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Article

Ti and Zr amino-tris(phenolate) catalysts for the synthesis of cyclic carbonates from CO_2 and epoxides

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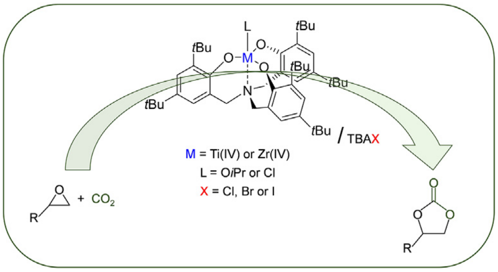
HIGHLIGHTS

- Ti and Zr amino-tris(phenolate) complexes in combination with TBA*X* (*X* = Cl, Br, I) are active catalysts for the synthesis of cyclic carbonates.
- First report of the application of Zr amino-tris(phenolate) complexes to catalyse the reaction of CO_2 with epoxides.
- Remarkably high TONs were obtained with the Zr amino-tris(phenolate) complex with isopropoxide as axial ligand.
- $\geq$ 98% selectivity towards the cyclic carbonate products was obtained with all terminal epoxides.

GRAPHICAL ABSTRACT



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ABSTRACT

Herein, we report the application of four amino-tris(phenolate)-based metal complexes incorporating Ti(IV) or Zr(IV) centres (**2a-3b**) as homogeneous catalysts for the conversion of CO_2 and epoxides into cyclic carbonates. The four complexes were synthesised, characterised and then evaluated in combination with tetrabutylammonium iodide, bromide or chloride as binary catalytic systems for the reaction of CO_2 with 1,2-epoxyhexane as epoxide substrate at 12 bar CO_2 pressure and 90 °C for 2 h. The catalytic systems comprising the two Ti(IV) complexes (**2a** and **2b**) showed similar performance. One notable exception was the catalytic system consisting of titanium complex **2b**, bearing an axial Cl-ligand, and tetrabutylammonium chloride, which displayed higher catalytic activity compared to other titanium-based systems. Even higher activity was achieved with Zr(IV) complex **3a,** bearing an axial isopropoxide ligand, which reached turnover numbers (TON_{metal}) up to 1920 for the reaction of CO_2 with 1,2-epoxyhexane at 12 bar CO_2 pressure and 90 °C for 2 h. This performance is comparable with that of state-of-the-art catalysts for this reaction. The catalytic system consisting of complex **3a** and tetrabutylammonium bromide was explored further by investigating its applicability with a broad substrate scope, achieving quantitative conversion of several epoxides with CO_2 into cyclic carbonate products at 90 °C and 12 bar CO_2 pressure for 18 h. The selectivity towards the cyclic carbonate products was $\geq$ 98% for all studied terminal epoxides and $\geq$ 80% for all examined cyclohexene-type epoxides.

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1. Introduction

In the context of the sustainable synthesis of chemical products, the use of CO_2 as feedstock is an attractive option as it allows the valorisation of a waste, greenhouse gas generated worldwide in enormous amounts. The challenges within CO_2-conversion are related to the high thermodynamic and kinetic stability of this molecule [1,2]. Reaction with high free-energy substrates such as epoxides and hydrogen can be employed to overcome the thermodynamic stability of CO_2, while catalysts are required to enhance the reaction kinetics in order to reach high reaction rates. Among the different routes for CO_2-utilisation [3–12], the reaction with epoxides to form cyclic or polymeric carbonates (Scheme 1) has received considerable attention [2,13–34]. Already since the first half of the 20th century, two widely-used carbonate compounds, ethylene carbonate and propylene carbonate, have been produced *via* the reaction of CO_2 with ethylene oxide and propylene oxide, respectively [35,36]. These two cyclic carbonates are employed in a variety of commercial applications, including in electrolytes for lithium-based batteries [37], as green polar aprotic solvents [38] and as intermediates for the synthesis of other chemicals, including polymers such as bisphenol-A-based polycarbonates [39] and polyurethanes [40]. The other possible product of the reaction between epoxides and CO_2, *i.e.* the polycarbonates, are commercially applied as polyols for polyurethane synthesis [41], as sacrificial binders for the production of ceramics and adhesives [42], and are being investigated for application as packaging material [43], performance coatings [44] and for utilisation in biomedical applications [45,46].

Numerous homogeneous catalytic systems have been developed for promoting the reaction of CO_2 with epoxides. The most studied among these catalysts consist of binary systems comprising a Lewis acid compound that coordinates and activates the epoxide, typically a metal-organic complex, and a Lewis base, which acts as a nucleophile in the ring-opening of the epoxide [14,47]. In the proposed reaction mechanism (Scheme 2), the titanium and zirconium complexes presented in this work act as Lewis acid compounds. In line with previous reports and based on our results (*vide infra*), we propose that during the catalytic cycle these complexes adopt a conformation in which the axial ligand remains coordinated to the metal centre [48].

A wide range of metal complexes in which the metal centre acts as Lewis acid active site have been studied, with the most common metals being zinc, chromium, cobalt, magnesium, aluminium and iron [49–63]. Together with the metal species, the nature of the organic ligand plays a key role in determining the activity of the complex and the selectivity towards either the cyclic or the polymeric carbonate. Well-known complexes researched for this reaction include metalloporphyrins [64,65], metal-salen/salphen complexes [66–71], bimetallic macrocyclic phenolates [72–74], and amino-bis/tris(phenolate)s [75–81]. Particularly, iron and aluminium amino-tris(phenolate) metal complexes have been found to display high activity towards the reaction of CO_2 with epoxides, with extremely high turnover frequency reached with the binary system consisting of aluminium amino-tris(phenolate) and bis(triphenylphosphine)iminium bromide (PPNBr) [75]. The remarkably high activity of iron and aluminium complexes prepared with amino-tris(phenolate) ligands inspired us to study this type of ligand in combination with titanium and zirconium as Lewis acid catalysts for the reaction of CO_2 with epoxides. So far, group(IV) metals such as titanium [82–95] and zirconium [82,91,95–97] have received limited attention concerning their application as homogeneous catalysts for this reaction. In this work, we report the synthesis of four amino-tris(phenolate)-type complexes with Ti(IV) or Zr(IV) metal centres (Scheme 3, complexes **2a-3b**) and demonstrate their promising catalytic activity in the conversion of CO_2 to cyclic carbonates employing a broad scope of epoxides. To the best of our knowledge, this is the first time that the synthesis of a zirconium amino-tris(phenolate) complex bearing an axial Cl-ligand is reported and also the first time that Zr-amino-tris(phenolate) complexes are reported for application as catalysts for the reaction of CO_2 with epoxides. Among the Ti-amino-tris(phenolate) complexes, **2a** has been recently reported in combination with PPNCl as catalytic system for the copolymerisation of CO_2 with cyclohexene oxide [48], whereas the activity of complex **2b** in this reaction was so far unexplored.

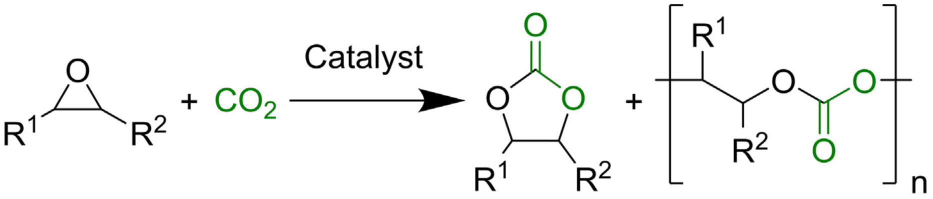
2. Experimental

2.1. Materials

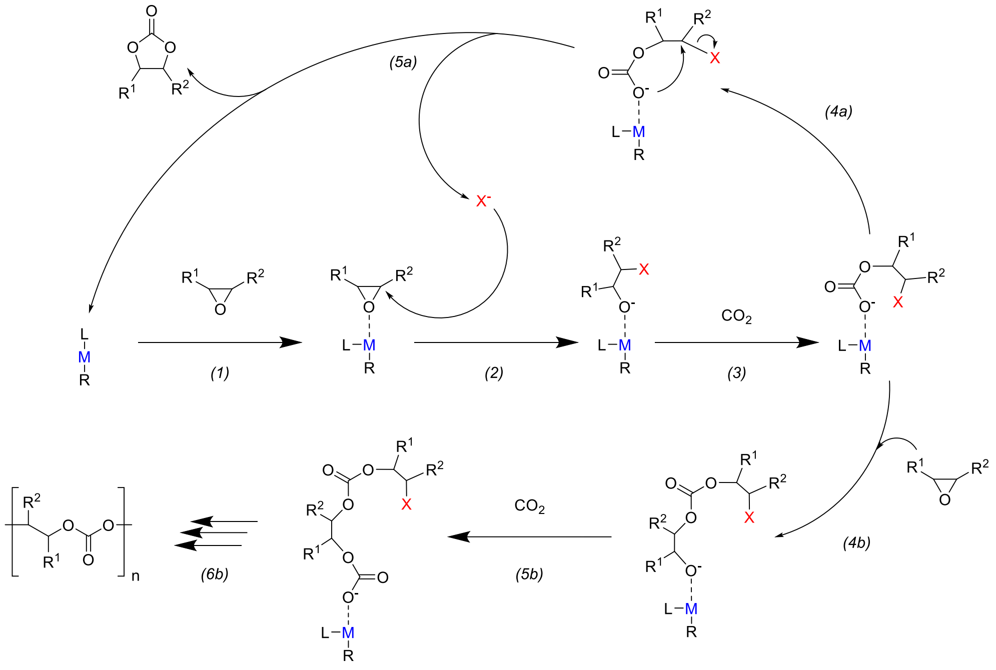
2,4-Di-*tert*-butylphenol (99%, Sigma-Aldrich), hexamethylenetetramine (≥ 99.8%, Sigma-Aldrich), aqueous formaldehyde (37 wt%, Sigma-Aldrich), titanium(IV) isopropoxide (97%, Sigma-Aldrich), benzene (≥ 99.0%, Sigma-Aldrich), chloroform-d (99.8%, Sigma-Aldrich), hydrochloric acid (37 wt%–38 wt%, Boom), magnesium sulphate (Boom), chloroform (≥ 99.8%, Macron), diethyl ether (≥ 99.0%, Macron), toluene (≥ 99.5%, Macron), hexane (≥ 95%, Macron), 1,2-epoxyhexane (97%, Sigma-Aldrich), cyclohexene oxide (97%, Sigma-Aldrich), 4-vinyl-1-cyclohexene-1,2-epoxide (mixture of isomers, 98%, Sigma-Aldrich), tetrabutylammonium iodide (≥ 99%, Sigma-Aldrich), tetrabutylammonium bromide (≥ 99%, Sigma-Aldrich), tetrabutylammonium chloride (≥ 97%, Sigma-Aldrich), mesitylene (98%, Sigma-Aldrich), epichlorohydrin (≥ 99%, Sigma-Aldrich), allyl glycidyl ether (≥ 99%, Sigma-Aldrich), styrene oxide (97%, Sigma-Aldrich), (+)-limonene oxide (mixture of *cis* and *trans*, 97%, Sigma-Aldrich), compressed nitrogen gas (N_2, ≥ 99.999%, Linde Gas) and compressed carbon dioxide (≥ 99.7%, Linde Gas) were used as received. Zirconium(IV) isopropoxide isopropanol complex (99.9%, Alfa Aesar) and zirconium(IV) chloride (> 99.5%, Alfa Aesar) were stored and used under N_2 atmosphere. Dry toluene, diethyl ether, hexane, and tetrahydrofuran were obtained by passing these solvents through a series of drying columns before storing them under nitrogen atmosphere. Tetrahydrofuran-d_8 (Euriso-top) and benzene-d_6 (> 99.8%, Sigma-Aldrich) were dried over a Na/K alloy, vacuum transferred to a Schlenk flask and stored under N_2. All air- and moisture-sensitive compounds were handled and stored under N_2 atmosphere using standard Schlenk and glovebox techniques.

2.2. Equipment

^1H NMR spectra were recorded on a Varian Oxford 300 MHz apparatus or on a Bruker 600 MHz apparatus with 64 scans and a relaxation time of 10 s, using chloroform-d, benzene-d_6, or tetrahydrofuran-d_8 as solvents. ^{13}C NMR spectra were recorded on a Bruker 600 MHz apparatus with 2048 scans and a relaxation time of 1 s or on a 300 MHz Varian Mercury PlusNMR apparatus with 8192 scans and a relaxation time of 1 s, using chloroform-d, benzene-d_6, or tetrahydrofuran-d_8 as solvents. ^1H NMR and ^{13}C NMR spectra were referenced using residual solvent resonances, ppm values are reported relative to tetramethylsilane (TMS). FT-



Scheme 1. General scheme of the reaction of CO_2 with epoxides, yielding cyclic and/or polymeric carbonates.



Scheme 2. Proposed mechanism of the formation of cyclic carbonates from the reaction of CO_2 with epoxides catalysed by the binary systems presented in this work, consisting of a metal complex (R-*M*-L, where *M* = Ti or Zr, R is the amino-tris(phenolate) ligand and L is the axial ligand, *i.e.* O*i*Pr or Cl; see Scheme 3 for the actual structure of the complex) with Lewis acid character for activating the epoxide towards the nucleophilic attack by a Lewis base (X^- = Cl^-, Br^- or I^-, originating from TBA*X*).

IR spectra were recorded using a Shimadzu IRtracer-100 equipped with an ATR sample unit with a resolution of 4 cm^{-1}, a wavenumber range of 4000–600 cm^{-1} and 64 scans.

2.3. Synthesis of the amino-tBu-tris(phenolate) ligand (1)

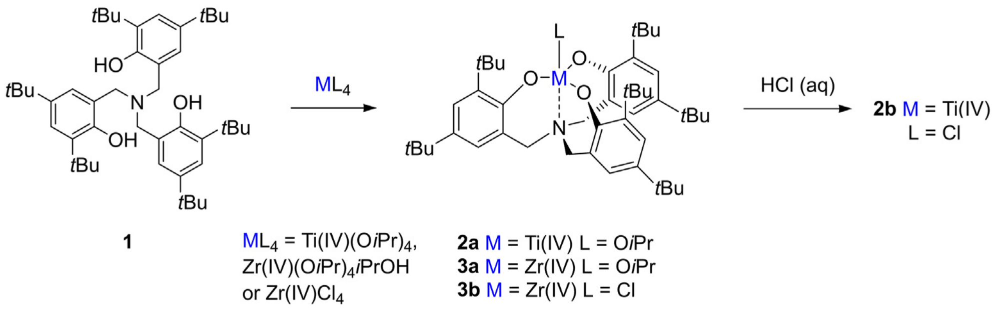
The synthesis of the ligand was performed according to a literature procedure [98]. Briefly, 2,4-di-*tert*-butylphenol (8.25 g, 40 mmol), hexamethylenetetramine (0.47 g, 3.3 mmol) and 37% aqueous formaldehyde (1.21 g, 14.2 mmol) were added into a 250 mL round-bottom flask equipped with a reflux condenser. The mixture was stirred at 125 °C for 48 h, after which the reaction was quenched with $CHCl_3$ (100 mL). The organic layer was washed with demineralised water (3 × 100 mL) and subsequently dried over $MgSO_4$. The organic phase was concentrated using rotary evaporation and the desired product was obtained as a white solid (6.46 g, 72%) after recrystallisation from diethyl ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, 3H, ArH), 6.99 (d, 3H, ArH), 6.56 (s, 3H, ArOH), 3.65 (s, 6H, CH), 1.40 (s, 27H, *t*Bu), 1.27 (s, 27H, *t*Bu). ^{13}C NMR (300 MHz, $CDCl_3$): δ 151.5, 142.2, 136.5, 125.7, 124.1, 121.9, 56.7, 35.0, 34.3, 31.7, 29.8. The full spectra can be found in the SI (Figs. S1 and S2).

2.4. Synthesis of titanium(IV) amino-tBu-tris(phenolate) isopropoxide (2a)

Titanium(IV) amino-*t*Bu-tris(phenolate) isopropoxide (**2a**) was synthesised according to a method from the literature [98]. A mixture of the amino-*t*Bu-tris(phenolate) ligand **1** (1.18 g, 1.75 mmol) and dry diethyl ether (50 mL) were added to a 100 mL three-necked round-bottom flask under N_2 atmosphere. Whilst stirring, titanium(IV) isopropoxide (0.52 mL, 1.75 mmol) was slowly added to the solution. The mixture was stirred at room temperature for 3 h and subsequently concentrated under reduced pressure, after which the obtained crude yellow product was slowly dissolved in hot hexane. The purified product was obtained after recrystallisation at −18 °C for 48 h, yielding yellow crystals (1.13 g, 83%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.45 (d, 3H, ArH), 6.82 (d, 3H, ArH), 5.48 (h, 1H, CH in $CH(CH_3)_2$), 3.97 (d, 3H, CH), 2.88 (d, 3H, CH), 1.49 (d, 6H, CH_3 in $CH(CH_3)_2$), 1.44 (s, 27H, *t*Bu), 1.27 (s, 27H, *t*Bu). ^{13}C NMR (300 MHz, C_6D_6): δ 161.2, 142.6, 135.6, 124.9, 124.5, 123.2, 79.8, 59.3, 35.4, 34.6, 32.0, 30.0, 27.0, 27.0, 23.1, 14.4. The full spectra can be found in the SI (Figs. S3 and S4).

2.5. Synthesis of titanium(IV) amino-tBu-tris(phenolate) chloride (2b)

Titanium(IV) amino-*t*Bu-tris(phenolate) chloride (**2b**) was synthesised from **2a** following an ion-exchange procedure reported in the literature [99]. Complex **2a** (0.25 g, 0.32 mmol) was dissolved in benzene (20 mL) and placed in a 100 mL separation funnel, after which 25 mL 1 M aqueous HCl was added. The mixture was shaken for 10 min, followed by removal of the aqueous layer and drying of the organic layer over $MgSO_4$. The desired product was obtained as an orange solid (0.18 g, 75%) by concentrating the organic solution under reduced



Scheme 3. Synthesis of complexes **2a-3b**.

pressure. ^{1}H NMR (400 MHz, C_6D_6): δ 7.43 (d, 3H, ArH), 6.75 (d, 3H, ArH), 3.95 (d, 3H, CH), 2.53 (d, 3H, CH), 1.66 (s, 27H, *t*Bu), 1.32 (s, 27H, *t*Bu). ^{13}C NMR (300 MHz, C_6D_6): δ 161.6, 144.3, 136.5, 124.3, 124.0, 123.8, 59.0, 35.4, 34.7, 31.9, 29.9. The full spectra can be found in the SI (Figs. S5 and S6).

2.6. *Synthesis of zirconium(IV) amino-tBu-tris(phenolate) isopropoxide* (**3a**)

Zirconium(IV) amino-*t*Bu-tris(phenolate) isopropoxide (**3a**) was synthesised according to a procedure from the literature [100]. A Schlenk flask was loaded with the zirconium(IV) isopropoxide isopropanol complex (0.47 g, 1.23 mmol) in a N_2-filled glovebox. Subsequently, the complex was dissolved in dry toluene (20 mL). The ligand **1** (0.84 g, 1.23 mmol) was dissolved in toluene (40 mL) under N_2 atmosphere in a second Schlenk flask equipped with a pressure-equalising dropping funnel. The mixture containing the zirconium complex was added dropwise to the ligand solution at 0 °C while stirring. The resulting mixture was stirred for 2 h while it was allowed to slowly return to room temperature. Subsequently, the mixture was concentrated under reduced pressure, and the obtained white crude solid was dissolved in hot dry toluene. After recrystallisation for 48 h at −18 °C, white crystals were obtained. The crystals were washed with dry hexane and dried under reduced pressure at 50 °C, which yielded the desired product (0.48 g, 48%). The product was stored and handled under strictly inert and moisture-free atmosphere. ^{1}H NMR (600 MHz, C_6D_6): δ 7.49 (d, 3H, ArH), 6.89 (d, 3H, ArH), 4.87 (h, 1H, CH in $CH(CH_3)_2$), 4.54 (d, 3H, CH), 3.01 (d, 3H, CH), 1.66 (s, 27H, *t*Bu), 1.55 (d, 6H, CH_3 in $CH(CH_3)_2$), 1.35 (s, 27H, *t*Bu). ^{13}C NMR (600 MHz, C_6D_6): δ 158.0, 141.1, 136.6, 125.3, 124.8, 123.8, 72.9, 60.5, 35.4, 34.4, 32.1, 31.1, 30.1, 27.8. The full spectra can be found in the SI (Figs. S7 and S8).

2.7. *Synthesis of zirconium(IV) amino-tBu-tris(phenolate) chloride* (**3b**)

Zirconium(IV) amino-*t*Bu-tris(phenolate) chloride (**3b**) was synthesised using a similar procedure to that employed for preparing **3a**. Zirconium(IV) chloride (0.500 g, 2.15 mmol) was dissolved in dry tetrahydrofuran (50 mL) and was slowly added to a solution of ligand **1** (1.44 g, 2.15 mmol) in dry tetrahydrofuran (50 mL) under N_2 atmosphere at 0 °C, after which the resulting mixture was stirred for 2 h and allowed to slowly return to room temperature. After concentrating the mixture under reduced pressure, the obtained white crude solid was dissolved in a minimum amount of hot dry tetrahydrofuran, after which dry toluene was added as non-solvent to produce a supersaturated solution. Recrystallisation for 48 h at −18 °C yielded needle-like white crystals, which were subsequently washed with dry toluene and dried at 50 °C under reduced pressure to obtain the final product (0.33 g, 19%). The product was stored and handled under strictly inert and moisture-free atmosphere. ^{1}H NMR (600 MHz, THF-d_8): δ 7.55 (s, 3H, ArH), 7.40 (s, 3H, ArH), 4.26 (s, 3H, CH_2), 3.58 (m, 4H, THF), 1.73 (m, 4H, THF), 1.40 (s, 27H, *t*Bu), 1.32 (s, 27H, *t*Bu). ^{13}C NMR (600 MHz, THF-d_8): δ 153.2, 143.8, 139.6, 126.5, 67.2, 50.6, 35.7, 34.9, 31.8, 30.3, 25.1. The full spectra can be found in the SI (Figs. S9 and S10).

2.8. *Catalytic tests*

The catalytic reactions between CO_2 and epoxides were carried out in a high-throughput reactor unit manufactured by ILS-Integrated Lab Solutions GmbH. This CO_2 reactor unit consists of: (i) a reactor block in which 10 reactions can be performed simultaneously in individually-stirred, separate batch reactors (84 mL volume each, 30 mm internal diameter), which was used in this work; and (ii) a single batch reactor with the same dimensions as the other batch reactors but equipped with a borosilicate glass window that allows visualising the phases present in the reaction mixture. The CO_2 reactor unit can be operated in a pressure range of 1–200 bar and a temperature range of 20–200 °C. For each test, the chosen amounts of group(IV) metal complex and of tetrabutylammonium halide, 30.0 mmol epoxide and 3.0 mmol internal standard (mesitylene) were weighed into a glass vial (30 mm external diameter, 46 mL volume) equipped with a magnetic stirring bar and closed with a screw cap containing a silicone/PTFE septum. Next, the closed glass vials were transferred into the 10-reactors block. To allow gas flow into and from the vials, each septum was pierced with two needles. Then, the 10-reactors block was closed and the reactors were purged 3 times with N_2 (5 bar) and then were pressurised with CO_2 (10 bar). Next, 10 min were waited (to prevent deterioration of the rubber O-rings), after which the reactors were depressurised to atmospheric pressure. After waiting an additional 10 min, the batch reactors were pressurised with 10 bar CO_2. Upon reaching 10 bar, the reactors were heated to 90 °C, which resulted in a final pressure of around 12 bar in each batch reactor. The described procedure of purging, pressurising and heating the 10-reactors block required approximately 1 h. After reaching the desired reaction temperature and pressure, the start of the catalytic test was defined as the moment at which the magnetic stirring was turned on. The reactions were performed for either 2 or 18 h at 900 r min^{-1} stirring speed. At the end of the catalytic test, the magnetic stirring was stopped, the reactor heating was turned off and the water-cooling system was switched on to cool down the reactors. Once room temperature was reached, the reactors were depressurised. The process of cooling and depressurising the 10-reactors block lasted approximately 45 min. Upon reaching atmospheric pressure, the 10-reactors block was opened and the test vials were removed. An aliquot of each sample was analysed by ^{1}H NMR and FT-IR.

3. Results and discussion

Four amino-tris(phenolate) complexes with Ti(IV) or Zr(IV) as metal centres (Scheme 3, complexes **2a-3b**) were synthesised and investigated in combination with a tetrabutylammonium halide as binary catalytic systems for the conversion of CO_2 and epoxides into cyclic carbonates. These group(IV) metals were chosen as catalytic sites because their ionic radius is larger than that of the more commonly employed Al(III) and their higher oxidation state implies that the complex contains an anionic axial ligand (L = Cl or O*i*Pr, see Scheme 3). These features are expected to influence the catalytic behaviour of the complex, with the larger ionic radius possibly providing enhanced accessibility to the metal centres. The amino-tris(phenolate) ligand bearing *t*Bu-groups on the phenolate rings (**1**) as well as complexes **2a** and **3a** were synthesised according to literature procedures [98,100]. Straightforward ion-exchange of **2a** with aqueous HCl resulted in the formation of complex **2b** [99]. Complex **3b** was synthesised here for the first time, by reacting $ZrCl_4$ with the amino-tris(phenolate) ligand **1** and following a procedure adapted from the one used for preparing **3a**. The successful synthesis of ligand **1** and of the four metal complexes was demonstrated by ^{1}H NMR and ^{13}C NMR analysis (Figs. S1–S10 in the SI).

We started the evaluation of the catalytic performance of the titanium(IV) amino-tris(phenolate) complexes **2a** and **2b** in the reaction of CO_2 with epoxides by testing them in combination with a tetrabutylammonium halide (TBAX, X = Cl, Br, I) in a benchmark reaction employing 1,2-epoxyhexane as epoxide substrate (12 bar CO_2, 90 °C, 2 h). The catalytic loading and the type of tetrabutylammonium halide acting as nucleophile were varied to study the influence of these parameters on the conversion and selectivity of the reaction (Table 1). No epoxide conversion was achieved without using a separate nucleophile source (Table 1, entries 1 and 11), indicating that complexes **2a** and **2b** cannot act as single-component catalysts. The tetrabutylammonium halides in the absence of complexes **2a** and **2b** display only low activity under the employed reaction conditions (Table 1, entries 21–23). A remarkable increase in 1,2-hexene carbonate yield was achieved when the metal complexes **2a** and **2b** were combined with the tetrabutylammonium halides in a binary catalytic system (Table 1, entries 2–10 and 12–20). Employing complex **2a**, the highest cyclic carbonate yields

Table 1
Reaction of CO_2 with 1,2-epoxyhexane catalysed by complexes **2a-2b** in combination with TBA*X*.

#	Ti-complex	Ti-complex loading, mol/mol[a]	Nucleophile source	Cyclic carbonate yield, %[b]	TON^{c}_{metal}
1	**2a**	0.05	–	0	–
2	**2a**	0.025	TBAI	10	400
3	**2a**	0.05	TBAI	18	360
4	**2a**	0.25	TBAI	38	152
5	**2a**	0.025	TBABr	25	1000
6	**2a**	0.05	TBABr	35	700
7	**2a**	0.25	TBABr	75	300
8	**2a**	0.025	TBACl	13	520
9	**2a**	0.05	TBACl	24	480
10	**2a**	0.25	TBACl	38	152
11	**2b**	0.05	–	0	–
12	**2b**	0.025	TBAI	14	560
13	**2b**	0.05	TBAI	18	360
14	**2b**	0.25	TBAI	42	168
15	**2b**	0.025	TBABr	25	1000
16	**2b**	0.05	TBABr	41	820
17	**2b**	0.25	TBABr	76	304
18	**2b**	0.025	TBACl	27	1080
19	**2b**	0.05	TBACl	43	860
20	**2b**	0.25	TBACl	83	332
21	**-**	–	TBAI	5	–
22	**-**	–	TBABr	4	–
23	**-**	–	TBACl	3	–

Reaction conditions: 30 mmol epoxide, 3 mmol mesitylene as NMR internal standard, 0.25 mol/mol nucleophile source (TBA*X*, with *X* = Cl, Br or I) relative to the epoxide (if applicable), 90 °C, 12 bar CO_2 pressure, 2 h. The selectivity towards the cyclic carbonate product was > 99% in all cases, as indicated by ^1H NMR spectroscopy (Fig. S11 for a representative spectrum). [a] Relative to the epoxide. [b] The yield of the cyclic carbonate (1,2-hexene carbonate) was determined based on the ^1H NMR signals of the carbonate product and epoxide substrate. [c] TON = turnover number, expressed as mol of converted epoxide per mol of metal complex.

were achieved using TBABr as nucleophile (Table 1, compare entries 5–7 to 2–4 and 8–10), obtaining TONs (relative to the metal complex) up to 1000. The nucleophilicity of the halide anions increases in the order $I^- < Br^- < Cl^-$ and their leaving group ability increases in the order $Cl^- < Br^- < I^-$, rendering I^- the worse nucleophile and Cl^- the worse leaving group. Taking this into account and considering the generally proposed reaction mechanism (Scheme 2) [14,47], it can be reasoned that the Br^- anion provides the optimal balance between nucleophilicity (step *2*) and leaving group ability (step *5a*) and, thus, results in the highest reaction rate when combined with this metal complex. Ion-exchange of the axial O*i*Pr-group of **2a** with a Cl-group, thereby forming complex **2b**, did not have a significant impact on the activity of the complex in combination with TBAI or TBABr as nucleophile (Table 1, compare entries 12–17 with entries 2–7). On the other hand, the combination of **2b** with TBACl as nucleophile displayed remarkably higher activity compared to the counterpart catalytic system based on complex **2a**, reaching the highest epoxide conversions and cyclic carbonate yields among the investigated titanium amino-tris(phenolate) complexes, with TONs up to 1080 (Table 1, entries 18–20). This unusual trend in catalytic activity could originate from differences in steric effects around the metal centre. Assuming that the axial ligands of **2a** and **2b** are not very labile, since it was shown that the isopropoxide and chloride groups do not act as nucleophiles in the benchmark reaction (Table 1, entries 1 and 11), we can conclude that the axial ligands remain coordinated to the metal centre during the catalytic cycle. This means that an anionic intermediate complex would form after steps *2* and *3* of the mechanism in Scheme 2, in line with what has been proposed in the literature for similar catalysts [48]. The rate of step *4a* is not only determined by the leaving ability of the halide that is involved in the nucleophilic attack (*vide supra*), but can also be promoted by the displacement of the carbonate intermediate by another halide [77]. This displacement may occur more readily when the axial ligand is the less sterically hindered Cl (compared to O*i*Pr) and when the halide promoting the displacement is smaller (and thus with Cl^- rather than with Br^- or I^-). This would explain the observed high activity of the binary catalytic system consisting of complex **2b** and TBACl.

For each binary catalytic system defined by the combination of a metal complex (**2a** or **2b**) and of a TBA*X* (*X* = Cl, Br, I), three different molar ratios between metal and organic halide were tested, *i.e.* 1:10, 1:5, and 1:1. In line with logical expectations, increasing the loading of metal complex (while keeping the TBA*X* loading constant) led to higher cyclic carbonate yields (with a maximum of 83% for the **2b**/TBACl system, Table 1, entry 20), though at the price of lower TONs on a metal content base. The amount and type of halide can also have a strong influence on the selectivity between cyclic and polymeric carbonate [77,80]. In general, higher relative amounts of organic halide promote the displacement of the carbonate intermediate, thus favouring the ring closure (steps *4a* and *5a* in Scheme 2), leading to the formation of the cyclic carbonate product [77]. As a consequence, higher selectivity towards the cyclic carbonate products are generally observed when the organic halide is used in excess relatively to the metal complexes, whereas the formation of the polycarbonate is more favourable when the metal to halide ratio is equal to 1 or lower [77]. With metal complex **2a** or **2b**, full selectivity (> 99%) towards the cyclic hexene carbonate was observed with all the tetrabutylammonium halides types and ratios. This is attributed to the nature of the epoxide and to the reaction being performed at relatively high temperature (90 °C), which promotes the formation of the thermodynamically-favoured cyclic carbonate product [1].

Stimulated by the promising results obtained with the titanium amino-tris(phenolate) complexes, we continued our study of group(IV) metals as Lewis acid centre catalysts for the reaction of CO_2 with epoxides with the corresponding zirconium-based complexes **3a** and **3b**. Zirconium(IV) has a relatively larger radius than titanium(IV) and, hence, is anticipated to be better accessible to the epoxide substrate. The zirconium-based amino-tris(phenolate) complexes **3a** and **3b** were tested as Lewis acid catalysts in combination with TBA*X* using the same reaction conditions employed for the titanium-based complexes (1,2-epoxyhexane as epoxide substrate, 90 °C, 12 bar CO_2, 2 h, Table 2). Similarly to complexes **2a** and **2b**, **3a** and **3b** did not display any activity without the presence of an additional nucleophile (Table 2, entries 1 and 11). Employing complex **3a** in combination with TBABr as nucleophile source, resulted in the highest observed activity in this work in terms of TONs (Table 2, entries 5–7), reaching a remarkably high TON_{metal} = 1920. Notably, no considerable differences in cyclic carbonate yields were observed upon employing either 0.05 mol/mol or 0.25 mol/mol of **3a** relative to the epoxide substrate. More specifically, in the case of TBACl (Table 2, entries 9 and 10) only a slightly higher conversion was achieved using 0.25 mol/mol **3a**, while for TBAI (Table 2, entries 3 and 4) and TBABr (Table 2, entries 6 and 7) even slightly lower conversions were obtained. This trend is significantly different from what we observed with the Ti-complexes **2a** and **2b** (*vide supra*). These results indicate that complex **3a** is highly active already at relatively low metal-to-nucleophile ratios. The fact that increasing the metal loading above a certain metal-to-nucleophile ratio (*i.e.* approximately 1:5) does not lead to higher product yield suggests that above this ratio the reaction kinetics is no longer influenced significantly by the amount of Lewis acid sites, but is controlled rather by the amount of nucleophile. However, a decrease in solubility of complex **3a** caused by the increased polarity of the reaction medium induced by the conversion of the epoxide into the cyclic carbonate might not be excluded as explanation of the observed behaviour.

In contrast to the results obtained with the titanium-based complexes, significantly lower cyclic carbonate yields were achieved for the zirconium complex bearing an axial chloride ligand (**3b**) compared to the complex bearing an axial isopropoxide ligand (**3a**) (Table 2, compare entries 12-20 with entries 2-10). We hypothesise that residual THF solvent molecules could coordinate to the zirconium metal centre, similarly

Table 2
Reaction of CO_2 with 1,2-epoxyhexane catalysed by complexes **3a**-**3b** in combination with TBA*X*.

#	Zr-complex	Zr-complex loading, mol/mol^{a}	Nucleophile source	Cyclic carbonate yield, %^{b}	TON$^{c}_{metal}$
1	**3a**	0.05	–	0	–
2	**3a**	0.025	TBAI	30	1200
3	**3a**	0.05	TBAI	44	880
4	**3a**	0.25	TBAI	39	156
5	**3a**	0.025	TBABr	48	1920
6	**3a**	0.05	TBABr	63	1260
7	**3a**	0.25	TBABr	57	228
8	**3a**	0.025	TBACl	35	1400
9	**3a**	0.05	TBACl	42	840
10	**3a**	0.25	TBACl	47	188
11	**3b**	0.05	–	0	–
12	**3b**	0.025	TBAI	8	320
13	**3b**	0.05	TBAI	9	180
14	**3b**	0.25	TBAI	27	108
15	**3b**	0.025	TBABr	8	320
16	**3b**	0.05	TBABr	10	200
17	**3b**	0.25	TBABr	21	84
18	**3b**	0.025	TBACl	6	240
19	**3b**	0.05	TBACl	7	140
20	**3b**	0.25	TBACl	12	48
21	**Al amino-*t*Bu-tris(phenolate)**	0.05	TBAI	45	900

Reaction conditions: 30 mmol epoxide, 3 mmol mesitylene as NMR internal standard, 0.25 mol/mol nucleophile source (TBA*X*, with *X* = Cl, Br or I) relative to the epoxide (if applicable), 90 °C, 12 bar CO_2 pressure, 2 h. The selectivity towards the cyclic carbonate product was > 99% in all cases as confirmed by ^{1}H NMR spectroscopy (Fig. S11 for a representative spectrum). ^{a} Relative to the epoxide. ^{b} The yield of the cyclic carbonate (1,2-hexene carbonate) was determined based on the ^{1}H NMR signals of the carbonate product and epoxide substrate. ^{c} TON = turnover number, expressed as mol of converted epoxide per mol of metal complex.

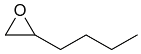
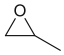
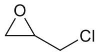
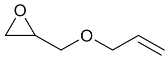
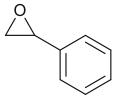
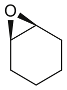
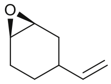
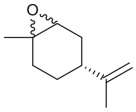
to what has been observed for aluminium-based amino-tris(phenolate) complexes [76]. This would hinder the coordination of the epoxide substrate and thus lead to lower catalytic activity in the reaction between 1,2-epoxyhexane and CO_2. Additionally, the axial chloride ligand is expected to lead to an increased Lewis acidity of the zirconium metal compared to the axial isopropoxide ligand. This increased Lewis acidity would hinder the release of the carbonate intermediate and thus the subsequent ring closure that yields the cyclic carbonate product (step *5a* in Scheme 2), thereby hampering the overall reaction rate.

Analogously to what observed with complexes **2a** and **2b**, complete selectivity towards the cyclic hexene carbonate product was obtained with complexes **3a** and **3b**, irrespectively of the type and relative amount of tetrabutylammonium halide that was employed.

In order to compare the activity of the most active metal complex identified in this work (**3a**) with the state-of-the-art aluminium amino-tris(phenolate) complex, we prepared the Al-complex with the same amino-*t*Bu-tris(phenolate) ligand following a literature procedure (see the SI for more details) [76]. The obtained Al-complex was tested under the same reaction conditions employed with complexes **2a**-**3b** and using TBAI as nucleophile, to recreate the conditions reported in the literature for this Al-complex as catalyst for the CO_2/epoxide reaction [76]. A 1,2-hexene carbonate yield of 45% with a TON of 900 was achieved (Table 2, entry 21), which indicates that our complex **3a** (Table 2, entry 3) has a virtually identical activity to this reference binary catalytic system. However, complex **3a** achieved significantly better performance with TBABr than with TBAI (Table 2), indicating that superior activity can be achieved by careful selection of the type and amount of metal amino-tris(phenolate) complex and tetrabutylammonium halide.

Based on the catalytic tests with 1,2-epoxyhexane as substrate, complex **3a** was selected as the most promising Lewis acid catalyst. To study the versatility of complex **3a** (in combination with TBABr) with regard to the reaction of CO_2 with epoxides, a substrate scope evaluation was performed using various terminal and internal epoxides (Table 3). Under the employed reaction conditions (90 °C, 12 bar CO_2, 18 h), all terminal epoxides (*i.e.* 1,2-epoxyhexane, propylene oxide, epichlorohydrin, allyl glycidyl ether and styrene oxide; Table 3, entries 1–5) were converted into the corresponding cyclic carbonates in nearly quantitative yields, with TONs up to 2000. This result confirms not only the notable activity of the binary system consisting of complex **3a** and TBABr, but also the complete selectivity towards the cyclic carbonate product regardless of the steric and electronic effects of the different functional groups of the terminal epoxides.

Table 3
Substrate scope of the reaction of CO_2 with various terminal and internal epoxides, catalysed by the binary catalytic system consisting of complex **3a** and TBABr.

#	Epoxide	Conv., %^{a}	Sel.$_{cyclic\ carbonate}$, %^{b}	TON$^{c}_{metal}$
1		> 99	> 99	2000
2		> 99	> 99	2000
3		99	98	1980
4		98	> 99	1960
5		> 99	> 99	2000
6		19	80	380
7		17	92	340
8		< 1	–	–

Reaction conditions: 30 mmol epoxide, 3 mmol mesitylene as NMR internal standard, 0.05 mol/mol of complex **3a** relative to the epoxide, 0.25 mol/mol TBABr relative to the epoxide, 90 °C, 12 bar CO_2 pressure, 18 h. ^{a} Conversion determined based on the ^{1}H NMR signals of the carbonate product and epoxide substrate. ^{b} Selectivity towards the cyclic carbonate determined by FT-IR analysis on the basis of the relative intensity of the C=O stretch signal of the cyclic carbonate and polycarbonate. ^{c} TON = turnover number, expressed as mol of converted epoxide per mol of metal.

The activity of complex **3a** was drastically lower when internal epoxides were used as substrates (Table 3, entries 6–8). For cyclohexene oxide and vinylcyclohexene oxide, only a moderate conversion was achieved (Table 3, entries 6 and 7, respectively), whereas in the case of limonene oxide no carbonate product was observed under the employed reaction conditions (Table 3, entry 8). The lower activity with these internal epoxides is in line with trends typically observed in the literature [75,80], and has been attributed to the higher steric hindrance around the epoxide group, which hampers the initial nucleophilic attack (step *2* in Scheme 2), and to the geometric strain that characterises the two adjacent rings of the obtained carbonates [101]. The inactivity in the conversion of limonene oxide is most probably related to the additional bulkiness of the methyl group adjacent to the epoxide moiety combined with the intrinsic conformation around the zirconium metal centre of **3a**. It was also observed that when cyclohexene oxide and vinylcyclohexene oxide were used as substrate, the selectivity towards the cyclic carbonate product was not complete (Table 3, entries 6 and 7) and a significant fraction of polycarbonate product was also observed (Figs. S12 and S13 for the FT-IR spectra). This is a well-known phenomenon, which presumably originates from the geometric ring strain of the two interconnected rings in the cyclic carbonate product, rendering it less thermodynamically favourable [67]. Although the selectivity towards the cyclic carbonate product was not complete, it was significantly higher compared to that observed in other reports of the reaction of CO_2 with cyclohexene oxide using related amino-tris(phenolate)-based metal complexes as catalysts, which instead were selective towards the polycarbonate [48]. Such difference in selectivity can be explained with the fact that in this work we used (i) a higher nucleophile-to-metal ratio and (ii) bromide (from TBABr) instead of chloride (from PPNCl) as nucleophile, with both features promoting the selectivity towards the cyclic carbonate product [77].

The activity of our optimum catalytic system, consisting of complex **3a** in combination with TBABr, was shown to be comparable to that of an Al amino-*t*Bu-tris(phenolate) complex in combination with TBAI under identical reaction conditions (Table 2). In order to expand the comparison, we compiled a selection of state-of-the-art binary catalytic systems for the synthesis of cyclic carbonates from CO_2 and epoxides (Table S1). For this purpose, we selected metal complexes that are either based on amino-tris(phenolate) ligands but with different metals (Al, Fe), or are based on Ti or Zr centres but with different ligands. It is important to note that these catalytic systems were tested under different conditions from each other and from our work. This means that a quantitative comparison of the catalytic performances is not possible, as this would require the tests to be carried out with the same epoxide substrate and under the same conditions in terms of temperature, CO_2 pressure, catalyst loading and reactor set-up. Still, if the TON and turnover frequency (TOF) values based on the moles of metal and those based on the moles of halide are considered while taking into account the different reaction conditions (Table S1), it can be concluded that the catalytic system based on complex **3a** is competitive with the most active counterparts reported in the literature [48,82,83,86,97,102,103].

4. Conclusions

In this work, we showed that amino-tris(phenolate)-based complexes incorporating group(IV) metal centres (*i.e.* titanium and zirconium) in combination with tetrabutylammonium halides (*i.e.* iodide, bromide and chloride) are highly active and fully selective binary catalysts for the atom-efficient reaction of CO_2 with terminal epoxides yielding the corresponding cyclic carbonate products. Titanium amino-tris(phenolate) complex **2b**, incorporating an axial chloride ligand, showed the highest catalytic activity among the titanium-based complexes, whereas zirconium amino-tris(phenolate) complex **3a**, bearing an axial isopropoxide ligand, provided the highest overall catalytic activity. The catalytic performance of complex **3a** in combination with TBAI is comparable with that of a state-of-the-art homogeneous catalytic system from the literature (consisting of an Al-amino-tris(phenolate) complex in combination with TBAI), and could be further optimised by using TBABr as nucleophile source. This binary catalytic system (complex **3a**, 0.05 mol/mol relative to the epoxide, in combination with 0.25 mol/mol TBABr), achieved remarkably high TONs (up to 2000) when tested at 90 °C, 12 bar CO_2 pressure, 18 h. This catalytic system was highly versatile in the reaction of terminal epoxides with CO_2, achieving quantitative conversion of a variety of terminal epoxides with different functionalities with full selectivity towards the corresponding cyclic carbonates. The presented results demonstrate the potential of group(IV) metal complexes based on amino-tris(phenolate) ligands as highly active catalysts for the conversion of CO_2 with epoxides into cyclic carbonates.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gce.2021.12.009.

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