

A Powerful Aluminum Catalyst for the Synthesis of Highly Functional Organic Carbonates

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Supporting Information

ABSTRACT: An aluminum complex based on an amino triphenolate ligand scaffold shows unprecedented high activity (initial TOFs up to 36 000 h⁻¹), broad substrate scope, and functional group tolerance in the formation of highly functional organic carbonates prepared from epoxides and CO₂. The developed catalytic protocol is further characterized by low catalyst loadings and relative mild reaction conditions using a cheap, abundant, and nontoxic metal.

Carbon dioxide (CO₂) can be considered as an abundant, low cost, and renewable carbon source, but its use as such is limited as a result of its high stability and therefore low reactivity. Synthetic procedures which utilize CO₂ as a carbon feedstock are currently generating great interest within the scientific community,¹ as these may offer viable alternative routes toward various organic structures that are currently derived from fossil fuel based resources.² The catalysis of the atom-efficient (cyclo)addition of CO₂ to epoxides which yields useful cyclic or polycarbonate products (Scheme 1)³ is gaining momentum, as a variety of industrial targets incorporating these carbonates have been developed.^{1a-d} Many different binary/

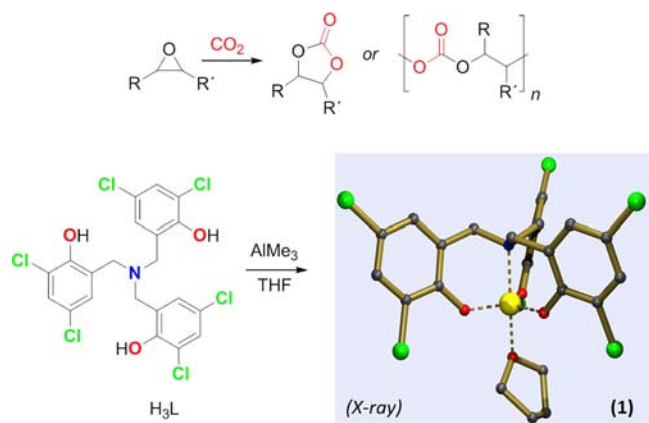
bifunctional catalyst systems for this reaction have been reported combining a Lewis acid and a nucleophile which is required for the ring opening of the epoxide.⁴

To date, most of the reported catalyst systems require relatively high catalyst loadings, and as a result (initial) turnover frequencies (TOFs) are rarely >200 h⁻¹ even at elevated temperatures (>100 °C), thus limiting their potential for industrial application. In this context, recent work reported by Sakai has shown important progress in the field communicating a bifunctional Mg(porphyrin) catalyst having TOFs as high as 12 000 h⁻¹.⁵ Though this is indeed a significant improvement, the catalyst system was only reported to be effective for the conversion of terminal epoxides (Scheme 1; R' = H). Previously, Minakata reported on a facile route toward more functional iodinated (unsaturated) cyclic carbonates elegantly making use of trapping a carbonic acid derivative by a hypoiodite source under mild conditions.⁶ Unfortunately, this procedure does not allow for the introduction of other functional groups and cannot address the synthesis of sterically encumbered disubstituted carbonates (Scheme 1, R and R') and oxetanes. Thus, the development of a catalyst system able to combine unusual reactivity (high TOF) with a broad substrate scope and high functional group tolerance to date still represents a challenging task.

The Lewis acidity of aluminum has already been successfully exploited to provide catalyst systems for the cycloaddition of CO₂ to epoxides.⁷ Of these reports, the most developed aluminum based catalysts are the bimetallic Al(salen) complexes reported by North and co-workers which provide a system active under ambient conditions, although due to the catalyst loadings required high TOFs were not achieved and only terminal epoxides proved to be suitable substrates.⁸ More recently, Darensbourg also studied a bifunctional Al(salen) framework in the context of organic carbonate formation.⁹ Motivated by these previous works and the fact that Al represents a nontoxic, earth-abundant metal, we set out to develop a catalyst system that shows the required features needed for the efficient conversion of a wide range of highly functional/substituted epoxides and oxetanes.

We reasoned that the use of an amino triphenolate ligand showing strong inductive effects (see Scheme 1) would favor the high oxophilic nature of the complexed metal center and

Scheme 1. Synthesis of Organic Carbonates from Epoxides and CO₂^a



^aBottom: synthesis of Al catalyst **1** from a hexachlorinated amino triphenol and its X-ray structure (Al center in yellow and one axial THF ligand is also present).

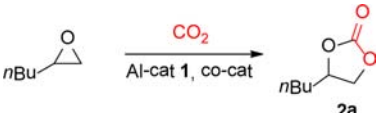
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create a new powerful catalyst with high potential for the activation of epoxides and oxetanes. The envisioned Al complex¹⁰ was easily synthesized in high yield (80%) and purity by treatment of the known ligand, H₃L,¹¹ and AlMe₃ in THF. The resultant complex was initially investigated as a catalyst for the cycloaddition of CO₂ to 1,2-epoxyhexane in combination with *n*-tetrabutylammonium iodide (TBAI) as a cocatalyst.

At a catalyst loading of 0.05 mol % and a TBAI loading of 0.25 mol % we were able to achieve quantitative conversion of this substrate at 90 °C within 2 h (Table 1, entry 2, TOF = 960

Table 1. Synthesis of Cyclic Carbonate 2a from CO₂ and 1,2-Epoxyhexane^a



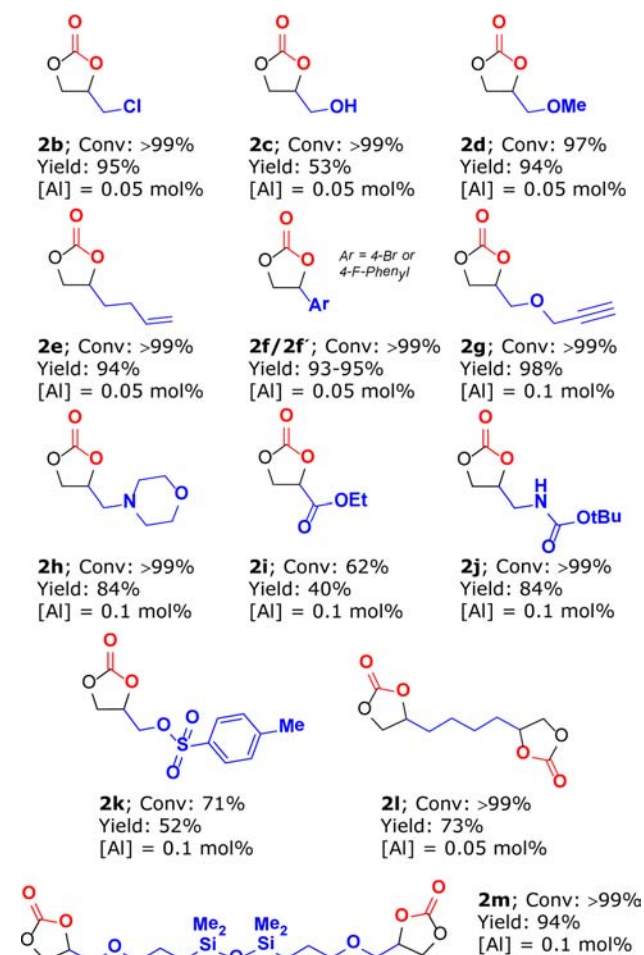
| entry | I (mol %) | cocat. (mol %) | t (h) | conv. ^{b,c} (%) | TOF ^d (h ⁻¹) |
|-----------------|-----------|----------------|-------|--------------------------|-------------------------------------|
| 1 | — | 0.25 | 2 | 17 | — |
| 2 | 0.05 | 0.25 | 2 | 96 | 960 |
| 3 | — | 0.05 | 2 | 13 | — |
| 4 ^e | 0.05 | 0.25 | 2 | 46 | 460 |
| 5 | 0.0025 | 0.05 | 2 | 38 | 7600 |
| 6 | 0.0010 | 0.05 | 2 | 33 | 16 500 |
| 7 | 0.0005 | 0.05 | 0.5 | 6 | 24 000 |
| 8 | 0.0005 | 0.05 | 1 | 13 | 26 000 |
| 9 | 0.0005 | 0.05 | 1.5 | 18 | 24 000 |
| 10 | 0.0005 | 0.05 | 2 | 24 | 24 000 ^f |
| 11 ^c | 0.0005 | 0.05 | 2 | 15 | 15 000 |
| 12 ^g | 0.0005 | 0.05 | 2 | 29 | 29 000 |
| 13 ^h | 0.0005 | 0.05 | 2 | 36 | 36 000 |

^aConditions: 1,2-epoxyhexane (1.00 g, 10.0 mmol), Al complex 1 (quantity indicated), TBAI (quantity indicated), 90 °C, 10 bar initial CO₂ pressure, 30 mL autoclave. ^bDetermined by ¹H NMR of the crude reaction mixture. ^cSelectivity for the cyclic carbonate product >99%. ^dInitial TOF/h/1 during the first 2 h. ^eUsing an Al(salen)₂O catalyst at the same [Al] loading. ^fTON = 112 000 after 18 h; average of three runs. ^gUsing PPN-I. ^hUsing PPN-Br.

h⁻¹). We then investigated the use of reduced amounts of Al complex 1 (entries 5–10) and were delighted to find that considerable conversions could still be achieved resulting in very high initial TOFs of up to 24 000 h⁻¹ per aluminum metal. To assess whether this activity was maintained throughout the reaction, the activities were also measured after 0.5, 1, and 1.5 h (entries 7–9) showing that the TOF reported after 2 h remains virtually unchanged in the initial stage of the reaction. Importantly, this indicates that the catalyst is stable under these conditions; under these same conditions the TON reached 112 000 after 18 h.¹² When compared to the TBAI cocatalyst alone (Table 1, entries 1 and 3) significantly higher conversions were observed in the presence of Al complex 1, with TOFs as high as 36 000 h⁻¹ when TBAI was replaced by PPN-I or PPN-Br as the cocatalyst (PPN = bis-(triphenylphosphine)iminium, entries 12 and 13). This high reactivity of the binary catalyst 1/TBAI was also observed with other substrates (Scheme 2) giving initial TOFs of 27 000 h⁻¹ (2h), 24 000 h⁻¹ (2d), and 17 000 h⁻¹ (2f).

When compared with a μ -oxo-Al(salen) dinuclear complex which may be regarded as one of the benchmark systems,⁸ the

Scheme 2. Scope in Terminal Epoxides^a



^aCyclic (bis)carbonates 2b–2m obtained from their corresponding epoxides using 1/TBAI as catalyst system. General conditions: neat, 1.00 g of substrate, molar ratio 1/TBAI = 1:5, 70 °C, 18 h, 10 bar initial CO₂ pressure, 30 mL autoclave. The observed selectivity for the cyclic carbonate product was >99% in all examples determined by ¹H NMR in CDCl₃. Note that in the synthesis of products 2f–2k 0.5 mL of MEK (co)solvent was used.¹³

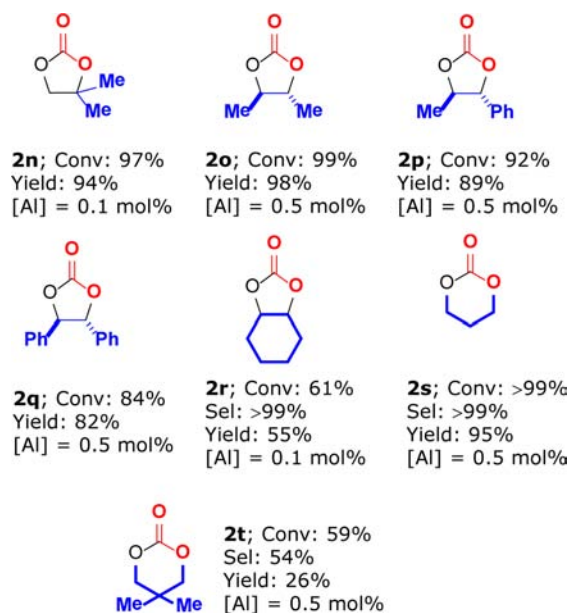
newly developed Al-complex 1 shows higher initial TOFs (entries 2 versus 4, and 10 versus 11).

Having established that Al complex 1 is a highly active catalyst for organic carbonate formation (Table 1), we then focused on further application of its promising reactivity potential and first investigated the scope of the cycloaddition of CO₂ to a variety of highly functionalized terminal epoxides providing organic carbonates 2b–2m (Scheme 2). In some cases it was necessary to use methylethylketone (MEK) as a (co)solvent during the conversion to prevent problems associated with either high viscosity and/or the solid nature of the reaction mixture. In general, low amounts of catalyst 1 (0.05–0.10 mol %) and cocatalyst (0.25–0.50 mol %) were already effective under comparatively mild conditions (70 °C, *p*CO₂⁰ = 10 bar).¹⁴ All of the substrates studied were conveniently converted into the corresponding (bis)carbonates 2b–2m with high selectivity (>99%), and the products were isolated in good to excellent yields, indicating the high versatility of this catalyst system. Interestingly, the catalyst system 1/TBAI not only tolerates functionalities such as alkene, alkyne, alkyl halide, alcohol, ether, and substituted aryl groups

(2b–2g) but also allows for conversion of even more challenging substrates that contain fragments having potentially competing O- or N-donor atoms that may be able to coordinate to the Al metal center and compromise catalytic conversion. Carbonates **2h–2k** incorporating morpholine, ester, amide, and sulfonate ester groups could also be obtained in reasonable to good isolated yields (40–84%); in some cases effects arising from isolation through column purification resulted in lower isolated yields. Bis-epoxide substrates were also cleanly converted into their bis-carbonate products **2l** and **2m** in good yields (73–94%). These combined results clearly demonstrate the catalytic potential of Al-complex **1** showing the amplified scope for the conversion of highly functional terminal epoxides.

To further exemplify and challenge the catalytic potential of Al-complex **1**, internal epoxides with increasing steric bulk and oxetanes were then chosen as reaction partners (Scheme 3,

Scheme 3. Scope for Internal Epoxides/Oxetanes^a



^aCyclic carbonates **2n–2t** obtained using **1**/TBAB as catalyst system. General conditions: 1.00 g of substrate, **1**/TBAB = 1:5, 70 °C, 18 h, 10 bar initial CO₂ pressure, 30 mL autoclave. Selectivity for the cyclic carbonate product >99% in all examples (unless stated otherwise) determined by ¹H NMR in CDCl₃. Further details: (i) for **2o–2q** the reaction time was 42 h and temperature was 90 °C using 0.5 mL of MEK¹³ as (co)solvent; (ii) for **2r** the ratio **1**/TBAB was 1:10; (iii) for **2s** and **2t** TBAI was used. For **2s** the reaction time was 4 h, and for **2t** it was 66 h; (iv) the selectivity toward the *trans* product in the case of **2o–2q** was >99% as determined by ¹H NMR in CDCl₃.

synthesis of **2n–2t**). These internal epoxides (except for **2r**) and oxetanes are widely considered to be very difficult substrates, and as a result much less success has been achieved with these substrates.¹⁵ The use of **1**/TBAB (TBAB = *n*-tetrabutylammonium bromide) as a catalyst system turned out to be most beneficial for the conversion of these internal epoxides into their cyclic carbonates using low loadings of **1** (0.1–0.5 mol %), whereas the use of TBAI gave poorer results.

To obtain reasonable yields of products **2p** and **2q**, a reaction temperature of 90 °C was required. The *trans* disposition of both substituents in carbonates **2o–2q** was easily determined by ¹H NMR spectroscopy; for **2o** and **2q** single-crystal X-ray

diffraction studies further supported the proposed configurations (see Supporting Information (SI)). It should be noted that there are very few reports of the synthesis of **2q**¹⁶ through catalytic cycloaddition of CO₂ to stilbene oxide, marking the current protocol as a rare example of a catalyst able to mediate this conversion affording a high yield of **2q**.

Oxetanes are the closest homologues to epoxides but have historically received far less attention. Their lower ring strain results in lower conversion rates, making these compounds significantly more challenging substrates, as ring opening is usually considered to be the rate-limiting step. There have been limited reports of vanadium, aluminum, chromium, and iron catalysts capable of catalyzing the cycloaddition of CO₂ to oxetanes.¹⁷ Conversion under various reaction conditions of two different oxetanes leading to the six-membered carbonates **1s** and **1t** are shown in Table S3 and Scheme S1 (SI) where again MEK was used as a (co)solvent due to the solid nature of the products, thus enabling optimization of these conversions (best results in Scheme 3).

It was possible to obtain almost quantitative and selective conversion to carbonate **2s** (95% yield) after only 4 h at 70 °C (Table S3, entry 3). Longer reaction times lead to a lower selectivity for **2s**, as the formation of increasing amounts of polycarbonates were observed in the product mixture (Table S3, entry 4). At a lower reaction temperature (50 °C), prolonged reaction times however did not lead to any detectable polymer formation (Table S3) pointing to a temperature onset for polymer formation starting from **2s**.¹⁸ It is known that cyclic carbonates derived from oxetanes are the kinetic products and are susceptible to polycarbonate formation unlike their epoxide-derived homologues. Carbonate **2t** is significantly less accessible as a result of the increased steric effects posed by the 3,3'-positioned substituents, and therefore increased reaction times were required. Though this led to a higher yield of **2t** (Scheme 3; 26%), much lower selectivities (54%) were observed due to polycarbonate/ether formation and partial decarboxylation.¹⁹ Also in this case, by lowering the reaction temperature to 50 °C virtually complete selectivity for **2t** was noted albeit at the expense of the substrate conversion (19%) and isolated yield (12%).

In conclusion, we have presented an easily accessible and new amino triphenolate complex based on a cheap, earth-abundant, and nontoxic metal (i.e., Al) that has been demonstrated to be a highly active and versatile catalyst for organic carbonate formation. Remarkably initial TOFs as high as 36 000 h⁻¹ during catalysis of the cycloaddition of CO₂ to epoxides were obtained with TONs exceeding 100 000. To the best of our knowledge, these TOFs are among the highest reported for a homogeneous catalyst system in the context of cyclic carbonate formation. The catalyst system also displays a wide substrate scope and functionality tolerance. It thus allows for the preparation of highly functional cyclic carbonate products derived from terminal, double, and internal epoxides, and oxetanes. We are currently investigating the catalytic potential of Al-complex **1** in the formation of organic products derived from CO₂ and other suitable substrates.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental procedures and full analytical data, and copies of relevant NMR and IR spectra for known and new compounds.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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- (12) The average TOF was further investigated up to a reaction time of 6 h showing a slight decrease to 12 700 h⁻¹; see the SI (Table S1). Additionally, the influence of air and water was also studied in the conversion of substrates **2b**, **2d**, and **2f'**; only a small effect of added water was noted on the product yield observed for the conversion of substrate **2d**; see the SI (Table S2). The combined data show that the used catalyst system is highly robust and, furthermore, can be handled in air.
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