf ^a	5.13	1650	1255, 1183, 1033, 647, 579, 520

^a $[(\text{H}_2\text{O})_x\text{Hf}(\text{NO}_3)](\text{OTf})_3$.

Inspection of the proposed 'nitrate capture' mechanism reveals that the putative species $[(\text{H}_2\text{O})_x\text{Ln}(\text{NO}_3)](\text{OTf})_2$ is the key intermediate. These novel salts (Ln = La–Lu) were prepared as air-stable solids by metathesis of the respective lanthanide chlorides in water [eqn. (5)]; analysis by IR spectroscopy



(Table 2) revealed the presence of outer sphere triflates and non-ionic, *i.e.* lanthanide-bound, nitrate.²⁸ For instance, the IR spectrum of $[(\text{H}_2\text{O})_x\text{La}(\text{NO}_3)](\text{OTf})_2$ revealed the characteristic signals for outer sphere triflate²⁹ (1247, 1188, 1031, 640, 581 and 524 cm^{-1} ; *cf.* $[\text{La}(\text{OH}_2)_9](\text{OTf})_3$; 1248, 1187, 1032, 641, 581 and 524 cm^{-1}) along with the requisite inner sphere nitrate absorptions at 1459 and 1318 cm^{-1} . Whilst these characteristic signals allowed for definitive assignment of the nitrate ion to the inner sphere, it is not possible to discriminate between the bidentate and unidentate modes of binding from this simple analysis.³⁰ Unfortunately attempted recrystallisation of this salt (or any of the other prepared members of the lanthanide series, *vide infra*) from H_2O or H_2O –MeOH failed to provide material suitable for single-crystal X-ray structure determination. That these observed bands were due to nitrate was confirmed by the preparation of the corresponding ¹⁵N labelled analogue (from $\text{Ag}^{15}\text{NO}_3$) which displayed isotopic shifts (*ca.* -30 cm^{-1} ; 1430 and 1294 cm^{-1}) entirely consistent from a consideration of their relative reduced masses. The remaining members of the series, $[(\text{H}_2\text{O})_x\text{Ln}(\text{NO}_3)](\text{OTf})_2$, displayed a steady shift to increasing wavenumber of the highest frequency nitrate band with decreasing ionic-radii (*i.e.* increasing Z/r) (Table 2). Located at 1459 cm^{-1} for the lanthanum salt, the corresponding band for lutetium was found at 1497 cm^{-1} . A similar, but much less pronounced shift has been reported for $\text{Ln}(\text{NO}_3)_3 \cdot 3[(\text{BuO})_3\text{PO}]$ (Ln = La–Lu).³¹ It has long been predicted by normal coordinate calculations that the highest frequency nitrate band in metal nitrates is shifted to increasing wavenumbers with an increase in the polarising power of the metal center,³² regardless of the mode (unidentate *versus* bidentate) of binding.³³ Since our experimental confirmation of this trend for these isostructural aqua-nitrato complexes correlates well with the decreasing ionic radii and concomitant increasing activity of the various lanthanide(III) triflates for nitration, we feel this structural investigation provides strong evidence in support of our proposed 'nitrate capture' model.

A plot of the highest nitrate stretching frequencies *versus* Z/r

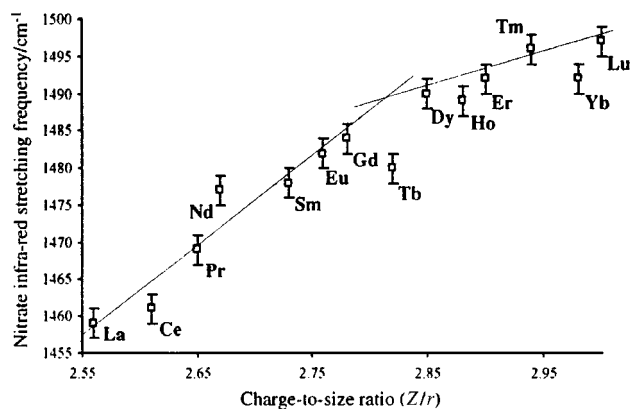


Fig. 2 Plot of nitrate stretching frequencies vs. charge-to-size (Z/r) ratios.

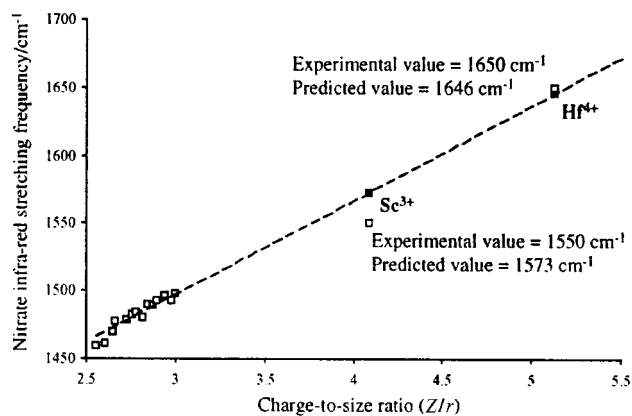


Fig. 3 Extrapolation of nitrate stretching frequencies to higher Z/r ratios.

of tripositive lanthanide ions for $[(\text{H}_2\text{O})_x\text{Ln}(\text{NO}_3)](\text{OTf})_2$ (Ln = La–Lu) reveals two straight lines with an intersection point located around atomic number $Z = 64$ (Fig. 2). This 'gadolinium break' can be interpreted as a change in coordination number where the hydration sphere is somewhat more compact for the heavier (and thus smaller) lanthanide ions.³⁴

With a view to the identification of superior catalysts, and as a further test of our model, extrapolation of this plot (*via* a best fit line to the data points $Z > 64$) to higher charge-to-size ratios led us to consider the use of hafnium(IV) and zirconium(IV) triflates which have previously been used, in their anhydrous form, as catalysts for Friedel–Crafts acylations^{35a} and Fries rearrangements.^{35b} With charge-to-size ratios of 5.13 and 5.14 for the tetrapositive centers respectively,³⁶ their mononitrate tris(triflate) salts should display nitrate bands at approximately 1646 cm^{-1} in their IR spectra (Fig. 3). Gratiatingly, these novel materials (which were readily prepared by simple metathesis of the chlorides with the relevant combinations of silver salts) displayed IR bands at 1650 and 1651 cm^{-1} respectively (along with the characteristic outer sphere triflate signals). Armed with this pleasing information and with a specific programme aim of nitrating *o*-nitrotoluene (ONT), where catalytic quantities of lanthanide(III) triflates were essentially ineffective, we prepared hydrated hafnium(IV) and zirconium(IV) triflates.¹⁴ When hydrated $\text{Hf}(\text{OTf})_4$ was utilised at a 10 mol% loading, smooth nitration of ONT occurred over a period of 24 h (>95% conversion); 2,4- and 2,6-dinitrotoluenes (DNTs) were isolated

§ The extrapolation was based on a best fit of the nitrate stretching frequencies of the $[(\text{H}_2\text{O})_x\text{Ln}(\text{NO}_3)](\text{OTf})_2$ salts with $Z > 64$. The corresponding band for $[(\text{H}_2\text{O})_x\text{Sc}(\text{NO}_3)](\text{OTf})_2$ ($Z/r = 4.10$) was predicted to appear at 1573 cm^{-1} . The authentic material displayed an IR stretch of 1550 cm^{-1} .

Table 3 Experimental data for $[(\text{H}_2\text{O})_x\text{Ln}(\text{NO}_3)](\text{OTf})_2$

Ln	Yield (%)	AgCl recovery (%)	x^a	Found (required) ^b		δ_F (ppm) (D ₂ O)	δ_C (ppm) ^c (D ₂ O)	-ve ion ESI (m/z) ^d
				Ln	S			
La	96	98	6	20.5 (22.9)	11.6 (10.6)	-78.0	122.5 (317)	473.7, 560.6, 647.7, 734.7
Ce	95	98	6	22.1 (23.0)	10.8 (10.5)	-78.0	122.5 (317)	474.7, 561.8, 648.8, 735.7
Pr	99	99	6	22.8 (23.1)	11.3 (10.5)	-78.0	122.4 (317)	475.9, 562.9, 649.8, 736.8
Nd	95	97	5	25.1 (24.3)	10.9 (10.8)	-78.0	122.5 (317)	476.9, 565.8, 652.7, 739.7
Sm	97	99	9	22.2 (22.3)	8.9 (9.5)	-78.0	122.5 (317)	487.0, 573.8, 662.8, 747.8
Eu	97	99	6	24.3 (24.5)	10.6 (10.3)	-78.0	122.5 (316)	486.9, 574.7, 661.8, 748.8
Gd	99	97	6	26.0 (25.1)	9.9 (10.2)	-78.0	122.4 (318)	491.4, 581.8, 668.7, 753.7
Tb	99	98	6	25.7 (25.3)	10.2 (10.2)	-79.0	119.0 (318)	495.9, 580.8, 667.9, 754.8
Dy	100	100	7	24.3 (25.0)	9.8 (9.9)	-78.7	120.6 (318)	497.5, 584.5, 672.5, 759.6
Ho	92	92	8	23.7 (24.6)	9.6 (9.6)	-78.2	121.2 (318)	499.6, 586.9, 673.8, 760.7
Er	97	93	9	22.9 (24.3)	9.0 (9.3)	-77.7	122.9 (317)	501.7, 587.8, 674.8, 763.9
Tm	99	100	5	27.9 (27.3)	10.2 (10.0)	-77.4	123.0 (317)	504.0, 590.9, 677.9, 764.8
Yb	98	98	4	27.5 (28.6)	11.1 (10.6)	-77.6	120.3 (317)	508.2, 595.1, 682.1, 769.0
Yb ^e	99	100	5	31.4 (32.3)	6.2 (6.0)	-77.5	120.3 (317)	508.2, 595.1, 611.9, 769.0
Lu	98	99	6	27.2 (27.2)	9.9 (10.0)	-77.9	122.5 (317)	509.9, 596.9, 683.8, 770.8
Hf ^f	99	96	7	21.8 (21.9)	11.8 (11.8)	-77.9	122.5 (317)	—

^a Best fit hydration number based on inductively coupled plasma-atomic emission spectroscopy (ICP) analysis. ^b ICP analysis. The figures in parentheses represent the required values based on hydration number x . ^c All signals observed as quartets. The figure in parenthesis is the coupling constant J in Hz. ^d Corresponding to $[\text{M}(\text{NO}_3)_3(\text{OTf})^-]$, $[\text{M}(\text{NO}_3)_2(\text{OTf})_2]^-$, $[\text{M}(\text{NO}_3)(\text{OTf})_3]^-$ and $[\text{M}(\text{OTf})_4]^-$. These ions were observed as clusters of isotopes, of which the most intense peak is quoted. ^e $[(\text{H}_2\text{O})_5\text{Yb}(\text{NO}_3)_2](\text{OTf})$. ^f $[(\text{H}_2\text{O})_7\text{Hf}(\text{NO}_3)](\text{OTf})_3$.

in 92% yield in a ratio of 63:37.¹⁴ Similarly, hydrated zirconium(IV) triflate was found to have comparable catalytic activity (95% conversion in 24 h) and 2,4- and 2,6-DNT were isolated in 87% yield in a 66:34 ratio.

Conclusion

On the basis of these results it is apparent that a simple consideration of charge-to-size ratio of a given metal ion allows a useful prediction of the relative reactivity of the metal triflate salt for nitrations. This 'nitrate capture' model features the lanthanide(III) ion as an Lewis acid which enhances the Brønsted acidity²⁴ of a protic acid (*i.e.* nitric acid), *via* binding of its conjugate base (*i.e.* nitrate anion). The similar trend in catalytic competence of the various lanthanide(III) triflates in our recent communication for the direct esterification of alcohols with acetic acid⁷ is readily attributed to a mechanistically analogous 'acetate capture' process. It seems reasonable to speculate that other various reported methodologies employing lanthanide(III) triflates may also involve the release of catalytically active quantities of triflic acid *via* reversible binding of conjugate bases of any available acids in the reaction medium, be they reagents, reaction adducts, substrates or solvents.³⁷¶

¶ In this respect, we have also noted accelerated H/D exchange for the α -protons of nitromethane, commonly employed as a solvent for lanthanide(III) triflate catalysis, when treated with ytterbium(III) triflate in D₂O. Thus nitromethane (10 μL) treated with ytterbium(III) triflate (12 mg) in D₂O (0.5 mL) in an NMR tube for 48 h at 65 °C revealed approximately 80% H/D exchange (all three sites). In the control [no Yb(OTf)₃] only 10% exchange was observed.

Such a release has an unmistakable parallel to the involvement of trimethylsilyl triflate as the active catalytic species in many metal triflate catalysed Mukaiyama aldol reactions.³⁸ Further, very recently, Répichet *et al.* have reported that bismuth(III) triflate is an effective catalyst for Friedel–Crafts acylation reactions and speculate that liberated triflic acid is crucial in the catalytic cycle.³⁹

Experimental

Materials and methods

All chemicals were purchased from Aldrich Chemical Co. The lanthanide(III) triflates were purchased as their hydrates $[\text{Ln}(\text{OH}_2)_n](\text{OTf})_3$ (Ln = La–Lu, n = variable), taken up in distilled water and evaporated to constant mass (freeze dryer) before use. Ag¹⁵NO₃ was prepared from a H¹⁵NO₃ 40 wt% solution in water (98 atom%) by neutralisation with silver carbonate in water, filtration and evaporation. All other chemicals were used as purchased. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP) was performed on a Thermo Electron ARL 3580B instrument (standard operating conditions) by B. Coles of the T. H. Huxley School of Environment, Earth Sciences and Engineering at Imperial College. IR spectra were recorded on a Mattson 5000 FTIR spectrometer. ¹⁹F and ¹³C NMR spectra were recorded on a Bruker DRX-400 spectrometer. Chemical shifts were measured in ppm and externally referenced to fluorotrichloromethane (δ_F 0.0) or sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) (δ_C 0.0). J Values are given in Hz. Negative ion electrospray (ESI) mass spectra were recorded on a VG platform spectrometer.

General procedure for lanthanide(III) triflate catalysed nitration of bromobenzene

To a solution of the respective lanthanide(III) triflate (10 mol%, 0.3 mmol) in nitric acid (69%, d 1.43, 0.192 mL, 3.0 mmol) was added a solution of bromobenzene (471 mg, 3.0 mmol) in 1,2-dichloroethane (2.0 mL). The mixture was refluxed with vigorous stirring. After 6 h an aliquot was withdrawn and subjected to GC/MS analysis (Table 1 and Fig. 1).

General procedure for the preparation of $[(\text{H}_2\text{O})_x\text{Ln}(\text{NO}_3)](\text{OTf})_2$

To a solution of the respective lanthanide(III) chloride hydrate (1.0 mmol) in distilled water (2.0 mL) was added a solution of AgNO_3 (170 mg, 1.0 mmol) and AgOTf (513 mg, 2.0 mmol) in distilled water (2.0 mL). The resultant slurry was allowed to settle for 1 h before being filtered. The filtrate was concentrated *in vacuo* (freeze dryer) to afford the desired product (Table 3). The relative proportions of materials were modified accordingly for the preparations of the $[(\text{H}_2\text{O})_x\text{Hf}(\text{NO}_3)](\text{OTf})_3$ and $[(\text{H}_2\text{O})_x\text{Yb}(\text{NO}_3)_2](\text{OTf})_2$ salts.

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Dedicated to the memory of Professor Ralph Raphael.

References

- 1 J. H. Forsberg, V. T. Spaziano, T. M. Balasubramanian, G. K. Liu, S. A. Kinsley, C. A. Duckworth, J. J. Poteruca, P. S. Brown and J. L. Miller, *J. Org. Chem.*, 1987, **52**, 1017.
- 2 S. Kobayashi, *Synlett*, 1994, 689.
- 3 (a) H. Ishitani and S. Kobayashi, *Tetrahedron Lett.*, 1996, **37**, 7357; (b) I. E. Marko and G. R. Evans, *Tetrahedron Lett.*, 1994, **35**, 2771; (c) T. Saito, M. Kawamura and J.-I. Nishimura, *Tetrahedron Lett.*, 1997, **38**, 3231.
- 4 A. Kawada, S. Mitamura and S. Kobayashi, *Chem. Commun.*, 1996, 183.
- 5 S. Kobayashi and S. Nagayama, *J. Org. Chem.*, 1997, **62**, 232.
- 6 (a) S. Kobayashi, I. Hachiya and Y. Yamanoi, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 2342; (b) H. Aspinall, A. F. Browning, N. Greeves and P. Ravenscroft, *Tetrahedron Lett.*, 1994, **35**, 4639.
- 7 A. G. M. Barrett and D. C. Braddock, *Chem. Commun.*, 1997, 351.
- 8 (a) S. Matsubara, M. Yoshioka and K. Utimoto, *Chem. Lett.*, 1994, 827; (b) S. Kobayashi, I. Hachiya, T. Takahori, M. Araki and H. Ishitani, *Tetrahedron Lett.*, 1992, **33**, 6815; (c) P. E. Harrington and M. A. Kerr, *Synlett*, 1996, 1047; (d) E. Keller and B. L. Feringa, *Synlett*, 1997, 842.
- 9 (a) M. Meguro, N. Asao and Y. Yamamoto, *J. Chem. Soc., Perkin Trans. 1*, 1994, 2579; (b) M. Chini, P. Crotti, L. Favero, F. Macchia and M. Pineschi, *Tetrahedron Lett.*, 1994, **35**, 433.
- 10 (a) T. Hanamoto, Y. Sugimoto, Y. Yokoyama and J. Inanaga, *J. Org. Chem.*, 1996, **61**, 4491; (b) S.-C. H. Diana, K.-Y. Sim and T.-P. Loh, *Synlett*, 1996, 263; (c) S. Kobayashi, H. Ishitani and M. Ueno, *Synlett*, 1997, 115.
- 11 (a) F. J. Waller, A. G. M. Barrett, D. C. Braddock and D. Ramprasad, *Chem. Commun.*, 1997, 613; (b) F. J. Waller, D. Ramprasad, A. G. M. Barrett and D. C. Braddock, *Catalysis of Organic Reactions*, ed. F. E. Herkes, Marcel Dekker, New York, 1998, p. 289.
- 12 M. Ouertani, P. Girard and H. B. Kagan, *Tetrahedron Lett.*, 1982, **23**, 4315.
- 13 B. M. Trost, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 259.
- 14 F. J. Waller, A. G. M. Barrett, D. C. Braddock and D. Ramprasad, *Tetrahedron Lett.*, 1998, **39**, 1641.
- 15 (a) G. A. Olah, R. Malhotra and S. C. Narang, *Nitration: Methods and Mechanisms*, VCH, New York, 1989; (b) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, 2nd edn., Cornell University Press, Ithaca, New York, 1969.
- 16 (a) J. M. Harrowfield, D. L. Kepert, J. M. Patrick and A. H. White, *Aust. J. Chem.*, 1983, **36**, 483; (b) A. Chatterjee, E. N. Maslen and K. J. Watson, *Acta Crystallogr.*, 1988, **B44**, 381.
- 17 (a) T. Kowall, F. Foglia, L. Helm and A. E. Merbach, *Chem. Eur. J.*, 1996, **2**, 285; (b) B. P. Hay, *Inorg. Chem.*, 1991, **30**, 2876 and references cited therein.
- 18 I. Abrahamer and Y. Marcus, *Inorg. Chem.*, 1967, **6**, 2103.
- 19 P. J. Breen and W. D. Horrocks Jr., *Inorg. Chem.*, 1983, **22**, 536.
- 20 A. Fratiello, V. Kubo-Anderson, E. Bolanos, O. Chavez, J. Ortega, R. D. Perrigan, F. Reyes, L. Saenz, S. M. Stoll and T. Thompson, *J. Solution Chem.*, 1996, **25**, 345 and references cited therein.
- 21 C. Bonal, J.-P. Morel and N. Morel-Desrosiers, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 4957.
- 22 H. Yokoyama and G. Johansson, *Acta. Chem. Scand.*, 1990, **44**, 567.
- 23 B. Piriou and D. R. Svoronos, *J. Less-Common Met.*, 1985, **112**, 275.
- 24 K. Ishihara, Y. Ishida, S. Nakamura and H. Yamamoto, *Synlett*, 1997, 758.
- 25 (a) R. J. Thomas, W. F. Anzilotti and G. F. Hennion, *Ind. Eng. Chem.*, 1940, **32**, 408; (b) G. F. Hennion, *U. S. Patent*, 1943, 2 314 212.
- 26 D. W. Amos, D. A. Baines and G. W. Flewett, *Tetrahedron Lett.*, 1973, 3191.
- 27 S. Dincturk and J. H. Ridd, *J. Chem. Soc., Perkin Trans. 2*, 1982, 961.
- 28 B. M. Gatehouse, S. E. Livingstone and R. S. Nyholm, *J. Chem. Soc.*, 1957, 4222.
- 29 D. H. Johnston and D. F. Shriver, *Inorg. Chem.*, 1993, **32**, 1045.
- 30 A. B. P. Lever, E. Mantovani and B. S. Ramaswamy, *Can. J. Chem.*, 1971, **49**, 1957 and references cited therein.
- 31 J. R. Ferraro, C. Cristallini and I. Fox, *J. Inorg. Nucl. Chem.*, 1967, **29**, 139.
- 32 (a) H. Brintzinger and R. E. Hester, *Inorg. Chem.*, 1966, **5**, 980; (b) R. E. Hester and W. E. L. Grossman, *Inorg. Chem.*, 1996, **5**, 1308.
- 33 C. C. Addison, N. Logan, S. C. Wallwork and C. D. Garner, *Quart. Rev.*, 1971, **25**, 289.
- 34 A. Habenschuss and F. Spedding, *J. Chem. Phys.*, 1979, **70**, 2797.
- 35 (a) I. Hachiya, M. Moriwaki and S. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 2053; (b) S. Kobayashi, M. Moriwaki and I. Hachiya, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 267.
- 36 *Handbook of Chemistry and Physics*, 66th edn., ed. R. C. Weast, CRC Press Inc., 1985–1986.
- 37 A. G. M. Barrett, D. C. Braddock, J. P. Henschke and E. R. Walker, *J. Chem. Soc., Perkin Trans. 1*, following paper.
- 38 T. K. Hollis and B. Bosnich, *J. Am. Chem. Soc.*, 1995, **117**, 4570.
- 39 S. Répichet, C. Le Roux, J. Dubac and J.-R. Desmurs, *Eur. J. Org. Chem.*, 1998, 2743.