

CO₂/Epoxide Reactions Catalyzed by Bimetallic Salalen Aluminum Complexes.

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Abstract: Four new bimetallic aluminum complexes bearing salalen ligands were synthesized and characterized. They were employed as catalysts in the reaction of CO₂ with both cyclohexene oxide and propylene oxide, by using tetrabutyl ammonium bromide as cocatalyst. The effect of the reaction conditions on the productivity and selectivity of the catalytic system was evaluated. Under the optimized reaction conditions, *cis*-cyclohexene carbonate (CHC) and propylene carbonate (PC) were obtained as exclusive products, respectively. Interestingly, in the production of *cis*-CHC, turnover frequencies comparable to those of the most active systems described in the literature were obtained. Moreover the catalytic system resulted active even operating under mild reaction conditions (100 °C, 0.2 MPa of CO₂ pressure) and with a low catalyst loading (0.04 mol%).

Introduction

The depletion of fossil fuel reserves is attracting both academic and industrial efforts towards the search of new routes for the synthesis of organic (macro)molecules from biorenewable resources. CO₂ is an advantageous one carbon source as it is an abundant and non-toxic compound. The drawback is its high stability which leads to a low reactivity. For this reason its activation requires highly reactive chemicals. Epoxides belong to this class of compounds due to their ring strain. Their reaction with CO₂ furnishes valuable products, namely aliphatic polycarbonates and/or cyclic organic carbonates (COCs).^[1] Aliphatic polycarbonates produced by these reactions have been commercialized as adhesive, binders and coatings. In the same way, COCs have various applications such as nonprotic solvents, intermediates in organic synthesis, and battery electrolytes.^[2] Cyclohexene oxide (CHO) and propylene oxide (PO) are representative epoxides often chosen to test the catalytic activity

and product selectivity of a given catalyst. The products of the CO₂/epoxide reactions strongly depend on the epoxide and on the conditions of the reaction, such as temperature, pressure, co-catalyst and solvent.^[3] For example, Al-salalen complexes typically afford alternating copolymers (polycyclohexene carbonate, PCHC) from carbon dioxide and CHO while produce cyclic propylene carbonate (PC) from PO and carbon dioxide. This is in agreement with thermodynamic studies on such processes, as cyclic carbonate formation competes with chain growth for PO copolymerizations while for reactions involving CHO^[4] the formation of the cyclic carbonate is generally prevented because of the ring strain associated to a bicyclic compound.^[5] As a consequence, while numerous catalysts have been found to selectively produce PCHC, the efficient and selective formation of CHC is more challenging. Promising catalysts have been reported in the recent literature,^[6,7] however these catalysts are often plagued by low turnover frequencies,^[6] in some cases higher values have been observed at low conversion^[7d] or by working with high catalyst loading.^[7a]

CHO is a *meso*-epoxide and the ring opening proceeds with inversion of one of its stereocentres to generate either (*R,R*)- or (*S,S*)-*trans*-1,2-cyclohexylene units. The closing of the carbonate intermediate may generate the *trans*-CHC, usually ascribed to the back-biting byproduct in the formation of the PCHC, or the *cis*-CHC whose formation requires a mechanism involving a double-inversion of CHO stereochemistry (i.e. formal retention of the original configuration of CHO).^[2b] Notably, switchable iron based systems, introduced by Williams and Kleij, have been found able to selectively produce *cis*-CHC or PCHC by modifying the experimental conditions.^[8]

The CO₂/epoxide reactions generally follow a coordination insertion mechanism which can be promoted by a metallic compound having general formula of L_nMR in which L_n is a set of ancillary ligands, R is an initiating group and M is the active metal centre. Among the explored metals, aluminum is particularly interesting as it is an abundant, non toxic, main group metal which generally leads to a good control of the reaction process. Aluminum complexes bearing salalen ligands, active in the CO₂/epoxide reactions, have been extensively studied^[9] and reviewed.^[2, 5a, 10] Interestingly, in most cases a bimetallic mechanism has been proposed for the reaction. As a fact, the dinuclear μ -oxo-bridged Al(salalen) complex reported by North's group, resulted active for the formation of cyclic carbonate even under mild reaction conditions and the participation of both metal centers in the catalytic event was demonstrated.^[11] For these reasons in this work we decided to synthesize bimetallic aluminum complexes and explore their behaviour in the CO₂/epoxide reactions. The choice of ligands fell on salalen ligands,^[12] hybrid structures between the much more explored salalen and salan ligands. We previously synthesized several monometallic aluminum complexes bearing

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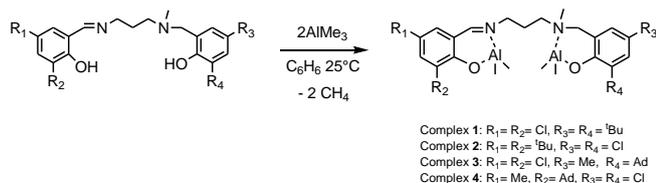
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salalen ligands with a two-carbon bridge between the imino and amino nitrogen atoms and different substituents on the ligand skeleton.^[13] Here we hypothesized that by increasing the length of the bridge by one carbon atom the tendency of all four donors to chelate to a single metal atom would diminish, while enough room would be created to include two aluminum atoms each coordinating to an individual ON-unit.

Results and Discussion

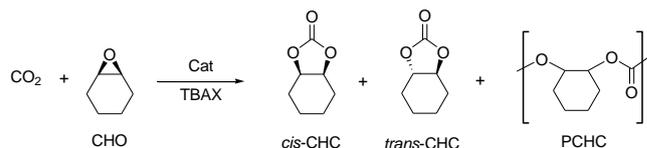
Complexes **1-4** were synthesized by reacting the proper salalen precursor ligand with 2 equivalents of trimethylaluminum in benzene at room temperature (Scheme 1).

NMR studies of the reactions indicated that the neutral proligands were deprotonated by two metal alkyls of trimethylaluminum with the release of 2 equiv of methane. The disappearance of the O-H signal of the free ligands and the appearance of four resonances for the protons of the methyls bound to the two aluminum atoms, in the high field region of the ¹H NMR spectra, suggested the formation of the desired bimetallic aluminum complexes. The four dialuminum complexes were characterized by ¹H, ¹³C, COSY NMR and elemental analysis. In all cases the CH₂ protons appear as A_xB_x patterns confirming the coordination of the neutral nitrogen atoms to the aluminum centers. However for complex **2**, some of these protons give broad signals, which narrow at lower temperature (see Supporting Information). Even in the ¹³C NMR spectrum some carbons give broad signals. In particular, this is observed for the methyl carbon bound to the nitrogen and for the six carbon atoms of the aromatic ring of the amino side. These observations may suggest the existence of a conformational equilibrium of the metallacycle in which the amino nitrogen is included.



Scheme 1. Synthesis of the aluminum complexes **1-4**.

We tested the catalytic activity and the product selectivity of complexes **1-4** in the reaction of CO₂ with cyclohexene oxide (CHO) and propylene oxide (PO). We first attempted the CO₂/CHO reaction in the presence of a quaternary ammonium salt as cocatalyst (Scheme 2). Polycyclohexencarbonate and cyclohexencarbonate are produced in different ratio depending on the experimental conditions (Tables 1-3).



Scheme 2. CO₂/CHO reaction promoted by complexes **1-4** in combination with a quaternary ammonium salt (TBAX).

The conversion of the epoxide was measured by ¹H NMR spectrometry by integrating the signal at 4.6 ppm (methine protons of both PCHC and *cis*-CHC) and the signal at 4.0 ppm (methine protons of the *trans*-CHC) with respect to the analogue protons of the CHO (3.1 ppm). Usually, the selectivity between the cyclic carbonate and the polycarbonate derived from cyclohexene oxide is determined by means of IR spectroscopy because the signals of the hydrogens on the carbonate ring in *cis*-CHC [H_a in Figure 1] and on the polymer backbone in PCHC [H_d in Figure 1] are partially overlapped in the ¹H NMR spectra. Interestingly, we found that by measuring the ¹H NMR spectra with a 600 MHz instrument a good resolution of the signals at 2.0 ppm (H_e) and 1.9 ppm (H_b) was obtained, enabling the determination of the ratio of the two products.

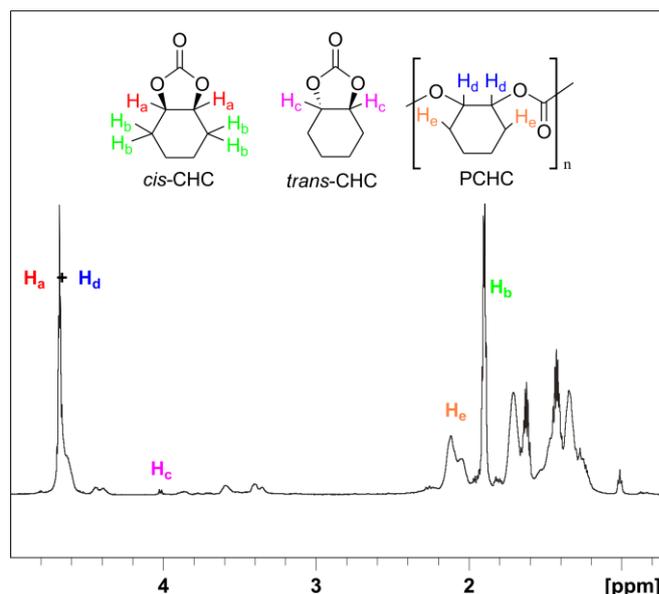


Figure 1. ¹H NMR spectrum of a mixture of CHC and PCHC (entry 3 in Table 1), (CDCl₃, 600 MHz, 298 K).

The effects of the experimental conditions (i.e., nature and equivalents of the cocatalyst, solvent, nature and loading of the catalyst, temperature, CO₂ pressure, number of equivalents and concentration of the cyclohexene oxide) on the outcome of the reactions have been investigated. The results are summarized in Tables 1-3.

Table 1. CO₂/CHO reaction promoted by complex **1** and quaternary ammonium salts (TBAX).^[a]

Entry	X	Time (h)	Conv %	A : B : C ^[b]	TON	TOF (h ⁻¹)
1	Br	20	29	87 : 2 : 11	305	15
2	Br	65	59	83 : 2 : 15	692	11
3	Cl	20	19	33 : 1 : 60	223	11
4	AcO	20	19	49 : - : 51	223	11
5 ^[c]	Br	20	17	90 : 3 : 7	199	10

[a] General conditions: **1** = 42.1 μmol, Cocat = 2 eq, CHO = 5 mL (1174 equiv), CH₂Cl₂ = 0.3 mL, Temperature = 80°C, P_{CO₂} = 3 MPa, time = 20 h. [b] A = *cis*-CHC, B = *trans*-CHC; C = PCHC. [c] CHO = 1.1 mL (250 equiv), CH₂Cl₂ = 4 mL.

Preliminary reactions carried out in the neat monomer showed that the cocatalyst is not soluble in the CHO and, under these conditions, the aluminum complex **1** homopolymerizes the CHO. Subsequent experiments have been conducted in the presence of a small amount of dichloromethane (0.3 mL) to dissolve the salt. In the presence of the cocatalyst the consecutive insertions of the epoxide and thus the formation of the polyether was hampered, in agreement with what reported in the literature.^[1c]

Complex **1** was found to be active in the CO₂/CHO reaction with TON values of up to 700. Comparing entries 1, 3 and 4 in which different cocatalysts have been employed, only small differences in the conversions can be observed, with the highest value obtained with the TBAB. Moreover, the highest percentage of *cis*-CHC is obtained when the counterion is a better leaving group (such as the bromide). Although the conversions were low, entry 2 demonstrates that higher conversion may be obtained by prolonging the reaction time, suggesting the stability of the active species in these conditions. Finally, adding a solvent and lowering the number of equivalents of the epoxide (entry 5) led to a higher selectivity for the *cis*-CHC product, although this implied a lower TON. Reasonably, in the presence of a lower monomer concentration the intermediate species of the CO₂/CHO coupling exists for an extended period of time allowing for the production of the cyclic carbonate.

Next, the performances of the aluminum complexes **1-4** were compared in the CO₂/CHO reaction in the presence of 4 equivalents of TBAB as cocatalyst (Table 2).

Complexes **2** and **4**, which feature chloro substituents on the amine-side phenol and bulky alkyl groups on the imine-side phenol, were found to be the most efficient. While, complexes **1** and **3** with the opposite phenolate substitution pattern, viz., bulky alkyl substituents on the amine-side phenol and halo groups on the imine-side phenol, showed a slightly lower activity. Complex **2** was also found to be the most selective toward the formation

of cyclic carbonate (95% of CHC vs 5% of PCHC, entry 2, Table 2).

Table 2. CO₂ / CHO reaction promoted by complexes **1-4** and TBAB.^[a]

Entry	Cat	Conv (%)	A : B : C ^[b]	TON	TOF (h ⁻¹)
1	1	60	89 : - : 11	704	35
2	2	67	87 : 8 : 5	786	39
3	3	54	80 : 2 : 18	634	32
4	4	75	77 : 5 : 18	880	44

[a] General conditions: cat **1-4** = 42.1 μmol, TBAB = 4 equiv, CH₂Cl₂ = 0.3 mL, CHO = 50 mmol (5 mL). Temperature = 80°C, P_{CO₂} = 3 MPa, time = 20 h. [b] A = *cis*-CHC, B = *trans*-CHC; C = PCHC.

For these reasons, we selected complex **2** to explore the effect of the cocatalyst equivalents, reaction temperature and CO₂ pressure on the products of the reaction. The increase of the equivalents of the cocatalyst leads to an improvement of the performance of the catalyst in terms of both activity and selectivity (cfr. entries 1 and 3, Table 3). This effect has been already reported in the literature and has been ascribed to the excess of nucleophile, whose availability for the coordination to the metal centre, may facilitate the displacement of the carbonate intermediate from the catalyst, thus favoring the ring closure reaction and the formation of cyclic carbonate.^[1c]

Table 3. CO₂ / CHO reaction promoted by complex **2** and TBAB.^[a]

Entry	TBAB (eq)	Temp (°C)	P _{CO₂} (MPa)	Conv (%)	A : B : C ^[b]	TON	TOF (h ⁻¹)
1	4	80	3	67	87 : 8 : 5	786	39
2	4	50	3	28	56 : - : 44	329	16
3	8	80	3	90	92 : 4 : 4	1060	53
4	8	80	1	64	93 : 5 : 2	750	38
5	8	100	1	75	96 : 3 : 1	880	63
6	16 ^[c]	100	1	65	>99 : - : -	1530	110
7	16 ^[c]	100	0.2	30	>99 : - : -	704	50

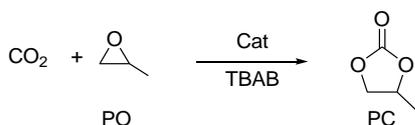
[a] General conditions: cat **2** = 0.08 mol % (42.1 μmol), CH₂Cl₂ = 0.3 mL, CHO = 50 mmol (5 mL), time: 20 h (entries 1-4), 14 h (entries 5-7). [b] A = *cis*-CHC, B = *trans*-CHC; C = PCHC. [c] cat **2** = 0.04 mol % (21.0 μmol).

In agreement with thermodynamic studies, the PCHC percentage increased by lowering the temperature (cfr entries 1 and 2, Table 3) while the selectivity versus *cis*-CHC products improved by raising the temperature (cfr entries 4 and 5, Table 3). Lowering the CO₂ pressure from 3 MPa to 1 MPa had only a small effect on the product selectivity furnishing a slightly higher percentage of CHC vs PCHC (cfr entries 3 and 4, Table 3). Predictably, keeping the number of TBAB equivalents constant, the highest TON values have been obtained at higher pressures and temperatures (cfr entries 3-5, Table 3). Next, we tried to lower the catalyst loading by working with 0.04 mol% of complex **2** (entry 6, Table 3; the amount of TBAB was not changed so 16 equiv of the salt were used). Rewardingly, under these conditions the catalyst was still able to convert 65% of CHO with a complete *cis*-CHC selectivity, giving one of the highest TOF (110 h⁻¹) reported in the literature for this class of reaction. Finally, we tried to save the CO₂ by diminishing the reaction pressure, our system was still active at 0.2 MPa of CO₂, however in these conditions only 30% of CHO were converted in 14 hours. Worth noting, a CO₂/CHO reaction carried out in the absence of catalysts, under the same conditions of entry 6, gave only 4% of *cis*-CHC, demonstrating that TBAB alone shows a very low activity under these conditions.

As known in the literature, monometallic salen aluminum complexes provide exclusively PCHC^[9a] or a mixture of PCHC and CHC^[9b] depending on both the reaction conditions and the ligand skeleton. Although, to the best of our knowledge, the behavior of these reported complexes was not studied in the conditions that we used in this work, the high selectivity towards *cis*-CHC product observed for the bimetallic salalen aluminum complexes could be ascribed either to the nature of the ligand or to the presence of two metallic centers in close proximity. To have more insight on this issue we synthesized a bimetallic aluminum complex bearing a salen ligand (N,N'-propylenebis(3,5-di-tert-butylsalicylimine)) with a structure similar to that of the salalen ligands (see Supporting Information). This salen complex was then tested in the CO₂/CHO reaction under the conditions detailed in entry 1 of Table 1.^[14] With respect to the salalen complex **1**, it showed a lower activity (conversion: 18% vs 29% for complex **1**) but a comparable selectivity towards *cis*-CHC (90% of *cis*-CHC vs 87% for complex **1**), thus suggesting a role of the bimetallic nature of those complexes in discriminating the reaction products.

Next the performance of this class of catalysts were investigated in the CO₂/PO reactions. Results are summarized in Table 4. Cyclic propylene carbonates (PCs) were obtained as exclusive product in all cases.

First, the reactions were carried out under the reaction conditions screened for CHO, by using complexes **1** and **2** in combination with two equivalents of TBAB (entries 1 and 2, Table 4).



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Table 4. CO₂ / PO reaction promoted by complexes **1-4** and TBAB.^[a]

Entry	Cat	Cat:TBAB:PO (equiv)	Time (h)	Temp (°C)	Conv (%)	TON	TOF (h ⁻¹)
1	1	1:2:1700	5	80	87	1477	296
2	2	1:2:1700	5	80	97	1646	329
3 ^[b]	2	1:25:6800	1	100	22	1493	1493
4 ^[b]	2	1:50:6800	1	100	41	2783	2783

[a] General conditions: cat = 42.1 μmol, CH₂Cl₂ = 0.3 mL, PO = 5 mL. [b] cat = 21.0 μmol, PO = 10 mL.

Both complexes showed very high activities, exceeding those reported for recently described bimetallic systems,^[15] allowing a conversion of at least 1500 equivalents of epoxide in 5 hours. As already observed for CO₂ / CHO reactions, complex **2** was found to be more active than complex **1** (cfr entries 1 and 2, Table 4) thus we employed it for exploring the effects of the reaction conditions. To improve the productivity of this system in terms of initial turnover frequency, the CO₂/PO reaction was performed at higher temperature (100°C), at a lower catalyst loading (0.015 %) and at a higher TBAB/catalyst ratio (entries 3 and 4, Table 4). The increasing of the percentage of the ammonium salt had beneficial effect on the catalytic activity and the system **2** / TBAB = 50 showed a very high turnover frequency, comparable to those reported for the most active metal complexes.^[2b, 7b, 16] It should be noted that the co-catalyst alone (TBAB), in the same conditions of entry 3, converted only 5 % of PO to propylene carbonate.

Conclusions

Bimetallic salalen aluminum complexes were found to be active in the CO₂/epoxide cycloaddition reaction with both cyclohexene oxide and propylene oxide. By proper choice of the reaction conditions *cis*-CHC was produced as the sole product. Excitingly, one of the highest turnover frequencies among those reported in literature was obtained (110 h⁻¹), even at relatively high epoxide conversions (65%), working under mild conditions (100 °C, 1 MPa of CO₂) and with a low catalyst loading (0.04 mol %). The behavior of the bimetallic salalen aluminum complex **1** in the CO₂/CHO reaction was compared with a similar bimetallic salen aluminum complex, properly synthesized. The latter was less active but showed a comparable selectivity towards *cis*-CHC, this result may suggest a role of the bimetallic nature of the catalytic systems in the observed selectivity. A more thorough study of the behavior of bimetallic salen aluminum complexes in the CO₂/epoxide reaction is in progress and it will be reported in due course.

Finally, in the CO₂/PO reaction a TOF of about 3000 h⁻¹, obtained with a low catalyst loading (0.015%), includes these systems among the most active reported in the literature.

Experimental Section

General Considerations.

All manipulations of air- and/or water-sensitive compounds were carried out under a dry nitrogen atmosphere using a Braun Labmaster glove box or standard Schlenk-line techniques. Glassware and autoclave used in the polymerization were dried in an oven at 120 °C overnight. Benzene and hexane were distilled over sodium benzophenone. Dichloromethane, cyclohexene oxide and propylene oxide were distilled over calcium hydride. CD_2Cl_2 and C_6D_6 were dried using molecular sieves. All other chemicals were commercially available and used as received unless otherwise stated. Elemental analyses were performed in the microanalytical laboratory of the Department of Chemistry and Biology. Synthesis and characterization of both ligands and the salen bimetallic aluminum complex are described in the Supporting Information.

Synthesis of complexes.

Complex 1. In a 20 mL vial with a magnetic stir bar, 62.9 mg (8.47×10^{-4} mol) of AlMe_3 (97% wt) were dissolved in 2 mL of dry benzene. In a 5 mL vial 203 mg (4.23×10^{-4} mol) of H_2L_1 were dissolved in 2 mL of dry benzene. The ligand solution was slowly dropped in the AlMe_3 solution. The reaction mixture was stirred for 2 hours at room temperature. The solvent was removed under vacuum, then 1 mL of hexane was added and after stirring for few minutes the compound was dried. Complex 1 was obtained as a yellow powder. Yield: 94%. ^1H NMR (600 MHz, CD_2Cl_2 , 298 K): δ -0.799 (s, 3H, Al-CH₃), -0.733 (s, 3H, Al-CH₃), -0.718 (s, 3H, Al-CH₃), -0.708 (s, 3H, Al-CH₃), 1.273 (s, 9H, CCH₃), 1.377 (s, 9H, CCH₃), 2.155 (m, 2H, CH₂), 2.346 (s, 3H, N-CH₃), 2.554 (m, 1H, CH₂), 2.913 (m, 1H, CH₂), 3.531 (d, J = 13.1 Hz, 1H, CH₂), 3.534 (m, 1H, CH₂), 3.657 (m, 1H, CH₂), 4.028 (d, J = 13.1 Hz, 1H, CH₂), 6.837 (d, J = 2.52 Hz, 1H, Ar-H), 7.166 (d, J = 2.7 Hz, 1H, Ar-H), 7.278 (d, J = 2.5 Hz, 1H, Ar-H), 7.569 (d, J = 2.6 Hz, 1H, Ar-H), 8.058 (s, 1H, C=N). ^{13}C NMR (100.6 MHz, C_6D_6 , 298 K): δ -9.73 (AlCH₃), -9.15 (AlCH₃), -8.47 (AlCH₃), -8.22 (AlCH₃), 24.03 (CH₂), 30.22 (CCH₃)₃, 31.97 (CCH₃)₃, 34.36 (CCH₃)₃, 35.51 (CCH₃)₃, 40.23 (N-CH₃), 54.04 (CH₂), 55.12 (CH₂), 61.66 (CH₂), 119.53 (Cq), 120.12 (Cq), 121.501 (Cq), 124.42 (CH), 125.19 (CH), 129.59 (Cq), 131.77 (CH), 136.51 (CH), 138.59 (Cq), 139.25 (Cq), 156.85 (Cq), 158.59 (Cq), 169.67 (CH=N). Elemental analysis calcd (%) for $\text{C}_{30}\text{H}_{46}\text{Al}_2\text{Cl}_2\text{N}_2\text{O}_2$: C, 60.91; H, 7.84; N, 4.74; found: C, 60.97; H, 7.79; N, 4.77.

Complex 2. The same procedure used for complex 1 was followed by using 62.0 mg (8.34×10^{-4} mol) of AlMe_3 (97% wt) and 200 mg (4.17×10^{-4} mol) of proper ligand. Complex 2 was obtained as a yellow powder in 89% yield. ^1H NMR (600 MHz, CD_2Cl_2 , 233 K): δ -0.818 (s, 3H, Al-CH₃), -0.801 (s, 6H, Al-CH₃), -0.723 (s, 3H, Al-CH₃), 1.248 (s, 9H, CCH₃), 1.341 (s, 9H, CCH₃), 2.078 (m, 2H, CH₂), 2.327 (s, 3H, N-CH₃), 2.550 (m, 1H, CH₂), 2.905 (m, 1H, CH₂), 3.441 (m, 2H, CH₂), 3.664 (m, 1H, CH₂), 4.028 (d, J = 12.3 Hz, 1H, CH₂), 6.899 (d, J = 2.0 Hz, 1H, Ar-H), 7.053 (d, J = 2.1 Hz, 1H, Ar-H), 7.306 (d, J = 2.3 Hz, 1H, Ar-H), 7.486 (d, J = 2.2 Hz, 1H, Ar-H), 8.139 (s, 1H, C=N). ^{13}C NMR (100.6 MHz, CD_2Cl_2 , 298 K): δ -10.99 (AlCH₃), -10.52 (AlCH₃), -9.75 (AlCH₃), -9.42 (AlCH₃), 25.07 (CH₂), 29.35 (CCH₃)₃, 31.37 (CCH₃)₃, 34.32 (CCH₃)₃, 35.49 (CCH₃)₃, 41.43 (N-CH₃), 55.60 (CH₂), 55.68 (CH₂), 60.60 (CH₂), 118.49 (Cq), 128.27 (CH), 129.12 (CH), 130.69 (CH), 132.64 (CH), 139.68 (Cq), 140.63 (Cq), 161.79 (Cq), 172.97 (CH=N). Elemental analysis calcd (%) for $\text{fC}_{30}\text{H}_{46}\text{Al}_2\text{Cl}_2\text{N}_2\text{O}_2$: C, 60.91; H, 7.84; N, 4.74; found: C, 61.01; H, 7.81; N, 4.71.

Complex 3. The same procedure used for complex 1 was followed by using 46.1 mg (6.38×10^{-4} mol) of AlMe_3 (97% wt) and 167.2 mg ($3.27 \times$

10^{-4} mol) of proper ligand. Complex 4 was obtained as a yellow powder in 90% yield. ^1H NMR (600 MHz, C_6D_6 , 298 K, TMS): δ = -0.427 (bs, 6H, Al-CH₃), -0.424 (s, 3H, Al-CH₃), -0.422 (s, 3H, Al-CH₃), 1.485 (m, 2H, CH₂), 1.694 (s, 3H, CH₃), 1.915 (m, 6H, CH₂), 1.924 (m, 1H, CH₂), 2.164 (bs, 3H, CH), 2.165 (m, 1H, CH₂), 2.350 (s, 3H, N-CH₃), 2.547 (m, 7H, CH₂), 2.613 (m, 1H, CH₂), 3.057 (d, J = 13.1 Hz, 1H, CH₂), 3.269 (d, J = 13.1 Hz, 1H, CH₂), 6.423(d, J = 2.7 Hz, 1H, Ar-H), 6.499 (d, J = 2.0 Hz, 1H, Ar-H), 6.688 (s, 1H, C=N), 7.177 (d, J = 2.0 Hz, 1H, Ar-H), 7.241(d, J = 2.7 Hz, 1H, Ar-H). ^{13}C NMR (150 MHz, C_6D_6 , 298 K, TMS): δ = -10.44 (AlCH₃), -9.81 (AlCH₃), -9.08(AlCH₃), -8.94 (AlCH₃), 21.07 (Cq), 23.58 (CH₂), 29.76 (CH₃), 37.39 (CH), 37.72 (CH₂), 40.27 (N-CH₂), 40.92 (N-CH₃), 53.47 (CH₂), 54.90 (CH₂), 60.95 (CH₂), 119.50 (Cq), 120.52 (Cq), 121.42 (Cq), 125.72 (Cq), 127.15 (CH), 129.17 (CH), 131.82 (CH), 136.44 (CH), 139.31 (Cq), 157.03 (Cq), 158.55 (Cq), 169.67 (CH=N). Elemental analysis calcd (%) for $\text{C}_{33}\text{H}_{46}\text{Al}_2\text{Cl}_2\text{N}_2\text{O}_2$: C, 63.15; H, 7.39; N, 4.46; found: C, 63.12; H, 7.35; N, 4.48.

Complex 4. The same procedure used for complex 1 was followed by using 57.7 mg (7.77×10^{-4} mol) of AlMe_3 (97% wt) and 200.2 mg (3.88×10^{-4} mol) of proper ligand. Complex 4 was obtained as a yellow powder in 93% yield. ^1H NMR (600 MHz, CD_2Cl_2 , 298 K, TMS): δ = -0.770 (s, 3H, Al-CH₃), -0.757 (s, 3H, Al-CH₃), -0.749 (s, 3H, Al-CH₃), -0.696 (s, 3H, Al-CH₃), 1.775 (bs, 6H, CH₂), 2.049 (bs, 3H, CH), 2.121 (bs, 6H, CH₂), 2.239(s, 3H, CH₃), 2.392 (s, 3H, N-CH₃), 2.619 (m, 1H, CH₂), 2.934(m, 1H, CH₂), 3.358 (m, 1H, CH₂), 3.556 (d, J = 13.8 Hz, 1H, CH₂), 3.604 (m, 1H, CH₂), 3.999 (d, J = 13.8 Hz, 1H, CH₂), 6.875 (d, ^4J = 2.7 Hz, 1H, Ar-H), 6.904 (d, ^4J = 2.6 Hz, 1H, Ar-H), 7.213 (d, ^4J = 2.6 Hz, 1H, Ar-H), 7.326 (d, ^4J = 2.7 Hz, 1H, Ar-H), 8.065 (s, 1H, C=N). ^{13}C NMR (100.6 MHz, C_6D_6 , 298 K, TMS): δ = -10.304 (AlCH₃), -9.601 (AlCH₃), -8.808 (AlCH₃), -8.489 (AlCH₃), 20.93 (CH₃), 24.14 (Cq), 29.90 (CH₂), 37.89 (CH₂), 38.00(CH), 40.42(N-CH₂), 40.98(N-CH₃), 54.51 (CH₂), 55.05 (CH₂), 69.81 (CH₂), 119.49 (Cq), 121.74 (Cq), 122.62 (Cq), 125.85 (Cq), 126.53 (Cq), 128.40 (CH), 131.18 (CH), 132.60 (CH), 136.76 (CH), 141.85 (Cq), 155.28 (Cq), 162.73 (Cq), 172.42(CH=N). Elemental analysis calcd (%) for $\text{C}_{33}\text{H}_{46}\text{Al}_2\text{Cl}_2\text{N}_2\text{O}_2$: C, 63.15; H, 7.39; N, 4.46; found: C, 63.18; H, 7.42; N, 4.50.

CO₂/epoxide reaction procedure.

In a typical experiment, in a glovebox, the catalyst and the cocatalyst (TBAX) were dissolved in CH_2Cl_2 (0.3 mL) in a 20 mL vial. Then the epoxide (5 or 10 mL) was added to the vial and the reaction mixture was transferred into the autoclave. The autoclave was pressurized to the prescribed pressure of CO_2 , whilst the reaction mixture was stirred for 20 minutes at room temperature, in order to facilitate CO_2 dissolution. The autoclave was heated to the appropriate temperature and the mixture was stirred for the necessary reaction time. After the prescribed time the reaction mixture was quenched by dipping the autoclave in an ice bath, opened at air and a ^1H NMR spectrum of the crude reaction mixture was recorded. Then 0.5 mL of methanol were added and the residual epoxide was removed under vacuum.

Acknowledgements

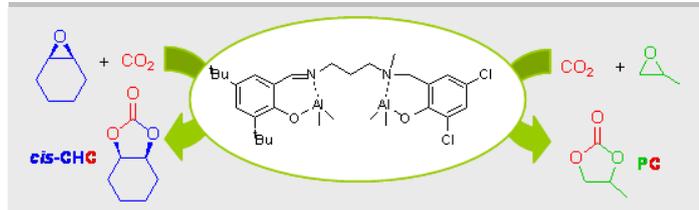
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Keywords: aluminum • carbon dioxide fixation • homogeneous catalysis • renewable resources • salalen ligands

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FULL PAPER



Bimetallic salalen aluminum complexes catalyzed the cycloaddition reaction of CO_2 with both cyclohexene oxide and propylene oxide, producing *cis*-cyclohexene carbonate and propylene carbonate as exclusive product with high turnover frequencies.

Mariachiara Cozzolino, Konstantin Press, Mina Mazzeo, Marina Lamberti*

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CO_2 /Epoxide Reactions Catalyzed by

Bimetallic Salalen Aluminum

Complexes.