Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron 60 (2004) 1531–1539
Tetrahedron

Group 3 metal (Sc, La) triflates as catalysts for the carbomethoxylation of aliphatic amines with dimethylcarbonate under mild conditions

Monica Distaso[a] and Eugenio Quaranta[a,b,*]

[a]*Dipartimento di Chimica, Campus Universitario, Università di Bari, 70126 Bari, Italy*
[b]*ICCOM-CNR, Dipartimento di Chimica, Campus Universitario, 70126 Bari, Italy*

Received 10 September 2003; revised 12 November 2003; accepted 4 December 2003

Abstract—The activity of $Sc(OTf)_3$ and $La(OTf)_3$ ($OTf{=}SO_3CF_3$) as catalysts for the phosgene-free synthesis of carbamate esters via carbomethoxylation of aliphatic amines with dimethylcarbonate (DMC) has been investigated. In the presence of $M(OTf)_3$ (M=Sc, La), primary and secondary aliphatic amines easily react with dimethylcarbonate, under very mild conditions (20 °C), to afford carbamate esters with good yield and excellent selectivity ($\cong 100\%$). $Sc(OTf)_3$ is a more effective catalyst than the homologue La salt. The carbomethoxylation reaction requires as strict anhydrous conditions, as, at 20 °C, the presence of water inhibits markedly the catalytic activity of both triflate salts. Temperature influences carbamate selectivity, which is lower at higher temperature because of deleterious formation of N-methylation side-products.

1. Introduction

The search for new synthetic methods that minimize energy requirements and reduce or eliminate the utilization of hazardous reagents is a major target for 'Green Chemistry'.[1] Much effort is currently being focussed on replacing phosgene,[2] which, because of its toxicity, is being less and less employed in chemical industry as a starting material for the synthesis of a number of chemicals, such as carbamates, ureas, isocyanates and organic carbonates.[3]

We have shown that carbon dioxide can be an effective substitute for phosgene in the synthesis of carbamate esters $RR'NHC(O)OR''$ (R=alkyl, aryl; R′=H, alkyl; R″=alkyl).[2] These compounds are largely used as pharmaceuticals and agrochemicals and also play a key role as intermediates in chemical industry for the production of fine and commodity chemicals.[4] The development of phosgene-free routes to carbamates is an important synthetic task and several other approaches, based, for example, on the use of either CO[5] or carbonic acid diesters,[6] are currently under study.

Aminolysis of organic carbonates has gained growing attention as an alternative clean route to carbamate esters in the last few years.[2] This is favoured by the fact that innovative phosgene-free methodologies for the industrial synthesis of organic carbonates have been implemented.[7] Aliphatic amines easily react with diphenylcarbonate,[8] or other organic carbonates having fairly good leaving groups.[6,9] However, carboalkoxylation of aliphatic amines by unactivated organic carbonates, such as dialkylcarbonates (Eq. 1; R=alkyl; R′=H, alkyl; R″=alkyl), usually needs a suitable catalyst in order to observe satisfactory conversion rate and selectivity.[10–13] We have demonstrated that CO_2 itself is an effective catalyst for the synthesis

$$RR'NH + (R''O)_2CO \xrightarrow{\text{Cat.}} RR'NC(O)OR'' + R''OH \qquad (1)$$

of *N*-alkyl methylcarbamates from aliphatic primary amines and dimethylcarbonate (DMC).[2,12] However, Lewis acid metal catalysts have been more usually used to this end.[10,13] A few of them have been studied as catalysts for the carbamation of aromatic amines.[10,13,14] Such processes (Eq. 1; R=aryl; R′=H, alkyl, aryl; R″=alkyl or aryl) can be catalysed both by organo-phosphorous Brönsted acids[2,8,15] and organic or inorganic bases.[16] In most cases, quite severe experimental conditions, such as high temperatures (>90 °C), are required, which often promote the formation of undesired by-products, such as ureas and/or N-alkylation products, lowering the selectivity to give the carbamate.

Despite the number of metal systems investigated, so far the behaviour of early transition metal derivatives and, more specifically, d^0 transition metal systems as catalysts in the aminolysis reaction of unactivated carbonic acid diesters still remains very poorly documented.[13] To date, no report has ever described the activity of Group 3 metal salts as

---

Keywords: Carbamate esters; Scandium triflate; Lanthanum triflate; Dimethylcarbonate; Amines.
* Tel./fax: +39-080-544-20-83;
e-mail address: quaranta@chimica.uniba.it

0040–4020/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2003.12.020

catalysts for this particular purpose. As a continuation to our previous studies,[2,15] we have therefore focused our attention on the use of Group 3 metal triflates $M(OTf)_3$ (M=Sc, La; $OTf=SO_3CF_3$) as potential catalysts for amine carbomethoxylation. We have investigated the catalytic activity of these salts at ambient temperature (20 °C), because of the current widespread interest for new synthetic protocols requiring mild experimental conditions,[1] scarcely investigated so far. In the last few years, Group 3 metal triflates and, more generally, rare-earth metal (Ln) triflates have been receiving great attention for their ability to promote a wide variety of organic reactions selectively, under not severe conditions.[17] Interestingly, they have been shown to exhibit excellent catalytic properties even in the presence of Lewis bases containing N, O, P, S donor atoms.

Herein, we describe, for the first time, the activity of both $Sc(OTf)_3$ and $La(OTf)_3$ as catalysts for carbomethoxylation of primary and secondary aliphatic amines with DMC and document a few examples of utilization of these salts as effective catalysts for the selective synthesis of carbamate esters via aminolysis of DMC at ambient temperature.

2. Results and discussion

2.1. Carbomethoxylation of aliphatic primary amines with DMC promoted by $M(OTf)_3$ (M=Sc, La) salts

Table 1 compares the behaviour of a few Group 3 metal (Sc, La) salts as catalysts for the carbomethoxylation of benzylamine with anhydrous DMC, at 20 °C. Anhydrous $LaCl_3$, or hydrated La salts, such as $LaCl_3\cdot 7H_2O$ and $La(NO_3)_3\cdot 7H_2O$, show no or poor catalytic activity (entries 2–4, Table 1).[18] Conversely, under otherwise comparable reaction conditions, both $La(OTf)_3$ and $Sc(OTf)_3$ effectively promote the carbomethoxylation of the amine (entries 6 and 8, Table 1).[19]

Whatever $M(OTf)_3$ (M=Sc or La) catalyst salt is used, the carbomethoxylation reaction requires strict anhydrous conditions. We have ascertained that addition of water to the reaction markedly inhibits the catalytic activity of both $M(OTf)_3$ salts (M=Sc, La; Table 2).

Table 1. Carbomethoxylation of $PhCH_2NH_2$ with DMC in the presence of a Group 3 metal (La, Sc) salt at ambient temperature (20 °C)[a]

Entry	Metal salt	*M* (La, Sc) (mmol)	Time (h)	Carbamate yield (%)[b]
1	None	—	17	2
2	$LaCl_3$	0.067	23.5	2
3	$LaCl_3\cdot 7H_2O$	0.067	6	1
4	$La(NO_3)_3\cdot 7H_2O$	0.067	4	10
5	$La(OTf)_3$	0.067	0.5	27
6	$La(OTf)_3$	0.067	24.0	71
7	$Sc(OTf)_3$	0.072	0.7	34
8	$Sc(OTf)_3$	0.072	20.9	75

[a] To the used Sc or La salt in DMC, the amine was added. $PhCH_2NH_2$: 0.100 mL, 0.916 mmol; DMC: 1.0 mL, 11.87 mmol (in all the runs).

[b] GC-yield versus the amine (internal standard: *n*-undecane (30 μL)).

Table 2. Carbomethoxylation of $PhCH_2NH_2$ with DMC in the presence of $M(OTf)_3$ (M=La, Sc) at ambient temperature (20 °C): influence of H_2O on the catalytic activity of the triflate salts[a]

Entry	Metal salt	*M* (La, Sc) (mmol)	Time (h)	Carbamate yield (%)[b]
1	$La(OTf)_3$	0.067	24.0	71
2	$La(OTf)_3/H_2O$[c]	0.065	9.5	7
3	$Sc(OTf)_3$	0.072	20.9	75
4	$Sc(OTf)_3/H_2O$[d]	0.079	24	10

[a] $PhCH_2NH_2$: 0.100 mL, 0.916 mmol; DMC: 1.0 mL, 11.87 mmol (in all the runs).

[b] GC-yield versus the amine (internal standard: *n*-undecane (30 μL)).

[c] H_2O (8 μL; mol H_2O/mol La=7:1) was added to the suspension of the salt in DMC before adding the amine.

[d] H_2O (8.5 μL; mol H_2O/mol Sc=6:1) was added to the DMC solution of the salt before adding the amine.

In principle, water is expected to effectively compete with other donor species (amine, OTf anion, DMC itself, etc.) for the coordination sites on the metal centre and, therefore, can inhibit the activation of the substrate (DMC). Anhydrous conditions are required also to prevent the precipitation of poorly soluble metal-carbamato-species (see Section 4.2), which can easily form as a result of DMC hydrolysis in the presence of the amine.

Table 3 summarizes the results obtained when linear or branched aliphatic primary amines RNH_2 (R=benzyl, *n*-butyl, allyl, *iso*-butyl) were reacted with DMC at 20 °C, at a DMC/amine molar ratio close to 13:1, in the absence of any catalyst (entries 3, 6, 9, and 12, Table 3) or in the presence of catalytic amounts of $M(OTf)_3$ (7–8% (mol/mol) vs RNH_2; M=Sc or La). The triflate salts $M(OTf)_3$ smoothly promote the carbomethoxylation of the investigated amines which are converted into the corresponding carbamate esters in good yield (Table 3).

An analogous catalytic effect is clearly evident also when an amine/DMC molar ratio higher than unity (RNH_2/DMC=2.5–3 (mol/mol), Table 4) is used together with catalytic amounts of $M(OTf)_3$ (3–4% (mol/mol) vs DMC; M=Sc or La).

The carbomethoxylation reaction is very selective. In all cases (Tables 3 and 4), the metal triflate promotes the carbamation of the amine in a selective way (≌ 100%).

2.2. Kinetic and mechanistic considerations

After addition of amine to the $M(OTf)_3$ salt in DMC, the separation of poorly soluble metal species from the reaction medium may occur. In only a few cases (entries 2 and 8, Table 3; entries 3 and 9, Table 4), the reaction mixture remains homogeneous throughout the catalytic run. These features make it difficult to compare, for each amine, the catalytic efficiency of the $M(OTf)_3$ (M=Sc, La) salts quantitatively (as measured, for instance, by turnover-numbers (TONs)). A better insight into this issue is provided by the inspection of Figure 1 which shows the profile of formation of RNHC(O)OMe (R=benzyl, *n*-butyl, allyl, *iso*-butyl) carbamates in the presence of the $M(OTf)_3$ (M=Sc, La) salts, under the experimental conditions reported in Table 3. Curves (c) and (d) for (*n*-butyl)NHC(O)OMe and (g) and (h) for (*iso*-butyl)NHC(O)OMe show that carbamate

Table 3. Carbomethoxylation of aliphatic amines RNH_2 with DMC at ambient temperature (20 °C): catalytic effect of $M(OTf)_3$ (M=Sc, La) salts[a]

Entry	R	RNH_2 (mmol)	DMC (mmol)	$Sc(OTf)_3$ (mmol)	$La(OTf)_3$ (mmol)	Time (h)	RNHC(O)OMe yield (%)[b]
1	Benzyl	0.916	11.87	0.0723	—	20.9	75
2	Benzyl	0.916	11.87	—	0.0669	24.0	71
3	Benzyl	0.916	11.87	—	—	17	2
4	*n*-Butyl	0.908	11.87	0.0680	—	24.8	79
5	*n*-Butyl	0.908	11.87	—	0.0699	24.8	69
6	*n*-Butyl	0.908	11.87	—	—	20	15
7	Allyl	0.868	11.87	0.0642	—	22.5	76
8	Allyl	0.868	11.87	—	0.0678	25.4	77
9	Allyl	0.868	11.87	—	—	26	3
10	*i*-Butyl	0.897	11.87	0.0670	—	25.0	70
11	*i*-Butyl	0.897	11.87	—	0.0695	78.3	58[c]
12	*i*-Butyl	0.897	11.87	—	—	25	7

[a] To the $M(OTf)_3$ salt in DMC, the amine and *n*-undecane (internal standard) were in sequence added.

[b] GC-yield versus amine.

[c] Carbamate yield was equal to 49% after a reaction time of 22.5 h.

Table 4. Aminolysis of DMC by aliphatic amines RNH_2 (excess), at ambient temperature (20 °C), in the presence of $M(OTf)_3$ (M=Sc, La) salts

Entry	R	RNH_2 (mmol)	DMC (mmol)	$Sc(OTf)_3$ (mmol)	$La(OTf)_3$ (mmol)	Time (h)	RNHC(O)OMe yield (%)[a]
1	Benzyl	4.58	1.78	—	—	24	23
2	Benzyl	4.58	1.78	0.0657	—	21.2	82
3	Benzyl	4.58	1.78	—	0.0698	48	83
4	Allyl	5.04	1.78	—	—	24	43
5	Allyl	5.35	1.78	0.070	—	4	83
6	Allyl	5.35	1.66	—	0.0665	4	69
7	*i*-Butyl	6.85	1.78	—	—	24	59
8	*i*-Butyl	4.68	1.78	0.0657	—	24.3	86
9	*i*-Butyl	4.88	1.78	—	0.0693	23.5	76

[a] GC-yield versus DMC (internal standard: *n*-undecane).

formation is more efficient under $Sc(OTf)_3$ catalysis. For (benzyl)NHC(O)OMe (curves (a) and (b)) and (allyl)NH-C(O)OMe (curves (e) and (f)) the curves of formation in the presence of $La(OTf)_3$ or $Sc(OTf)_3$ almost overlap, although the reaction mixture remains homogeneous throughout the reaction time in the former case (M=La), while is heterogeneous in the latter (M=Sc), because of the precipitation of poorly soluble Sc-derivatives. These features suggest that $Sc(OTf)_3$ is a more effective catalyst than $La(OTf)_3$ in this reaction.[20]

The higher catalytic activity of the Sc salt can be related with the higher Lewis acidity of Sc(III) with respect to La (III),[21] as a result of their different ionic radii (0.89 Å for $Sc^{3+}$and 1.17 Å for La^{3+}).[22] The higher the acidity of the metal centre, the higher the reactivity of the substrate (DMC), which is more strongly activated towards the nucleophilic attack by amine.

The curves reported in Figure 1 indicate that, with the exception of the system $La(OTf)_3$/*iso*-butylamine/DMC

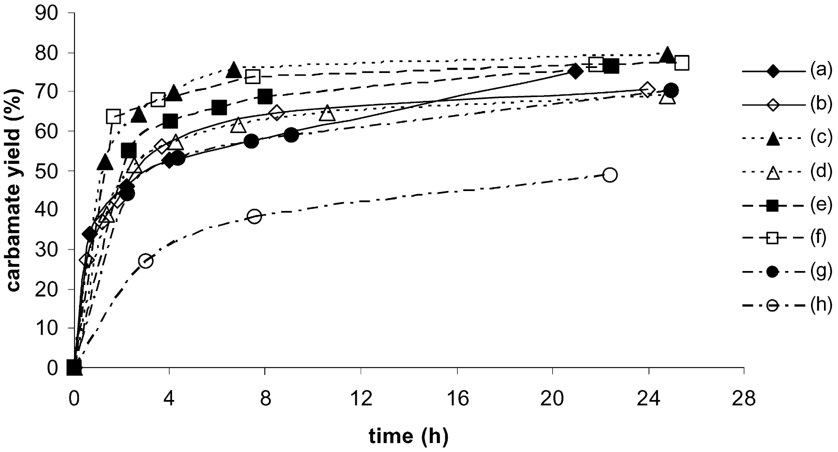

Figure 1. Curves of formation (20 °C) of RNHC(O)OMe carbamate esters by carbomethoxylation of aliphatic primary amines RNH_2 with DMC (1.0 mL, 11.87 mmol) in the presence of $M(OTf)_3$ (M=Sc, La). Experimental conditions: (a) $PhCH_2NH_2$: 0.916 mmol; $Sc(OTf)_3$: 0.0723 mmol. (b) $PhCH_2NH_2$: 0.916 mmol; $La(OTf)_3$: 0.0669 mmol. (c) $CH_3(CH_2)_3NH_2$: 0.908 mmol; $Sc(OTf)_3$: 0.0680 mmol. (d) $CH_3(CH_2)_3NH_2$: 0.908 mmol; $La(OTf)_3$: 0.0699 mmol. (e) $CH_2{=}CHCH_2NH_2$: 0.868 mmol; $Sc(OTf)_3$: 0.0642 mmol. (f) $CH_2{=}CHCH_2NH_2$: 0.868 mmol; $La(OTf)_3$: 0.0678 mmol. (g) $(CH_3)_2CHCH_2NH_2$: 0.897 mmol; $Sc(OTf)_3$: 0.0670 mmol. (h) $(CH_3)_2CHCH_2NH_2$: 0.897 mmol; $La(OTf)_3$: 0.0695 mmol. Carbamate yield was equal to 58.3% after a reaction time of 78.3 h.

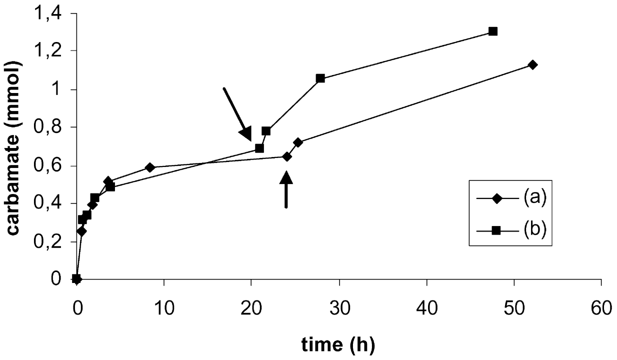

Figure 2. Carbomethoxylation of $PhCH_2NH_2$ with DMC in the presence of $M(OTf)_3$ (M=Sc, La) at ambient temperature (20 °C): effect of further addition of amine at the plateau. Experimental conditions: (a) $La(OTf)_3$: 0.0669 mmol, $PhCH_2NH_2$: 0.916 mmol, DMC: 11.87 mmol. After 24 h, 0.100 mL (0.916 mmol) of benzylamine were added. (b) $Sc(OTf)_3$: 0.0723 mmol, $PhCH_2NH_2$: 0.916 mmol, DMC: 11.87 mmol. After 21 h, 0.100 mL (0.916 mmol) of benzylamine were added.

(curve (h), Fig. 1), a quite interesting initial conversion is observed as the carbamate yield ranges between 50 and 65%, at ambient temperature, within a reaction time of 3 h. Figure 2 shows that, for the system $M(OTf)_3/PhCH_2NH_2/$DMC (M=Sc, La) at 20 °C, if amine is added to the reaction mixture at the plateau, the reaction restarts with an appreciable production of more carbamate ester. This demonstrates that the catalyst is still active, although not so effective as at the beginning. The restart of the reaction upon addition of fresh amine indicates that the residual unreacted amine may be in a form that is not prone to react with DMC: the nucleophilicity of the amine must be reduced in some way. Also, the diminished catalytic activity is indicative of a modification of the catalyst which may progressively deactivate by converting into a catalytically less active species.

In order to shed light on these issues, we have carried out a complete analysis of the reaction solution. We have found that the amine can undergo protonation and convert into the corresponding alkylammonium cation RNH_3^+, that is not reactive towards DMC and can be recovered at the end of the reaction as alkylammonium triflate salt, $(RNH_3)OTf$. This particular issue has been investigated in detail for the system $Sc(OTf)_3/PhCH_2NH_2/DMC$ (Sc/amine/DMC$\cong$ 1:13:172 (mol/mol)). IR monitoring of the reaction solution revealed the formation of $(PhCH_2NH_3)OTf$ (characteristic absorptions at 3258, 3166, 643 cm^{-1}) soon after (about 30–45 min) the reactants were mixed. The work-up of the reaction mixture, at the end of the catalytic run, allowed to isolate the salt $(PhCH_2NH_3)OTf$ (1.80 mol of salt per mol of Sc), that was characterized by IR and NMR spectroscopy.[23]

Most likely, the proton source is the coproduced methanol,[24] as suggested in Eq. 2.

$$L_nM(OTf)_3 + xMeOH + xRR'NH \rightarrow L_nM(OMe)(OTf)_{3-x} + x(RR'NH_2)OTf \qquad (2)$$

M=Sc, La and L=ligand, R′=H, alkyl.

The reactivity described by Eq. 2 is not completely new, as it has been documented in the literature and used for the synthesis of rare-earth alkoxides, $Ln(OR)_3$, by reaction of the corresponding chlorides, $LnCl_3$, with alcohols in the presence of bases (Eq. 3).[25]

$$LnCl_3 + 3ROH + 3NH_3 \rightarrow Ln(OR)_3 + 3(NH_4)Cl \qquad (3)$$

Ln=rare-earth metal

Ad hoc experiments allowed us to exclude that $(RR'NH_2)$ OTf salts may play a significant role as carbomethoxylation catalysts. In fact, as shown in Table 5 for the carbamation of $PhCH_2NH_2$ with DMC at 20 °C, $(PhCH_2NH_3)OTf$ (0.06585 g, 0.257 mmol; completely soluble in DMC (1 mL)) exhibits only a modest catalytic activity,[26] which is, however, somewhat lower than that of the $M(OTf)_3$ (M=Sc, La) salts.

2.3. Influence of temperature

Benzylamine has been used for studying the influence of temperature on the carbomethoxylation reaction. Table 6 summarizes the results obtained with $Sc(OTf)_3$ as catalyst.[28]

At 90 °C, the carbamation of the amine, albeit faster, takes place less selectively than at room temperature (see entries 1 and 2, Table 6).

Entries 3 and 4 (Table 6) illustrate the results obtained at 90 °C under conditions different from those used in entry 2. In entry 3, the use of a higher (vs entry 2) amount of the amine ($Sc(OTf)_3$/amine=3.1% vs 8.04% (mol/mol) in entry 2), without appreciably changing the analytical concentration of the catalyst ($[Sc(OTf)_3]$=0.06 mol/L vs 0.07 mol/L in entry 2) results in a better carbamate yield, but the selectivity is lower (95%), albeit still good. A marked reduction of selectivity and yield is observed in entry 4, where a significantly lower (vs entry 2) catalyst loading is used with respect to both the amine ($Sc(OTf)_3$/amine= 0.62% (mol/mol)) and DMC ($[Sc(OTf)_3]$=0.005 mol/L).

Analogous trends are found when $La(OTf)_3$ is used as catalyst in place of $Sc(OTf)_3$ (90 °C). Figure 3 shows the curve of formation of $PhCH_2NHC(O)OMe$ by carbomethoxylation of $PhCH_2NH_2$ with DMC in the presence of $La(OTf)_3$, under conditions otherwise comparable with

Table 5. Carbomethoxylation of $PhCH_2NH_2$ with DMC at ambient temperature (20 °C): $(PhCH_2NH_3)OTf$ vs $M(OTf)_3$ (M=Sc, La) catalytic activity

Catalyst	$PhCH_2NH_2$ (mmol)	DMC (mmol)	Catalyst/amine (mol/mol)%	Time (h)	$PhCH_2NHC(O)OMe$ yield (%)[a]
None	0.916	11.87	0	17	2
$(PhCH_2NH_3)OTf$	0.916	11.87	28	19	10
$Sc(OTf)_3$	0.916	11.87	7.9	20.9	75
$La(OTf)_3$	0.916	11.87	7.3	24.0	71

[a] GC-yield versus the amine (internal standard: *n*-undecane).

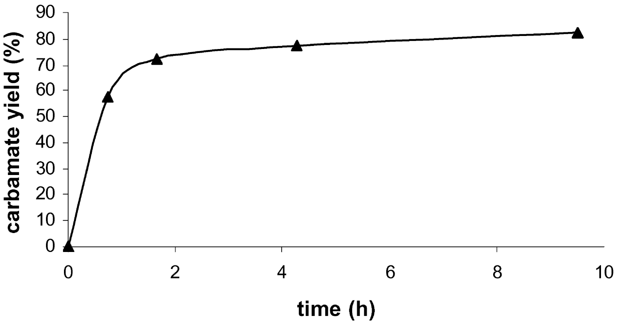

Figure 3. Carbomethoxylation of $PhCH_2NH_2$ with DMC in the presence of $La(OTf)_3$ at 90 °C. Experimental conditions: $La(OTf)_3$: 0.0681 mmol, $PhCH_2NH_2$: 2.29 mmol, DMC: 11.87 mmol.

those used in entry 3, Table 6. After 9.5 h at 90 °C, a carbamate yield close to 83% is obtained, with a selectivity to the carbamate ester around 95%.

2.4. Synthetic applications

The carbomethoxylation of a few amines was carried out at ambient temperature (20 °C) under conditions more appealing from the synthetic point of view than those employed in Table 3, by using a lower catalyst/amine molar ratio (≌ 3% vs ≌ 8% (mol/mol)). In order to realize a higher concentration of both nucleophile and catalyst in the reaction mixture, a markedly lower DMC/triflate salt molar ratio (75–95 vs 160–185 (mol/mol)) was also used. We focused our attention on the use of $Sc(OTf)_3$ as the catalyst, because of its higher catalytic activity with respect to the homologue La salt.

Table 6. Carbomethoxylation of $PhCH_2NH_2$ with DMC in the presence of $Sc(OTf)_3$ under different experimental conditions

Entry	RNH_2 (mmol)	DMC (mmol)	$Sc(OTf)_3$ (mmol)	T (°C)	Time (h)	Yield[a] (%)	Selectivity[b] (%)
1	0.916	11.87	0.0723	20	20.9	75	> 99.5
2[c]	0.916	11.87	0.0737	90	9.1	75	98
3	2.29	11.87	0.0701	90	8.7	84	95
4	9.16	118.7	0.0569	90	27.4	57[d]	89

[a] Carbamate GC-yield vs the amine (internal standard: *n*-undecane).

[b] Selectivity to carbamate ester. The observed side-products were $(PhCH_2)N(Me)H$ and $(PhCH_2)N(Me)_2$.

[c] The reaction mixture was heated at 90 °C for 9.1 h and analyzed by GC. Then, 0.100 mL (0.916 mmol) of $PhCH_2NH_2$ were further added and the reaction mixture heated at 90 °C for 6 h longer. After this time, the overall carbamate yield (vs the total amount of amine used) was 70% (95% selectivity).

[d] After the first 2 h, the carbamate yield was equal to 16% and selectivity >99%. However, the selectivity decreased with time and, after 27.4 h, the overall yield of N-alkylation products was close to 7%.

Under the described conditions, aliphatic primary amines, such as benzylamine, *n*-butylamine and allylamine, are selectively (≌ 100%) converted into the corresponding methylcarbamate esters in good yields (Table 7).

This study has been extended to secondary aliphatic amines, such as morpholine and piperidine. At 20 °C, under the conditions reported in Table 7, also these amines are very selectively (≌ 100%) carbomethoxylated, but at a lower rate than the primary ones. After ~24 h, in both cases, the amount of unreacted amine was still close to 20%. The carbamation of morpholine was carried out also at higher temperature. At 65 °C (Sc/amine=3.0% (mol/mol); DMC/Sc=76.0 (mol/mol)), as expected, a marked decrease in selectivity is observed due to the appreciable side-formation of *N*-methylmorpholine.[29]

As for the fate of the catalyst, we have emphasized above that, to some extent, Sc(III) precipitates during the reaction in the form of unsoluble species that have been recovered at the end of the catalytic run by filtration.[30] Unfortunately, their poor solubility in common organic solvents precluded any re-crystallization and in no case have we been able to isolate well defined compounds.[31] When reused at 20 °C, the crude precipitate still exhibits a catalytic activity. However, this results in lower activity as compared to the starting catalyst.

3. Conclusions

For the first time Group 3 metal salts have been employed as catalysts for the carbamation of amines with dimethylcarbonate. Both $Sc(OTf)_3$ and $La(OTf)_3$ effectively promote the carbomethoxylation of aliphatic amines with DMC at 20 °C to afford the corresponding carbamate esters with good yields and excellent selectivity (≌ 100%). $Sc(OTf)_3$ exhibits a higher catalytic activity than $La(OTf)_3$. The presence of water in the reaction medium inhibits the catalytic activity of both triflate salts at ambient temperature. Temperature affects the selectivity of the carbomethoxylation reaction, being less selective at higher temperature, because of the increased incidence of the N-methylation processes.

4. Experimental

4.1. General

Unless otherwise stated, all reactions and manipulations were conducted under a dinitrogen atmosphere, by using vacuum line techniques. All solvents were dried according

Table 7. Synthesis of methyl carbamates from amines and DMC in the presence of $Sc(OTf)_3$, at ambient temperature (20 °C)

Amine	Sc/amine (mol/mol)%	DMC/Sc (mol/mol)	Time (h)	RNHC(O)OMe isolated yield (%)
$PhCH_2NH_2$	3.0	97.0	24	83
$CH_2{=}CHCH_2NH_2$	3.0	94.7	24	77
$CH_3(CH_2)_3NH_2$	3.0	90.1	24	82
Piperidine	3.1	78.9	48	81
Morpholine	3.0	75.2	48	80

to literature methods[32] and stored under N_2. DMC (Fluka) was dried over 5 Å molecular sieves for 24 h, filtered, distilled, and stored under N_2. The amines (Fluka or Aldrich products) were dried over KOH, distilled, and stored under N_2. $M(OTf)_3$ (M=Sc, La) salts (Fluka, Aldrich) were used as received and manipulated under an inert gas atmosphere.

IR spectra were obtained with a Perkin Elmer 883 spectrophotometer or with a Perkin Elmer FTIR 1710 instrument. NMR spectra were run on a Varian XL-200 or a Bruker AM 500 instrument, as specified in the text. ^1H and ^{13}C chemical shifts are in ppm versus TMS and referenced to the solvent peak. GC–MS analyses were carried out with a Shimadzu GC-17A linked to a Shimadzu GCMS-QP5050 selective mass detector (capillary column: Supelco MDN-5S, 30 m×0.25 mm, 0.25 μm film thickness). GC analyses were performed with a HP 5890 Series II gas-chromatograph (capillary column: Heliflex AT-5, 30 m×0.25 mm, 0.25 μm film thickness).

4.2. Carbomethoxylation of $PhCH_2NH_2$ with DMC: influence of H_2O on the catalytic activity of the $M(OTf)_3$ (M=Sc, La) salts

To the solution of $Sc(OTf)_3$ in DMC, or to the suspension of $La(OTf)_3$ in the same solvent,[19] H_2O was added (see Table 2). Upon addition of $PhCH_2NH_2$ to the resulting homogeneous solutions, the fast separation of a poorly soluble colorless solid was observed. The resulting mixture was allowed to react at 20 °C and then analyzed by GC (Table 2).

The separated solids, isolated by centrifugation after their precipitation (30 min) or at the end of the catalytic run (Table 2), were found to contain Sc(III) or La(III)[33] (according to the used $M(OTf)_3$ salt) and evolved CO_2 upon acidolysis with diluted HCl. Moreover, their IR spectra showed strong absorptions at 3350–3340, 1570–1500, 1345–1340 cm^{-1}, consistent with the presence of a carbamate group.[34] The low solubility of these species in D_2O, where decomposition is also observed, and other common organic solvents has precluded their purification and full characterization.

4.3. Synthesis of carbamate methyl esters by aminolysis of DMC in the presence of $Sc(OTf)_3$ at ambient temperature (20 °C)

Product yields were not optimized. The MS, IR, ^1H and ^{13}C NMR of $PhCH_2NHC(O)OMe$ and $CH_2{=}CHCH_2NHC(O)OMe$ were identical with those of authentic samples.[12a]

4.3.1. Synthesis of $PhCH_2NHC(O)OMe$ by reaction of $PhCH_2NH_2$ with DMC in the presence of $Sc(OTf)_3$. Benzylamine (1.30 mL, 11.91 mmol) was added to the solution of $Sc(OTf)_3$ (0.18055 g, 0.367 mmol) in DMC (3.0 mL, 35.60 mmol) and the reaction mixture was allowed to react for 24 h at ambient temperature. After filtration, the mother solution and washing (DMC) liquors, collected together, were concentrated in vacuo. Upon addition of CH_2Cl_2 (15 mL) and cooling to 0 °C, pure $(PhCH_2NH_3)OTf$ separated and was isolated by filtration, washed with CH_2Cl_2 and dried in vacuo (0.13670 g, 0.531 mmol) [IR (Nujol, cm^{-1}): 3181, 3093 (s, br), 1617 (m), 1499, 1385, 1245 (vs), 1165 (s), 1115, 1056, 1032 (s), 967, 918, 865, 788, 749, 723, 699, 635, 585, 574, 515, 487. ^1H NMR (THF-d_8, 500.138 MHz): δ 4.22 (s, 2H, CH_2), 7.34–7.42 (m, 3H, $H_{aromatic}$), 7.52 (m, 2H, $H_{aromatic}$), 7.82 (br, 3H, NH_3). ^{13}C NMR (THF-d_8, 125.760 MHz): δ 44.39 (CH_2), 121.76 (q, CF_3, J_{CF}=320.5 Hz), 129.67, 129.85, 134.52 ($C_{aromatic}$)].

The resulting solution was washed with H_2O, which extracted more $(PhCH_2NH_3)OTf$ together with minor amounts of carbamate ester. The organic solution was dried (Na_2SO_4) and concentrated in vacuo to give the pure carbamate $PhCH_2NHC(O)OMe$ (83%, mp: 65–67 °C). Anal. Calcd for $C_9H_{11}NO_2$: C, 65.45; H, 6.67; N, 8.47. Found: C, 65.55; H, 6.73; N, 8.40.

4.3.2. Synthesis of $CH_2{=}CHCH_2NHC(O)OMe$ by reaction of $CH_2{=}CHCH_2NH_2$ with DMC in the presence of $Sc(OTf)_3$. Allylamine (0.930 mL, 12.43 mmol) was added to the solution of $Sc(OTf)_3$ (0.18505 g, 0.376 mmol) in DMC (3.0 mL, 35.60 mmol). The reaction mixture was stirred at 20 °C for 24 h, diluted with diethylether (30 mL) and filtered.

The resulting solution was treated with H_2O, which extracted allylammonium triflate [IR (Nujol, cm^{-1}): 3171 (vs, br), 1651 (m, sh), 1614 (m, br), 1505 (m), 1430, 1250 (vs), 1198, 1168 (s), 1130, 1032 (s), 991, 951, 876, 763, 645, 582, 517. ^1H (CD_3CN, 500.138 MHz): δ 3.58 (dt, 2H, CH_2, $^3J_{H-H}$=6.29 Hz, $^4J_{H-H}$=1.3 Hz), 5.38 (dm, 1H, H_{cis}), 5.43 (dm, 1H, H_{trans}), 5.91 (ddt, 1H, $CH_2{=}CH$, J_{cis}=10.34 Hz, J_{trans}=17.30 Hz, $^3J_{H-H}$=6.3 Hz), 6.51 (br, 3H, NH_3). ^{13}C (CD_3CN, 125.760 MHz): δ 43.05 ($C_{allylic}$), 119.08 (q, CF_3, $^1J_{CF}$=320 Hz), 122.00 ($H_2C{=}CH$), 129.76 ($CH_2{=}CH$)] together with minor amounts of carbamate. The organic phase was dried (Na_2SO_4) and concentrated in vacuo to give the pure carbamate $CH_2{=}CHCH_2NHC(O)OMe$ (77%). Anal. Calcd for $C_5H_9NO_2$: C, 52.16; H, 7.88; N, 12.16. Found: C, 52.10; H, 7.93; N, 12.10.

4.3.3. Synthesis of $CH_3(CH_2)_3NHC(O)OMe$ by reaction of $CH_3(CH_2)_3NH_2$ with DMC in the presence of $Sc(OTf)_3$. *n*-Butylamine (1.30 mL, 13.18 mmol) was added to the solution of $Sc(OTf)_3$ (0.19445 g, 0.395 mmol) in DMC (3.0 mL, 35.60 mmol). The reaction mixture was reacted at room temperature for 24 h, diluted with diethylether (10 mL), and filtered. To the resulting solution *n*-pentane (70 mL) was added. Upon cooling to −20 °C overnight, colorless needles of pure $[(CH_3(CH_2)_3NH_3]OTf$ separated from the solution and were isolated by filtration (0.07395 g, 0.331 mmol) [IR (Nujol, cm^{-1}): 3178 (vs, br), 1613 (m-s), 1514, 1248 (vs, br), 1170 (vs), 1037 (s), 914, 794, 762, 738, 641, 581, 517. ^1H (CD_3CN, 200 MHz): δ 0.91 (t, 3H, CH_3, $^3J_{H-H}$=7.23 Hz), 1.37 (m, 2H, CH_2CH_3), 1.59 (m, 2H, $CH_2CH_2CH_3$), 2.93 (m, 2H, NCH_2), 6.27 (br, 3H). ^{13}C (CD_3CN, 125.760 MHz): δ 13.65 (CH_3), 20.07 (CH_2CH_3), 29.53 ($CH_2CH_2CH_3$), 40.93 (NCH_2), 122.58 (q, CF_3, $^1J_{CF}$=320.7 Hz)].

The solution was extracted with H_2O (15 mL) from which residual amounts of $[(CH_3(CH_2)_3NH_3]OTf$ were recovered (as established by IR), but not further purified. From the organic solution, dried over Na_2SO_4 and concentrated in vacuo, pure carbamate $CH_3(CH_2)_3NHC(O)OMe$ was isolated (82%). Anal. Calcd for $C_6H_{13}NO_2$: C, 54.94; H, 9.99; N, 10.67. Found: C, 54.87; H, 10.07; N, 10.50. IR (neat, cm^{-1}): 3338 (m-s, br), 2961, 2874, 1707 (vs), 1535 (vs), 1458, 1381, 1260 (vs), 1193, 1142, 1113, 1057, 1025, 781. ^1H NMR ($CDCl_3$, 500.138 MHz): δ 0.82 (t, 3H, CH_3, $^3J_{H-H}$=7.35 Hz), 1.24 (m, 2H, CH_2CH_3), 1.38 (quintuplet, 2H, $CH_2CH_2CH_3$, J=7.3 Hz), 3.07 (quartet, 2H, NCH_2, J=6.6 Hz), 3.55 (s, 3H, OCH_3), 5.2 (br, 1H, NH). ^{13}C NMR ($CDCl_3$, 125.760 MHz): δ 13.76 (CH_3), 19.91 (CH_2CH_3), 32.14 ($CH_2CH_2CH_3$), 40.80 (NCH_2), 51.91 (OCH_3), 157.23 (C(O)O). MS (*m/z*): 131 ($M^{+\cdot}$), 116, 102, 88, 76, 59, 44.

4.3.4. Synthesis of 1-carbomethoxypiperidine by reaction of piperidine with DMC in the presence of $Sc(OTf)_3$. To the solution of $Sc(OTf)_3$ (0.17785 g, 0.361 mmol) in DMC (2.4 mL, 28.51 mmol) piperidine (1.15 mL, 11.62 mmol) was added. The reaction mixture was stirred for 48 h at ambient temperature, treated with diethylether (35 mL) and cooled to −20 °C. After filtration, the mother liquor and washing ethereal solutions (2×10 mL), collected together, were extracted with H_2O. The organic layer, dried over Na_2SO_4, was concentrated in vacuo to give pure carbamate with 81% yield. Anal. Calcd for $C_7H_{13}NO_2$: C, 58.72; H, 9.15; N, 9.78. Found: C, 58.65; H, 9.20; N, 9.70. IR (neat, cm^{-1}): 1702 (s), 1535, 1474, 1446, 1410, 1372, 1352, 1282, 1265, 1238, 1190, 1152, 1090, 1029, 947, 900, 854, 839, 791, 719. ^1H NMR ($CDCl_3$, 200 MHz): δ1.41 (m, 6H, $CH_2CH_2CH_2$), 3.26 (m, 4H, CH_2-N-CH_2), 3.53 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, 125.760 MHz): δ 24.44 and 25.33 ($CH_2-CH_2-CH_2$), 44.45 (CH_2-N-CH_2), 52.03 (OCH_3), 155.60 (C(O)O). MS (*m/z*): 143 ($M^{+\cdot}$), 128, 102, 84, 70, 56, 42.

Formed piperidinium triflate could be isolated in a pure form according to the following experimental procedure. The reaction mixture ($Sc(OTf)_3$: 0.18450 g, 0.375 mmol; DMC: 2.40 mL, 28.51 mmol; $C_5H_{11}N$: 1.15 mL, 11.62 mmol), prepared as previously described and stirred for 48 h at 20 °C, was filtered. The solution, after addition of diethylether (60 mL), was cooled to −20 °C overnight. The separated colorless solid was isolated by filtration, washed with diethylether, dried in vacuo and identified as pure piperidinium triflate (0.10170 g, 0.432 mmol) [IR (Nujol, cm^{-1}): 3163 (br, vs), 1592 (s), 1480, 1435, 1318, 1239 (vs), 1158 (s), 1082, 1029, 953, 922, 872, 866, 816, 761, 722, 633, 576, 547. ^1H NMR (CD_3CN, 200 MHz): δ 1.74 (m, 2H, $CH_2CH_2CH_2$), 1.92 (m, 4H, $CH_2CH_2CH_2$), 3.10 (t, 4H, CH_2-N-CH_2, J_{H-H}=5.7 Hz), 6.6 (br). ^{13}C NMR (CD_3CN, 125.760 MHz): δ 22.31 and 22.98 ($CH_2CH_2CH_2$), 45.87 (CH_2-N-CH_2), 121.79 (q, CF_3, $^1J_{CF}$=320 Hz)].

Upon treating the filtered solution with H_2O and concentrating in vacuo the aqueous layer, a solid residue (0.075 g; not further purified) was obtained, that resulted to contain more piperidinium triflate (as established by IR).

4.3.5. Synthesis of 1-carbomethoxymorpholine by reaction of morpholine with DMC in the presence of $Sc(OTf)_3$. To the solution of $Sc(OTf)_3$ (0.18655 g, 0.379 mmol) in DMC (2.4 mL, 28.51 mmol) morpholine (1.10 mL, 12.61 mmol) was added. The reaction mixture was reacted for 48 h at 20 °C, then diluted with diethylether (30 mL) and cooled to −20 °C overnight. After filtration, the solution was evaporated in vacuo, and the residue chromatographed on silica gel with diethylether/*n*-hexane (2:1, v/v) as eluent to give pure carbamate with 80% yield. Anal. Calcd for $C_6H_{11}NO_3$: C, 49.65; H, 7.64; N, 9.64. Found: C, 49.57; H, 7.72; N, 9.57. IR (neat, cm^{-1}): 2960, 2900, 2859, 1702 (vs), 1466, 1445, 1407, 1363, 1301, 1280, 1245, 1222 (vs), 1191, 1117, 1073, 1025, 958, 917, 851, 800, 769, 656, 568, 524, 475. ^1H NMR ($CDCl_3$, 200 MHz): δ 3.36 (m, 4H, CH_2-N-CH_2), 3.56 (m, 4H, CH_2-O-CH_2), 3.62 (s, 3H, CH_3). ^{13}C NMR (125.760 MHz, $CDCl_3$): δ 43.61 (CH_2-N-CH_2), 52.34 (CH_3), 66.07 (CH_2-O-CH_2), 155.32 (C(O)O). MS(*m/z*): 145 ($M^{+\cdot}$), 130, 114, 100, 86, 70, 56, 42.

Formed morpholinium triflate could be isolated in a pure form according to the experimental procedure reported below. The reaction mixture ($Sc(OTf)_3$: 0.18570 g, 0.377 mmol; DMC: 2.40 mL, 28.51 mmol; C_4H_9NO: 1.10 mL, 12.61 mmol), prepared as previously described and stirred for 48 h at 20 °C, was filtered. The solution, after addition of diethylether (60 mL), was cooled to −20 °C overnight. The solid precipitated was isolated by filtration, washed with diethylether, dried in vacuo and identified as pure morpholinium triflate (0.15255 g, 0.643 mmol) [IR (Nujol, cm^{-1}): 3066, 1604, 1276 (br), 1197, 1165, 1107, 1031, 903, 876, 763, 723, 638, 591, 575, 518, 476, 440, 420. ^1H NMR (CD_3CN, 200 MHz): δ 3.18 ppm (m, 4H, CH_2-N-CH_2), 3.83 (m, 4H, CH_2-O-CH_2), 6.8 (br, NH_2). ^{13}C NMR (CD_3CN, 125.760 MHz): 44.81 ppm (CH_2-N-CH_2), 64.19 (CH_2-O-CH_2), 121.78 (q, CF_3, $^1J_{CF}$= 320.4 Hz)]. The IR and NMR spectra reported above were carried out on the aged product (stored under dinitrogen, for 1 month, at ambient temperature) and were identical to those shown by a sample of morpholinium triflate prepared from morpholine and triflic acid in ether at 20 °C. The IR spectrum (Nujol) of the fresh product, registered soon after the isolation (see above), shows absorptions at 3022, 1554, 1417, 1262 (vs), 1233, 1221, 1161, 1098, 1043, 884, 867, 760, 645, 587, 515, 431, 410 cm^{-1}.

4.4. Isolation of $(PhCH_2NH_3)(OTf)$ from the reaction of MeOH with $PhCH_2NH_2$ in the presence of $Sc(OTf)_3$

To a CH_2Cl_2 (9 mL) solution of $Sc(OTf)_3$ (0.22870 g, 0.465 mmol) and MeOH (0.270 mL, 6.657 mmol) benzylamine (0.155 mL, 1.420 mmol) was added and the resulting suspension stirred at ambient temperature (20 °C) for 3 h. After filtration, the mother solution and washing (THF) liquors, collected together, were concentrated in vacuo. Upon addition of *n*-pentane and cooling to −20 °C, colorless crystals of $(PhCH_2NH_3)(OTf)$ separated and were isolated by filtration (0.22580 g; 0.88 mmol; $mol_{(RNH_3)OTf}/mol_{Sc} = 1.89$).

Acknowledgements

Financial support from Italian MIUR is gratefully acknowledged. M.D. wishes to thank the MIUR (L488/92) for a fellowship. The authors are indebted with Professor Michele Aresta (University of Bari) for helpful suggestions.

References and notes

1. Anastas, P. T.; Kirchoff, M. M. *Acc. Chem. Res.* **2002**, *35*, 686.
2. Aresta, M.; Quaranta, E. *ChemTech* **1997**, *27*(3), 32 and references therein.
3. Babad, H.; Zeiler, A. G. *Chem. Rev.* **1973**, *73*, 75.
4. (a) Barthelemy, J. *Lyon Pharm.* **1986**, *37*(6), 297. (b) Wu, T.-T.; Huang, J.; Arrington, N. D.; Dill, J. M. *J. Agric. Food Chem.* **1987**, *35*, 817. (c) Kato, T.; Suzuki, K.; Takahashi, J.; Kamashita, K. *J. Pestic. Sci.* **1984**, *9*, 489. (d) Rivetti, F.; Romano, U.; Sasselli, M. G. U.S. Patent 4514339, 1985. (e) Green, T. W.; Wuts, P. G. M. *Protective groups in organic synthesis*; 3rd ed. Wiley: New York, 1999; pp 503–550.
5. Cenini, S.; Pizzetti, M.; Crotti, C. *Aspects of homogeneous catalysis*; Ugo, R., Ed.; Riedel: Dordrecht, The Netherlands, 1998; Vol. 6, pp 97–108.
6. Hagemann, C. Kolhensaure derivate. In *Methoden der organishen chemie*; 4th ed., Houben-Weil, Ed.; Georg Thieme: Stuttgart, 1983; p 159 Band E4.
7. (a) Massi Mauri, M.; Romano, U.; Rivetti, F. *Ing. Chim. Ital.* **1985**, *21*(6), 6 and references cited therein. (b) Rivetti, F. *Comptes Rendus Acad. Sci., Series II: Chimie* **2000**, *3*(6), 497 and references therein.
8. Aresta, M.; Berloco, C.; Quaranta, E. *Tetrahedron* **1995**, *51*, 8073.
9. Kita, Y.; Haruta, J.; Yasuda, H.; Fukunaga, K.; Shirouchi, Y.; Tamura, Y. *J. Org. Chem.* **1982**, *47*, 2697.
10. (a) Porta, F.; Cenini, S.; Pizzotti, M.; Crotti, C. *Gazz. Chim. Ital.* **1985**, *115*, 275. (b) Garcia Deleon, R.; Kobayashi, A.; Yamauchi, T.; Ooishi, J.; Baba, T.; Masaki, S.; Hiarata, F. *Appl. Catal. A: Gen.* **2002**, *225*, 43. (c) Baba, T.; Fujiwara, M.; Oosaku, A.; Kobayashi, A.; Deleon, R. G.; Ono, Y. *Appl. Catal. A: Gen.* **2002**, *227*, 1. (d) Curini, M.; Epifano, F.; Maltese, F.; Rosati, O. *Tetrahedron Lett.* **2002**, *43*, 4895. (e) Baba, T.; Ono, Y. JP 089435, 2001. (f) Smith, R. C.; Hunns, J. C. B. WO 9856758, 1998. (g) Shimazaki, Y.; Kambe, N.; Sotozono, M. JP 07328435, 1995. (h) Shimazaki, Y.; Kambe, N.; Sotozono, M. JP 07330708, 1995. (i) Calderoni, C.; Mizia, F.; Rivetti, F.; Romano, U. EP 391473, 1990. (j) Bosetti, A.; Cesti, P.; Calderazzo, F. EP 752413, 1997. (k) Gurgiolo, A. E. US 4268684, 1981. (l) Onoda, T.; Tano, K.; Hara, Y. JP 55004316, 1980. (m) Romano, U.; Tesei, R. DE 2714540, 1977.
11. (a) Vauthey, I.; Valot, F.; Gozzi, C.; Fache, F.; Lemaire, M. *Tetrahedron Lett.* **2000**, *41*, 6347. (b) Gupte, S. P.; Shivarcar, A. B.; Chaudari, R. V. *J. Chem. Soc., Chem. Commun.* **2001**, 2620. (c) Carloni, S.; De Vos, D. E.; Jacobs, P. A.; Maggi, R.; Sartori, G. *J. Catal.* **2002**, *205*, 199. (d) Sima, T.; Guo, S.; Shi, F.; Deng, Y. *Tetrahedron Lett.* **2002**, *43*, 8145. (e) Orsat, B.; Alper, P. B.; Moree, W.; Mak, C.-P.; Wong, C.-H. *J. Am. Chem. Soc.* **1996**, *118*, 712. (f) Hacking, M. A. P. J.; van Rantwijk, F.; Sheldon, R. A. *J. Mol. Catal. B: Enzym.* **2000**, *9*, 201.
12. (a) Aresta, M.; Quaranta, E. *Tetrahedron* **1991**, *47*, 9489. (b) Aresta, M.; Dibenedetto, A.; Quaranta, E.; Boscolo, M.; Larsson, R. *J. Mol. Catal.* **2001**, *174*, 7. (c) See also Selva, M.; Tundo, P.; Perosa, A. *Tetrahedron Lett.* **2002**, *43*, 1217.
13. (a) Brill, W. F. DE 2160111, 1972. (b) Cong, J.-S.; Xue, W.; Zhao, X.-Q.; Wang, Y.-J. *Hebei Gongye Daxue Xuebao* **2001**, *30*, 32. *Chem. Abstr.* *135*, 228449. (c) Baba, T.; Kobayashi, A.; Yamauchi, T.; Tanaka, H.; Aso, S.; Inomata, M.; Kawanami, Y. *Catal. Lett.* **2002**, *82*, 193.
14. (a) Fu, Z.-H.; Ono, Y. *J. Mol. Catal.* **1994**, *91*, 399. (b) Fu, Y.; Baba, T.; Ono, Y. *J. Catal.* **2001**, *197*, 91.
15. (a) Aresta, M.; Dibenedetto, A.; Quaranta, E. *Green Chem.* **1999**, 237. (b) Aresta, M.; Dibenedetto, A.; Quaranta, E. *Tetrahedron* **1998**, *54*, 14145.
16. (a) Onoda, T.; Tano, K.; Hara, Y. JP 54163527, 1979. (b) Romano, U.; Fornasari, G.; Di Gioacchino, S. DE 3202690, 1982. (c) Lissel, M.; Rohani-Dezfuli, A. R.; Vogt, G. *J. Chem. Res. (S)* **1989**, 312.
17. For a recent comprehensive review, see: Kobayashi, S.; Sugiura, M.; Kitagawa, H.; Lam, W. W.-L. *Chem. Rev.* **2002**, *102*, 2227.
18. $LaCl_3$, $LaCl_3\cdot 7H_2O$, and $La(NO_3)_3\cdot 7H_2O$ resulted to be poorly soluble in DMC (Table 1). No solubilization of the used salt was observed upon subsequent addition of the amine.
19. Lanthanum triflate was not completely soluble in anhydrous DMC. Addition of benzylamine (Table 1) to the DMC suspension of $La(OTf)_3$ caused the complete solubilization of the salt. $Sc(OTf)_3$ easily dissolved in anhydrous DMC (Table 1), but a heterogeneous reaction mixture was obtained upon subsequent addition of $PhCH_2NH_2$ to the DMC solution of the Sc salt (see later in the text).
20. Analogous conclusions can be drawn also when an amine/DMC molar ratio higher than 1 is used (Table 4).
21. Tsuruta, H.; Yamaguchi, K.; Imamoto, T. *J. Chem. Soc., Chem. Commun.* **1999**, 1703.
22. Cotton, F. A.; Wilkinson, G. *Advanced inorganic chemistry*: 5th ed., Wiley: New York, 1988; p 973.
23. The formation of amine triflate salts has been documented also for amines other than benzylamine (see Section 4). The spectroscopic features of the isolated salts fully agree with those exhibited by authentic samples obtained by reacting the amine (1 equiv.) with CF_3SO_3H (1 equiv.) in diethylether.
24. In support of this, we note that, at 20 °C, a CH_2Cl_2 solution of $Sc(OTf)_3$ and MeOH (added in excess vs Sc to dissolve the metal triflate salt in the solvent used) immediately reacted with benzylamine to afford $(PhCH_2NH_3)(OTf)$ (see Section 4). In good agreement with what reported above, only two of the three used equivalents of benzylamine were protonated, as demonstrated by the fact that the moles of isolated $(PhCH_2NH_3)(OTf)$ salt per mole of Sc were close to 2 ($mol_{(RNH_3)}OTf/mol_{Sc}=1.89$). Work is in progress to purify and full characterize the very hygroscopic scandium derivative that co-precipitated with $(PhCH_2NH_3)(OTf)$ upon addition of the amine. IR (Nujol, cm^{-1}): 1331 (vs, OTf) and 1310 (s, shoulder, OTf), 1238 (s, shoulder, OTf), 1212 (vs, OTf) and 1195 (s, shoulder), 1044 (vs, C–O) and 1030 (s, shoulder, OTf), 639 (s, OTf). The IR spectrum in hexachlorobutadiene showed medium–weak absorptions at 2942, 2833 and 1463 cm^{-1} consistent with the presence of methoxo-groups.[25]
25. (a) Turevskaya, E. P.; Belokon, A. I.; Starikova, Z. A.; Yanovsky, A. I.; Kirushenkov, E. N.; Turova, N. Ya. *Polyhedron* **2000**, *19*, 705. (b) Mehrotra, R. C.; Batwara, J. M. *Inorg. Chem.* **1970**, *9*, 2505. (c) Funk, H.; Kohler, B. Z. *Anorg. Allg. Chem.* **1963**, *325*, 67.
26. This result is reminiscent of the modest catalytic effect played by pirrolidinium ion, when added as perchlorate salt, in the aminolysis of phenyl or *p*-chlorophenyl *p*-nitrobenzoate by pirrolidine.[27]
27. Menger, F. A.; Smith, J. N. *J. Am. Chem. Soc.* **1972**, *94*, 3824.
28. At 90 °C, in the presence of $Sc(OTf)_3$, the reaction mixture, initially heterogeneous, became homogeneous within 1.5 h.
29. The formation of *N*-methylmorpholine was confirmed by GC

and GC–MS (*m*/*z*: 101 (M$^{+\cdot}$), 87, 57, 42) analyses. After 8 h at 65 °C, the selectivity (determined by GC) of the carbomethoxylation process was equal to 92% and decreased to 87% after 23 h.

30. Minor amounts of Scandium (III) remain in solution and can be recovered, together with residual amounts of alkylammonium triflate, by means of extractions with water (see Section 4).
31. The IR spectra of the crude precipitates shows some common features, independently from the used amine. In all cases, an intense absorption is found between 1069 and 1056 cm^{-1}, that may be suggestive of metal-bonded-methoxo-groups. Strong bands, due to triflate anion, are located at 1300–1200, 1180–1170, 1031 and 639 cm^{-1}. A medium–strong band is also observed between 1665 and 1675 cm^{-1}, which we tentatively assign to the carbonyl stretching of carbamate ester molecules, most probably weakly coordinated to Scandium (as the low-frequency shift suggests). Accordingly, the intensity of the latter band markedly reduces upon washing the crude precipitate with DMC. Moreover, the GC–MS analysis of the DMC washing solution shows the presence of carbamate ester, that is further confirmed, by IR spectroscopy, on the residue of the DMC solution after evaporation of solvent (band at approximately 1700 cm^{-1} (see Section 4) due to $\nu_{C=O}$ in free carbamate esters).
32. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of laboratory chemicals*; Pergamon: Oxford, 1986.
33. Feigl, F.; Anger, V. *Spot texts in inorganic analysis*; 6th ed., Elsevier: Amsterdam, 1972; pp 125 and 407.
34. (a) Chisolm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* **1977**, *99*, 782. (b) Aresta, M.; Dibenedetto, A.; Quaranta, E. *J. Chem. Soc., Dalton Trans.* **1995**, 3359.