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Catalytic activity of solvated and unsolvated lanthanide halides in Friedel–Crafts acylations

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Abstract

Anhydrous lanthanide halides — chlorides and bromides — can act as homogeneous catalysts of Friedel–Crafts acylations. The catalytic activity is related to the solubility of these anhydrous salts. More soluble THF or dioxane (Diox.) neodymium and samarium adducts are more active catalysts. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The environmental problems due to the use of the ubiquitous catalysts of Friedel–Crafts reactions — AlCl_3 , BF_3 , etc. . . — have aroused for many years a great interest for alternative solutions [1], and this challenge continues to attract the attention of chemists. For this purpose, a large number of catalytic systems including smectite clays: montmorillonites [2] or zeolites [3,4], supported [5] or unsupported d-transition metals salts [6] and main group metals salts [7] have been and are again widely

investigated. Lanthanide trichlorides were also tested and Olah claimed that these salts were very weak catalysts for the Friedel–Crafts reaction [8]. More recently, Mine et al. [9] found that the lanthanide anhydrous trihalides — chlorides and bromides (except lanthanum and scandium) — were efficient and reusable catalysts of alkylation reactions. The use of soluble lanthanide and also scandium trifluoromethanesulfonates (triflates) [10–16] or bis(trifluoromethylsulfonyl)amidates (triflimidates) [17] as homogeneous catalysts of alkylation and acylation has also been investigated. Nevertheless, in spite of the good yields in acylation products and of the good selectivity of the reactions, the very high cost of these catalysts and the hazards related to the use of trifluoromethanesulfonic acid or related compounds and their salts hindered considerably their use on a wide scale.

In an effort to promote lanthanide salts as catalysts for Friedel–Crafts electrophilic substitutions,

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we reported previously the good results obtained in alkylation [18,19] and acylation [20] reactions of activated benzene rings using reusable supported lanthanide salts as heterogeneous catalysts. We report here the decline in the activity of anhydrous lanthanide halides, compared to the increased activity of their more soluble ether adducts, as homogeneous catalysts of acylation reactions.

2. Results and discussion

2.1. Catalytic activity of anhydrous halides

Previous experiments [20] showed that lanthanum trichloride deposited on silica (this support is inert towards acylation reactions) acted as a much more active catalyst (51% vs. 4% yield) than anhydrous LaCl_3 alone for anisole benzoylation ($\text{PhCOCl}/\text{Ln} = \text{PhOCH}_3/\text{Ln} = 1000$, 5 h, 154°C). In another way, LaCl_3 deposited on montmorillonite K10 was recovered quite quantitatively on the support after use, whereas for the analogous scandium catalyst used in the same conditions, only 12% of the scandium salt was recovered on the support, 88% was present in the solution after reaction. Then, it was interesting to know how active really lanthanide halides were — as homogeneous or as heterogeneous catalysts. To answer this question, we have investigated the catalytic activity of lanthanide trihalides in Friedel–Crafts acylations. This activity was compared in the reaction of benzoyl chloride with an excess (5/1) of anisole. Five percent of lanthanide trichloride was added and the mixture was refluxed (158°C) for 5 h. Table 1 summarises the experimental results.

It was clear that the trichlorides of the largest lanthanides were quite inactive, whereas good yields were obtained from the smaller. It is noteworthy that the mixture became rapidly homogeneous for SmCl_3 , GdCl_3 and YCl_3 , but remained heterogeneous for

Table 1
Yield of 4-methoxybenzophenone from 5% anhydrous lanthanide trichlorides as catalysts (5 h, 158°C)

LnCl_3	La	Ce	Nd	Sm	Gd	Y
Yield%	5 ^a	11 ^b	5 ^b 27 ^a	32 ^a	70 ^b	50 ^b

^aFreshly prepared samples. (see below).

^bCommercial samples.

Table 2
Yield (%) of 4-methoxybenzophenone using 10% of anhydrous lanthanide trichlorides

Time (h)	LaCl_3	NdCl_3	DyCl_3	YbCl_3	GdCl_3
0.5	3	33	72	50	37
1	4	34	80	67	60
3	5.5	44	88	76	90
5	8	79	90	82	95
22	14	85	88	76	92

LaCl_3 , CeCl_3 and NdCl_3 . Then, the activity of these salts can be directly related to their solubility in the mixture anisole/benzoyl chloride. The low yield obtained with commercial NdCl_3 was surprising, other experiments were performed using various samples of NdCl_3 . The best result (27% after 5 h) was obtained using a sample freshly prepared from $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ and trimethylorthoformate [21].

The evolution of the reaction on a longer time (Table 2) has been followed by GPC using samples of commercial anhydrous trichlorides of Dy, Yb and Gd, $\text{LaCl}_3 \cdot \text{NdCl}_3$ were prepared as above. To reduce the reaction time, 10% of catalyst was used.

The low yield (5% after 5 h) obtained from 5% of lanthanum trichloride was weakly enhanced (8%) when 10% of this salt was used, whereas for NdCl_3 , in the same conditions, the yield reached 79%, instead 27%. The yield of 4-methoxybenzophenone normally decreased slowly after a long time of refluxing, secondary reactions giving heavier products.

After cooling, the mixture was filtered and the filtrate was analysed by inductive coupling plasma–optical emission spectroscopy (ICP–OES) to know the amount of dissolved lanthanide salt (Table 3).

The yield of acylation product was related to the amount of dissolved salt. Nevertheless, if the solubility seemed to be the major parameter, the good yield

Table 3
Amount of dissolved lanthanide salt after acylation reaction (5% catalyst, 5 h, 158°C)

Element	La	Nd	Dy	Yb	Gd	Sc.
% in sol. ^a	0.067	0.4	2.45	2.5	1.85	2.5
% dissolv. ^b	3	17	94	88	72	88

^ag of trichloride/100 g of solution.

^bg of trichloride in solution/100 g added anhydrous trichloride.

Table 4
Yield of 4-methoxybenzophenone, DyCl₃ as catalyst

Time (h)	25% DyCl ₃	15% DyCl ₃	10% DyCl ₃	1% DyCl ₃
0.5	80	82	72	25
2	80	92	89	38
3	92	92	88	44
18	91	94	91	76

obtained with poorly soluble NdCl₃ establishes clearly the good catalytic activity of this element.

The amount of catalyst also had a great importance on the reaction time. Then, a series of reactions was performed with various amounts of dysprosium trichloride. Table 4 summarises the results.

All these results were in good conformity with those obtained by Mine et al. [9] on the catalytic activity of lanthanide salts in alkylation reactions.

2.2. Catalytic activity of lanthanide halides ether adducts

It is well known that the ether adducts of these halides are monomer and more soluble in organic media than the polymeric trihalides. For example, the solubility of some lanthanide trichlorides and tribromides in THF was reported in Table 5.

The THF adducts of the above-mentioned chlorides and bromides were prepared by Soxhlet extraction of the anhydrous halide with THF and removal of the solvent. The crystalline powders so obtained were used without further purification. Their activity was evaluated in the reaction of anisole with benzyle chloride (Fig. 1), the results are summarised in Table 6.

Soluble anhydrous or solvated gadolinium and yttrium chlorides showed the same high activity whereas poorly soluble THF adducts of lanthanum and cerium chlorides were only slightly more active

Table 5
Solubility of lanthanides trichlorides in THF (from Ref. [22])

Sol., g/l	La	Ce	Nd	Sm	Gd
Chloride	1.26	5.93	11.6	14.9	19.1
Bromide	5.7	6.0	7.1	5.5	3.8

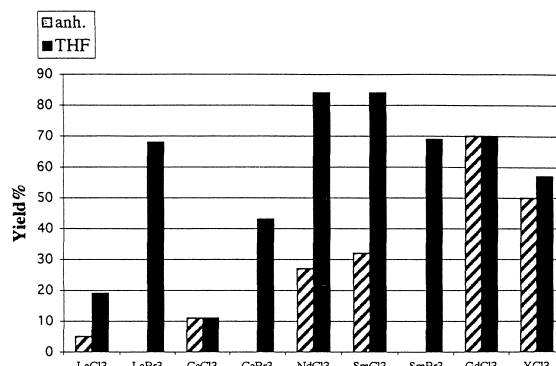


Fig. 1. Comparison of the activity of lanthanide halides, anhydrous or THF adducts (yield of 4-methoxybenzophenone — 5% catalyst).

than the anhydrous chlorides. At the opposite, the use of soluble THF adducts of samarium and especially neodymium unsteady anhydrous chlorides increased drastically the activity of these catalysts. The lanthanum and cerium tribromides were more soluble, hence, more active than the corresponding chlorides.

The nature of the ether coordinated to the metal has been studied for two elements: the large neodymium and the small yttrium. The dimethoxyethane (DME), dioxane (Diox.), and diglyme (Digl.) adducts of neodymium and yttrium dichlorides have been obtained from the THF adducts by displacement of the THF with a large excess of ether and removal of the solvent. The stoichiometry of these adducts was not exactly established, therefore, ¹H NMR recorded in D₂O showed the complete displacement of THF. Elemental analysis showed that the neodymium Digl. adduct contained only c. 0.7 Digl. per neodymium corresponding to an oligomeric or polymeric structure (Fig. 2). Table 7 summarises the catalytic performances of these

Table 6
Yield of 4-methoxybenzophenone, THF adducts of lanthanide trichlorides as catalysts (5% catalyst, 158°C, 5 h)

Lanthanide	La	Ce	Nd	Sm	Gd	Y
Cl, Yield%	19	11	83	83	70	57
Br, Yield%	68	43	—	69	—	—

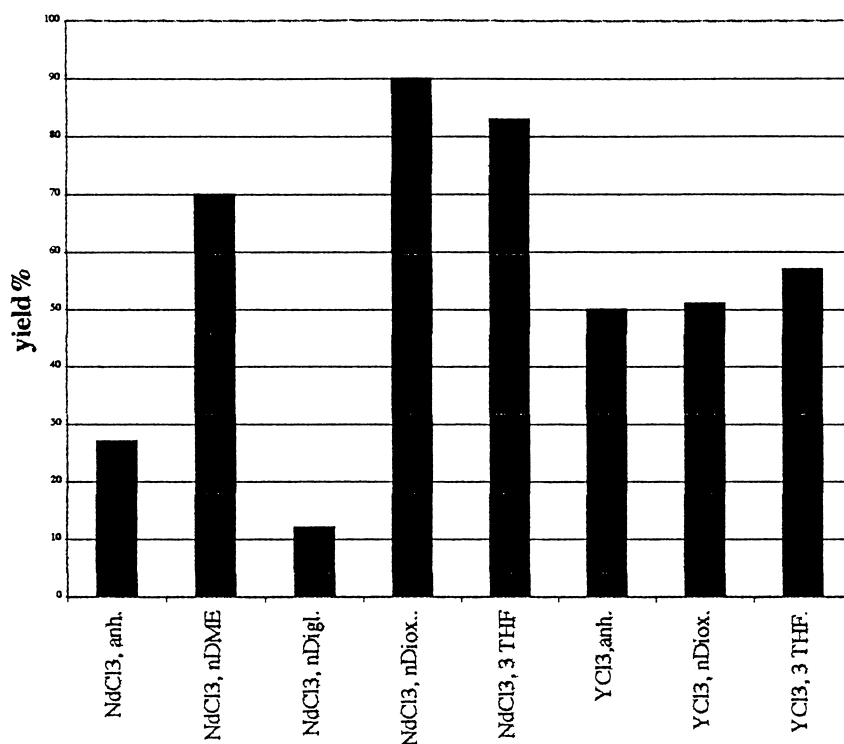


Fig. 2. Comparison of the activity of neodymium and yttrium chlorides, anhydrous or ether adducts (yield of 4-methoxybenzophenone — 5% catalyst).

adducts, compared to the anhydrous salts, for the acylation of anisole.

The best yields were obtained from the neodymium Diox. adduct. The low yield obtained from the Digl. adduct was surprising; this fact can be related to the low solubility of this salt as a consequence of its associated structure.

The catalytic activity of the more active neodymium trichloride Diox. adduct has been tested towards the acylation of some substituted benzene rings: fluorobenzene, toluene, anisole, phenetole (ethoxybenzene) and veratrole (1,2-dimethoxybenzene) with a slight excess (5%) of acyl chloride (Table 8).

Weakly activated fluorobenzene or toluene did not react. At the opposite, the reaction was complete or quite complete for activated aromatic ethers. Nevertheless, the yields of acylation products were very different.

From anisole, the expected product was obtained in very high yield (91%), whereas veratrole afforded 53% of 3,4-dimethoxy,4'-chlorobenzophenone and many secondary products and only 30% of 4-ethoxy,4'-chlorobenzophenone were obtained from phenetole. In this last case, two major secondary products were obtained. Those are identified by elemental, IR, GPC-MS and NMR analyses as the ester **A** and the ketoester **B**. The formation of these com-

Table 7

Yield of 4-methoxybenzophenone from neodymium and yttrium chlorides ether adducts. (5% catalyst, 158°C, 5 h)

Catalyst	NdCl ₃ Anh.	NdCl ₃ THF	NdCl ₃ DME	NdCl ₃ Diox.	NdCl ₃ Digl.	YCl ₃ Anh.	YCl ₃ THF	YCl ₃ Diox.
Yield%	27	84	70	91	12	50	56	51

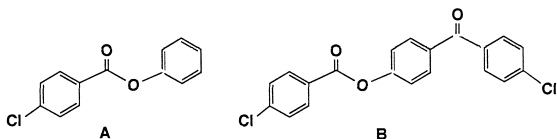
Table 8

Catalytic activity of $\text{NdCl}_3 \cdot n\text{Diox.}$ in acylation of substituted benzenes (5% catalyst, 5 h)

Arom.-ArCOCl	T°C	Arom. TR%	ArCOCl TR%	Yield/Arom.
$\text{C}_6\text{H}_5\text{F}-\text{C}_6\text{H}_5\text{COCl}$	85	0		
$\text{C}_6\text{H}_5\text{CH}_3-\text{C}_6\text{H}_5\text{COCl}$		0		
Anisole- $\text{C}_6\text{H}_5\text{COCl}$	158	100	100	91
Phenetole- $\text{C}_6\text{H}_5\text{COCl}$	170	79	100	41
Phenetole- $p\text{ClC}_6\text{H}_4\text{COCl}$	170	80	100	30
Veratrole- $p\text{ClC}_6\text{H}_4\text{COCl}$	206	87	100	53

TR = transformation rate.

pounds implied the deethylation of phenetole. The formation of **A** could be explained by successive deethylation/OH benzylation of phenetole and **B** could be formed from **A** by benzylation of after a Fries rearrangement followed by OH benzylation. This is currently under investigation.



3. Conclusion

It appears that lanthanide halides can act as heterogeneous catalysts when deposited and bonded on a mineral inactive support or as homogeneous catalysts if soluble in the reaction mixture. The catalytic activity is closely related to the solubility, but depends also on the element, the best results are obtained with neodymium and samarium.

4. Experimental

4.1. Materials

Commercially available organic and inorganic reagents were used without further purification. Ethers — tetrahydrofuran, Digl., Diox., DME — were previously dried on molecular sieves and distilled before use. The pure hydrated lanthanide salts were purchased by Rhodia Chimie. The anhydrous

lanthanide salts were provided from Aldrich or Strem and used without further treatment. The anhydrous salts were also prepared following the described procedures [21–23].

4.2. Analytical techniques

Composition and yields of the reaction products were determined with a GC 8000 Series gas chromatograph equipped with a flame ionisation detector, a data jet integrator (Thermo Separation Products) and a 25 m \times 0.32 mm OVI capillary column or a 30 m \times 0.53 mm OV 624 semi-capillary column.

^1H and ^{13}C NMR data were recorded on a Bruker AC 200 in D_2O or CDCl_3 .

Mass spectra were recorded on a Hewlett Packard G1800 A GCD apparatus equipped with a 30 m \times 0.25 mm HPS capillary column.

The amount of lanthanide salts in solution was measured with an ICP–OES spectrometer MAXIM III, and the results were obtained with the Plasma Vision program.

Elemental (C, H) analyses were carried on an EA 1108 CHNS-O (Fisons Instruments). IR spectra were recorded in nujol on a Bruker IFS 66 V apparatus.

4.3. Preparation of the ethers adducts

4.3.1. THF adducts

4.3.1.1. From anhydrous chlorides: (*La*, *Ce*, *Nd*, *Sm*) Cl_3 . A total 5 g of lanthanide chloride was extracted for 24 h with 100 ml of refluxing THF in a Soxhlet apparatus. After concentration of the solution at 10 ml and cooling, the crystalline powder was

filtered and dried under vacuum at room temperature. Yields: 40–90%.

4.3.1.2. From hydrated salts: $(La, Ce, Sm)Br_3$; $(Nd, Sm, Y)Cl_3$. A total of 2.40 g (4.75 mmol) of $LaBr_3 \cdot 7H_2O$ and 5.2 ml (47.5 mmol) of trimethylorthoformate were stirred for 30 min under argon. After removal of the excess of reagent and of methanol and methanoic acid formed, the white solid was extracted with 3×50 ml of THF. After evaporation of the solvent, $LaBr_3 \cdot 3THF$ was obtained analytically pure (2.77 g, 98% yield).

4.3.2. Diox. adducts

A total of 0.506 g (1.22 mmol) of $YCl_3 \cdot 3THF$ was stirred under argon at room temperature with 50 ml of Diox. After 15 h, the clear solution was evaporated to dryness to give $YCl_3 \cdot nDiox.$ as a white powder. 1H NMR recorded in D_2O showed only the signal of Diox. at 3.71 ppm. $NdCl_3 \cdot nDiox.$ was obtained in the same manner.

4.3.3. DME adduct

A total of 0.499 g (1.06 mmol) of $NdCl_3 \cdot 3THF$ was stirred under argon at room temperature with 15 ml of DME. After removal of the solvent, a violet powder was isolated. 1H NMR recorded in D_2O showed only the signals of DME: $\delta = 3.55$, s, 2H; 3.32, s, 3H.

4.3.4. Digl. adduct

A total of 0.93 g (2 mmol) of $NdCl_3 \cdot 3THF$ was dissolved in 30 ml of refluxing THF and 30 ml of Digl. were slowly added to the solution. THF was distilled and the solution was heated for one night, then filtered. After concentration, precipitation of the adduct by addition of 50 ml of pentane, the pale blue salt was filtered and dried under vacuum at room temperature. 1H NMR showed only the signals of Digl.: $\delta = 3.61$, s, 4H; 3.35, s 3H. Elemental analysis (C 16.6%; H 3.3%) corresponded to the formula $NdCl_3 \cdot 0.7$ Digl.

4.4. Acylation reaction, typical experiments

4.4.1. Anhydrous salt as catalyst

In a glove box, 0.35 g (0.725 mmol) of $DyCl_3 \cdot 3THF$ were weighed in a 50 ml vessel. Benzoyl

chloride, 1.75 g (12.5 mmol) and anisole, 6.76 g (62.5 mmol) were added with a syringe under nitrogen. The mixture was vigorously magnetically stirred and refluxed at 158°C for 5 h. After cooling, a 0.05-ml sample was dissolved in 1 ml THF and analysed by GPC. Yield: 70%.

4.4.2. Ether adduct as catalyst

In a glove box, 0.48 g (1.25 mmol for $NdCl_3 \cdot 1.5Diox.$) of $NdCl_3 \cdot nDiox.$ was weighed in a 100-ml vessel. 4-Chloro benzoyl chloride, 4.37 g (25 mmol) and veratrole, 3.79 g (27.5 mmol) were added with a syringe under nitrogen and the vigorously stirred mixture was refluxed for 5 h. A sample was analysed by GPC (yield 50%). After cooling, 50 ml of diethylether were added, the organic layer was filtered, washed with 3×25 ml water, dried on $MgSO_4$, and the solvent was removed. The crude product was recrystallised in pentane to give 2.42 g (35% yield) of pure 4-chloro-3',4'-dimethoxybenzophenone.

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