FULL PAPER

Stereodivergent Carbamate Synthesis by Selective In Situ Trapping of Organic Carbonate Intermediates

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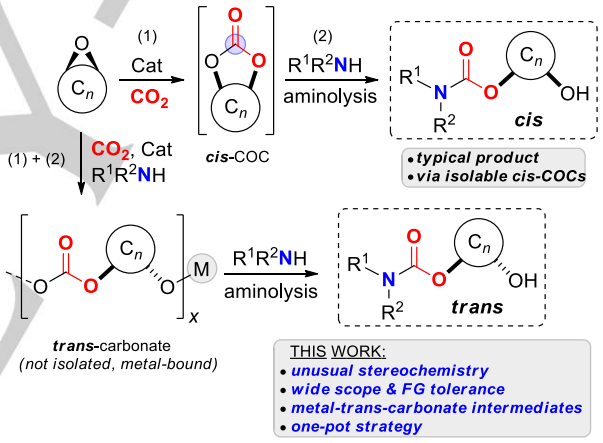
Abstract: *Trans*-carbamate structures can be prepared in a diastereoselective approach by a judicious one-pot combination of *in situ* prepared organic carbonates and suitable amine reagents under appropriate reaction conditions. This unprecedented approach allows for stereo-divergence from a single oxirane substrate with easy access to both *cis* and *trans* carbamate isomers with high stereo-selectivity (*dr* > 19:1). Key to control the diastereo-selective nature of the conversions leading to the *trans* carbamates is the *in situ* formation of *trans*-configured oligo/polycarbonates through Al-catalysis providing the targeted products after aminolysis. The present results demonstrate the valorization of a renewable carbon-based reagent (CO_2) into new valuable scaffolds and an unusual stereo-control exerted through carbonate intermediates. A series of control experiments support the proposed mechanistic rationale towards the *trans*-carbamate products which is based on the trapping of an *in situ* formed *trans*-configured oligo/polycarbonate.

Introduction

Carbamates are ubiquitous scaffolds found in a range of synthetic products of general use in agrochemical and pharmaceutical applications,[1] and in polymer science.[2] Their seemingly privileged incorporation into a wide range of chemical structures has been enabled by methodologies that are conventionally based on the use of toxic reagents including phosgene and its derivatives.[3] Driven by the need for more sustainable approaches towards carbamates, both linear[4] and cyclic organic carbonates[5] have become common reaction partners for amines to afford these widely targeted molecules. The latter category of carbonate structures can be easily obtained through epoxide/CO_2 coupling reactions[6] thus providing a way towards the valorization of a waste combustion product being safe, cheap and readily accessible.

The aminolysis reaction of cyclic organic carbonates (COCs) is well-documented and typically proceeds under mild reaction conditions when using simple alkylamines and mono-substituted COC reagents.[7] The efficient aminolysis of di- and tri-substituted COCs has been seldom reported and should proceed with retention of configuration (Scheme 1). *Cis*-carbamates are produced straightforwardly from their respective *cis*-COCs derived from cyclic oxiranes and CO_2 for which the synthetic methodology has advanced significantly over the years.[8] However, the *trans*-carbamates cannot be easily accessed as there exists no general method for the formation of *trans*-COCs from cyclic oxirane precursors and CO_2.[9]



Scheme 1. Divergent approach towards carbamate synthesis using carbonate intermediates via a sequential (1→2; *cis*) or one-pot (1+2; *trans*) approach. C_n stands for a cycloalkyl skeleton with *n* representing the number of C-atoms.

In order to chase this synthetic challenge, we envisioned that *in situ* formation of a *trans* oligo/polycarbonate from cyclic oxiranes and CO_2 could trigger the formation of a *trans*-carbamate by aminolysis. The use of appropriate catalytic copolymerization conditions would selectively lead to a growing *trans*-configured oligo-carbonate chain with subsequent aminolysis of the metal-bound oligomer giving rise to *trans*-carbamates in a one-pot approach (Scheme 1). Here we report on a general, stereo-divergent method for a wide range of functionalized carbamate structures derived from organic carbonate intermediates. Both the *cis* and *trans* diastereoisomers of these carbamate scaffolds can be formed with excellent stereo-control, with the family of unusual *trans*-configured products being generated through a conceptually new approach.

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Results and Discussion

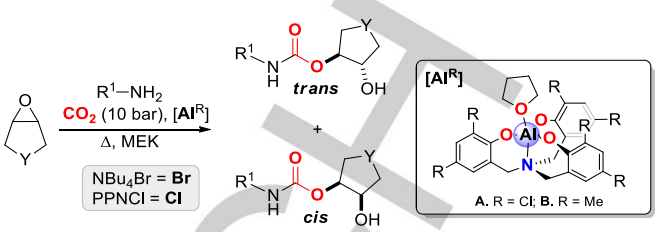
As part of a screening study we first considered the one-pot conversion of cyclopentene oxides (cyclopentene oxide, CPO, and 3,4-epoxyfuran), three different primary amines R´-NH_2 (R´ = Cy, Bu, Oc) and CO_2 using Al-catalysis (Table 1).[10] Suitable nucleophilic additives, including NBu_4Br (**Br**) and PPNCl (**Cl**; PPN = bis(triphenylphosphine)iminium) were used as these were previously shown to have the best potential in the formation of polymeric carbonates using aminotriphenolate complexes.[11] It should be noted that cyclohexene oxide (CHO) generally has excellent copolymerization potential, whereas cyclopentene oxides (Y = C or O; Scheme to Table 1) are known to be more challenging substrates. Thus, we envisioned that successful *in situ* formation of oligomeric carbonates derived from cyclopentene oxides would serve better to validate a more general approach towards *trans* carbamates.

First, 3,4-epoxyfuran was investigated using both Al-catalysts **A** and **B** varying the co-catalyst nature and amount, and the amount of solvent (MEK; methylethyl ketone), see entries 1–11 of Table 1. In the absence of Al-catalyst and nucleophile no conversion was noted (entry 1), while the use of complex **A** or nucleophile (TBAB) alone gave poor carbamate yields of 15% and 9%, respectively (entries 2 and 3). Combination of both catalyst components gave more productive catalysis and afforded the desired carbamate product in much higher yields of up to 76% with excellent stereo-control (*dr* > 99:1, entry 4). Additional variation of the amount of solvent, changing TBAB for PPNCl or using Al-complex **B** (entries 5–11) did not further improve these results, and at higher tem-peratures (90ºC, entry 10 versus 4) loss of stereo-selectivity was noted.

In the case of cyclopentene oxide as substrate (entries 12–21), similar observations were done although in these reactions Al-complex **B** combined with PPNCl provided the best compromise in terms of yield and diastereo-selectivity: the results reported in Table 1 show that the use of typical copolymerization conditions (*i.e.,* using Cl as nucleophile, Al-catalyst **B**, 60ºC)[10,11] leads to the preferred formation of the targeted *trans*-carbamate product with high *dr´*s of up to 96:4 (entry 14) when *n*-octylamine is used, and 89:11 in the case of *n*-butylamine (entry 19). Again, in the absence of nucleophilic additive (as noted with 3,4-epoxyfuran), much lower yields of carbamate are noted (entries 16, 17 and 20) likely to be the result of a relatively slow background reaction based on a carbamate nucleophile derived from the amine and CO_2 (Figure 1).[12] Longer reaction times do not seem to significantly affect the yield of carbamate (*cf.* entries 16 versus 17) under low-pressure conditions (10 bar).

We therefore tried the carbamate synthesis also under more severe pressure conditions (40 bar, entry 20 Table 1; *cf*. entry 21) and found only a small increase in the yield of the carbamate derived from CPO. This further confirms that for efficient formation of the *trans*-carbamate product under these relatively mild reaction conditions the presence of an external nucleophile is required, and offers the major pathway leading to *trans*-carbamate product through *in situ trans*-carbonate formation.

Stands for nucleophile additive, Cy for cyclohexyl, Oc for *n*-octyl and Bu for *n*-butyl.



Entry	Y/R^1	Cat [mol%]	Nu [mol%]	T/t [ºC]/[h]	Yield [%][b]	*trans*/*cis*[c]
1[d]	O/Cy	–	–	70, 70	<1	-
2[d]	O/Cy	**A**, 0.5	–	70, 70	15	>99:1
3[d]	O/Cy	–	Br, 2.0	70, 70	9	36:64
4	O/Cy	**A**, 0.5	Br, 2.0	70, 70	76[e]	>99:1
5[d]	O/Cy	**A**, 0.5	Br, 2.0	70, 70	81	76:24
6	O/Cy	**A**, 0.5	Cl, 2.0	70, 70	57	79:21
7[f]	O/Cy	**A**, 0.5	Cl, 2.0	70, 70	55	63:37
8[g]	O/Cy	**B**, 1.0	Cl, 1.0	70, 70	29	91:9
9[d]	O/Cy	**B**, 2.0	Cl, 2.0	70, 70	35	57:43
10[f]	O/Cy	**A**, 0.5	Br, 2.0	70, 70	46	70:30
11[f]	O/Cy	**A**, 2.0	Br, 2.0	70, 70	26	27:73
12	C/Oc	**A**, 0.5	Br, 2.0	70, 70	45	72:28
13	C/Oc	**B**, 0.5	Cl, 1.0	60, 24	7	85:15
14	C/Oc	**B**, 2.0	Cl, 2.0	60, 60	45[e]	96:4
15	C/Oc	**B**, 2.0	Cl, 2.0	70, 60	49	83:17
16	C/Oc	**B**, 2.0	–	60, 24	5	>99:1
17	C/Oc	**B**, 2.0	–	60, 60	9	>99:1
18	C/Bu	**A**, 0.5	Br, 2.0	70, 70	73[e]	57:43
19	C/Bu	**B**, 2.0	Cl, 2.0	60, 24	51[e]	89:11
20	C/Bu	**B**, 2.0	–	60, 24	4	>99:1
21[h]	C/Bu	**B**, 2.0	–	60, 24	11	>99:1

[a] Conditions: epoxide (4 mmol), R^1-NH_2 (1.2 equiv; R = Oc, Cy: 4 equiv.; R = Bu) using 0.5 mL MEK (methylethyl ketone), $p(CO_2)$º = 10 bar. [b] NMR yields using mesitylene as internal standard. [c] Determined by ^{1}H NMR. [d] Using 1.0 mL of MEK. [e] Isolated yields. [f] Using 2.0 mL of MEK. [g] Neat conditions. [h] Reaction carried out at 40 bar.

Table 1. Screening of suitable catalytic conditions to form the *trans*-carbamate products from cyclopentene oxides (Y = C, O), Amines R´-NH_2 and CO_2.[a] Nu

Similar behavior in carbamate formation was also noted for one other cyclic and one acyclic epoxide when they were probed under similar temperature/pressure conditions (see Tables S1 and S2). In these latter cases good to excellent selectivity for the *trans*-carbamates (*dr* >99:1) was noted validating further the current approach using an external nucleophilic additive.

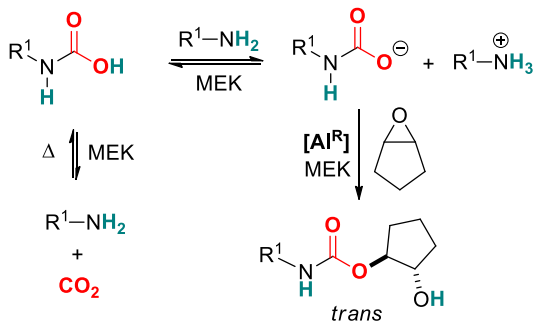


Figure 1. Potential background reaction to form a *trans* carbamate through the formation of a carbamate nucleophile from an amine and CO_2.

Having established a set of suitable reaction conditions leading selectively to *trans*-configured carbamates, we then investigated the scope in more detail (**1–15**, see Figure 2). As reference materials for the assignment of the *trans*-products **1b–15b**, the *cis*-carbamates **1a–15a** were separately prepared by *prior* formation of their *cis* cyclic carbonates derived from the respective epoxides under appropriate conditions.[6d] The aminolysis reaction was then carried out by addition of the appropriate amine and details are reported in the Supporting Information. In general, the stereo-control towards the *trans*-carbamates **1b–15b** is excellent providing the compounds with *dr´*s of ≥93:7 (apart from **4b** and **13b**; *dr* = 89:11 and 77:23, respectively). The approach is applicable towards various five- and six-membered cyclic and also acyclic epoxides (*cis*-2-butene oxide, *cf*. formation of **12b** and **13b**) without compromising significantly the diastereo-selectivity of the reaction. Various functionalized amines are tolerated bearing allyl (**2b** and **15b**), cyclopropyl (**8b**), thiophenelyl (**9b**), and pyridyl (**11b**) groups whereas the use of more functional epoxides allows for the incorporation of potentially useful furan (**3b**, **5b**, **7b** and **8b**) or cyclohexenyl (**2b** and **14b**) fragments.

The molecular structures for carbamates **1–15** (both diastereoisomers) were fully supported by 1D/2D NMR and IR spectroscopic techniques, and HRMS; for **5a** and **5b** the X-ray molecular structures (see Figure 3 and Supporting Information)[13] were determined and further supported their *cis* and *trans* assignment in line with the spectroscopic data. The isolated yields for the *cis*-carbamates **1a–15a** are generally higher than those obtained for the *trans* diastereo-iosmers **1b–15**; this suggest that the one-pot approach with the amine present at the early stage of the reaction may, as expected, slow down overall kinetics as the amine may compete with epoxide coordination to the Al-center in complexes **A** or **B**.

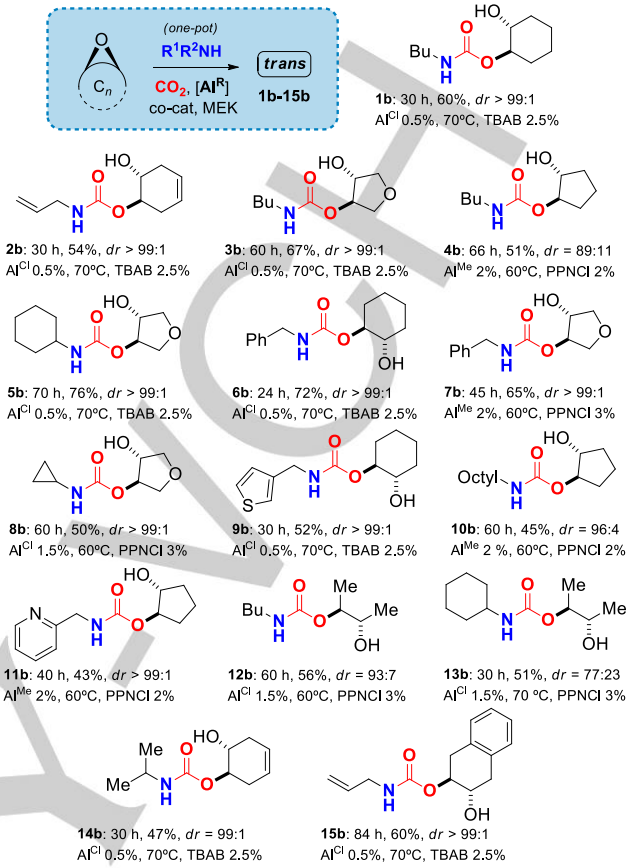


Figure 2. Scope for the formation of the *trans*-carbamates **1b–15b**. All reactions were carried out on a 4 mmol scale using 0.5 mL MEK, $p(CO_2)^o$ = 10 bar, cat/co-cat amounts are in mol%, and Al^{Cl} = complex **A**; Al^{Me} = complex **B**. All *dr* values were determined by ^{1}H NMR.

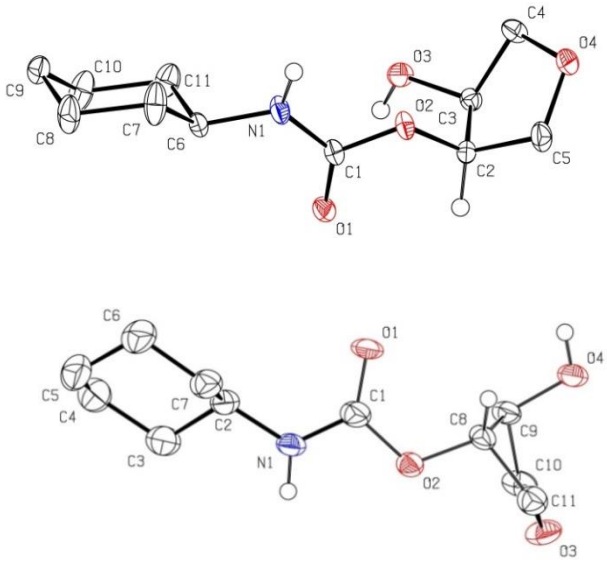
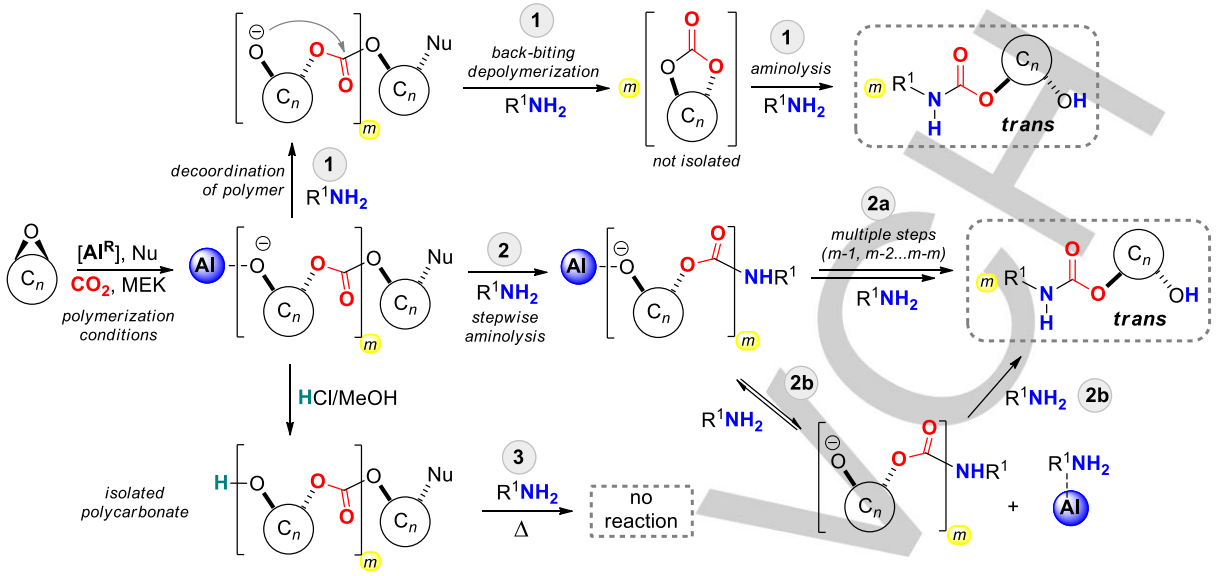


Figure 3. X-ray molecular structures determined for *cis*-**5a** (top) and *trans*-**5b** (below) together with part of the numbering scheme.



Scheme 2. Proposed mechanism for the formation of *trans*-carbamates through (1) formation of a *trans*-configured cyclic carbonate intermediate following aminolysis, or (2) a stepwise aminolysis of a metal-bound oligo/polycarbonate; pathway (3) shows the control experiment done with an isolated polycarbonate sample. The cation of the initial nucleophile is not shown here.

The isolated yields for the *cis*-carbamates **1a–15a** are generally higher than those obtained for the *trans* diastereoisomers **1b–15b**; this suggest that the one-pot approach with the amine present at the early stage of the reaction may, as expected, slow down overall kinetics as the amine may compete with epoxide coordination to the Al-center in complexes **A** or **B**. In order to investigate the mechanism of *trans*-carbamate formation, several additional experiments were conducted (see Scheme 2).

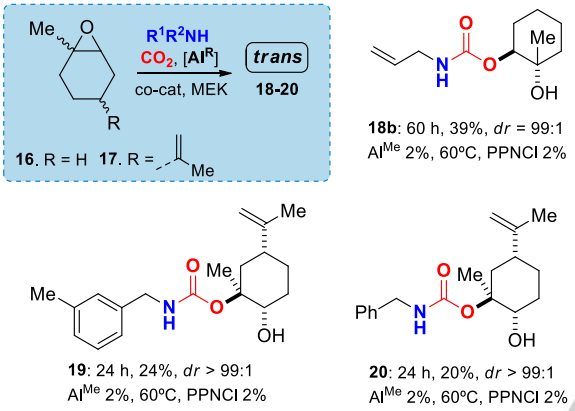
First, an *isolated* sample of a copolymer based on CHO/CO_2 (*cf.*, path 3, Scheme 2) was subjected to the general reaction conditions of the one-pot carbamate formation (*i.e.*, in the presence of [Al] complex **A**, TBAB, MEK, 70ºC, 18 h) but the presence of the *n*-butyl amine did not provoke any observable aminolysis between 25-80ºC as evidenced by ^{1}H NMR comparative studies (Supporting Information). Then we decided to freshly prepare the CHO/CO_2 copolymer in the absence of the amine using [Al^{Cl}] catalyst **A** (0.5 mol**%**) and TBAB (2.5 mol%) at 70ºC for 24 h; at this stage ^{1}H NMR analysis showed virtually full conversion into a fully alternating poly(cyclohexene)carbonate (PCHC, 99% polymer selectivity) with trace amount (1%) of *trans*-cyclohexene carbonate (*trans*-CHC). This copolymer (without applying the usual work up and with the metal likely still bound to the polymer)[14] was treated with 3 equiv of *n*-butyl amine for 10 h at 70ºC and then again analysed by ^{1}H NMR. Fortunately, conversion (65%) to the carbamate **1b** (*dr* > 99:1) was noted with the remaining 35% consisting of a mixture of 85% PCHC and 15% of *trans*-CHC (*i.e.,* a clear increase in the cyclic carbonate/polymer ratio is noted). The relative increase in *trans*-CHC can be explained by a depolymerisation of the metal-free copolymer[15e] when adding the amine which may compete for coordination to the Al-center (Scheme 2, pathway 1). The decoordinated polymer then leads to *trans*-CHC by a relatively fast alkoxide back-biting process towards the *trans*-carbonate and *in situ* aminolysis to give *trans*-configured **1b** as product.

A similar polymer degradation/aminolysis sequence (Scheme 2, pathway 1) seems plausible for the acyclic *cis*-2-butene oxide case. Control experiments were performed in the absence of amine reagent following the reaction conditions reported for **12b**-*trans* and **13b**-*trans* (Figure 2). The ^{1}H NMR analysis showed the mixture to contain only the cyclic carbonate product with a *trans* selectivity of up to 83% which is in reasonable agreement with the reported *dr* values for the two carbamate products derived from *cis*-2-butene oxide. Copolymers derived from *cis*-2-butene oxide have been reported recently by Darensbourg *et al*.[9c] showing that polymer-selective bifunctional M(salen) catalysts (M = Co, Cr) give virtually only *trans*-carbonate upon alkoxide backbiting; this suggests that the *trans*-carbamates derived from *cis*-2-butene oxide also originate from pre-polymer formation.

However, the diastereoselective formation of *trans*-carbamates using substrates such as CPO and 3,4-epoxyfuran cannot be explained via pathway 1 (Scheme 2). The group of Darensbourg has demonstrated that such a pathway is thermodynamically not feasible due to a high ring strain present in this *trans* cyclic carbonate, and therefore preferably results in degradation towards the starting epoxide and CO_2. Under high pressure conditions, carbonate rather than alkoxide backbiting is facilitated resulting in exclusive *cis*-carbonate formation,[15] excluding *trans*-carbamate formation through a *trans* cyclic carbonate intermediate.

We have recently shown by a combined experimental/computational approach that the coupling between limonene oxide (LO; Scheme 3) and CO_2 gives exclusive

formation of a fully alternating copolymer with a relative high barrier for (*trans*) cyclic carbonate formation.[10] In this Al-mediated copolymerization process the CO_2 insertion step was shown to be rate-limiting, suggesting that possible polymer degradation would have to proceed through alkoxide back-biting; both metal-bound and metal-free oligo/polycarbonates based on LO, however, are kinetically incompetent to give a *trans* cyclic carbonate via depolymerisation. This behaviour is reminiscent of copolymers derived from CPO which also cannot produce *trans*-COC through alkoxide back-biting. Therefore, another degradation process (*i.e.*, pathway 2 in Scheme 2) leading to formal *trans*-carbamate formation was considered.



Scheme 3. Carbamate formation reactions using tri-substituted epoxides as reagents. Conditions: 4 mmol scale, 0.5 mL MEK, $p(CO_2)^o$ = 10 bar, cat/co-cat amounts in mol%. All *dr* values were determined by ^{1}H NMR.

In order to investigate this in more detail, we envisioned that carbamate formation from tri-substituted cyclic oxiranes such as LO (Scheme 3) could serve to mimic the reactivity of CPO and related cyclic oxiranes. When we subjected both **16** (methyl-cyclohexene oxide) and **17** (*cis*-LO) to reaction conditions typically used for the formation of carbamates **1b–15b**, we only observed the formation of *trans*-carbamates **18–20**. The origin of the *trans*-selectivity is ascribed to an attack of the amine on the oligo/polycarbonate itself being either metal-bound (pathway 2a) or metal-devoid (pathway 2b) through aminolysis at a carbonate linkage retaining thus the *trans* configuration in the final carbamate product.[16]

Conclusions

In summary, we here present an unprecedented catalytic approach towards *trans*-configured carbamates by selectively trapping of *trans*-carbonate intermediates with amine reagents. Supporting experiments have revealed that either *in situ* aminolysis of *trans* cyclic carbonates obtained through polycarbonate backbiting or aminolysis of *in situ* prepared *trans*-configured (metal-bound) oligo/polycarbonates is a new approach to exert a high degree of diastereo-selective control. Such a control is a new tool in the synthesis of CO_2-derived fine chemicals showing potential in other types of synthetic transformations focusing on this renewable C_1 building block.

Experimental Section

Typical procedure for the formation of the *cis*-carbamates

The cyclic carbonates were first synthesized from carbon dioxide according to reported literature procedures[6d,17] using Al(III) amino-triphenolate complex [Al^{Cl}] as catalyst. After that, the respective carbonate (1 mmol, 1 eq.) and the corresponding amine (1.2 eq. for non-volatile amines; 4 eq. for volatile amines) were charged into a 5 mL round bottom flask and the reaction mixture was stirred at 50-70 ºC for an appropriate time frame. After the reaction, the analytically pure carbamate product was isolated by flash chromatography. The Supporting Information contains all details regarding these *cis*-carbamates.

Typical procedure for the formation of the *trans*-carbamates

The respective epoxide (4 mmol, 1 eq.), Al-complex (Al^R , 0.5–2.0%; R = Cl or Me), amine (1.2 eq. for non-volatile amines; 3 eq. for volatile amines), TBAB/PPNCl and MEK (1 mL) were charged into a 30 mL stainless steel autoclave. The autoclave was then subjected to three cycles of pressurization and depressurization with carbon dioxide (0.5 MPa, 5 bar), before final stabilization to a pressure of 1 MPa (10 bar). The autoclave was sealed and heated to 60–90 ºC and left stirring for an appropriate time frame. Then, the autoclave was cooled to rt and carefully depressurized. The analytically pure carbamate product was then isolated by flash chromatography. The Supporting Information contains all details regarding these *trans*-carbamates.

Acknowledgements

We thank ICIQ, ICREA, and the Spanish Ministerio de Economía y Competitividad (MINECO) through projects CTQ-2014–60419-R, and the Severo Ochoa Excellence Accreditation 2014–2018 through project SEV-2013–0319. Dr. Noemí Cabello, Sofía Arnal, and Vanessa Martínez are acknowledged for the mass analyses. WG thanks the Cellex foundation for further financial support and VL acknowledges the Generalitat de Catalunya for a FI predoctoral fellowship.

Keywords: aluminium • carbamates • carbon dioxide • diastereoselective synthesis • organic carbonates

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[8] a) J. Martínez, J. A. Castro-Osma, A. Earlam, C. Alonso-Moreno, A. Otero, A. Lara-Sánchez, M. North, A. Rodríguez-Diéguez, *Chem. Eur. J.* **2015**, *21*, 9850–9862; b) C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin, A. W. Kleij, *J. Am. Chem. Soc*. **2013**, *135*, 1228-1231; c) C. J. Whiteoak, E. Martin, M. Martínez Belmonte, J. Benet-Buchholz, A. W. Kleij, *Adv. Synth. Catal*. **2012**, *354*, 469-476; d) C. Beattie, M. North, P. Villuendas, C. Young, *J. Org. Chem.* **2013**, *78*, 419-426.

[9] Only a few contributions report the formation of trace or very low amounts of *trans*-COCs from the depolymerisation of poly(carbonate) precursors; these COCs were neither isolated nor used in further synthesis. See: a) A. Buchard, M. R. Kember, K. G. Sandeman, C. K. Williams, *Chem. Commun*. **2011**, *47*, 212-214; b) D. J. Darensbourg, P. Bottarelli, J. R. Andreatta, *Macromolecules* **2007**, *40*, 7727-7729; c) D. J. Darensbourg, W.-C. Chung, *Macromolecules* **2014**, *47*, 4943-4948; The selective formation of a *trans*-carbonate from *cis*-2-butene oxide was also reported recently: d) C. J. Whiteoak, E. Martin, E. C. Escudero-Adán, A. W. Kleij, *Adv. Synth. Catal.* **2013**, *355*, 2233-2239.

[10] Al(aminotriphenolate) complexes are effective epoxide/CO_2 copolymerization catalysts, see: L. Peña Carrodeguas, J. González-Fabra, F. Castro-Gómez, C. Bo, A. W. Kleij, *Chem. Eur. J.* **2015**, *21*, 6115-6122.

[11] For Fe(III) based aminotriphenolates a selective switch in chemo-selectivity between the cyclic and polycarbonate was observed in cyclohexene oxide/CO_2 couplings, see: M. Taherimehr, S. M. Al-Amsyar, C. J. Whiteoak, A. W. Kleij, P. P. Pescarmona, *Green Chem*. **2013**, *15*, 3083-3090.

[12] Under the reaction conditions, the amine may react with CO_2 to form a carbamate species which can ring-open the epoxide to form the *trans*-carbamate albeit in very low yield. Thus, this is a much slower reaction than the ones studied here with added nucleophiles. This background reaction proceeds somewhat better under much harsher pressure conditions (*i.e*., 50 bar) with concomitant formation of substantial aminoalcohol side-product, see: F. Kojima, T. Aida, S. Inoue, *J. Am. Chem. Soc*. **1986**, *108*, 391-395. Apparently, under the mild conditions reported here the formation of a carbamate nucleophile derived from the amine and CO_2 is either catalytically incompetent or only formed in very low concentration. The use of secondary amine reagents leads only to amino alcohol formation, *i.e*. aminolysis of the oxirane substrate occurs.

[13] For more details: CCDC-1039414 and CCDC-1423217.

[14] For living copolymerisation see: J. G. Kim, C. D. Cowman, A. M. LaPointe, U. Wiesner, G. W. Coates, *Macromolecules* **2011**, *44*, 1110-1113.

[15] a) D J. Darensbourg, A. D. Yeung, *Macromolecules* **2013**, *46*, 83-95; b) D. J. Darensbourg, A. D. Yeung, S.-H. Wei, *Green Chem*. **2013**, *15*, 1578-1583; c) D. J. Darensbourg, S.-H. Wei, A. D. Yeung, W. Chadwick Ellis, *Macromolecules* **2013**, *46*, 5850-5855. See also: d) D. J. Darensbourg, A. D. Yeung, *Polymer Chem*. **2014**, *5*, 3949-3962; e) D. J. Darensbourg, A. D. Yeung, *Polymer Chem*. **2015**, *6*, 1103-1117.

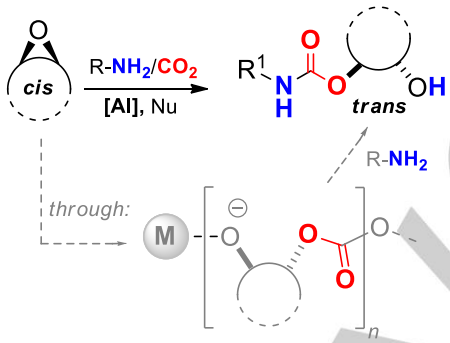
[16] Note that the regio-selectivity for the formation of **18b** is different from the ones observed for *trans* **19** and **20**. This is likely a function of the amine reagent as the formation of other carbamates from methyl-cyclohexene oxides using *p*-methoxy-benzylamine under similar reaction conditions was shown to give a regio-isomeric mixture (combined yield 32%; regio-selectivity 58:42). See for full details the Supporting Information.

[17] C. J. Whiteoak, N. Kielland, V. Laserna, F. Castro-Gómez, E. Martin, E. C. Escudero-Adán, C. Bo, A. W. Kleij, *Chem. Eur. J.* **2014**, *20*, 2264-2275.

Entry for the Table of Contents:

FULL PAPER

Cuts both ways: Stereodivergence in carbamate synthesis has been achieved through a selective trapping of carbonate intermediates under Al-catalysis using cyclic oxiranes, amines and CO_2 as reaction partners. Both *trans* and *cis* carbamates were produced with *dr* values >19:1. Mechanistic investigations support the view of a key *trans*-configured oligo/polycarbonate intermediate controlling the stereo-selectivity in this conceptually new catalytic CO_2 conversion approach.



- *Operationally simple, under mild Al-catalysis*
- *dr > 19:1, isolated yield up to 82%*
- *18 examples based on (a)cyclic oxiranes*
- *In situ trapping of trans-carbonate intermediate*

*Wusheng Guo, Victor Laserna, Eddy Martin, Eduardo C. Escudero-Adán and Arjan W. Kleij**

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Stereodivergent Carbamate Synthesis by Selective In Situ Trapping of Organic Carbonate Intermediates