Lewis Acids

Highly Active Aluminium Catalysts for the Formation of Organic **Carbonates from CO₂ and Oxiranes**

Christopher J. Whiteoak,^[a] Nicola Kielland,^[a] Victor Laserna,^[a] Fernando Castro-Gómez,^[a] Eddy Martin,^[a] Eduardo C. Escudero-Adán,^[a] Carles Bo,^[a, c] and Arjan W. Kleij*^[a, b]

Abstract: Al^{III} complexes of amino-tris(phenolate) ligand scaffolds have been prepared to attain highly Lewis acidic catalysts. Combination of the aforementioned systems with ammonium halides provides highly active catalysts for the synthesis of organic carbonates through addition of carbon dioxide to oxiranes with initial turnover frequencies among the highest reported to date within the context of cyclic carbonate formation. Density functional theory (DFT) studies

Introduction

The use of carbon dioxide (CO₂) as a renewable carbon feedstock is of both academic and industrial relevance.^[1] However, there are only a limited number of chemical processes that have been successfully developed in which CO₂ is used as a reagent^[2] and even less that classify as truly sustainable from the point view of energy use and carbon recycling.^[3] One method of increasing the sustainability of a chemical process is through the use of catalysis and therefore use of such may enable the realization of truly sustainable CO₂ conversions.^[4] The largest challenge in CO₂ conversion is its relative high kinetic and thermodynamic stability; whereas catalysis can be used to effectively lower the barriers associated with the kinetic stability, the choice for higher-energy substrates can help to overcome the thermodynamic hurdle. With this latter aspect in mind, the use of epoxides (oxiranes) has the advantage that the ring strain is released upon ring opening and its conversion in the presence of CO₂ providing either organic poly-^[5] or cyclic carbonates^[6] (Scheme 1) is indeed exothermic. This addi-

[a] Dr. C. J. Whiteoak, Dr. N. Kielland, V. Laserna, F. Castro-Gómez, Dr. E. Martin, E. C. Escudero-Adán, Prof. Dr. C. Bo, Prof. Dr. A. W. Kleij Institute of Chemical Research of Catalonia (ICIQ) Av. Països Catalans 16, 43007 Tarragona (Spain) Fax: (+ 34) 977-920-828 E-mail: akleij@iciq.es [b] Prof. Dr. A. W. Kleij Catalan Institute of Research and Advanced Studies (ICREA) Pg. Lluís Companys 23, 08010 Barcelona (Spain) [c] Prof. Dr. C. Bo Departament de Química Física i Inorgánica Universitat Rovira i Viraili Marcel·lí Domingo s/n 43007 Tarragona (Spain) http://dx.doi.ora/10.1002/chem.201302536.

combined with kinetic data provides a rational for the relative high activity found for these Al[™] complexes, and the data are consistent with a monometallic mechanism. The activity and versatility of these Al^{III} complexes has also been evaluated against some state-of-the-art catalysts and the combined results compare favorably in terms of catalyst construction, stability, activity, and applicability.

tion^[7] of CO₂ to epoxides is a well-documented area of research in which a number of different catalytic solutions have been proposed using ionic liquids,^[8] binary,^[9] or bifunctional (metallosalen) complexes,^[10] and simple organic motifs such as "onium salts".^[11] However, only in a limited amount of cases have these catalytic efforts resulted in systems with (very) high activities expressed in high turnover frequencies (TOFs) and high turnover numbers (TONs).

In addition, when taking into account possible application of catalysts in an industrial setting^[12] long-term stability, recycling features, accessibility, cost-effectiveness, toxicity, and catalyst modularity are features that are of crucial importance.

Recently, Ema, Sakai, and co-workers reported on bifunctional metalloporphyrin catalysts (M=Mg, Zn) that were able to produce cyclic carbonates based on terminal epoxides with high TOFs of up to $12000 h^{-1}$ and TONs up to 103000.^[10b] This work inspired us to design and construct catalyst systems with similar or even improved potential in this area with a focus on high reactivity and wide application potential (substrate scope). We became interested in using amino-tris(phenolate) scaffolds^[9b, 13a] as ligand alternatives for the widely used salen and/or salans,^[14] because these provide different molecular conformations upon complexation of suitable metal ions.^[13] We envisioned that the presence of fewer donor atoms in the plane of the metal would be beneficial for those cases in which the steric requirement of the coordinating epoxide substrate would limit catalytic turnover. Because in the majority of cases binary catalyst systems are employed (i.e., a metal complex combined with a suitable nucleophile), the nucleophile needed in the ring-opening step of the coordinated epoxide would have difficulty approaching the substrate and entering the coordination sphere of the metal. We have recently reported that Fe^{III}-based amino-tris(phenolate) complexes are efficient catalysts for the formation of a wide series of cyclic car-

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Results and Discussion

Synthesis and analysis of complexes

The amino-tris(phenol) ligands 1 and 2 were prepared by a known Mannich condensation reaction,^[18] whereas 3 was prepared in stepwise manner.^[19] The ligand bearing chloride substituents (ligand 4) has been reported by Kol and co-workers^[20] but the preparation was achieved by using a different work-up procedure to that reported; after heating 2,4-dichlorophenol and hexamethyltetramine (HMTA) together at reflux at 110°C for 2.5 h, an (unexpected) adduct of HMTA and the desired ligand, 4-HMTA, was isolated (X-ray structure, see the Supporting Information). The HMTA could be removed by an acid/base workup to yield the desired ligand 4

cessful catalyst systems (A–C) based on aluminium for this reaction. Note that catalyst systems A and C are binary systems and are combined with NBu₄X (X = Br or I) whereas catalyst B is a one-component, bifunctional system.

bonates under virtually ambient conditions $(25 \,^{\circ}C, P(CO_2) = 2 \text{ bar})$ and also effectively mediate the conversion of internal epoxides.^[9b] Further to that, computational analyses^[15] on the Zn(salphen)-mediated formation of cyclic carbonates^[4c,9e] have indicated that metallosalen catalyst systems may have limitations concerning the more sterically demanding substrates. The fact that amino-tris(phenolate) complexes show better catalytic potential is in line with these theoretical studies.

In an attempt to create even more powerful catalyst systems, we have turned our focus to aluminium systems, because recent literature has demonstrated that complexes based on AI can be attractive within the context of organic carbonate formation (Scheme 1; see systems A-C).^[16] Our preliminary results using an [Al{amino-tris(phenolate)}] complex (Scheme 1, C) demonstrated unprecedented activity (initial TOFs up to 36000 h⁻¹ and TONs exceeding 118000) and substrate scope,^[17] here we will demonstrate that these kind of complexes based on this earth-abundant metal can be easily fine-tuned giving rise to catalyst systems with activities among the highest reported to date. Further theoretical, kinetic, stability, and structural studies are also presented that clearly show a combination of attractive properties for these powerful catalyst systems during CO₂ conversion into value-added commodities such as cyclic carbonates. Computational investigations have shed important insight on reasons for the observation of high activities of these new Al-based catalysts.

in good purity although low yield. This ligand is difficult to prepare selectively as a result of the poor solubility of both the corresponding amino-bis(phenol) and the amino-tris(phenol) in the reaction medium. Upon formation of the amino-tris-(phenol) ligands, a degradation may occur towards the aminobis(phenol) as reported by Solomon and co-workers for ligand 1.^[21] In the case of **4** this degradation reaction appears to be rapid as the poor solubility of the amino-bis(phenol) drives the equilibrium towards this undesired product as soon as the amino-tris(phenol) is obtained, thereby limiting the yield of the desired ligand.

The [Al{amino-tris(phenolate)}] complexes were obtained through the reaction of the ligand precursors **1–4** with trimethylaluminium ([AlMe₃]) in THF (Scheme 2). The characterization data for complexes **5**, **6**, and **8** are consistent with monomeric complexes, in which a THF ligand occupies the apical



Scheme 2. Synthesis of [Al{(amino-tris(phenolate)}] complexes 5–8 from precursor ligands 1–4.





Figure 1. Displacement ellipsoid plot of the molecular structure of 8-THF together with a partial numbering scheme. Co-crystallized solvent molecules and rotational disorder in the THF ligand is omitted for clarity. Selected bond lengths [Å] and angles [$^{\circ}$]: Al(1)–O(1) = 1.7604(14), Al(1)–O(2) = 1.7527(15), Al(1)–O(3) = 1.7689(15), Al(1)–O(4) = 1.9216(15), Al(1)–N(1) = 2.0715(17); O(4)-Al(1)-N(1) = 178.11(7), O(1)-Al(1)-O(2) = 120.94(7), O(2)-Al(1)-O(3) = 117.02(7), O(1)-Al(1)-O(4) = 87.31(7), O(2)-Al(1)-O(4) = 89.50(7), N(1)-Al(1)-O(1) = 90.94(7), N(1)-Al(1)-O(3) = 91.43(7).

position of trigonal-bipyrimidal coordination geometry. Complex **7** is presumed to exist as a dimeric species (as is its Fe^{III} analogue)^[13] considering its lower solubility in most solvents. The molecular structure for **8**-THF (Figure 1) was determined by X-ray crystallography from crystals obtained from THF/hexane. The molecular structures of **5**-THF and **6**-THF were reported previously.^[22]

Further fine-tuning of the amino-tris(phenol) scaffold can also be accomplished through the synthesis of nonsymmetrical ligands. In this respect, an aminobis(phenol) (i.e., a secondary amine) may serve as a suitable precursor, since simple alkylation of the amine with an appropriate reagent directly affords nonsymmetrical systems. This was probed for the secondary amine **9**,^[23] which was alkylated with the commercially available alkyl bromide **10**; the desired nonsymmetrical amino-tris(phenol) ligand **11** was isolated in 68% yield. Metalation, as described for Al

complexes **5–8**, was achieved similarly to furnish **12** in 78% yield. The identity of **12** was first established by ¹H NMR spectroscopy (details in the Supporting Information) and further affirmed by using X-ray crystallography (Figure 2). The structure reported for **12** represents, to our knowledge, the first crystallographically characterized nonsymmetrical amino-tris(phenolate) complex (Scheme 3).

Complex **12** crystallized as a dimeric structure comprising two μ_2 -phenoxo bridges. Such dimerization potential has been well-documented in the literature and recently we have shown that dimers of [Fe{amino-tris(phenolate)}] complexes can be easily disrupted by addition of a suitable, competing ligand



Figure 2. Displacement ellipsoid plot of the dimeric structure of **12** together with a partial numbering scheme. Co-crystallized solvent molecules and rotational disorder are omitted for clarity. The bond lengths/angles around both Al centers are rather similar. Selected lengths [Å] and angles [°]: Al(1)–O(1) = 1.740(3), Al(1)–O(2) = 1.734(3), Al(1)–O(3) = 1.846(2), Al(1)–O(8) = 1.948(2), Al(1)–N(1) = 2.003(3); O(1)-Al(1)-O(2) = 124.28(13), O(1)-Al(1)-O(3) = 115.08(12), O(1)-Al(1)-O(8) = 91.15(11), O(1)-Al(1)-N(1) = 93.50(12), O(2)-Al(1)-O(8) = 91.14(11), O(3)-Al(1)-O(8) = 76.99(10), Al(1)-O(8)-Al(2) = 39.94(8), Al(1)-O(8)-Al(2)-O(3) = 176.71(18).



Scheme 3. Synthesis of nonsymmetrical [Al{(amino-tris(phenolate)}] complex 12.

(THF, pyridine) or substrate (epoxide)^[9b, 13] providing monomeric species which is a prerequisite for application in catalysis (see below).

Catalysis screening with Al complexes 5-8 and 12

The catalytic potential of the Al complexes was first evaluated under mild conditions (T=30 °C, $P(CO_2)=1.0$ MPa=10 bar) using 1,2-epoxyhexane (**13**) as a benchmark substrate and NBu₄I as the co-catalyst (Table 1, entries 1–14). In general, at catalyst loadings of 0.05 mol% low conversions were noted, whereas increasing this by at least tenfold (0.5–0.7 mol%) re-

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initial pressure, 2 h, 30 °C. [b] Catalyst concentration calculated on a per-Al-atom basis and amount related to the substrate. [c] Determined by ¹H NMR spectroscopy of the crude reaction mixture; selectivity in all cases > 99%. Conversions were found to be reproducible within $\pm 2\%$ in four independent runs for selected experiments. [d] Average turnover frequency (TOF h⁻¹) during the first 2 h. [e] By using NBu₄Br as co-catalyst.

sulted in high conversion levels of up to 94% (Table 1, entry 4). The AI complexes themselves proved to be inactive (Table 1, entries 1 and 10). The best result, in terms of initial TOF, was obtained for Al complex 8 (Table 1, entry 11) which gave an average TOF of 100 h⁻¹. It should be noted that the co-catalyst alone (NBu₄I) under similar conditions reported for the AI complexes (either at 0.05 or 0.5 mol% catalyst loading) proved to be ineffective and no conversion into carbonate was detected (Table 1, entries 15 and 16). Further to that, upon comparison with two benchmark catalyst systems (North's bimetallic [Al-(salen)] A combined with NBu₄I (Table 1, entry 18) or NBu₄Br (entry 19) and our previously reported [Zn(salphen)] catalyst D) we found that these latter systems were less effective and showed about half the activity (TOFs are 50 and 46 h⁻¹, respectively; Table 1, entries 17 and 19) compared with Al complex 8 at the same metal loading (entry 12; $TOF = 91 h^{-1}$).^[24] The lowest activities (expressed in initial TOFs) were found for the nonsubstituted AI complex 7 and the nonsymmetrical AI complex **12**. It is known that these complexes have a higher tendency to form dimeric structures, which can compete with the required substrate coordination. Temperature is an important factor controlling the monomer–dimer equilibrium, with higher temperatures favoring higher concentrations of the more reactive monomeric species.^[13] Therefore, to compare and better evaluate the catalytic potential of Al complexes **5–8** and **12**, we then focused on higher reaction temperatures to further increase the turnover frequencies (Table 2).

	nBu1;	$\frac{CO_2 (10)}{NBu_4 I, r}$	bar) → O eat - <i>n</i> Bu	° /	5. R = Me 6. R = <i>t</i> Bu 7. R = H 8. R = Cl	
Entry	Cat. [mol	%]	Co-cat. [mol%]	<i>Т</i> [°С]	Conv. [%] ^[c]	TOF $[h^{-1}]^{[d]}$
1	5	0.05	0.25	50	41	410
2	5	0.05	0.25	70	60	600
3	5	0.05	0	90	0	0
4	5	0.05	0.25	90	89	890
5	5	0.005	0.025	110	22	2200
6	6	0.05	0.25	50	20	200
7	6	0.05	0.25	70	52	520
8	6	0.05	0.25	90	74	740
9	6	0.01	0.05	90	23	1150
10	6	0.005	0.025	110	17	1700
11	7	0.05	0.25	50	15	150
12	7	0.05	0.25	70	58	580
13	7	0.05	0.25	90	78	780
14	7	0.005	0.025	110	21	2100
15	8	0.05	0.25	50	41	410
16	8	0.05	0.25	70	82	820
17	8	0.05	0	90	0	0
18	8	0.05	0.25	90	96	960
19	8	0.01	0.05	90	42	2100
20	8	0.005	0.025	110	26	2600
21	-	-	0.25	50	2	-
22	-	-	0.25	70	15	-
23	-	-	0.25	90	17	-
24	-	_	0.025	110	22	_
[a] Read initial p atom b	ction conc pressure, pasis and	ditions: 1,2- 2 h. [b] Cat amount r	epoxyhexane alyst concent elated to the	(1.0 g, 9.9 tration cal	8 mmol), 1.0 culated on e. [c] Deter) MPa CO; a per-Al- mined by

Table 2. Catalysis results obtained for the synthesis of the cyclic carbonate derived from 1,2-epoxyhexane at various temperatures using NBu₄I as the co-catalyst.^[a,b]

[a] Reaction conditions: 1,2-epoxyhexane (1.0 g, 9.98 mmol), 1.0 MPa CO₂ initial pressure, 2 h. [b] Catalyst concentration calculated on a per-Alatom basis and amount related to the substrate. [c] Determined by ¹H NMR spectroscopy of the crude reaction mixture; selectivity in all cases > 99%. Conversions were found to be reproducible within $\pm 2\%$ in four independent runs for selected experiments. [d] Average turnover frequency (TOF h⁻¹) during the first 2 h.

For this second stage of the catalysis screening, temperatures up to 110 °C were considered and Al complexes **5–8** were utilized because their substitution pattern allows for a direct comparison of activities within this series. As expected, at higher temperatures complexes **5–8** display higher reactivity and an increase in the observed average TOFs for all complexes, with the complexes in the absence of NBu₄I being inactive (Table 2, entries 3 and 17; 90 °C). For instance, for the Al complex **5** at 50 °C an increase in the TOF is noted to 410 h⁻¹,



which reaches 2200 h⁻¹ at 110 °C at a catalyst loading of only 0.005 mol% (Table 2, entries 1–5). For the other catalysts **6–8** similar features were noted, that is, an increase in the TOF with the highest reactivity was noted at 110 °C. The Al complex **7**, which is likely to form (at least in part) a dimeric structure in solution shows, as expected, higher reactivity at higher temperatures as a result of a more favorable monomer–dimer equilibrium.^[13] Nonetheless, clearly for Al complex **8** at all temperatures the highest TOFs were observed suggesting that this system has the highest catalytic potential with a notable TOF of up to 2600 h⁻¹ (Table 2, entry 20).

At increased reaction temperatures there are two crucial features to consider: first, at elevated temperatures the efficacy of the co-catalyst alone (i.e., the ammonium salt)^[11] is needed for comparison.^[25] Critical assessment of the conversion data at 110°C shows that the absence/presence of any Al complex (Table 2, entries 5, 10, 14, and 20 versus 24) gives rise to almost the same amount of product formation and the effect of the presence of the Lewis acidic Al complex is thus minimal. At 90 °C however, a significant difference in conversion is still noted (compare, for instance, Table 2, entries 18 and 23; 96 vs. 17% conversion) in line with the hypothesis that the Al complex under these conditions plays an imperative role. Second, whereas up to a 90°C reaction temperature the selectivity for the cyclic carbonate is maintained (\geq 99% as determined by ¹H NMR spectroscopy), at 110 °C in some cases we observed trace amounts of side products that probably arise from thermal decomposition of the carbonate target. Therefore, because of the above-mentioned reasons further optimization/investigations of the TOF were carried out with Al complex 8 at a maximum temperature of 90 °C.

Optimization of the performance of Al complex 8 and stability tests

To assess the catalytic potential of Al complex 8 in the formation of cyclic carbonates, initial TOFs were then determined at various concentrations of 8 (Table 3). In each case, a comparison was made between the efficiency of the binary catalyst couple (i.e., Al complex 8 and NBu₄I) versus the co-catalyst alone to ensure that the Al complex shows a significant contribution in the observed activity. At a loading of 0.05 mol% (Table 3, entry 1, 96%) a TOF of 960 h^{-1} is attained, whereas the co-catalyst alone (entry 2) shows much lower conversion (17%). Lowering the loading of Al complex 8 to 0.01 mol% (Table 3, entry 3) increases the TOF value to 2100 h^{-1} ; it is important to note here that the actual potential of a catalyst should be measured at the initial stage of the reaction (i.e., at low conversion levels) when substrate concentration limitation on the observed activity is minimal. On decreasing the amount of 8 while maintaining a co-catalyst amount of 0.05 mol%, very high initial TOFs of 7600 (Table 3, entry 5; 0.0025 mol% of **8**), 16500 (entry 7; 0.0010 mol% of **8**), and 24000 h⁻¹ (entry 8; 0.0005 mol% of 8) were observed whereas the co-catalyst alone provided a significantly lower conversion (entry 6; 13%). One of the benchmark systems ([Al(salen)] dimer A, Scheme 1) from the literature was again compared with our best-perform-



ing complex 8. At a total Al loading of 0.01 mol% (entries 3 and 4 in Table 3), catalyst **8** gave an initial TOF of 2100 h^{-1} , which is four times higher than observed for dimeric [Al(salen)] complex \boldsymbol{A} (550 $h^{-1}).$ Other substrates (14–16) were then tested with Al complex 8 to see whether such high initial TOFs could also be achieved as observed for 1,2-epoxyhexane 13 (Table 3, entries 9-11). With these alternative epoxides 14-16, initial TOFs amounted to 27000 (14), 24000 (15), and 17000 h^{-1} (16), respectively, demonstrating the wider applicability of catalyst 8 and a very high activity in general. As a final part of the optimization of the activity of the binary catalyst couple (Al complex 8 and a suitable co-catalyst) we then focused on the use of bis(triphenylphosphoranylidene)ammonium (PPN) salts of bromide and iodide because these have been shown to give excellent results in the context of (cyclic/ poly) carbonate formation.^[26] Whereas the use of Al complex 8/PPN-I (Table 3, entry 12) showed a modest increase in initial TOF to 29000 h^{-1} (cf., 24000 h^{-1} in the case in which NBu_4I

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was used; entry 8), the use of PPN-I alone (entry 13) showed slightly lower conversion of the substrate. The combination of Al complex **8** and PPN-Br, however, showed significantly higher activity than the co-catalyst alone (Table 3, compare entries 14 and 15) and a remarkably high initial TOF of 36000 h⁻¹ was achieved.

To establish the robustness of Al complex **8** several further experiments were conducted. First, at a loading of 0.0005 mol% of **8** using the conditions reported in entry 8 (Table 3) the TON was determined after 18 h, being a notable 112 000. This shows that the catalyst is stable enough in the course of time at 90 °C providing further turnover when compared with the initial stage of the reaction (Table 3, entry 8; 2 h).

Following the average TOF in time (Table 4, entries 1–8) the $TOF h^{-1}$ stays stable within the first two hours of the reaction

Table 4. Reactivity in time and stability studies using Al-catalyst **8** in the synthesis of cyclic carbonates derived from epoxides **13** and **15–17** at 70–90 °C using NBu₄I as co-catalyst and comparison with reactions using only the co-catalyst.^[a,b]



atom basis and amount related to the substrate. [c] Determined by ¹H NMR spectroscopy of the crude reaction mixture; selectivity in all cases >99%. Conversions were found to be reproducible within $\pm 2\%$ in four independent runs for selected experiments. [d] Average turnover frequency (TOF h⁻¹) during the first 2 h. [e] At $P(CO_2) = 1$ MPa together with P(Air) = 0.2 MPa at 70 °C. [f] The yield of the isolated product is in parenformed at 70 °C.

and amounts to $12666 h^{-1}$ after 6 h; this lower value may be expected when the kinetics of a process follows a non-zeroorder dependency on the substrate(s) concentration. Then, the stability of the catalyst system was further probed by investigating the turnover under more competitive reaction conditions, that is, in the presence of air or water (Table 4) and comparing the conversion/yield for three different substrates with those reported previously. $\ensuremath{^{[17]}}$

Interestingly, the results from entries 9–14 in Table 4 show that neither the presence of air nor water has a dramatic long-term effect (cf., TON) on the conversion of the epoxide nor the yield of the isolated carbonate product with typical yields under these conditions being high (up to 98%). Therefore, by combining the results from Tables 1–4 it may be concluded that Al complex **8** is both a highly active as well as robust system that upon combination with a suitable nucleophile (NBu₄X, PPN–X; X=Br, I) gives rise to a binary catalyst couple with initial activities amongst the highest reported to date.

Mechanistic considerations

As the mechanism for dimeric [Al(salen)] complexes has been recently investigated by North and co-workers,^[9d] we have further focused on some of the features of the operative mechanism^[27] when using Al complexes based on amino-tris(phenolate) scaffolds. Previously, the first step in the [Zn(salphen)]-catalyzed formation of cyclic carbonates was proposed to be the coordination of the epoxide to the metal center.^[9e,28] We were able to grow crystals of a similar structure based on Al complex **8** and oxetane; its structure is presented in Figure 3.

The structure for **8**-oxetane simply serves to demonstrate a likely starting point in the conversion of any substrate converted by the [Al{amino-tris(phenolate)}] complexes reported in this work. Kinetic studies (see the Experimental Section for more details) were performed with the objective to examine the order in the binary catalyst. These kinetic studies were per-



Figure 3. Displacement ellipsoid plot of the structure of **8**-oxetane together with a partial numbering scheme. Co-crystallized solvent molecules are omitted for clarity, and only one of the crystallographically independent molecules in the unit cell is shown. Selected bond lengths [Å] and angles [°]: Al(1B)–O(1B) = 1.742(2), Al(1B)–O(2B) = 1.759(2), Al(1B)–O(3B) = 1.768(2), Al(1B)–O(4B) = 1.907(3), Al(1B)–N(1B) = 2.073(3); O(1B)-Al(1B)-O(2B) = 124.84(12), O(1B)-Al(1B)-O(3B) = 115.79(11), O(2B)-Al(1B)-O(4B) = 84.56(10), O(1B)-Al(1B)-O(4B) = 88.67(11), O(1B)-Al(1B)-N(1B) = 92.11(12), O(4B)-Al(1B)-N(1B) = 175.76(10).

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formed with Al complex **8** in the range 0.063-0.25 mol% (the range wherein most of the experiments were carried out with complexes **5–8** and **12**) with respect to the substrate 1,2-epoxyhexane **13** at 30 °C and an initial CO₂ pressure of 1 MPa (10 bar) with an iodide loading of 0.5 mol%. A reaction temperature of 30 °C was chosen to isolate the activity of the binary catalyst system from that of the background conversion related to the co-catalyst, which occurs at higher temperatures; the iodide nucleophile itself (at 0.5 mol%) does not lead to any observable conversion at this temperature (separately checked; 0% conversion). Activity is only observed at 30° C when both the Al complex **8** and the iodide nucleophile are present; the absence of either component results in a non-observable formation of product. The results of the kinetic stud-



ies are highlighted in Figure 4. The conversion of the substrate

Figure 4. Double logarithmic plot of the order determination in binary catalyst under pseudo-steady-state conditions using 1,2-epoxyhexane/CO₂ as substrates and different concentrations of the Al complex **8** at 30 °C.

was determined by ¹H NMR spectroscopic analysis after 2 h in all experiments by analyzing the crude reaction mixture aliquots. Interestingly, these kinetic studies appear to reveal a pseudo-second-order dependence (2.1; Figure 4) on the (binary) catalyst system. The rate law for this process may be written as [Equation (1)]:

$$Rate = k \cdot [CO_2]^a \cdot [epoxide]^b \cdot [AI]^c \cdot [I]^d$$
(1)

in which, *k* represents the rate constant, and [Al] and [I] the concentration of complex **8** and the iodide, respectively. Assuming steady state conditions at the beginning of the reaction (and thus CO_2 and epoxide concentrations being more or less constant) Equation (1) can be rewritten as Equation (2) and (3)

 $Rate = k_{obs} \cdot [AI]^{c} \cdot [I]^{d} with \ k_{obs} = k \cdot [CO_{2}]^{a} \cdot [epoxide]^{b}$ (2)

Rate = $k_{obs} \cdot [Cat]^e$ with [Cat] = binary catalyst system (3)

Both the Al complex **8** as well as the iodide nucleophile are considered to be equally important for catalytic turnover; they do not act separately and as a result one can assume that c=d and e=c+d. Therefore Equation (2) can be simplified in the form shown in Equation (3). By taking the natural logarithm of Equation (3), Equation (4) is obtained:

$$\ln(\text{Rate}) = \ln(k_{\text{obs}}) + e\ln[\text{Cat}]$$
(4)

The kinetic data from the double logarithmic plot revealed that *e* is close to 2.0 suggesting a (pseudo) second order dependence on the binary catalyst system. As the rate-determining step likely involves the Al complex **8** as well as the iodide, this suggests that only one metal center is actively involved in the mechanistic cycle in contrast with the cycle previously reported for dinuclear [Al(salen)] complexes.^[9d] Also, the computational investigations appear to confirm the requirement of a single Al complex for effective catalytic turnover as will be discussed below in further detail.

To obtain further details about the individual reaction steps and their energy requirements, computational studies were performed by using DFT-based methods and considering a monometallic mechanism. We recently reported on the computational analysis of the full reaction mechanism based on the binary catalyst [Zn(salphen)] D/NBu₄I examining various epoxide substrates.^[15] A number of the previously examined substrates^[17] converted by Al complex 8 required methyl ethyl ketone (MEK) as co-solvent, whereas the former DFT studies (BP86) were carried out with the [Zn(salphen)]-based catalyst by using CH_2CI_2 as medium. Therefore, we have now recalculated the free energies of all transition states (TSs) and intermediates that are involved in the [Zn(salphen)]/NBu₄l-catalyzed reaction using MEK as medium, and have compared these computational results with those obtained for the binary catalyst system 8/NBu₄I using propylene oxide at 25 °C at the B3LYP/6-311G**/LANL2DZ level of theory (see Figure 5 including schematic representations of the involved intermediates and transition states).

Considering a similar type of monometallic mechanism for both types of catalysts, the reaction starts with coordination of the epoxide (propylene oxide) forming an initial complex **IC**. Then, the iodide mediates the ring opening of the coordinated epoxide at the β position; this step involves the breaking of the C_{β}-O bond and the simultaneous formation of a C_{β}-I bond through **TS1** leading to the metal-alkoxide intermediate **Int-1**. It can be observed that this process is energetically more favorable by 21.6 kcal mol⁻¹ for the AI complex **8** compared with the same step involving the [Zn(salphen)] complex. The next step is the insertion of the CO₂ molecule into the metaloxygen bond of intermediate **Int-1**, leading to the formation of linear carbonate **Int-2** through transition state **TS2**.

Unlike for the [Zn(salphen)] catalyst system, for the Al-catalyzed reaction this process involves two possible pathways (i.e., path **a** and path **b**, see Figure 5). Thus, two **TS2** structures could be obtained depending on the relative orientation (cf.,

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Figure 5. Free-energy profiles for the ring-expansion addition of CO_2 to propylene oxide catalyzed by [Zn(salphen)]/NBu₄I (in blue) and AI complex 8/NBu₄I (in red) considering the β pathway (i.e., initial ring opening occurs at the non-substituted carbon center). As a solvent, MEK was considered at 25 °C. IC stands for initial complex formation; FC stands for the intermediate complex having the carbonate product coordinated.

axial or equatorial coordination position of O1 in Figure 6) of the incoming CO₂ molecule with respect the metal center as shown in Figure 6. Interestingly, in these transition states, a hexacoordinated Al center is observed, which helps to decrease the energy requirement of the CO₂ insertion step. Although TS2-a and TS2-b are lower in energy than the corresponding transition state for the [Zn(salphen)] system by 11.3 and 20.2 kcalmol⁻¹, respectively, **TS2-b** would be the most favorable route due to the lower barrier required to afford Int2-b. However, since axial-to-equatorial interconversion between intermediates Int2-a and Int2-b should be fairly easy, it is proposed that these species can undergo isomerization. Intermediate Int2-a was found more stable than Int2-b by 7 kcal mol⁻¹, thus suggesting that the reaction proceeds through path a. Following the reaction coordinate, the subsequent step is ring closing, which occurs through the non-coordinating O-atom (O2) of the carbonate fragment (Figure 6) through TS3 giving the final intermediate FC. Herein, the transition states TS3-a and TS3-b also could afford intermediates FC-a and FC-b, respectively. Thus, path a still continues to be the most likely pathway because of the higher stability of TS3-a over TS3-b by 14.1 kcal mol⁻¹, and also because the lower absolute value of most other barriers. In addition, path a has an activation energy of 34.2 kcal mol⁻¹, with the CO₂ insertion being the rate-limiting step; whereas for path b, a higher activation energy was found (39.3 kcalmol⁻¹), and the rate-limiting step corresponds to the ring-closing step. Once the coordinated cyclic carbonate is formed, it is released from the complex allowing for further epoxide turnover. The overall reaction is exergonic with a release of 2.4 kcal mol⁻¹ in the case of both catalyst systems.

The competing mechanism was also examined by using the energetic span (δE) model.^[29] Computed free-energy spans for path **a** and path **b** are fairly high (δE = 34.2 and 39.3 kcal mol⁻¹, respectively); these are identical to the activation barrier of each pathway. **IC** was found to be the TOF-determining intermediate (TDI) for both catalytic cycles, and **TS2-a** and **TS3-b** correspond to the TOF-determining TS (TDTS) of the alternative cycles. On the other hand, by mixing both pathways (considering the most stable intermediates and **TS**), a smaller energetic span of 25.3 kcal mol⁻¹ was obtained, in which **IC** is the TDI. However, the exact position of the TDTS is difficult to distinguish because of the small difference between **TS2-b** (15.4 kcal mol⁻¹) and **TS3-a** (15.3 kcal mol⁻¹). Consequently, a similar degree of TOF control of 0.54 for **TS2-b** and 0.46 for **TS3-a** is observed.

The energetic span of the catalytic cycle involving the [Zn-(salphen)] complex **D** was found to be higher (δE = 35.6 kcal mol⁻¹) compared with the energetic span of the binary Al-containing catalyst system. The latter, together with the fact that for Al complex **8** all the involved **TSs** and intermediates are significantly less energy-demanding, is in line with the observation that complex **8** is a much more efficient catalyst than [Zn-(salphen)] **D** (see also Table 1 for experimental evidence). Of particular note is the fact that the initial coordination of the epoxide in the case of the [Zn(salphen)] complex is endothermic (+5.6 kcal mol⁻¹), whereas the coordination of propylene oxide to Al complex **8** is exothermic by 9.9 kcal mol⁻¹. This



Figure 6. Optimized structures of the transition states **TS1-TS3** for the Al complex **8**/NBu₄l catalyzed reaction, together with the most relevant calculated distances (in Å) and the values of the negative (imaginary) vibrational frequencies.

result also demonstrates that **8** is a much more powerful Lewis acid mediator than [Zn(salphen)] complex **D**.

Conclusion

We have reported on a new family of powerful [Al{amino-tris-(phenolate)]] catalysts for the addition of CO₂ to epoxides with initial activities among the highest reported to date in this area and turnover numbers exceeding 100000. Furthermore, the most active catalyst based on Al complex **8** is a highly robust system as shown by various stability and activity studies. Kinetic data and DFT calculations appear to support that a monometallic mechanism is likely operative, with the CO₂ insertion step being rate-limiting and the initial coordination of the epoxide to the Lewis acidic center more favorable by around 15 kcal mol⁻¹ compared with our previously reported [Zn(salphen)]/NBu₄l binary catalyst system. The potential of Al complex 8 to form a less energy-demanding hexacoordinated transition state is a unique feature (cf., DFT studies) and together with its associated lower energetic span these are features that help to explain the higher catalytic potential of this system versus the catalyst based on [Zn(salphen)] **D**. The simple access to Al complex 8 and its high potential as a strong Lewis acid mediator make this system a highly potent system for other types of Lewis acid-mediated transformations such as the formation of polycarbonates under appropriate conditions. Studies towards this objective are currently ongoing in our laboratory.

Experimental Section

General Procedures

All epoxide substrates and reagents were commercially available and were used as received. Carbon dioxide was purchased from PRAXAIR and used without further purification. Solvents used in the synthesis of the complexes were dried using an Innovative Technology PURE SOLV solvent purification system. The ligands 1,^[18] 2,^[18] 3,^[19] and 4^[20] were prepared as described previously although 4 was isolated by a modified procedure. The synthesis of [Al{amino-tris(phenolate)}] complexes was carried out using standard vacuum line and Schlenk or cannular techniques and once synthesized the products were stored in a vial kept in air. ¹H NMR spectra were recorded on a Bruker AV-400 or AV-500 spectrometer and referenced to the residual NMR solvent signals. Elemental analysis was performed by the Unidád de Análisis Elemental at the Universidad de Santiago de Compostela. Mass spectrometric analysis and X-ray diffraction studies were performed by the Research Support Group at the ICIQ.

Syntheses

Ligand precursor 4: 2,4-dichlorophenol (4.0 g, 24.5 mmol) and hexamethylene tetramine (HMTA; 1.2 g, 8.5 mmol) were heated at 110°C for 2.5 h. Cold MeOH (20 mL) was then added to the yellow solution before being kept at 0°C for 30 min. The solution was sonicated and the precipitate which subsequently formed was filtered off and dried under vacuum. The white solid was found to be a co-crystal with the formula 4.HMTA (790 mg, 14%). Crystals suitable for single-crystal X-ray diffraction studies of this co-crystallized adduct were obtained by storing the MeOH solution at $-30\,^{\circ}\text{C}$ for a further 3 days. ¹H NMR (400 MHz, 298 K, CDCl₃): $\delta =$ 7.23 (d, ${}^{3}J_{HH} = 2.3$ Hz, 3 H, ArH), 7.01 (d, ${}^{3}J_{HH} = 2.3$ Hz, 3 H, ArH), 6.92 (brs, 3H, ArOH), 4.80 (s, 12H, NCH₂N), 3.69 ppm (s, 6H, ArCH₂N); ¹³C{¹H} NMR (125 MHz, 298 K, CDCl₃): $\delta = 150.50$, 129.03, 128.63, 125.22, 124.19, 121.16 (all aromatic C), 74.34 (NCH₂N), 55.59 ppm (ArCH₂N); elemental analysis calcd (%) for C₂₈H₂₉N₅O₃Cl₆: C 47.53, H 3.99, N 10.27; found: C 47.33, H 3.86, N 10.39. The resulting 4-HMTA compound was then suspended in water (20 mL) and acidified to pH 2 with HCl (37% in water) with stirring before being basified to pH 11, at which point the compound was fully dissolved. The solution was neutralized using HCl, during which the product precipitated. It was then filtered and dried under vacuum. The resulting yellowish solid was dissolved in a small amount of CH₂Cl₂ and hexane added to precipitate the product, which was finally filtered and dried to yield a white powder (680 mg, 37%). ¹H NMR (400 MHz, 298 K, CDCl₃): δ = 7.24 (d, ³ J_{HH} = 2.4 Hz, 3 H, ArH), 7.04 (d, ³J_{HH}=2.4 Hz, 3 H, ArH), 5.53 (brs, 3 H, ArOH), 3.73 ppm (s, 6H, ArCH₂N); ¹³C{¹H} NMR (125 MHz, 298 K,



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CDCl₃): δ = 149.83, 129.10, 128.54, 124.84, 124.72, 121.09 (all aromatic C), 55.35 ppm (ArCH₂N); MS (ESI, MeOH): *m/z* calcd: 540.9 [*M*]⁺; found: 541. elemental analysis calcd (%) for C₂₁H₁₅NO₃Cl₆: C 46.53, H 2.79, N 2.58; found: C 46.73, H 2.73, N 2.57.

Al complex 5^[22a]: [AlMe₃] (2 mu in heptane, 1.19 mL, 2.38 mmol) was slowly added to a solution of ligand precursor 1 (1.0 g, 2.38 mmol) in THF (20 mL). The solution was stirred at RT for 2 h and then concentrated. Hexane was added to the concentrate resulting in precipitation of the complex, which was isolated by filtration and further dried under vacuum to yield a white powder (963 mg, 78%). ¹H NMR (400 MHz, 298 K, CDCl₃): δ = 6.90 (d, ³J_{HH} = 1.4 Hz, 3H, ArH), 6.63 (d, ³J_{HH} = 1.4 Hz, 3H, ArH), 4.59 (br, 4H, THF), 4.28 (br d, ²J_{HH} = 13.5 Hz, 3H, ArCH₂N), 2.86 (br d, ²J_{HH} = 13.5 Hz, 3H, ArCH₂N), 2.20 (s, 9H, ArCH₃), 2.21 (s, 9H, ArCH₃), 2.18 ppm (br, 4H, THF); ¹³C{¹H} NMR (125 MHz, 298 K, CDCl₃): δ = 154.29, 131.02, 126.97, 126.89, 125.83, 120.63 (all aromatic C), 71.31 (THF), 58.67 (ArCH₂N), 25.60 (THF), 20.40 (ArCH₃), 16.98 ppm (ArCH₃); MS (MALDI+, dctb): *m/z* calcd: 443.2 [*M*-THF]⁺; found: 443.

Al complex 6^[22b]: This compound was prepared in a similar manner to 5 by treatment of ligand precursor 2 (1.0 g, 1.49 mmol) with [AlMe₃] (2 μ in heptane, 0.75 mL, 1.49 mmol) to yield a white powder (869 mg, 76%). ¹H NMR (400 MHz, 298 K, CDCl₃): δ = 7.25 (d, ³J_{HH} = 2.5 Hz, 3 H, ArH), 6.87 (d, ³J_{HH} = 2.5 Hz, 3 H, ArH), 4.36–4.27 (m, 7H; overlapping ArCH₂N and THF), 2.95 (brs, 3 H, ArCH₂N), 2.06 (m, 4H, THF), 1.43 (s, 27 H, ArC(CH₃)₃), 1.29 ppm (s, 27 H, ArC(CH₃)₃); 1³C{¹H} NMR (125 MHz, 298 K, CDCl₃): δ = 154.82, 139.37, 137.11, 123.78, 123.60, 121.43 (all aromatic C), 70.26 (THF), 58.83 (ArC(L₃N)), 34.88 (ArC(CH₃)₃), 34.03 (ArC(CH₃)₃), 31.71 (ArC(CH₃)₃), 29.70 (ArC(CH₃)₃), 25.42 ppm (THF); MS (MALDI +, dctb): *m/z* calcd: 695.5 [*M*-THF]⁺; found: 695.

Al complex 7: This compound was prepared in a similar manner to 5 by treatment of ligand precursor **3** (350 mg, 1.04 mmol) with [AlMe₃] (2 μ in heptane, 0.51 mL, 1.04 mmol) to yield a white powder (286 mg, 76%). ¹H NMR (400 MHz, 298 K, [D₃]pyridine): $\delta = 7.37$ (ddd, ³ $J_{HH} = 7.6$ and 7.7, ⁴ $J_{HH} = 1.5$ Hz, 3 H, ArH), 7.18 (dd, ³ $J_{HH} = 7.6$, ⁴ $J_{HH} = 1.5$ Hz, 3 H, ArH), 7.06 (dd, ³ $J_{HH} = 7.7$, ⁴ $J_{HH} = 0.9$ Hz, 3 H, ArH), 6.92 (ddd, ³ $J_{HH} = 7.6$ and 7.7, ⁴ $J_{HH} = 0.9$ Hz, 3 H, ArH), 4.49 (brs, 3 H, ArCH₂N), 3.14 ppm (brs, 3 H, ArCH₂N); ¹³C{¹H} NMR (125 MHz, 298 K, [D₃]pyridine): $\delta = 160.21$, 130.77, 130.52, 123.50, 120.69, 119.09 (all aromatic C), 59.46 ppm (ArCH₂N); MS (MALDI +, dctb): *m/z* calcd: 359.11 [*M*]⁺; found: 359.4; elemental analysis calcd (%) for C₂₁H₁₈NO₃Al·H₂O· $J/_4$ (C₆H₁₄): C 67.74, H 5.94, N 3.51; found: C 67.41, H 5.95, N 3.25.

Al complex 8: This compound was prepared in a similar manner to 5 by treatment of ligand precursor 4 (500 mg, 0.92 mmol) with [AlMe₃] (2 m in heptane, 0.46 mL, 0.92 mmol) to yield a white powder (350 mg, 60%). Crystals suitable for single-crystal X-ray diffraction studies were obtained by layering of a concentrated THF solution of the complex with hexane. ¹H NMR (400 MHz, 298 K, CDCl₃): δ = 7.33 (d, ³_{HH} = 2.6 Hz, 3 H, ArH), 6.90 (d, ³_{JHH} = 2.6 Hz, 3 H, ArH), 4.69 (m, 4H, THF), 4.18 (br d, ²_{JHH} = 13.3 Hz, 3 H, ArCH₂N), 2.95 (br d, ²_{JHH} = 13.3 Hz, 3 H, ArCH₂N), 2.23 ppm (m, 4 H, THF); ¹³C{¹H} NMR (125 MHz, 298 K, CDCl₃): δ = 152.46, 129.75, 127.13, 124.68, 123.08, 122.16 (all aromatic C), 72.38 (THF), 58.25 (ArCH₂N), 25.48 ppm (THF); MS (MALDI +, dctb): *m/z* calcd: 564.9 [*M*-THF]⁺; found: 565; elemental analysis calcd (%) for C₂₅H₂₀AlCl₆NO₄: C 47.05, H 3.16, N 2.19; found: C 46.75, H 3.22, N 2.12.

Ligand precursor 11: NEt₃ (123 μ L, 1.76 mmol) was added with stirring to a solution of 6,6'-(azanediyl-bis(methylene))-bis(2,4-ditert-butylphenol) (0.80 g, 1.76 mmol) and 2-(bromomethyl)-4-nitrophenol (204 mg, 1.76 mmol) in THF (20 mL). The reaction mixture was stirred at reflux temperature for 18 h and filtered after cooling. The volatiles were removed from the filtrate and the obtained residue was purified by column chromatography (EtOAc/hexane, 20:80 v/v) to yield a yellow powder (721 mg, 68%). ¹H NMR (400 MHz, 298 K, CDCl₃): $\delta = 8.04$ (dd, ³J_{HH} = 8.9 Hz, ⁴J_{HH} = 2.8 Hz 1 H, ArH), 7.96 (d, ⁴J_{HH} = 2.8 Hz, 1 H, ArH), 7.24 (d, ⁴J_{HH} = 2.4 Hz, 2 H, ArH), 6.98 (d, ⁴J_{HH} = 2.4 Hz, 2 H, ArH), 6.86 (d, ³J_{HH} = 8.9 Hz, 1 H, ArH), 5.91 (br s, 3 H, ArOH), 3.85 (s, 2 H, ArCH₂N), 3.78 (s, 4 H, ArCH₂N), 1.41 (s, 18H, ArC(CH₃)₃), 1.28 ppm (s, 18H, ArC(CH₃)₃); ¹³C{¹H} NMR (125 MHz, 298 K, CDCl₃): $\delta = 162.40$, 151.31, 142.59, 140.41, 135.92, 126.45, 125.69, 125.62, 124.20, 123.19, 121.68, 116.73 (all aromatic C), 57.68, 56.94 (both ArCH₂N), 34.60, 34.19 (both ArC(CH₃)₃), 31.55, 29.88 ppm (both ArC(CH₃)₃); MS (ESI–, MeOH): *m/z* calcd: 603.4 [*M*-H]⁻; found: 603; elemental analysis calcd (%) for C₃₇H₃₂N₂O₅-¹/₂H₂O: C 72.40, H 8.70, N 4.56; found: C 72.57, H 8.63, N 4.47.

Al complex 12: This compound was prepared in a similar manner to 5 by treatment of 11 (500 mg, 0.82 mmol) with $[AIMe_3]$ (2 μ in heptane, 0.41 mL, 0.82 mmol) to yield a white powder (422 mg, 78%). Crystals suitable for single-crystal X-ray diffraction studies were obtained by layering of a concentrated THF solution of the complex with hexane. ¹H NMR (400 MHz, 298 K, [D₅]pyridine): $\delta =$ 8.27 (dd, ${}^{3}J_{HH} = 8.9$, ${}^{4}J_{HH} = 2.8$ Hz, 1 H, ArH), 8.13 (d, ${}^{4}J_{HH} = 2.8$ Hz, 1 H, ArH), 7.51 (d, ${}^{4}J_{HH} = 2.3$ Hz, 2H, ArH), 7.12 (brs, 2H, ArH), 7.03 (d, ³J_{HH} = 8.9 Hz, 1 H, ArH), 4.15 (brs, 3 H, ArCH₂N), 3.25 (brs, 3 H, ArCH₂N), 1.43 (s, 18H, ArC(CH₃)₃), 1.34 ppm (s, 18H, ArC(CH₃)₃); ¹³C{¹H} NMR (125 MHz, 298 K, [D₅]pyridine): $\delta = 165.44$, 155.13, 139.77, 139.07, 137.48, 135.53, 125.82, 125.75, 124.30, 123.70, 123.53, 119.59 (all aromatic C), 58.83, 56.90 (both ArCH₂N), 34.61, 34.11 (both ArC(CH₃)₃), 31.71, 29.52 ppm (both ArC(CH₃)₃); m/z calcd: 628.35 [M]⁺; found: 628.4; elemental analysis calcd (%) for C₃₇H₄₉N₂O₅Al·H₂O·¹/₂(C₆H₁₄): C 69.64, H 8.47, N 3.91; found: C 69.59, H 8.78, N 3.80.

Typical catalysis procedure

1,2-epoxyhexane (1.0 g), the aluminium complex (0.005 mol%), and Bu₄NI (0.025 mol%) were charged into a stainless steel autoclave (30 mL). The autoclave was then subjected to three cycles of pressurization and depressurization with CO₂ (0.5 MPa, 5 bar), before final stabilization of the pressure to 1.0 MPa (10 bar). The autoclave was sealed and heated to the required temperature and left stirring for 2 h. An aliquot of the resulting mixture was taken and conversion analyzed by means of ¹H NMR spectroscopy using CDCl₃ as the solvent. The identity of the cyclic carbonate product was confirmed by comparison to previously reported literature values. For a photo of the reactor please refer to the Supporting Information.

Kinetic experiments

The AMTEC vessels were charged with NBu₄I and connected to the hardware. A leak test was first performed with 1.5 MPa (15 bar) of CO_2 , with the pressure finally reduced to 0.2 MPa (2 bar). The reactors were filled with 0.4 MPa (4 bar) of CO_2 , and degassed to 2 bar, and this cycle was repeated three times. A solution of the Al catalyst **8** in 1,2-epoxyhexane **13** (1.20 mL) was injected into the reaction vessel, the pressure was raised to 1.5 MPa (15 bar), and the temperature was set to 30 °C. The reactions were stirred for 2 h at 600 rpm. The stirrer was then stopped and degassed. Hereafter, an aliquot of the resultant reaction mixture was taken and the conversion was determined by means of ¹H NMR spectroscopy using CDCl₃ as the solvent. For a photo of the reactor system please refer to the Supporting Information.

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X-ray diffraction studies

The measured crystals were stable under atmospheric conditions; nevertheless they were treated under inert conditions immersed in perfluoropolyether as protecting oil for manipulation. Data Collection: Measurements were made on a Bruker-Nonius diffractometer equipped with an APPEX II 4K CCD area detector, a FR591 rotating anode with Mo_{ka} radiation, Montel mirrors and a Kryoflex low temperature device (T=-173 °C). Full-sphere data collection was used with ω and ϕ scans. Programs used: Data collection Apex2V2011.3 (Bruker-Nonius 2008), data reduction Saint + Version 7.60A (Bruker AXS 2008) and absorption correction SADABS V. 2008–1 (2008). Structure Solution: SHELXTL Version 6.10 (Sheldrick, 2000) was used. Structure Refinement: SHELXTL-97-UNIX VERSION.

Crystallographic details for Al-complex 8-THF: Formula: $C_{25}H_{20}Cl_6NO_4Al; M_w = 638.10$; crystal size $0.30 \times 0.15 \times 0.05 \text{ mm}^3$; orthorhombic; space group *Pbca*; a = 17.2360(19), b = 15.7823(17), c = 19.047(2) Å; $a = \beta = \gamma = 90.0^{\circ}$; $V = 5181.2(10)^{\circ}$; Z = 8; $\rho_{calcd} =$ 1.636 mg m^{-13} ; $\mu(Mo_{Ka}) = 0.733 \text{ mm}^{-1}$; T = 100(2) K; $\theta(\text{min/max}) =$ 2.05/26.25; F(000) = 2592; 93.683 reflections collected; 5209 unique reflections ($R_{int} = 0.0535$); absorption correction empirical; refinement method: full-matrix least-squares on F^2 ; data/restraints/parameters: 5209/86/364; GoF on $F^2 = 1.074$; $R_1 = 0.0287$ and $wR_2 =$ 0.0663 [$I > 2\sigma(I)$]; $R_1 = 0.0404$ and $wR_2 = 0.0728$ (all data); largest diff. peak and hole: 0.333 and $-0.305 \text{ e}^3 \text{ Å}^{-3}$. CCDC-902502 contains the supplementary crystallographic data for this structure. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic details for Al complex 12: Formula: $C_{95}H_{122}N_4O_{10}AI_2$; $M_w = 1533.93$; crystal size $0.15 \times 0.05 \times 0.05$ mm³; monoclinic; space group P21/c; a=29.417(3), b=10.9419(12), c= 30.189(3) Å; $\alpha = \gamma = 90$, $\beta = 118.896(4)$; $V = 8507.2(17)^{\circ}$; Z = 4; $\rho_{\text{calcd}} = 1.198 \text{ mg m}^{-13}; \ \mu(\text{Mo}_{\text{K}\alpha}) = 0.095 \text{ mm}^{-1}; \ T = 100(2) \text{ K}; \ \theta(\text{min}/$ max) = 0.79/24.80; F(000) = 3304; 79528 reflections collected; 14140 unique reflections ($R_{int} = 0.1388$); absorption correction empirical; refinement method: full-matrix least-squares on F²; data/restraints/parameters: 14140/441/1127; GoF on $F^2 = 1.015$; $R_1 =$ 0.0643 and $wR_2 = 0.1280 [I > 2\sigma(I)]$; $R_1 = 0.1523$ and $wR_2 = 0.1658$ (all data); largest diff. peak and hole: 0.546 and $-0.554 e^{3} Å^{-3}$. This structure is a toluene solvate and has a *tert*-butyl group disordered. CCDC-938872 contains the supplementary crystallographic data for this structure. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Crystallographic details for Al-complex 8-oxetane: Formula: $C_{25}H_{19.75}NO_{4.25}CI_{6.75}AI; M_w = 668.44; crystal size <math>0.50 \times 0.05 \times$ 0.05 mm³; triclinic; space group P-1; a = 13.702(4), b = 14.048(4), c = 14.784(3) Å; $\alpha = 94.689(7)$, $\beta = 93.252(7)$, $\gamma = 100.374(10)^{\circ}$; V =2782.5(12) °; Z=4; $ho_{
m calcd}$ = 1.596 mg m⁻¹³; μ (Mo_{Ka}) = 0.757 mm⁻¹; T = 100(2) K; $\theta(\min/\max) = 1.39/28.23$; F(000) = 1354; 21763 reflections collected; 21763 unique reflections ($R_{int} = 0.000$); absorption correction empirical; refinement method: full-matrix least-squares on *F*²; data/restraints/parameters: 21763/72/758; GoF on *F*²=1.021; $R_1 = 0.0570$ and $wR_2 = 0.1528$ [$l > 2\sigma(l)$]; $R_1 = 0.0928$ and $wR_2 = 0.0570$ 0.1898 (all data); largest diff. peak and hole: 0.881 and -0.940e³Å⁻³. The disorder in co-crystallized solvent molecules and the coordinated oxetane was done with TWINABS.^[30] CCDC-938873 contains the supplementary crystallographic data for this structure. . These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The structure for **4**-HMTA can be found in the Supporting Information; CCDC-938871 contains the supplementary crystallographic data for this structure. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Computational details

All calculations were performed by using the Gaussian 09 package^[31] with the hybrid B3LYP functional.^[32] The standard 6–311G(d,p) basis set was used to describe the H, C, N, and O atoms. The relativistic effective core pseudo potential LANL2DZ was used, together with its associated basis set, for Al, Zn, Cl, and I atoms. Full geometry optimizations were performed without constrains. The nature of the stationary points encountered was characterized either as minima or transition states by means of harmonic vibrational frequencies analysis. The zero-point, thermal, and entropy corrections were evaluated to compute enthalpies and Gibbs free energies (T=298 K, p=1 bar). Solvent effects for MEK have been introduced by using the Polarizable Continuum Model (PCM).

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