ChemPubSoc Europe
DOI: 10.1002/chem.201504305
CHEMISTRY A European Journal Full Paper

Homogeneous Catalysis |*Hot Paper*|

Synthesis of Cyclic Carbonates Catalysed by Chromium and Aluminium Salphen Complexes

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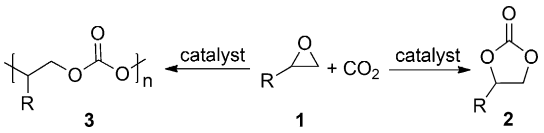
Abstract: Chromium and aluminium salphen complexes have been found to display remarkable catalytic activity in the synthesis of cyclic carbonates from a range of epoxides and carbon dioxide. The Al(salphen) complex is more reactive towards terminal epoxides at ambient temperature and pressure, whereas the Cr(salphen) complex exhibits higher catalytic activity towards more challenging internal epoxides at elevated temperature and pressure.

Introduction

Direct chemical fixation of carbon dioxide into organic compounds has received much attention recently, as carbon dioxide is a cheap, abundant, non-toxic, and versatile carbon source[1,2] as well as being one of the most significant greenhouse gases.[3] In particular, the transformation from epoxides **1** and carbon dioxide into either cyclic carbonates **2**[4] or polycarbonates **3**[5] is of commercial importance (Scheme 1). There are a number of applications associated with cyclic carbonates, such as their use as electrolytes in lithium ion batteries, polar aprotic solvents, and intermediates in organic synthesis.[6]



Scheme 1. Synthesis of cyclic and polycarbonates.

The biggest challenge in carbon dioxide utilisation is its relatively high kinetic and thermodynamic stability. The thermodynamic stability can only be overcome by adding energy to the reaction, either directly or in the form of high energy reactants such as epoxides or hydrogen whilst the kinetic stability can be overcome by the use of catalysts. A number of catalytic systems for the synthesis of cyclic carbonates from epoxides and carbon dioxide have been developed.[4] In view of the large scale of production of cyclic carbonates, especially due to the burgeoning demand for lithium ion batteries, it is highly desirable that catalysts for cyclic carbonate synthesis are derived from inexpensive, Earth-crust abundant metals, such as aluminium.[7] Amongst these, bimetallic aluminium salen complex **4**, reported by North and co-workers (Figure 1),[8] is amongst the most active catalysts for cyclic carbonate synthesis at room temperature and pressure in the presence of tetrabutylammonium bromide as a cocatalyst. Moreover, aluminium complex **4** was shown to have high reusability,[9] as well as being compatible with carbon dioxide generated by the combustion of methane in a pure oxygen atmosphere.[10] A one-component aluminium complex, which does not require a separate cocatalyst, has been prepared and immobilised analogues have been developed.[11] The catalytic activity of the immobilised catalysts were tested in the synthesis of cyclic carbonates from ethylene and propylene oxide in a gas-phase reactor,[12] and were shown to be compatible with both simulated[12b] and real flue gas.[13] More recently, aluminium complex **4** was shown to be an effective catalyst for the synthesis of cyclic carbonates from a range of terminal epoxides in the absence of cocatalysts at elevated temperature and pressure.[14]

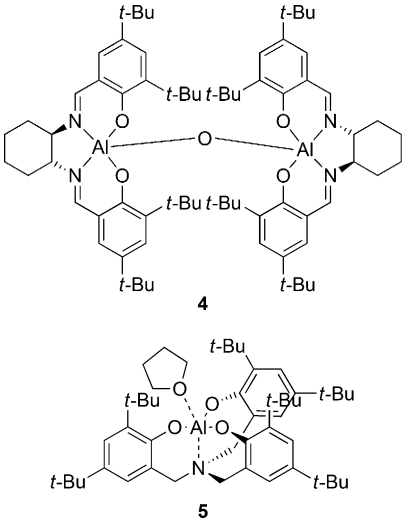


Figure 1. Aluminium-based catalysts **4** and **5**.

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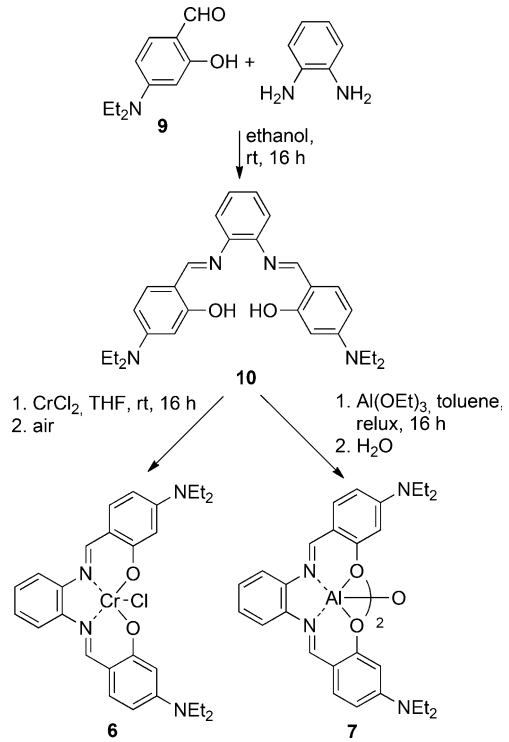
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201504305.

Kleij and co-workers have developed a number of amino(triphenolate) based aluminium complexes.[15] Although using slightly elevated temperature and pressure, aluminium(III) amino(triphenolate) **5** exhibits high catalytic activity with a wide range of substrates bearing various functional groups. Furthermore, aluminium complex **5** was also shown to be effective for the conversion of oxetanes into the corresponding six-membered ring cyclic carbonates.[16]

Although chromium is considered to be a more endangered element than aluminium,[7] several remarkable catalysts based around this metal have been reported, particularly for the preparation of polycarbonates.[5b,d,17] Fewer examples have been reported for the synthesis of cyclic carbonates. Recently, Deng and co-workers reported the synthesis of a chromium-based conjugated microporous polymer and its use as a heterogeneous catalyst in the formation of cyclic carbonates from epoxides and carbon dioxide.[18] Therefore, there is still potential for chromium-based catalysts to be developed as catalysts for cyclic carbonate synthesis.

In continuation of our efforts to further develop highly active catalytic systems for the reaction between epoxides and carbon dioxide, herein, we report the synthesis of chromium and aluminium based catalysts **6** and **7**, both of which contain a salphen scaffold, as efficient catalysts for the formation of cyclic carbonates from epoxides and carbon dioxide.



Scheme 2. Synthesis of chromium complex **6** and aluminium complex **7**.

Results and Discussion

A new one-component aluminium-based catalyst system **8** has recently been developed for the reaction between epoxides and carbon dioxide (Figure 2).[19] However, aluminium complex

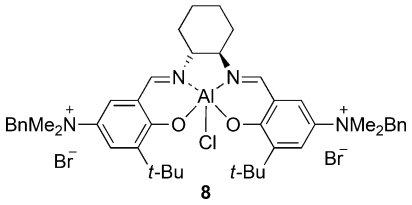
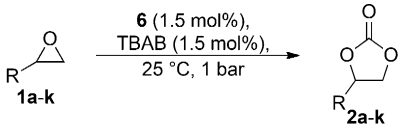


Figure 2. Aluminium-based catalyst **8**.

8, which has the trialkylammonium groups directly attached to the aromatic ring of the salen ligand, requires a multistep synthesis. Catalysts that exhibit high efficiency as well as being readily accessible are more attractive. Therefore, the use of commercially available 4-(diethylamino)salicylaldehyde **9** as one of the components for the ligand synthesis was investigated. Given the high catalytic activity previously reported by Kleij et al. for salphen complexes,[20] it was decided to combine aldehyde **9** with 1,2-diaminobenzene to prepare salphen ligand **10** and hence complexes **6** and **7**.

The syntheses of chromium complex **6** and aluminium complex **7** are presented in Scheme 2. Condensation of 4-(diethylamino)salicylaldehyde **9** with 1,2-diaminobenzene provided salphen ligand **10** as a yellow solid. Treatment of ligand **10** with chromium(II) chloride in THF followed by oxidation with air afforded Cr^{III}(salphen) chloride **6** as a brown solid. For the synthesis of aluminium complex **7**, salphen ligand **10** was added to a solution of aluminium triethoxide in refluxing toluene.[7] After a 16 h reflux, an aqueous work-up afforded Al(salphen) complex **7** as a bright orange solid.

The conversion of styrene oxide **1a** into styrene carbonate **2a** (Scheme 3) was chosen as the reaction to test the catalytic



1,**2**: a, R = Ph; b, R = Me; c, R = Bu; d, R = Hex; e, R = Dec; f, R = Oct; g, R = CH_2Cl; h, R = CH_2OH; i, R = CH_2OPh; j, R = 4-ClC_6H_4; k, R = 4-BrC_6H_4.

Scheme 3. Synthesis of cyclic carbonates **2a**–**k** using complex **6**.

activity of complexes **6** and **7** and the reactions were monitored by ^{1}H NMR spectroscopy. The chromium salphen complex **6** was initially investigated as a catalyst with *n*-tetrabutylammonium bromide (TBAB) as a cocatalyst, at 25 °C and 1 bar carbon dioxide pressure under solvent free conditions for 24 h. At a catalyst and cocatalyst loading of 2.5 mol%, 63% conversion of styrene oxide to styrene carbonate was achieved after 3 h and this increased to 87% after 6 h and 100% after 24 h (Table 1, entry 1). Control experiments involving the sole use of either complex **6** or TBAB gave only trace amounts of cyclic carbonate product (Table 1, entries 2 and 3), highlighting the strong synergistic effect observed when using complex **6** and

Table 1. Optimisation of the synthesis of cyclic carbonate **2a** using complex **6** and TBAB.[a]

Entry	Catalyst [mol%]	TBAB [mol%]	Conversion [%][b]
1	2.5	2.5	63, 87, 100
2	2.5	0	<1
3	0	2.5	<1
4	0.5	0.5	9, 19, 57
5	1.0	1.0	21, 39, 86
6	1.5	1.5	33, 55, 96
7	2.0	2.0	43, 66, 100

[a] Reactions were carried out at 25 °C and 1 bar carbon dioxide pressure using complex **6** and TBAB in the absence of a solvent. [b] Determined by ^{1}H NMR spectroscopy after 3, 6, and 24 h.

TBAB together. Subsequently, a range of catalyst concentrations were investigated to further reduce the catalyst loading, whilst keeping the catalyst to cocatalyst molar ratio at 1:1. At a catalyst loading of 0.5 mol%, low conversions were observed (Table 1, entry 4), but these increased linearly as the catalyst concentration was increased to 2 mol% (Table 1, entries 5–7). It was therefore decided that 1.5 mol% was the optimal loading for both the catalyst and cocatalyst, affording conversions to styrene carbonate of 33%, 55% and 96% after 3, 6 and 24 h, respectively (Table 1, entry 6). All the above reactions gave cyclic carbonate **2a** as the only product and there was no evidence for formation of polymeric or hydrolysis products.

The influence of the cocatalyst on the reaction between carbon dioxide and styrene oxide **1a** was also investigated and the results are summarized in Table 2. As expected,[8] it

Table 2. Influence of cocatalyst on the catalytic activity of complex **6**.[a]

Entry	Cocatalyst	Conversion [%][b]	TOF [h^{-1}][c]
1	TBAF	3, 7, 31	0.67, 0.78, 0.86
2	TBACl	8, 14, 54	1.78, 1.56, 1.50
3	TBAB	33, 55, 100	7.33, 6.11, 2.78
4	TBAI	33, 55, 100	7.33, 6.11, 2.78
5	DMAP	3, 5, 9	0.67, 0.56, 0.25
6	NMI	1, 2, 6	0.22, 0.22, 0.17
7	PPNCl	15, 24, 66	3.33, 2.67, 1.83
8	PPNBr	41, 63, 100	9.11, 7.00, 2.78

[a] Reactions were carried out at 25 °C and 1 bar carbon dioxide pressure using 1.5 mol% of complex **6** and 1.5 mol% of cocatalyst. [b] Determined by ^{1}H NMR spectroscopy after 3, 6, and 24 h. [c] TOF = moles of product/(moles of catalyst × time).

was found that the nucleophilicity and leaving-group ability of the cocatalyst determined its activity. Thus, *n*-tetrabutylammonium fluoride and chloride were poor cocatalysts (Table 2, entries 1 and 2), whilst TBAB and *n*-tetrabutylammonium iodide (TBAI) had much higher and similar activity, giving identical conversions at 25 °C and 1 bar carbon dioxide pressure (Table 2, entries 3 and 4). 4-Dimethylaminopyridine (DMAP) and *N*-methylimidazole (NMI) were not good cocatalysts as only 9% and 6% conversions were observed even after 24 h (Table 2, entries 5 and 6). The bis(triphenylphosphine)iminium halides were slightly more active than the corresponding *n*-tetrabutylammonium salts (Table 2, entries 7 and 8) and bis(triphenylphosphine)iminium bromide (PPNBr) was the most active cocatalyst, giving 41% conversion to styrene carbonate **3a** after 3 h (Table 2, entry 8). However, since TBAB is available at much lower cost than PPNBr, it was selected as the optimal cocatalyst.

Having determined the optimal reaction conditions to be 1.5 mol% of chromium complex **6** and TBAB at 25 °C and 1 bar carbon dioxide pressure, a series of terminal epoxides **1a–k** were then studied as substrates for the formation of the corresponding cyclic carbonates **2a–k**. The results are summarised in Table 3, and in general, good to excellent conversions to the

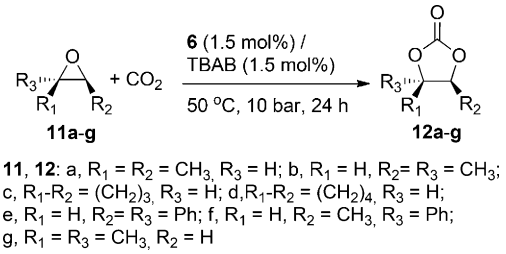
Table 3. Synthesis of cyclic carbonates **2a–k** using complex **6** and TBAB.[a]

Entry	Substrate	Conversion [%][b]	Yield [%][c]
1	**1a**	33, 55, 100	84
2	**1b**	–[d]	59
3	**1c**	51, 79, 100	78
4	**1d**	57, 75, 100	75
5	**1e**	4,20, 99	78
6	**1f**	5, 19, 89	74
7	**1g**	7, 29, 80	75
8	**1h**	13,34, 81	61
9	**1i**	46,85, 100[e]	87
10	**1j**	27, 45, 93	79
11	**1k**	25, 58, 100[e]	73

[a] Reactions were carried out using 1.5 mol% of complex **6** and 1.5 mol% of TBAB at 25 °C and 1 bar carbon dioxide pressure. [b] Determined by ^{1}H NMR spectroscopy after 3, 6, and 24 h. [c] Yield of isolated product after purification by column chromatography. [d] Not determined owing to the volatility of epoxide **1b**. [e] Reactions were carried out at 50 °C.

cyclic carbonates were achieved and the products were isolated in high yields. Epoxides **1i**,**k** are solids at 25 °C, so, for these substrates, reactions were carried out at 50 °C to give a homogeneous reaction mixture. Cyclic carbonates **2a–k** were again, the only product formed in these reactions.

A series of internal epoxides **11a–g** were then examined as substrates to further expand the substrate scope. Internal epoxides are considered to be more challenging substrates for cyclic carbonate synthesis although an effective method has recently been reported by Kleij and co-workers.[16] In view of the known synthetic challenge, reactions with internal epoxides were carried out using 1.5 mol% of complex **6** and TBAB, at 50 °C and 10 bar carbon dioxide pressure under solvent free conditions for 24 h (Scheme 4). Under these conditions, cyclic carbonates **12a–g** were isolated in good to excellent yields except for that derived from epoxide **11d**, illustrating the versatility of catalyst **6** (Table 4). Indeed, this is the first example of the successful conversion of internal epoxides into the corresponding cyclic carbonates using a chromium-based catalyst. Control experiments using epoxide **11f** as substrate (Table 4, entries 1–3) showed that under these conditions, no reaction occurred in the absence of both complex **6** and TBAB and neg-



11, **12**: a, $R_1 = R_2 = CH_3$, $R_3 = H$; b, $R_1 = H$, $R_2 = R_3 = CH_3$; c, R_1-$R_2 = (CH_2)_3$, $R_3 = H$; d, R_1-$R_2 = (CH_2)_4$, $R_3 = H$; e, $R_1 = H$, $R_2 = R_3 = Ph$; f, $R_1 = H$, $R_2 = CH_3$, $R_3 = Ph$; g, $R_1 = R_3 = CH_3$, $R_2 = H$

Scheme 4. Synthesis of cyclic carbonates **12a–g**.

Table 4. Synthesis of cyclic carbonates **12a–g** using complex **6** and TBAB.[a]

Entry	Substrate	**6** [mol%]	TBAB [mol%]	Conversion [%][b]	Yield [%][c]
1	**11f**	0	0	0	
2	**11f**	0	1.5	3	
3	**11f**	1.5	0	25	
4	**11a**	1.5	1.5	–[d]	68[e]
5	**11b**	1.5	1.5	–[d]	68[f]
6	**11c**	1.5	1.5	93	85
7	**11d**	1.5	1.5	–[d]	80[g]
8	**11e**	1.5	1.5	65[h]	63
9	**11f**	1.5	1.5	72	68
10	**11g**	1.5	1.5	–[d]	61

[a] Reactions were carried out at 50 °C and 10 bar carbon dioxide pressure. [b] Determined by ^{1}H NMR spectroscopy. [c] Yield of isolated product after purification by column chromatography. [d] Not determined. [e] Mixture of 86% *cis*- and 14% *trans*-cyclic carbonate product. [f] Yield of *trans*-cyclic carbonate product. [g] Yield of polymer. [h] Reaction carried out at 90 °C.

ligible conversion occurred in the presence of TBAB alone. Complex **6** alone did have some catalytic activity, but this was much lower than that observed when complex **6** and TBAB were both present (compare Table 4 entries 3 and 9).

In the case of 1,2-dimethyloxirane, both *cis*- and *trans*-isomers **11a,b** were used as substrates for the formation cyclic carbonates **12a,b**. It was observed that when the pure *trans*-epoxide **11b** was used, the cyclic carbonate product was obtained with retention of configuration and was exclusively *trans*-isomer **12b** (Table 4, entry 5). The *cis* epoxide **11a**, however, gave an 86:14 mixture of *cis*- and *trans*-isomers **12a,b** of the cyclic carbonate (Table 4, entry 4). It has been reported that the synthesis of cyclic carbonates from *cis*-1,2-dimethyloxirane **11a** is more challenging than from the *trans*-isomer **11b**.[21] We were delighted therefore to find that using complex **6** under moderate reaction conditions, both *cis*- and *trans*-epoxides **11a** and **11b** gave cyclic carbonates with the same isolated yields.

Cyclopentene oxide **11c** was an excellent substrate, giving cyclic carbonate **12c** in 85% yield (Table 4, entry 6). Cyclohexene oxide **11d** was also a substrate for catalyst **6** (Table 4, entry 7), but gave polycarbonate **3** rather than cyclic carbonate **12d**. This was confirmed by comparing ^{1}H NMR data with previously reported data.[19] GPC showed that the polycarbonate had a $M_n = 1320$ and $M_w = 2639$ relative to polystyrene standards. A MALDI-TOF mass spectrum of the polymer showed a repeating unit of 142 Daltons as expected, and showed the presence of oligomers composed of 3 to 18 monomer units with alcohols at both chain ends. This indicates that a chain-transfer process involving moisture within the reactor occurred during the polymerisation (see the Supporting Information for GPC and MALDI-TOF traces). Catalysts capable of formation of both cyclic carbonates and polymeric products have been reported previously.[5b,d,17,18] This further demonstrates the ability of chromium-based catalysts to form either cyclic- or polycarbonates depending on the monomer structure.

Stilbene oxide **11e** was also used as a substrate and gave *trans*-1,2-diphenylethylene carbonate **12e** in 63% isolated yield (Table 4, entry 8). In this case, the reaction temperature was raised to 90 °C as the epoxide is a solid at 50 °C. There are very few examples of the synthesis of **12e** via catalytic addition of carbon dioxide to stilbene oxide,[15a,b,22] making complex **6** a rare example of a catalyst able to transform bulky epoxide **11e** into cyclic carbonate **12e** in high yield. Complex **6** was also active with other sterically hindered epoxides, **11f** and **11g**, and provided cyclic carbonates **12f** and **12g** in good yields (Table 4, entries 9 and 10).

To test the catalytic activity of aluminium salphen complex **7** in the synthesis of cyclic carbonates from epoxides and carbon dioxide, styrene oxide was again used as a benchmark substrate. The reaction was carried out using 1.5 mol% of aluminium complex **7** and TBAB at 25 °C and 1 bar carbon dioxide pressure under solvent free conditions. A 50% conversion to styrene carbonate **2a** was achieved after 3 h (Table 5, entry 1),

Table 5. Synthesis of cyclic carbonates **2a–k** using complex **7** and TBAB.[a]

Entry	Substrate	Conversion [%][b]	Yield [%][c]
1	**1a**	50, 75, 100	83
2	**1b**	–[d]	72
3	**1c**	86, 97, 100	79
4	**1d**	97, 100	72
5	**1e**	45, 85, 100	90
6	**1f**	34, 73, 100	88
7	**1g**	60, 75, 100	77
8	**1h**	60, 76, 100	83
9	**1i**	77, 100[e]	77
10	**1j**	41, 60, 100	88
11	**1k**	57, 78, 100[e]	67

[a] Reactions were carried out using 1.5 mol% of aluminium complex **7** and 1.5 mol% of TBAB at 25 °C and 1 bar carbon dioxide pressure. [b] Determined by ^{1}H NMR spectroscopy after 3, 6 and 24 h. [c] Yield of isolated product after purification by column chromatography. [d] Not determined. [e] Reactions were carried out at 50 °C.

a result which was significantly higher than that was obtained with chromium complex **6** (33%; Table 1, entry 6). Furthermore, even when compared with dinuclear aluminium salen complex **4** (38% conversion using 1.0 mol% and 62% conversion using 2.5 mol% catalyst after 3 h[8a]), which maybe be regarded as the state of the art catalyst system, aluminium salphen complex **7** exhibits higher activity. Therefore, a series of terminal

epoxides **1a**–**k** were examined as substrates under the same reaction conditions and gave high conversions to the corresponding cyclic carbonates **2a**–**k** which were also isolated in high yields (Table 5). All the terminal epoxides tested gave considerably higher conversions in the first few hours of reaction than were obtained using chromium salphen complex **6** (compare Tables 3 and 5).

To investigate the catalytic activity of aluminium complex **7** in the synthesis of disubstituted cyclic carbonates, cyclopentene oxide **11c** was first used as a substrate. Using 1.5 mol% of complex **7** together with TBAB at 50 °C and 10 bar carbon dioxide pressure, a conversion of 95% was observed by ^{1}H NMR and cyclic carbonate **12c** was isolated in 73% yield (Table 6, entry 5). When the same reaction conditions were applied to cyclohexene oxide **11d**, *cis*-cyclohexene carbonate **12d** was isolated in 60% yield (Table 6, entry 6). When 1.5 mol% of complex **7** and TBAB were used with other disubstituted cyclic carbonates **11a,b,e**–**g**, very low conversions were observed. By increasing the catalyst concentration to 5 mol%, epoxides **11a,b,e**–**g** were successfully converted into cyclic carbonates **12c**–**g** in 37–83% yield. Control experiments with epoxide **11f** again showed that under these conditions complex **7** or TBAB alone gave only 5–15% conversion (Table 6, entries 1 and 2). The same trend was observed for 1,2-dimethyloxirane as seen when chromium-based complex **6** was employed. The *cis*- and *trans*-cyclic carbonates **12a** and **12b** were isolated in a similar yield (Table 6, entries 3 and 4), albeit both were much lower than that obtained using complex **6** (*cf.* entries 4 and 5 of Table 4). Compared to complex **6**, complex **7** catalysed the reaction with much higher retention of stereochemistry using *cis*-1,2-dimethyloxirane **11a**, and a 94:6 ratio of *cis*- and *trans*-isomers of cyclic carbonates **12a,b** was observed. While the sterically hindered epoxides **11e** and **11f** were successfully converted into the cyclic carbonate products **12e** and **12f** (Table 6, entries 7 and 8), the reaction with 1,1-dimethyloxirane **11g** was very sluggish and its cyclic carbonate product **12g** was isolated in only 37% yield (Table 6, entry 9).

Table 6. Synthesis of cyclic carbonates **12a**–**g** using complex **7** and TBAB.[a]

Entry	Substrate	**7** [mol%]	TBAB [mol%]	Conversion [%][b]	Yield [%][c]
1	**11f**	0	5	5	
2	**11f**	5	0	15	
3	**11a**	5	5	49	37[d]
4	**11b**	5	5	54	39[e]
5	**11c**	1.5	1.5	95	73
6	**11d**	1.5	1.5	76	60
7	**11e**	5	5	60[f]	50
8	**11f**	5	5	87	83
9	**11g**	5	5	–[g]	37

[a] Reactions were carried out at 50 °C and 10 bar carbon dioxide pressure. [b] Determined by ^{1}H NMR spectroscopy. [c] Yield of isolated product after purification by column chromatography. [d] Mixture of 94% *cis*- and 6% *trans*-cyclic carbonate product. [e] Yield of *trans*-cyclic carbonate product. [f] Reaction carried out at 90 °C. [g] Not determined.

For a direct comparison of the rate of conversion of styrene oxide **1a** into styrene carbonate **2a** reactions involving catalysts **4, 6** and **7** were carried out with TBAB as cocatalyst at 25 °C and 1 bar carbon dioxide pressure. The reactions were carried out for 7 h and samples were removed at intervals for ^{1}H NMR analysis to determine the conversion to cyclic carbonate **2a** with time. Figure 3 shows that under the same reaction conditions, the catalytic activity of aluminium salphen complex **7** is higher than either aluminium salen complex **4** or chromium salphen complex **6**.

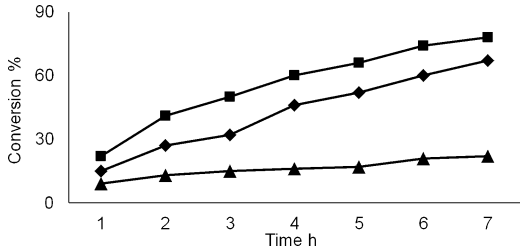


Figure 3. Plot of conversion versus time for styrene carbonate synthesis using catalysts **4**, **6**, and **7**. Triangles, Reaction profiles: ▲ catalyst **4**, ◆ catalyst **6**, ■ catalyst **7**.

The differences in catalytic activity of chromium salphen complex **6** and aluminium salphen catalyst **7** could be explained in term of Lewis acidity. Thus, aluminium salphen complex **7** is more Lewis acidic owing to the electron-withdrawing nature of the bridging oxygen atom, giving it a much faster rate of conversion for terminal epoxide than complex **6**. However, the bulky nature of bimetallic complex **7** makes it difficult for it to react with sterically hindered internal epoxides and monometallic chromium salphen complex **6** is better for these substrates.

Conclusion

Novel chromium **6** and aluminium **7** salphen complexes derived from 4-(diethylamino)salicylaldehyde **9** and 1,2-diaminobenzene have been synthesised. A catalytic system using complex **6** or **7** in the presence of TBAB as a cocatalyst has been developed for the synthesis of cyclic carbonates from epoxides and carbon dioxide. At 25 °C and 1 bar carbon dioxide pressure, aluminium salphen complex **7** exhibits higher catalytic activity for the formation of cyclic carbonates from terminal epoxides than chromium salphen complex **6**. However, chromium salphen complex **6** is more efficient for sterically congested disubstituted epoxides at elevated temperature and pressure. Both complex **6** and **7** display higher reactivity towards cyclopentene oxide than cyclohexene oxide.

Although there are a number of catalyst systems that have been developed for the synthesis of cyclic carbonates from epoxides and carbon dioxide, only a handful of these are active under mild reaction conditions. Within these, there are even fewer that can transform internal epoxides to their correspond-

ing cyclic carbonates. We have shown that both chromium and aluminium salphen complex **6** and **7** are efficient catalysts for the synthesis of cyclic carbonates from sterically challenging epoxides.

Experimental Section

Synthesis of ligand 10: 4-(Diethylamino)salicylaldehyde (5.0 g, 0.026 mol, 2.0 equiv) was added to a stirred solution of 1,2-diaminobenzene (1.4 g, 0.013 mol, 1.0 equiv) in ethanol (250 mL) and the resulting solution was stirred at room temperature for 16 h. A bright yellow precipitate was formed and the solution was filtered. The solid was then washed with cold ethanol and dried to give ligand **10** as a bright yellow solid (4.8 g, 80%). m.p. 147–148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.42$ (s, 2H, 2×NC=H), 7.22–7.12 (m, 4H, Ph), 6.24–6.20 (m, 4H, Ph), 3.38 (q, $J = 8.0$ Hz, 8H, 4×CH_2), 1.90 ppm (t, $J = 8.0$ Hz, 12H, 4×CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 164.4$ (ArC), 160.8 (ArCH), 151.7 (ArC), 142.5 (ArC), 133.7 (ArCH), 126.1 (ArCH), 119.2 (ArCH), 109.5 (ArC), 103.5 (ArCH), 98.1 (ArCH), 44.5 (CH_2), 12.7 ppm (CH_3); IR (neat): $\tilde{\nu} = 3356$, 2967, 1611, 1347, 1188, 1013, 961, 784, 751, 698 cm^{-1}; HRMS (ESI$^+$): calcd. for $C_{28}H_{34}N_4O_2$ $[M+H]^+$ 459.2755, found 459.2762.

Synthesis of chromium salphen complex 6: Salphen ligand **10** (0.5 g, 1.09 mmol, 1.0 equiv) was dissolved in dry THF (50 mL) under argon. Then, anhydrous $CrCl_2$ (0.138 g, 1.09 mmol, 1.0 equiv) was added and the mixture was stirred for 24 h under argon. Air was bubbled through the flask for another 24 h. Then, Et_2O was added and the organic layer was washed with a saturated solution of ammonium chloride (2×25 mL) and brine (2×50 mL). The organic layer was dried (Na_2SO_4) and the solvent was evaporated under reduced pressure to give chromium salphen complex **6** as a red-brown solid (0.53 g, 91%). m.p. 230–233 °C; IR (neat): $\tilde{\nu} =$ 2972, 1610, 1562, 1347, 1201, 1141, 1014, 825, 788, 754, 650 cm^{-1}; HRMS (LIFDI): calcd. for $C_{28}H_{32}CrN_4O_2Cl$ $[M]^+$: 543.16, found 543.14.

Synthesis of aluminium salphen 7: Aluminium triethoxide (2.12 g, 13.08 mmol, 2.0 equiv) in toluene (200 mL) was stirred and heated to reflux for 1 h. Then, ligand **10** (3.0 g, 6.54 mmol, 1.0 equiv) was added to the resulting suspension and the reaction refluxed for 16 h. After cooling to room temperature, the solvent was reduced under reduced pressure and the residue was dissolved in CH_2Cl_2 (300 mL) and water (300 mL) was added. The resulting mixture was stirred for 15 min. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3×100 mL). The combined organic extracts were washed with brine, dried with $MgSO_4$ and evaporated under reduced pressure to give the crude product. Purification by washing the crude product with Et_2O gave aluminium salphen **7** as an orange powder (3.84 g, 60%). m.p. 219–221 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.39$ (br s, 2H, 2×N=CH), 7.58–7.31 (m, 3H, Ar), 7.18–6.93 (m, 9H, Ar), 6.93–6.21 (m, 8H, Ar), 3.41 (q, $J = 4.0$ Hz, 16H, 8×NCH_2), 1.22 ppm (t $J = 8.0$ Hz, 24H, 8×CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 168.1$ (ArC), 156.2 (ArCH), 154.4 (ArC), 137.7 (ArC), 136.1 (ArCH), 125.1 (ArCH), 114.4 (ArCH), 110.5 (ArC), 104.0 (ArCH), 101.4 (ArC), 44.5 (CH_2), 13.0 ppm (CH_3); IR (neat): $\tilde{\nu} = 2968$, 1601, 1568, 1494, 1343, 1209, 1178, 1011, 779, 707, 649, 518 cm^{-1}; HRMS (ESI$^+$): calcd. for $C_{56}H_{65}Al_2N_8O_5$ $[M+H]^+$ 983.4727, found 983.4703.

General procedure for catalyst screening at 1 bar pressure

An epoxide (1.66 mmol), catalyst **6** or **7** (0.025 mmol) and Bu_4NBr (8 mg, 0.025 mmol) were placed in a sample vial fitted with a magnetic stirrer bar and placed in a large conical flask. Cardice pellets were added to the conical flask which was then fitted with a rubber stopper pierced by a deflated balloon. The reaction mixture was stirred at 25 °C for 24 h. The conversion of epoxide to cyclic carbonate was determined by analysis of a sample by ^{1}H NMR spectroscopy.

General procedure for catalyst screening at 50 °C and 10 bar pressure

An epoxide (1.66 mmol), catalyst **6** (13 mg, 0.025 mmol) and Bu_4NBr (8 mg, 0.025 mmol) or **7** (82 mg, 0.083 mmol) and Bu_4NBr (27 mg, 0.083 mmol) were placed in a stainless steel autoclave fitted with a magnetic stirrer bar, and the reactor was heated to 50 °C before charged with 10 bar pressure of carbon dioxide. The reaction mixture was stirred for 24 h. The conversion of epoxide to cyclic carbonate was determined by analysis of a sample by ^{1}H NMR spectroscopy.

Cyclic carbonates **2a–k** and **12a–g** are all known compounds and the spectroscopic data of samples prepared using catalysts **6** and **7** were consistent with those previously reported.[8,11,12,15,23,24]

Styrene carbonate (2a): Purification by flash column chromatography with n-hexane/EtOAc (6:4) gave a white solid. m.p. 49–51 °C (lit.[8,11,12,23] 50–51 °C); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.41$–7.31 (m, 5H, Ph), 5.64 (t, $J = 8.0$ Hz, 1H, OCH), 4.76 (t, $J = 8.0$ Hz, 1H, CH_2), 4.28 ppm (t $J = 8.0$ Hz, 1H, CH_2);^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 154.7 (C=O), 135.6 (ArC), 129.4 (ArCH), 128.9 (ArCH), 125.7 (ArCH), 77.8 (OCH), 70.9 ppm (OCH_2); IR (neat): $\tilde{\nu} = 3060$, 3029, 2961, 2903, 1791, 1599 cm^{-1}; HRMS (ESI$^+$): calcd. for $C_9H_8O_3$ $[M+Na]^+$ 187.0366, found 187.0361.

Propylene carbonate (2b): Purification by flash column chromatography with n-hexane/EtOAc (8:2) gave a colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.89$–4.80 (m, 1H, OCH), 4.54 (t, $J =$ 8.0 Hz, 1H, CH_2), 4.01 (t, $J = 8.0$ Hz, 1H, CH_2), 1.47 ppm (d, $J =$ 4.0 Hz, 1H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.0$ (C=O), 73.5 (OCH), 70.6 (OCH_2), 19.3 ppm (CH_3); IR (neat): $\tilde{\nu} = 2961$, 2902, 1781 cm^{-1}; HRMS (ESI$^+$): calcd for $C_4H_6O_3$ $[M+Na]^+$ 125.0209 found 125.0207.

1,2-Butylene carbonate (2c): Purification by flash column chromatography with n-hexane/EtOAc (8:2) gave a colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.68$–4.53 (m, 1H, OCH), 4.50 (t, $J =$ 8.0 Hz, 1H, CH_2), 4.07 (t, $J = 8.0$ Hz, 1H, CH_2), 1.87–1.70 (m, 2H, CH_2), 1.02 ppm (t, $J = 8.0$ Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 155.1 (C=O), 78.0 (OCH), 69.0 (OCH_2), 26.8 (CH_2), 8.4 ppm (CH_3); IR (neat): $\tilde{\nu} = 2938$, 2917, 1801 cm^{-1}; HRMS (ESI$^+$): calcd for $C_5H_8O_3$ $[M+Na]^+$ 139.0366, found 139.0364.

1,2-Hexylene carbonate (2d): Purification by flash column chromatography with n-hexane/EtOAc (6:4) gave a colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.72$–4.70 (m, 1H, OCH), 4.51 (t, $J =$ 8.0 Hz, 1H, CH_2), 4.05 (t, $J = 8.0$ Hz, 1H, CH_2), 1.84–1.63 (m, 2H, CH_2), 1.48–1.33 (m, 4H, 2×CH_2), 0.91 ppm (t, $J = 8.0$ Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.1$ (C=O), 76.8 (OCH), 69.4 (OCH_2), 35.6 (CH_2), 26.4 (CH_2), 22.3 (CH_2), 13.8 ppm (CH_3); IR (neat): $\tilde{\nu} =$ 2941, 2922, 2899, 1796 cm^{-1}; HRMS (ESI$^+$): calcd for $C_7H_{12}O_3$ $[M+$ Na$]^+$ 167.0679, found 167.0682.

1,2-Dodecylene carbonate (2e): Purification by flash column chromatography with n-hexane/EtOAc (8:2) gave a colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.73$–4.66 (m, 1H, OCH), 4.52 (t, $J =$ 8.0 Hz, 1H, CH_2), 4.06 (t, $J = 8.0$ Hz, 1H, CH_2), 1.84–1.70 (m, 2H, CH_2), 1.63–1.26 (m, 16H, 8×CH_2), 0.88 ppm (t, $J = 8.0$ Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.1$ (C=O), 77.1 (OCH), 69.4 (OCH_2), 33.9 (CH_2), 31.8 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 24.3 (CH_2), 22.6 (CH_2), 14.1 ppm (CH_3); IR (neat): $\tilde{\nu} =$

2931, 2832, 1798 cm^{-1}; HRMS (ESI^+): calcd for $C_{13}H_{24}O_3$ $[M+Na]^+$ 251.1618, found 251.1621.

1,2-Decylene carbonate (2 f): Purification by flash column chromatography with n-hexane/EtOAc (8:2) gave a colourless liquid. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.73–4.66$ (m, 1H, OCH), 4.52 (t, $J = 8.0$ Hz, 1H, CH_2), 4.06 (t, $J = 8.0$ Hz, 1H, CH_2), 1.85–1.64 (m, 2H, CH_2), 1.50–1.26 (m, 12H, $6\times CH_2$), 0.87 ppm (t, $J = 8.0$ Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.1$ (C=O), 77.0 (OCH), 69.4 (OCH_2), 33.9 (CH_2), 31.8 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 24.3 (CH_2), 22.6 (CH_2), 14.1 ppm (CH_3); HRMS (ESI^+): calcd for $C_{11}H_{20}O_3$ $[M+Na]^+$ 223.1305, found 223.1315.

3-Chloropropylene carbonate (2 g): Purification by flash column chromatography with n-hexane/EtOAc (6:4) gave a white solid. m.p. 67–69 °C (lit.[8,11,12,23] 68–69 °C); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.98–4.92$ (m, 1H, OCH), 4.58 (t, $J = 8.0$ Hz, 1H, OCH_2), 4.40 ppm (t, $J = 8.0$ Hz, 1H, OCH_2), 3.78–3.70 ppm (m, 2H, CH_2Cl); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.2$ (C=O), 74.3 (OCH), 66.9 (OCH_2), 43.7 ppm (CH_2Cl); IR (neat): $\tilde{\nu} = 2973$, 2698, 2121, 2017, 1971, 1793 cm^{-1}; HRMS (ESI^+): calcd for $C_4H_5ClO_3$ $[M+Na]^+$ 158.9819, found 158.9815.

Glycerol carbonate (2 h): Purification by flash column chromatography with n-hexane/EtOAc (6:4) gave a colourless liquid. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.83–4.77$ (m, 1H, CH), 4.51 (t, $J = 8.0$ Hz, 1H, OCH_2), 4.41 (dd, $J = 8.0$, 4.0 Hz, 1H, OCH_2), 3.96 (dd, $J = 16.0$, 4.0 Hz, 1H, C*H*OH), 3.68 ppm (dd, $J = 16.0$, 4.0 Hz, 1H, C*H*OH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.4$ (C=O), 76.6 (OCH), 65.8 (OCH_2), 61.6 ppm (CH_2OH); IR (neat): $\tilde{\nu} = 3382$, 2901, 1799 cm^{-1}; HRMS (ESI^+): calcd for $C_4H_6O_4$ $[M+Na]^+$ 141.0158, found 141.0159.

3-Phenoxypropylene carbonate (2 i): Purification by flash column chromatography with n-hexane/EtOAc (8:2) gave a white solid. m.p. 94–96 °C (lit.[8,11,12,23] 94–95 °C); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.30$ (t, $J = 8.0$ Hz, 2H, *m*-Ph), 7.05 (t, $J = 8.0$ Hz, 1H, *p*-Ph), 6.92 (d, $J = 8.0$ Hz, 2H, *o*-Ph), 5.10–5.02 (m, 1H, OCH), 4.71–4.52 (m, 2H, OCH_2), 4.26 (dd, $J = 11.0$, 4.0 Hz, 1H, CH_2), 4.16 ppm (dd, $J = 11.0$, 4.0 Hz, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 157.7$ (C=O), 154.6 (ArC), 129.7 (ArCH), 122.0 (ArCH), 114.6 (ArCH), 74.0 (OCH), 66.8 (OCH_2), 66.2 ppm (CH_2); HRMS (ESI^+): calcd for $C_{10}H_{10}O_4$ $[M+Na]^+$ 217.0471, found 217.0473.

4-Chlorostyrene carbonate (2 j): Purification by flash column chromatography with n-hexane/EtOAc (6:4) gave a white solid. m.p. 67–69 °C (lit.[8,11,12,23] 68–69 °C); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.43$ (d, $J = 8.0$ Hz, 2H, ArH), 7.30 (d, $J = 8.0$ Hz, 2H, ArH), 5.66 (t, $J = 8.0$ Hz, 1H, CH), 4.80 (t, $J = 8.0$ Hz, 1H, CH_2), 4.31 ppm (t, $J = 8.0$ Hz, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.5$ (C=O), 135.8 (ArC), 134.2 (ArC), 129.5 (ArCH), 127.2 (ArCH), 77.2 (OCH), 71.0 ppm (OCH_2); IR (neat): $\tilde{\nu} = 2973$, 2698, 2121, 2017, 1971, 1793 cm^{-1}; HRMS (ESI^+): calcd for $C_9H_7ClO_3$ $[M+H]^+$ 220.9984, found 220.9976.

4-Bromostyrene carbonate (2 k): Purification by flash column chromatography with n-hexane/EtOAc (8:2) gave a white solid. m.p. 70–72 °C (lit.[8,11,12,23] 68–69 °C); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.58$ (d, $J = 8.0$ Hz, 2H, ArH), 7.24 (d, $J = 8.0$ Hz, 2H, ArH), 5.64 (t, $J = 8.0$ Hz, 1H, CH), 4.80 (t, $J = 8.0$ Hz, 1H, CH_2), 4.30 ppm (t, $J = 8.0$ Hz, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.5$ (C=O), 134.8 (ArC), 132.5 (ArCH), 127.4 (ArCH), 123.9 (ArC), 77.2 (CH), 70.9 ppm (CH_2); IR (neat): $\tilde{\nu} = 2951$, 2522, 2161, 2017, 1981, 1801, 1771 cm^{-1}; HRMS (ESI^+): calcd for $C_9H_7BrO_3$ $[M+Na]^+$ 264.9471, found 264.9470.

***cis*-2,3-Butene carbonate (12 a)**: Purification by flash column chromatography with n-hexane/EtOAc (7:3) gave a white solid as a mixture of *cis* and *trans* isomers. m.p. 30–31 °C (lit).[15,16,24] 29–30 °C); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.84–4.82$ (m, 2H, $2\times CH$), 1.35 ppm (d, $J = 8.0$ Hz, 6H, $2\times Me$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.6$ (C=O), 76.0 (CH), 14.3 ppm (CH_3); IR (neat): $\tilde{\nu} = 2960$, 2899, 1787 cm^{-1}; HRMS (ESI^+): calcd for $C_5H_8O_3$ $[M+Na]^+$ 139.0366, found 139.0365.

***trans*-2,3-Butene carbonate (12 b)**: Purification by flash column chromatography with n-hexane/EtOAc (7:3) gave a white solid. m.p. 30–32 °C (lit).[15,16,24] 29–30 °C); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.34–4.32$ (m, 2H, $2\times CH$), 1.45 ppm (d, $J = 4.0$ Hz, 6H, $2\times Me$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.3$ (C=O), 79.9 (CH), 18.4 ppm (CH_3); IR (neat): $\tilde{\nu} = 2955$, 2871, 1776 cm^{-1}; HRMS ($ESI+$): calcd for $C_5H_8O_3$ $[M+Na]^+$ 139.0366, found: 139.0364.

1,2-Cyclopentene carbonate (12 c): Purification by flash column chromatography with n-hexane/EtOAc (8:2) gave a white solid. m.p. 30–33 °C (lit.[15,16,24] 29–30 °C); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 5.11–5.10$ (m, 2H, $2\times CH$), 2.17–2.12 (m, 2H, CH_2), 1.83–1.61 ppm (m, 4H, $2\times CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.4$ (C=O), 81.8 (CH), 33.1 (CH_2), 21.5 ppm (CH_2); IR (neat): $\tilde{\nu} = 2967$, 2871, 1789 cm^{-1}; HRMS (ESI^+): calcd for $C_6H_8O_3$ $[M+Na]^+$ 151.0366, found 151.0368.

***cis*-1,2-Cyclohexene carbonate (12 d)**: Purification by flash column chromatography with n-hexane/EtOAc (8:2) gave a white solid. m.p. 35–37 °C (lit.[15,16,24] 34–35 °C); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.70–4.65$ (m, 2H, $2\times CH$), 1.91–1.87 (m, 4H, $2\times CH_2$), 1.68–1.57 (m, 2H, CH_2), 1.46–1.32 ppm (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.2$ (C=O), 75.7 (CH), 26.8 (CH_2), 19.2 ppm (CH_2); IR (neat): $\tilde{\nu} = 2933$, 2861, 1784 cm^{-1}; HRMS (ESI^+): calcd for $C_7H_{10}O_3$ $[M+Na]^+$ 165.0522, found 165.0521.

***trans*-1,2-Diphenylethylene carbonate (12 e)**: Purification by flash column chromatography with n-hexane/EtOAc (8:2) gave a white solid. m.p. 109–110 °C (lit.[15,16,24] 110–111 °C); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.54–7.43$ (m, 6H, ArH), 7.33–7.31 (m, 4H, ArH), 5.44 ppm (s, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.8$ (C=O), 134.8 (ArC), 129.8 (ArCH), 129.2 (ArCH), 126.0 (ArCH), 85.4 ppm (CH); IR (neat): $\tilde{\nu} = 3051$, 2977, 1812, 1458 cm^{-1}; HRMS (ESI^+): calcd for $C_{15}H_{12}O_3$ $[M+H]^+$ 241.0859, found 241.0863.

***trans*-1-Phenyl-2-methylethylene carbonate (12 f)**: Purification by flash column chromatography with n-hexane/EtOAc (8:2) gave a white solid. m.p. 112–114 °C (lit.[15,16,24] 110–111 °C); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.54–7.43$ (m, 3H, ArH), 7.37–7.35 (m, 2H, ArH), 5.13 (d $J = 8.0$ Hz, 1H, PhCH), 4.64–4.57 (m, 1H, CHMe), 1.56 ppm (d, $J = 8.0$ Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.3$ (C=O), 135.0 (ArC), 129.7 (ArCH), 129.2 (ArCH), 126.0 (ArCH), 84.9 (CH), 80.7 (CH), 18.3 ppm (CH_3); IR (neat): $\tilde{\nu} = 3010$, 2950, 1800, 1459 cm^{-1}; HRMS (ESI^+): calcd for $C_{10}H_{10}O_3$ $[M+H]^+$ 179.0703, found 179.0704.

1,1-Dimethylethylene carbonate (12 g): Purification by flash column chromatography with n-hexane/EtOAc (8:2) gave a white solid. m.p. 30–32 °C (lit.[15,16,24] 29–30 °C); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.14$ (s, 2H, CH_2), 1.52 ppm (s, 6H, $2\times Me$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.6$ (C=O), 81.7 (CMe_2), 75.4 (CH_2), 26.0 ppm (CH_3); IR (neat): $\tilde{\nu} = 2955$, 2833, 1780 cm^{-1}; HRMS (ESI^+): calcd for $C_5H_8O_3$ $[M+Na]^+$ 139.0366, found 139.0366.

Acknowledgements

We gratefully acknowledge financial support from the European Union Seventh Framework Programme FP7-NMP-2012 under grant agreement number 309497.

Keywords: aluminium · chromium · cyclic carbonates · epoxides · homogeneous catalysis · salphen ligands

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Received: October 27, 2015
Revised: November 26, 2015
Published online on January 7, 2016