Heterogeneous & Homogeneous & Bio- & Nano-
CHEMCATCHEM
CATALYSIS

Accepted Article

Title: Amidinate aluminium complexes as catalysts for carbon dioxide fixation into cyclic carbonates

Authors: Danay Meléndez, agustin Lara-Sánchez, Javier Martínez, Xiao Wu, Antonio Otero, Jose Castro-Osma, Michael North, and Rene Rojas

To be cited as: *ChemCatChem* 10.1002/cctc.201702014

Link to VoR: http://dx.doi.org/10.1002/cctc.201702014

A Journal of
ChemPubSoc Europe

WILEY-VCH

www.chemcatchem.org

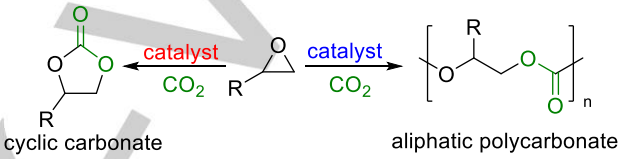
Amidinate aluminium complexes as catalysts for carbon dioxide fixation into cyclic carbonates

Danay Osorio Meléndez,[a] Agustín Lara-Sánchez,[c] Javier Martínez,[c] Xiao Wu,[d] Antonio Otero,[c] José A. Castro-Osma,*[b] Michael North,*[d] and René S. Rojas*[a]

Abstract: A series of inexpensive and sustainable amidinate aluminium complexes has been developed as catalysts for the chemical fixation of carbon dioxide into cyclic carbonates. The reactions using terminal epoxides as substrates were carried out at room temperature and one bar of carbon dioxide pressure in the presence of tetrabutylammonium iodide as co-catalyst in the absence of solvent. Under these reaction conditions, excellent conversions and selectivities were achieved for a broad range of terminal epoxides. Moreover, the optimal catalyst could be used for the synthesis of disubstituted cyclic carbonates from internal epoxides and carbon dioxide, highlighting the potential of these amidinate aluminium complexes as catalysts.

Introduction

Carbon dioxide is considered to be an inexpensive, nontoxic and sustainable C1 feedstock for the synthesis of value-added products, and its chemical utilization is a rapidly growing research area in the scientific community.[1,2] Although being chemically attractive, the inherent thermodynamic and kinetic stability of carbon dioxide is the major impediment for its incorporation into organic frameworks. To date, a number of valuable chemicals have been produced by incorporating carbon dioxide, these include amides,[3] methanol[4] and formic acid.[5] Meanwhile, the reaction between epoxides and carbon dioxide has also been developed into a successful carbon dioxide utilisation process, producing cyclic carbonates and polycarbonates (Scheme 1).[6,7,8] The synthesis of ethylene and propylene carbonates has been commercialised for over 50 years,[9] and nowadays cyclic carbonates are widely used as polar aprotic solvents,[10] electrolytes for lithium ion batteries[11] and organic synthetic intermediates.[12] Aliphatic polycarbonates have promising applications including as precursors for the synthesis of non-isocyanate derived polyurethanes[13] and are currently being commercialized as replacements for aromatic polycarbonates.[14,15]



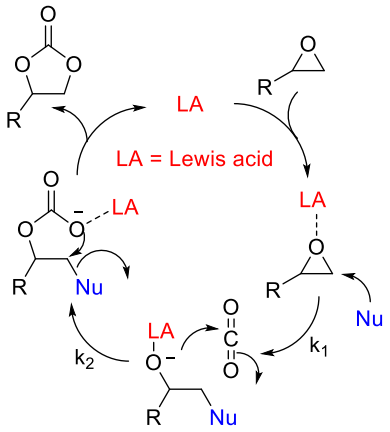
Scheme 1. Reaction between epoxides and carbon dioxide.

Over recent years, many research groups have made significant contributions and a variety of catalytic systems have been developed for the synthesis of cyclic carbonates from epoxides and carbon dioxide, some of which operate under ambient reactions (25 °C, carbon dioxide pressure ≤ 1 bar). These systems are mainly based on metal complexes,[16] metal organic frameworks[17] and some organocatalysts.[18] In particular, metal-salen complexes have been well investigated and among them, aluminium,[19] chromium[20] and cobalt[21] complexes have been most widely studied for the reaction between epoxides and carbon dioxide. These systems usually require a halide salt as a cocatalyst, though single-component, bifunctional catalysts in which one or more quaternary ammonium or phosphonium halides are covalently linked to a catalyst have also been developed.[22] For example, the combination of 2.5 mol% of a bimetallic aluminium(salen) complex and tetrabutylammonium bromide catalyses the synthesis of cyclic carbonates from terminal epoxides at 25 ºC and one bar carbon dioxide pressure.[19] It is worth noting that the bimetallic aluminium(salen) complex is capable of carrying out the kinetic resolution of the epoxides[23] and single-component versions of this catalyst system have been developed.[24] Furthermore, acen[25] and heteroscorpionate[26] and aminophenolate[27] complexes have also been studied, and showed high catalytic activity towards cyclic carbonate formation under mild reaction conditions.

A generally accepted mechanism for the metal-mediated coupling reaction between epoxides and carbon dioxide to afford cyclic carbonates is shown in Scheme 2. First, the Lewis-acidic metal center coordinates to the epoxide followed by ring-opening by the cocatalyst to give an alkoxide ion. Then, carbon dioxide is inserted followed by ring-closing to afford the five-membered cyclic carbonate. This also leads to the regeneration of both the catalyst and the cocatalyst.

[a] Dr. D. A. Meléndez, Prof. R. S. Rojas*
Nucleus Millennium Chemical Processes and Catalysis (CPC),
Laboratorio de Química Inorgánica, Facultad de Química
Universidad Católica de Chile
Casilla 306, Santiago-22 6094411, Chile.
E-mail: rrojasg@uc.cl
[b] Dr. J. A. Castro-Osma*
Departamento de Química Inorgánica, Orgánica y Bioquímica, and
Centro de Innovación en Química Avanzada (ORFEO-CINQA),
Facultad de Farmacia
Universidad de Castilla-La Mancha
02071-Albacete, Spain.
E-mail: JoseAntonio.Castro@uclm.es
[c] Dr. A. Lara-Sánchez, Dr. J. Martínez, Prof. A. Otero
Departamento de Química Inorgánica, Orgánica y Bioquímica, and
Centro de Innovación en Química Avanzada (ORFEO-CINQA),
Facultad de Ciencias y Tecnologías Químicas
Universidad de Castilla-La Mancha
Campus Universitario, 13071-Ciudad Real, Spain.
[d] Dr. X. Wu, Prof. M. North*
Green Chemistry Centre of Excellence, Department of Chemistry
The University of York
York, YO10 5DD (UK).
E-mail: Michael.north@york.ac.uk

Supporting information including: experimental, copies of the ^{1}H and ^{13}C NMR spectra for cyclic carbonates and details of the kinetic analyses for this article is given via a link at the end of the document



Scheme 2. General mechanism for cyclic carbonate synthesis.

Amidinate metal complexes have been shown to catalyse important reactions including: polymerisations,[28] hydrogenations,[29] hydrosilylations,[30] Kharasch reactions,[31] amidations[32] and hydrophosphination reactions.[33] In our effort to investigate and take advantage of the catalytic properties of amidinate systems as described above, recently we have reported the application of a series of aluminium bisamidinates towards ring-opening polymerization (ROP) of cyclic esters.[34] It was observed that all complexes were active for the ROP of *ε*-caprolactone. Moreover, the most active catalyst displayed significant catalytic activity towards the ROP of *L*-lactide and copolymerization of *ε*-caprolactone and *L*-lactide, producing biodegradable materials with narrow polydispersities. Taking into account the high catalytic activity shown by these complexes for the ROP of cyclic esters, their catalytic activity for cyclic carbonates formation from epoxides and carbon dioxide was investigated and the results are reported herein.

Results and Discussion

Aluminium complexes **1**–**6** (Figure 1) were synthesized by reaction of the bis(amidine) precursors and a trialkylaluminium in toluene in excellent yield and purity, as previously reported.[34] A catalyst screening for the conversion of styrene oxide **7a** and CO_2 into styrene carbonate **8a** was initially carried out using a combination of 5 mol% of complexes **1**–**4** or 10 mol% of complexes **5**–**6** and 5 mol% of tetrabutylammonium bromide (TBAB) as the catalyst system at 25°C and 1 bar of CO_2 for 24 hours under solvent free conditions (Scheme 3). Each reaction was analysed by ^{1}H-NMR spectroscopy to determine the conversion of epoxide **7a** into cyclic carbonate **8a** (Table 1). In all cases, the selectivity towards the cyclic carbonate was higher than 99%.

As can be seen from entries 1–6, bimetallic complexes **1**–**4** were more active than either of the monometallic complexes **5**–**6** using the same aluminium loading. Moreover, ethyl containing complexes **2**, **4** and **6** are more active than methyl complexes **1**, **3** and **5** (entries 1–6). Amongst the

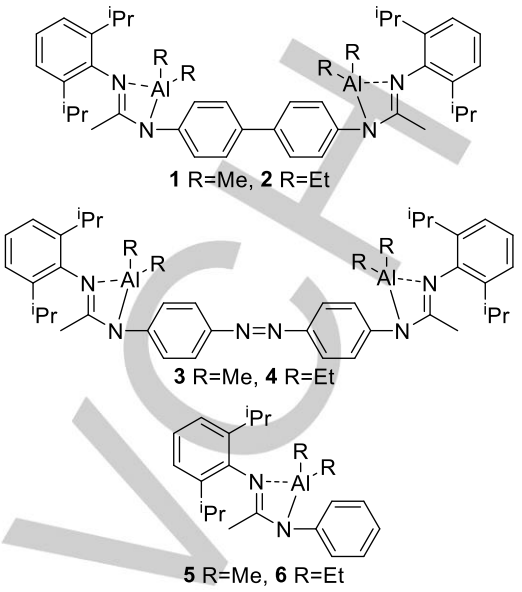
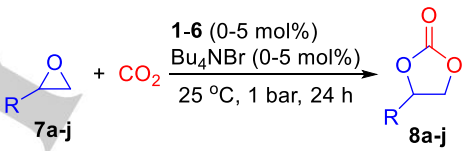


Figure 1. Aluminium based bis(amidinate) catalysts.



a) R=Ph **b)** R=Me **c)** R=Et **d)** R= Bu **e)** R= Oct **f)** R=CH_2Cl
g) R= CH_2OH **h)** R= CH_2OPh **i)** R= 4-ClC_6H_4 **j)** R= 4-BrC_6H_4

Scheme 3. Synthesis of cyclic carbonates **8a–j**.

Table 1. Conversion of styrene oxide **7a** into styrene carbonate **8a** using catalyst **1-6** and Bu_4NBr.[a]

Entry	Complex	Conversion (%)[b] 3h	Conversion (%)[b] 6h	Conversion (%)[b] 24h
1	**1**	12	27	56
2	**2**	16	30	67
3	**3**	10	23	53
4	**4**	20	31	57
5	**5**[c]	5	11	22
6	**6**[c]	8	18	34
7[d]	-	2	4	8
8[e]	**2**	0	0	0

[a] Reactions carried out at 25°C and 1 bar of CO_2 for 24 hours using 5 mol% of both complex **1**–**4** and Bu_4NBr. [b] Conversion determined by ^{1}H-NMR spectroscopy of the reaction mixture. [c] 10 mol% of monometallic complex was used. [d] 5 mol% of Bu_4NBr added. [e] No Bu_4NBr was added.

Table 2. Influence of cocatalyst on the synthesis of styrene carbonate **8a** catalysed by complex **2**.[a]

Entry	Cocatalyst	Conversion (%)[b] 3h	Conversion (%)[b] 6h	Conversion (%)[b] 24h
1	Bu_4NF	0	0	0
2	Bu_4NCl	9	13	38
3	Bu_4NBr	16	30	67
4	Bu_4NI	18	42	87
5	PPNCl[c]	6	10	25
6	DMAP[d]	0	0	0

[a] Reactions were carried out at 25°C and 1 bar CO_2 for 24 hours using 5 mol% of both complex **2** and cocatalyst. [b] Conversion determined by ^{1}H-NMR spectroscopy of the reaction mixture. [c] Bis(triphenylphosphine)iminium chloride . [d] 4-Dimethylaminopyridine.

Table 3. Conversion of styrene oxide **7a** into styrene carbonate **8a** using catalyst **1-6** and TBAI.[a]

Entry	Catalyst	Conversion (%)[b] 3h	Conversion (%)[b] 6h	Conversion (%)[b] 24h
1	**1**	15	30	58
2	**2**	18	42	87
3	**3**	12	25	53
4	**4**	11	32	56
5	**5**	6	13	27
6	**6**	10	21	38

[a] Reactions carried out at 25°C and 1 bar of CO_2 for 24 hours using 5 mol% of catalyst and TBAI. [b] Conversion determined by ^{1}H-NMR spectroscopy of the reaction mixture.

catalysts studied, complex **2** was the most effective catalyst for this transformation. Control experiments (entries 7–8) showed that the combination of an aluminum complex and a nucleophile source is needed in order to achieve good conversions, which is consistent with other aluminum systems, where reaction at room temperature only occurs in the presence of a cocatalyst.[23-27]

A combination of complex **2** with a range of nucleophile sources was chosen as a catalyst system to optimize the cocatalyst for styrene carbonate synthesis as shown in Table 2. It was found that the combination of complex **2** and tetrabutylammonium iodide (TBAI) formed an efficient catalyst system for styrene carbonate synthesis at 25 °C and 1 bar carbon dioxide pressure (Table 2, entry 4). Other cocatalysts such as tetrabutylammonium fluoride, tetrabutylammonium chloride, 4-dimethylaminopyridine and bis(triphenylphosphine)iminium chloride were also tested, but lower activities were obtained (Table 2, entries 1, 2, 5 and 6). Thus, the best results were obtained when the cocatalyst has the potential to generate a good leaving group. Hence, the results suggest that for catalysis using complex **2**, the final step of the catalytic cycle shown in Scheme 2 (ring-closure with elimination of the nucleophile) is the rate determining step of the catalytic cycle.

In order to establish, if the change of cocatalyst from tetrabutylammonium bromide to tetrabutylammonium iodide has a positive effect for each of complexes **1-6**, the conversion of styrene oxide **7a** into styrene carbonate **8a** was investigated under same reaction conditions and the results are summarized in Table 3. For complexes **1** and **3-6** there was no significant difference between the two cocatalysts, whilst for complex **2**, tetrabutylammonium iodide was significantly more active than tetrabutylammonium bromide (Table 1 and 3 respectively). These results may be due to a change in the relative rates of epoxide ring-opening, in which the halide of the cocatalyst acts as a nucleophile (rate limiting for catalysts **1** and **3-6**) and cyclic carbonate ring-closure, in which the halide acts as a leaving group, (rate limiting for catalyst **2**).

The most active complex **2** has four ethyl-aluminium bonds which could hydrolyse during the reaction. This has been previously observed for heteroscorpionate aluminium complexes where water has been shown to have a significant influence on the catalytic activity.[26] Therefore, to further optimize the reaction conditions, the addition of known, small amounts of water to the reaction mixture was investigated. As shown in Figure 2, under the standard reaction conditions, (25°C, 1 bar CO_2, 24 hours, 5 mol% of **2** and tetrabutylammonium iodide, using styrene oxide as substrate) the addition of just 1 mol% of water, the amount needed to hydrolyse just one in every twenty aluminium-ethyl bonds had a dramatic effect on the catalytic activity, decreasing the conversion from 87% to 54%. However, the addition of up to 8 mol% of water, enough to hydrolyse one in every 2.5 aluminium-ethyl bonds, had no further impact on the catalytic activity.

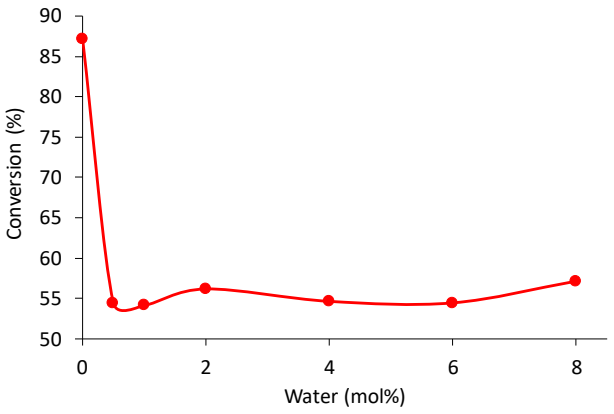


Figure 2. Effect of added water on the conversion of styrene oxide **7a** into cyclic carbonate **8a** catalysed by 5 mol% of complex **2** and TBAI.

Having determined the optimal reaction conditions, the formation of ten monosubstituted cyclic carbonates (**8a–j**), from their corresponding terminal epoxides and carbon dioxide was carried out using 5 mol% of catalysts **2** and **4** with TBAI as a cocatalyst. Reactions were carried out at 25°C and 1 bar CO_2, except when propylene oxide **7b** was used as a substrate when the reaction was carried out at 0°C due to the volatility of epoxide **7b**. As can be seen in Table 4, both catalysts converted the terminal epoxides into their corresponding cyclic carbonates in good yields under mild reaction conditions.

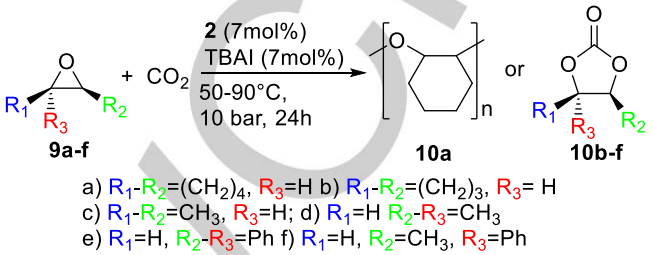
Table 4. Epoxide conversion into cyclic carbonates using catalyst **2** and **4**.[a]

			Complex **2**		Complex **4**	
Entry	Epoxide	T (°C)	Conversion (%),[b] [TOF][c]	Yield (%)[c]	Conversion (%),[b] [TOF] [c]	Yield (%)[d]
1	R=Ph (**7a**)	25	87 [0.7]	80	57 [0.5]	53
2	R=Me (**7b**)	0	--[e] [0.8]	97	--[e] [0.7]	81
3	R=Et (**7c**)	25	53 [0.4]	46	38 [0.3]	30
4	R=Bu (**7d**)	25	97 [0.8]	84	81 [0.7]	73
5	R= Oct (**7e**)	25	78 [0.7]	71	29 [0.2]	20
6	R=CH_2Cl (**7f**)	25	92 [0.8]	89	91 [0.8]	87
7	R=CH_2OH (**7g**)	25	52 [0.4]	43	51 [0.4]	42
8	R=CH_2OPh (**7h**)	25	69 [0.6]	66	36 [0.3]	32
9	R= 4-ClC_6H_4 (**7i**)	25	40 [0.3]	35	53 [0.4]	42
10	R= 4-BrC_6H_4 (**7j**)	25	51 [0.4]	47	60 [0.5]	53

[a] Reactions carried out at 1 bar CO_2 for 24 hours, using 5 mol% of catalyst **2** or **4** and TBAI. [b] Conversion determined by ^{1}H-NMR of the reaction mixture. [c] TOF (h^{-1}) = moles of product/(moles of catalyst x reaction time). [d] Determined on purified product. [e] Conversion could not be determined because of the volatility of the substrate.

In general, good to excellent conversions and yields were obtained when non-functionalized and functionalized aliphatic epoxides were used (Table 4, entries 2-8). However, lower conversions were obtained when using functionalized aromatic epoxides **7i** and **7j** (Table 4, entries 9 and 10) due to the solidification of the reaction mixture which could affect the catalytic conversion. Moreover, this study, allowed the activity of catalysts **2** and **4** to be compared using a wider range of epoxides since the catalytic activity will depend on the solubility of the complex in the epoxide. In general, both catalysts showed good catalytic activity. However, complex **2** was a better catalyst for aliphatic epoxides **7b**-**7h** while complex **4** showed better catalytic activity towards functionalized aromatic epoxides **7i-j**.

In order to expand the range of substrates, the use of internal epoxides was investigated (Scheme 4). As most of the disubstituted epoxides are aliphatic, complex **2** was chosen for this study. Internal epoxides are less active than terminal epoxides, but recently some efficient catalytic systems have been described for this application.[6,23-27] Due to the lower reactivity of these epoxides, reactions were performed using 7 mol% of complex **2** and tetrabutylammonium iodide as catalyst system for 24 hours at 50°C and 10 bar CO_2, except when epoxide **9e** was used as a substrate for which a temperature of 90°C was used. Cyclic carbonates **10b**–**f** were synthesized in good yields (Table 5).



Scheme 4. Synthesis of disubstituted cyclic carbonates from internal epoxides.

Table 5. Synthesis of disubstituted cyclic carbonates using complex **2** as catalyst.[a]

Entry	Substrate	Conversion (%)[b] [TOF][c]	Yield (%)[d]
1	**9a**	100[e]	83[e]
2	**9b**	85 [0.5]	80
3	**9c**	--[f] [0.5]	85
4	**9d**	--[f] [0.5]	87
5	**9e**[g]	62 [0.4]	57
6	**9f**	81 [0.5]	76

[a] Reactions carried out at 10 bar CO_2 for 24 hours, using 7 mol% of both complex **2** and TBAI. [b] Conversion determined by ^{1}H-NMR of the crude product. [c] TOF (h^{-1}) = moles of product/(moles of catalyst x reaction time). [d] Determined on the purified product. [e] Polycyclohexene oxide was obtained as product. [f] Conversion could not be determined because of the substrate volatility. [g] Reaction carried out at 90°C.

When epoxide **9a** was used as the substrate, polycyclohexene oxide was obtained, indicating that the ring opening polymerisation of the epoxide took place without insertion of carbon dioxide under these reaction conditions. On the other hand, when epoxides **9b**-**f** were used as substrate, the cyclic carbonate products were obtained with 100% selectivity. Under these reactions conditions, epoxide **9b** was an excellent substrate, allowing the formation of cyclic carbonate **10b** in 80% isolated yield (Table 5, entry 2). Cyclic carbonates **10c** and **10d** were obtained in high yield, considering the volatility of epoxides **9c,d** (Table 5, entry 3 and 4). When the *cis*-isomer **9c** was used, a mixture of *cis*- and *trans*-cyclic carbonates **10c,d** was obtained in a 36:64 *cis*:*trans* ratio. However, when epoxide **9d** was used as a substrate, cyclic carbonate **10d** was obtained with a

stereoselectivity higher than 95%. In the case of stilbene oxide **9e** (Table 5, entry 5) it was necessary to increase the temperature since the substrate is solid at lower temperatures, and under these reaction conditions 57% of **10e** was obtained. Finally, sterically hindered cyclic carbonate **10f** was obtained in 76% yield with 100% retention of the stereochemistry.

To achieve a better understanding of the catalyst system, a kinetic study for the synthesis of styrene carbonate **8a** using catalyst **2** and tetrabutylammonium iodide was carried out at 50°C and 1 bar CO_2 in the absence of a solvent (See Supporting information). Samples were collected from the reaction mixture every 30 minutes and were analysed by ^{1}H-NMR spectroscopy to determine conversion of styrene oxide **7a** into styrene carbonate **8a**. It has been shown in previous reports[26] that, under these reaction conditions, the reaction follows zero order kinetics at low conversions of the epoxide since it acts as both substrate and reaction solvent. However, when the cyclic carbonate is the main product in the reaction mixture, the reaction follows first order kinetics.

The order with respect to the concentrations of TBAI and catalyst **2** were determined and the plots of log[TBAI] *vs* logk_{0obs}, log[TBAI] *vs* logk_{1obs}, log[**2**] *vs* logk_{0obs} and log[**2**] *vs* logk_{1obs} have gradients of 0.86, 1.01, 0.90 and 1.23 respectively (Figures 3 and 5). This indicates that the reaction is first order with respect to the concentration of both TBAI and complex **2**. This was confirmed by plotting k_{0obs} or k_{1obs} *vs* [TBAI] and k_{0obs} or k_{1obs} *vs* [**2**] (Figures 4 and 6), which showed a good fit to a straight line with intercepts very close to the origin.

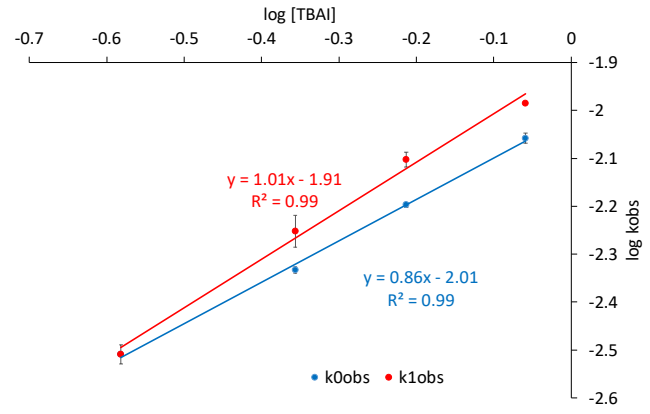


Figure 3. Logarithmic plots of k_{0obs} and k_{1obs} *vs* [TBAI]. Reactions were carried out at 50 °C under solvent-free conditions with [**2**] = 440 mM and [TBAI] = 262 – 873 mM. Data shown are the average of two experiments, with the individual experiments being used to indicate the error bars.

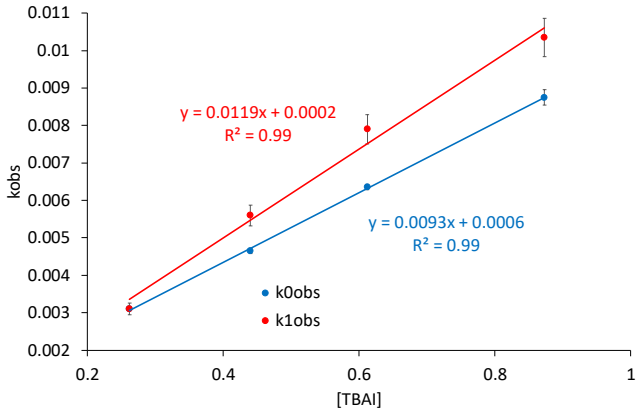


Figure 4. Plots of k_{0obs} and k_{1obs} vs [TBAI]. Reactions were carried out at 50 °C under solvent-free conditions with [**2**] = 440 mM and [TBAI] = 262–873 mM. Data shown are the average of two experiments, with the individual experiments being used to indicate the error bars.

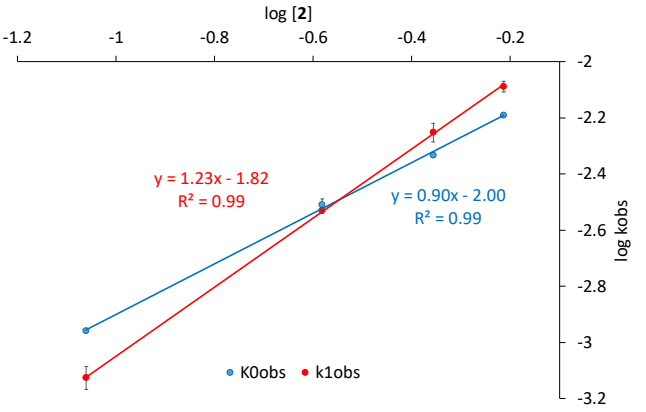


Figure 5. Logarithmic plots of k_{0obs} and k_{1obs} vs [**2**]. Reactions were carried out at 50 °C under solvent-free conditions with [**2**] = 87–612 mM and [TBAI] = 440 mM. Data shown are the average of two experiments, with the individual experiments being used to indicate the error bars.

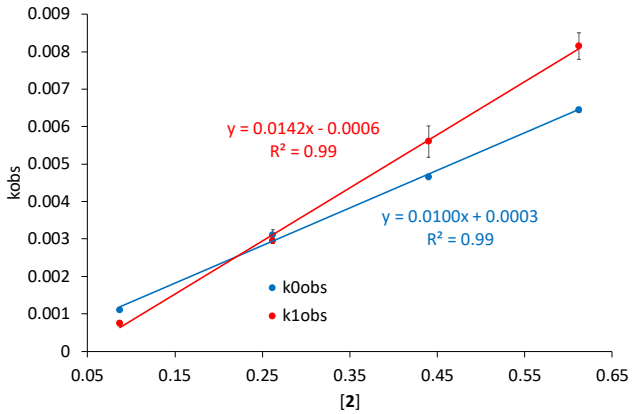


Figure 6. Plots of k_{0obs} and k_{1obs} *vs* [**2**]. Reactions were carried out at 50 °C under solvent-free conditions with [**2**] = 87–612 mM and [TBAI] = 440 mM. Data shown are the average of two experiments, with the individual experiments being used to indicate the error bars.

Based on the experimental results showing that cyclic carbonate formation occurs with retention of the epoxide stereochemistry and that the kinetic studies indicate that reactions are first order with respect to the concentration of the catalyst and tetrabutylammonium iodide, we propose that the reaction follows the mechanism shown in Scheme 2 with complex **2** acting as the Lewis acid. The epoxide ring-opening and cyclic carbonate ring-closing steps both involve an inversion of configuration and result in overall retention of stereochemistry. The first order kinetics with respect to complex **2** suggest that only one of the aluminium atoms within the complex is acting as a Lewis acid at any time. This is intriguing given that complex **2** is twice as active as the corresponding monometallic complex **6** (Table 1, entries 2 and 6). This difference in reactivity may be related to solubility or stability differences between the monometallic and bimetallic complexes under the reaction conditions.

Conclusions

Amidinate aluminium complexes **1**–**6**, in the presence of tetrabutylammonium iodide as a cocatalyst, have been developed as active and versatile catalyst systems for cyclic carbonates formation from terminal epoxides and carbon dioxide. The catalyst systems formed by the combination of complex **2** or complex **4** and tetrabutylammonium iodide display good catalytic activity at 25 ºC and one bar carbon dioxide pressure in the absence of a solvent. These catalyst systems displayed a broad substrate scope catalysing the formation of a cyclic carbonates from aryl, alkyl and functionalized terminal epoxides in good to excellent yields. Moreover, the combination of complex **2** and tetrabutylammonium iodide displayed good catalytic activity towards the synthesis of disubstituted cyclic carbonates from their corresponding internal epoxides and carbon dioxide under mild reaction conditions. The use of internal epoxides confirmed that cyclic carbonate synthesis occurs with retention of the epoxide stereochemistry.

A kinetic study was carried out and showed that reactions are first order with respect to the concentration of complex **2** and tetrabutylammonium iodide. Based on the experimental results obtained using internal epoxides as substrates and the kinetic study, a plausible mechanism cyclic carbonates formation catalysed by complex **2** and tetrabutylammonium iodide has been proposed.

It is worth highlighting that these aluminium complexes are the first amidinate aluminium catalysts to be developed for the synthesis of cyclic carbonates from epoxides and carbon dioxide. The ligands are easy to make, highly tunable and can be synthesised on a large scale, making them powerful candidates to design new highly active catalysts for cyclic carbonates production.

Acknowledgements

This work was supported by the Ministerio de Economía y Competitividad (MINECO), Spain (grant nos. CTQ2014-51912-REDC and CTQ2014-52899-R), Nucleus Millenum CPC (ICM No. 120082), FONDECYT project No. 1161091, and CONICYT (grant no 21130376), Chile.

Keywords: Carbon dioxide • sustainable catalysis • cyclic carbonates • aluminium • epoxide

REFERENCES

[1] For textbooks see: a) *Carbon Dioxide as Chemical Feedstock* (Ed. M. Aresta), Wiley-VCH, Weinheim, **2010**; b) *New and Future Developments in Catalysis: Activation of Carbon Dioxide* (Ed. S. L. Suib), Elsevier, Oxford, **2013**; c) *Carbon Dioxide Utilisation: Closing the Carbon Cycle* (Eds. P. Styring, A. Quadrelli, K. Armstrong), Elsevier, Oxford, **2015**.

[2] a) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kühn, *Angew. Chem. Int. Ed.* **2011**, *50*, 8510–8537; b) M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.* **2014**, *114*, 1709−1742; c) Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun.* **2015**, *6*, 5933; d) E. S. Sanz-Pérez, C. R. Murdock, S. A. Didas, C. W. Jones, *Chem. Rev.* **2016**, *116*, 11840−11876; e) A. W. Kleij, M. North, A. Urakawa, *ChemSusChem* **2017**, *10*, 1036–1038; f) Q.-W. Song, Z.-H. Zhou, L.-N. He, *Green Chem.* **2017**, *19*, 3707−3728.

[3] a) C. Das Neves Gomes, O. Jacquet, C. Villiers, P. Thuéry, M. Ephritikhine, T. Cantat, *Angew. Chem., Int. Ed.* **2012**, *51*, 187−190; b) O. Jacquet, C. Das Neves Gomes, M. Ephritikhine, T. Cantat, *J. Am. Chem. Soc.* **2012**, *134*, 2934−2937.

[4] a) J. Graciani, K. Mudiyanselage, F. Xu, A. E. Baber, J. Evans, S. D. Senanayake, D. J. Stacchiola, P. Liu, J. Hrbek, J. F. Sanz, J. A. Rodriguez, *Science* **2014**, *345*, 546−550; b) C. H. Lim, A. M. Holder, J. T. Hynes, C. B. Musgrave, *J. Am. Chem. Soc.* **2014**, *136*, 16081−16095; c) R. K. Yadav, G. H. Oh, N. J. Park, A. Kumar, K. J. Kong, J. O. Baeg, *J. Am. Chem. Soc.* **2014**, *136*, 16728−16731; d) S. Wesselbaum, V. Moha, M. Meuresch, S. Brosinski, K. M. mThenert, J. Kothe, T. v. Stein, U. Englert, M. Holscher, J. Klankermayer, W. Leitner, *Chem. Sci.* **2015**, *6*, 693−704.

[5] a) A. Bassegoda, C. Madden, D. W. Wakerley, E. Reisner, J. Hirst, *J. Am. Chem. Soc.* **2014**, *136*, 15473−15476; b) X. Q. Min, M. W. Kanan, *J. Am. Chem. Soc.* **2015**, *137*, 4701−4708; c) A. Klinkova, P. De Luna, C. T. Dinh, O. Voznyy, E. M. Larin, E. Kumacheva, E. H. Sargent, *ACS Catalysis* **2016**, *6*, 8115-8120.

[6] For recent reviews of cyclic carbonate synthesis see: a) C. Martín, G. Fiorani, A. W. Kleij, *ACS Catal.* **2015**, *5*, 1353−1370; b) B. Yu, L.-N. He, *ChemSusChem* **2015**, *8*, 52−62; c) M. Cokoja, M. E. Wilhelm, M. H. Anthofer, W. A. Herrmann, F. E. Kühn, *ChemSusChem* **2015**, *8*, 2436−2454; d) B.-H. Xu, J.-Q. Wang, J. Sun, Y. Huang, J.-P. Zhang, X.-P. Zhang, S.-J. Zhang, *Green Chem.* **2015**, *17*, 108−122; e) V. D'Elia, J. D. A. Pelletier, J.-M. Basset, *ChemCatChem* **2015**, *7*, 1906−1917; f) J. W. Comerford,; I. D. V. Ingram, M. North, X. Wu, *Green Chem.* **2015**, *17*, 1966−1987; g) M. Alves, B. Grignard, R. Mereau, C. Jerome, T. Tassaing, C. Detrembleur, *Catal. Sci. Technol.*, **2017**, *7*, 2651−2684; h) J. Rintjema, A. W. Kleij, *ChemSusChem* **2017**, *10*, 1274−1282; i) J. E. Gomez, A. W. Kleij, *Curr. Opinion Green Sus. Chem.* **2017**, *3*, 55−60.

[7] For recent reviews covering cyclic and polycarbonate synthesis see: a) R. Martín, A. W. Kleij, *ChemSusChem* **2011**, *4*, 1259−1263; b) X.-B. Lu, D. J. Darensbourg, *Chem. Soc. Rev.* **2012**, *41*, 1462−1484; c) W. N. R.

Wan Isahak, Z. A. Che Ramli, M. W. Mohamed Hisham,; M. A. Yarmo, *Renew. Sustainable Energy Rev.* **2015**, *47*, 93−106.

[8] For recent reviews of polycarbonate synthesis see: a) S. Klaus, M. W. Lehenmeier, C. E. Anderson, B. Rieger, *Coord. Chem. Rev.* **2011**, *255*, 1460−1479; b) M. R. Kember, A. Buchard, C. K. Williams, *Chem. Commun.* **2011**, *47*, 141−163; c) X.-B. Lu, W.-M. Ren, G.-P. Wu, *Acc. Chem. Res.* **2012**, *45*, 1721−1735; d) D. J. Darensbourg, S. J. Wilson, *Green Chem.* **2012**, *14*, 2665−2671; e) N. Ikpo, J. C. Flogeras, F. M. Kerton, *Dalton Trans.* **2013**, *42*, 8998−9006; f) D. J. Darensbourg, A. D. Yeung, *Polym. Chem.* **2014**, *5*, 3949–3962; g) M. Taherimehr, P. P. Pescarmona, *J. Appl. Polym. Sci.* **2014**, *131*, 41141; h) Y. Qin, X. Sheng, S. Liu, G. Ren, X. Wang, F. Wang, *J. CO2 Util.* **2015**, *11*, 3−9; i) S. Paul, Y. Zhu, C. Romain, R. Brooks, P. K. Saini, C. K. Williams, *Chem. Commun.* **2015**, *51*, 6459−6479; j) Y. Zhu, C. Romain, C. K. Williams, *Nature* **2016**, *540*, 354−362; k) D. J. Darensbourg, *Inorg. Chem. Front.* **2017**, *4*, 412−419.

[9] W. Peppel, *J. Ind. Eng. Chem.* **1958**, *50*, 767−770.

[10] B. Schäffner, F. Schäffner, S. P. Verevkin, A. Börner, *Chem. Rev.* **2010**, *110*, 4554−4581.

[11] A. Hofmann, M. Migeot, E. Thißen, M. Schulz, R. Heinzmann, S. Indris, T. Bergfeldt, B. Lei, C. Ziebert, T. Hanemann, *ChemSusChem* **2015**, *8*, 1892−1900; b) J. P. Vivek, N. Berry, G. Papageorgiou, R. J. Nichols, L. J. Hardwick, *J. Am. Chem. Soc.* **2016**, *138*, 3745−3751.

[12] a) Y. Hara, S. Onodera, T. Kochi, F. Kakiuchi, *Org. Lett.*, **2015**, *17*, 4850–4853; b) W. Guo, J. Gónzalez-Fabra, N. A. G. Bandeira, C. Bo, A. W. Kleij, *Angew. Chem., Int. Ed.* **2015**, *54*, 11686–11690; c) R. Ninokata, T. Yamahira, G. Onodera, M. Kimura, *Angew. Chem., Int. Ed.*, **2016**, *56*, 208–211; d) A. Cai, W. Guo, L. Martínez-Rodríguez, A. W. Kleij, *J. Am. Chem. Soc.*, **2016**, *138*, 14194–14197; e) L.-C. Yang, Z.-Q. Rong, Y.-N. Wang, Z. Y. Tan, M. Wang, Y. Zhao, *Angew. Chem., Int. Ed.* **2017**, *56*, 2927–2931.

[13] G. Rokicki, P. G. Parzuchowski, M. Mazurek, *Polym. Adv. Technol.*, **2015**, *26*, 707–761.

[14] A. Tullo, *Chem. Eng. News* **2008**, *86*, 21.

[15] a) C. Gürtler, J. Hofmann, T. E. Müller, A. Wolf, S. Grasser, B. Köhler, (Bayer Material Science) Method for producing polyether carbonate polyols; WO117332, 2011; b) J. Hofmann, C. Gürtler, H. Nefzger, N. Hahn, K. Lorenz, T. E. Müller, (Bayer Material Science) Method for producing polyether carbonate polyols having primary hydroxyl end groups and polyurethane polymers produced therefrom; WO080192, 2012; c) N. Von der Assen, A. Sternberg, A. Kätelhön, A. Bardow, *Faraday Discuss.* **2015**, *183*, 291−307.

[16] a) M. North, R. Pasquale, *Angew. Chem., Int. Ed.* **2009**, *48*, 2946−2948; b) A. Buchard, M. R. Kember, K. G. Sandeman, C. K. Williams, *Chem. Commun.* **2011**, *47*, 212−214; c) J. A. Castro-Osma, M. North, X. Wu, *Chem. Eur. J.* **2016**, *22*, 2100−2107.

[17] a) M. H. Beyzavi, R. C. Klet, S. Tussupbayev, J. Borycz, N. A. Vermeulen, C. J. Cramer, J. F. Stoddart, J. T. Hupp, O.K. Farha, *J. Am. Chem. Soc.* **2014**, *136*, 15861−15864; b) Z. –R. Jiang, H. Wuang, Y. Hu, J. Lu, H. –L. Jiang, *ChemSusChem* **2015**, *8*, 878−885; c) P. –Z. Li, X. –J. Wang, J. Liu, J. S. Lim, R. Zou, Y. Zhao, *J. Am. Chem. Soc.* **2016**, *138*, 2142−2145; d) A. C. Kathalikkattil, R. Roshan, J. Tharun, R. Babu, G. –S. Jeong, D. –W. Kim, S. J. Cho, D. –W. Park, *Chem. Commun.* **2016**, *52*, 280−283.

[18] a) A. M. Hardman-Baldwin, A. E. Mattson, *ChemSusChem* **2014**, *7*, 3275−3278; b) L. Wang, G. Zhang, K. Kodama, T. Hirose, *Green Chem.* **2016**, *18*, 1229−1233.

[19] a) M. North, *ARKIVOC* **2012**, 610−628; b) X. Wu, M. North, *ChemSusChem* **2016**, *10*, 74−78.

[20] a) Y. Liu, W.-M. Ren, J. Liu, X.-B. Lu, *Angew. Chem. Int. Ed.* **2013**, *2*, 11594−11598; b) Y. Liu, W.-M. Ren, K.-K. He, X.-B. Lu, *Nat. Commun.* **2014**, *5*, 5687; c) J. A. Castro-Osma, K. J. Lamb, M. North, *ACS Catal.* **2016**, *6*, 5012−5025.

[21] a) W.-M. Ren, G.-P. Wu, F. Lin, J.-Y. Jiang, C. Liu, Y. Luo, X.-B. Lu, *Chem. Sci.* **2012**, *3*, 2094−2102; b) T. Roy, R. I. Kureshy, N. H. Khan, S. H. R. Abdi, H. C. Bajaj, *Catal. Sci. Technol.* **2013**, *3*, 2661−2667; c) Z. Zhu, Y. Zhang, K. Wang, X. Fu, F. Chen, H. Jing, *Catal. Commun.* **2016**, *81*, 50−53; d) F. Zhou, S.-L. Xie, X.-T. Gao, R. Zhang, C.-H. Wang, G.-Q. Yin, J. Zhou, *Green Chem.* **2017**, *19*, 3908−3915.

[22] For examples see: a) C.-X. Miao, J.-Q. Wang, Y. Wu, Y. Du, L.-N. He, *ChemSusChem* **2008**, *1*, 236–241; b) C. J. Whiteoak, A. H. Henseler, C. Ayats, A. W. Kleij, M. A. Pericàs, *Green Chem.* **2014**, *16*, 1552–1559; c) T. Jose, S. Cañellas, M. A. Pericàs, A. W. Kleij, *Green Chem.* **2017**, *19*, 5488–5493.

[23] M. North, S. C. Z. Quek, N. E. Pridmore, A. C. Whitwood, X. Wu, *ACS Catal.* **2015**, *5*, 3398−3402.

[24] a) J. Meléndez, M. North, P. Villuendas, *Chem. Commun.* **2009**, 2577–2579; b) M. North, P. Villuendas, C. Young, *Chem. Eur. J.* **2009**, *15*, 11454–11457; c) M. North, C. Young, *ChemSusChem* **2011**, *4*, 1685–1693; d) J. Meléndez, M. North, P. Villuendas, C. Young, *Dalton Trans.* **2011**, *40*, 3885–3902; e) M. North, B. Wang, C. Young, *Energy Environ. Sci.* **2011**, *4*, 4163–4170; f) M. North, P. Villuendas, C. Young, *Tetrahedron Lett.* **2012**, *53*, 2736–2740; g) M. North, P. Villuendas, *ChemCatChem* **2012**, *4*, 789–794; h) Y. A. Rulev, Z. Gugkaeva, V. I. Maleev, M. North, Y. N. Belokon, *Beilstein J. Org. Chem.* **2015,** *11,* 1614–1623.

[25] M. North, C. Young, *Catal. Sci. Technol.* **2011**, *1*, 93−99.

[26] a) J. A. Castro-Osma, A. Lara-Sánchez, M. North, A. Otero, P. Villuendas, *Catal. Sci. Technol.* **2012**, *2*, 1021−1026; b) J. A. Castro-Osma, C. Alonso-Moreno, A. Lara-Sánchez, J. Martínez, M. North, A. Otero, *Catal. Sci. Technol.* **2014**, *4*, 1674−1684; c) J. Martinez, J. A. Castro-Osma, A. Earlam, C. Alonso-Moreno, A. Otero, A. Lara-Sanchez, M. North, A. Rodríguez-Diéguez, *Chem. Eur. J.* **2015**, *21*, 9850−9862; d) J. Martinez, J. A. Castro-Osma, C. Alonso-Moreno, A. Rodríguez-Diéguez, M. North, A. Otero, A. Lara-Sanchez, *ChemSusChem* **2017**, *10*, 1175−1185.

[27] a) C. J.Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin, A. W. Kleij, *J. Am. Chem. Soc.* **2013**, 135, 1228–1231; b) V. Laserna, G. Fiorani, C. J. Whiteoak, E. Martin, E. C. Escudero-Adán, A. W. Kleij, *Angew. Chem., Int. Ed.* **2014**, *53*, 10416–10419; c) G. Fiorani, M. Stuck, C. Martín, E. Martin, M. Martínez-Belmonte, E. C. Escudero-Adán, A. W. Kleij, *ChemSusChem* **2016**, *9*, 1304–1311; d) C. Miceli, J. Rintjema, E. Martin, E. C. Escudero-Adán, C. Zonta, G. Licini, A. W. Kleij, *ACS Catal.* **2017**, *7*, 2367–2373.

[28] a) Y. Luo, Z. Gao, J. Chen, *J. Organomet. Chem.* **2017**, *846*, 18–23; b) W. Li, S.-D. Bai, F. Su, S.-F. Yuan, X.-E. Duan, D.-X. Liu, *New. J. Chem.* **2017**, *41*, 661–670; c) S. Bambirra, E. Otten, D. van Leusen, A. Meetsma, B. Hessen, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1950–1952; d) R. A. Collins, A. F. Russell, R. T. W. Scott, R. Bernardo, G. H. J. van Doremaele, A. Berthoud, P. Mountford, *Organometallics* **2017**, *36*, 2167–2181.

[29] L. M. Martínez-Prieto, I. Cano, A. Márquez, E. A. Baquero, S. Tricard, L. Cusinato, I. del Rosal, R. Poteau, Y. Coppel, K. Philippot, B. Chaudret, J. Cámpora, P. W. N. M. van Leeuwen, *Chem. Sci.* **2017**, *8*, 2931–2941.

[30] S. Ge, A. Meetsma, B. Hessen, *Organometallics*, **2008**, *27*, 3131–3135.

[31] H. Nagashima, M. Gondo, S. Masuda, H. Kondo, Y. Yamaguchi, K. Matsubaraac, *Chem. Commun.* **2003**, 442–443.

[32] J. Wang, J. Li, F. Xu, Q. Shen, *Adv. Synth. Catal.* **2009**, *351*, 1363–1370.

[33] H. Hu, C. Cui, *Organometallics* **2012**, *31*, 1208–1211.

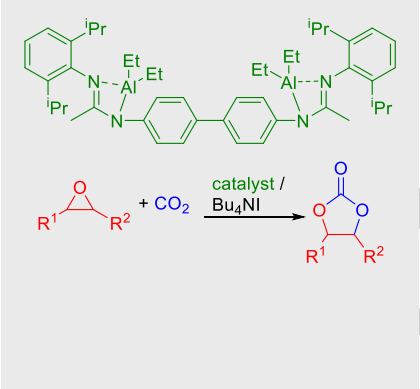
[34] D. Osorio Meléndez, J. A. Castro-Osma, A. Lara-Sánchez, R. S. Rojas, A. Otero, *J. Polym. Sci. Part A Polym. Chem.* **2017**, *55*, 2397–2407.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Amidinate Et-Al catalyse cyclic carbonate synthesis. In the presence of a tetrabutylammonium iodide cocatalyst, bimetallic amidinate aluminium complexes are effective catalysts for cyclic carbonate synthesis from carbon dioxide and both terminal and internal epoxides.



*Author(s), Corresponding Author(s)**

Page No. – Page No.

Amidinate aluminium complexes as catalysts for carbon dioxide fixation into cyclic carbonates