Synthesis of cyclic carbonates from epoxides and CO_2

Michael North,* Riccardo Pasquale and Carl Young

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The synthesis of cyclic carbonates by the 100% atom economical reaction between epoxides and CO_2 is reviewed in the context of reducing global emissions of waste CO_2 and converting waste CO_2 into industrially useful chemical feedstocks.

1 Introduction

Humankind relies on fossil fuels as the primary source of energy; producing, as a by-product, CO_2 which is released into the atmosphere and believed to be partly responsible for changes to the global climate. The scientific community is currently researching alternative energy sources and developing systems for the chemical utilization of CO_2. At the present time, however, carbon capture and storage (CCS) from fossil fuel power stations is the only strategy being investigated to reduce carbon emissions, though it is highly demanding in terms of energy. An attractive alternative to CCS would be to utilize the waste CO_2 in the production of commercially important chemicals under mild reaction conditions, thus simultaneously reducing atmospheric CO_2 emissions and providing an alternative, renewable feedstock for the chemicals industry. However, because of its low reactivity, there are very few feasible processes that could recover and use carbon dioxide as a sustainable resource.

1.1 Overview of CO_2 chemistry

Fossil fuel burning is the primary source of non-natural CO_2 emissions,[1] and is the basis of worldwide primary energy production: 85% of the global energy production comprises oil, coal and gas, whilst the remaining 15% includes nuclear power and alternative renewable sources, such as solar heat, wind and biomass.[2] Fossil fuels are a non-renewable approach to energy production[3] and their global levels are predicted to peak in the next 10–40 years,[4] though coal deposits could last for another 200 years.[5] Thus, the present reserves will not sustain future demand, and it is therefore desirable to develop novel technologies based on renewable energy sources, to help to prevent any further increase in the atmospheric level of CO_2.

CO_2 is a renewable source of carbon and has the advantages of being abundant, economical and non-toxic.[6] Concerns about anthropogenic emissions have recently sparked interest in the chemical transformation of CO_2, although the high cost and a lack of effective, feasible processes, often limit commercial applicability. At present, industrial transformations utilize around 110 Mt of CO_2 per year as a synthetic building block, which is less than 1% of global emissions.[6d] The largest single use is in the synthesis of urea ($\Delta H_r = -101$ kJ mol^{-1}) which is currently carried out on about a 90 Mton per annum scale[6a] and has been a commercial process since 1922. The synthesis of salicyclic

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School of Chemistry and University Research Centre in Catalysis and Intensified Processing, Bedson Building, Newcastle University, Newcastle upon Tyne, UK NE1 7RU. E-mail: Michael.north@ncl.ac.uk; Fax: +44 (0)191 222 6929; Tel: +44 (0)191 222 7128

Michael North

Michael North obtained his BSc from Durham University and his DPhil from the University of Oxford. After a postdoctoral position at the University of Nottingham, and academic posts at the University of Wales and the University of London, he was appointed to his current position as Professor of organic chemistry at the University of Newcastle upon Tyne. He has published over 170 papers and holds six patents. His research interests are centered on the design of new catalysts for asymmetric carbon–carbon bond formation and carbon dioxide chemistry. In 2001 he was awarded the Descartes Prize by the European Commission.

Riccardo Pasquale

Riccardo Pasquale graduated from the University of Padua in Italy and in 2006 moved to Newcastle to start his doctoral studies on the development of highly active catalysts for the synthesis of cyclic carbonates from CO_2 and epoxides. His PhD work has resulted in the publication of four papers and has led to the filing of a series of patents that form the basis of a University of Newcastle upon Tyne spin-out company to exploit the chemistry he developed. Riccardo is currently writing his PhD thesis.

acid from phenol and CO_2 ($\Delta H_r = -31.4$ kJ mol^{-1}) has been a commercial process since 1890.[6] Other applications of CO_2 are as refrigerants,[7a] fire-extinguishers,[7b] supercritical solvents[7c,d] and extraction media, though their contribution to reducing CO_2 emissions is still negligible. However, chemical reutilization of CO_2 could accomplish a decrease in carbon emissions and would also lead to economic benefits, if CO_2 could be converted into a chemical for which there is significant demand.

As highlighted by Sakakura,[6b] reutilization of CO_2 is restricted as most processes require large amounts of energy, though some reactions do have negative enthalpies of reaction. For example, $\Delta H_r = -40.7$ kJ mol^{-1} for the synthesis of benzoic acid from benzene and CO_2[8] and $\Delta H_r = -16.6$ kJ mol^{-1} for the synthesis of acetic acid from CO_2 and methane.[8] In general however, the high oxidation state of the carbon in CO_2 results in elevated thermodynamic stability, and therefore CO_2 utilization requires reaction with high energy substrates or alternative processes such as electroreduction.[6c] The major approaches being investigated for CO_2 transformation involve:

The use of high-energy starting materials, such as hydrogen, unsaturated compounds or organometallics.

The synthesis of low energy target molecules, such as organic carbonates.

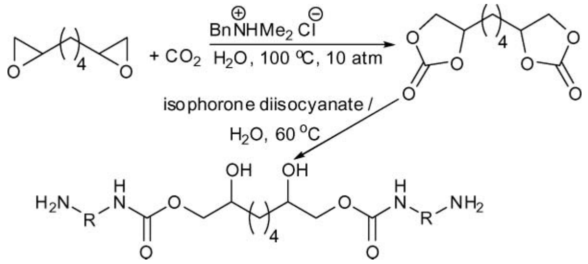
The design of processes in which the equilibrium is shifted towards the products by the removal of by-products.

The addition of significant energy, such as light or electricity, in order to perform the transformation.

1.2 Organic Carbonates

Incorporation of CO_2 into carbonates is a potentially significant transformation for the decrease of carbon emissions. Carbonates are usually grouped into inorganic (metal) and organic derivatives[6e] and organic carbonates can be further classified as cyclic carbonates, acyclic carbonates and polycarbonates. Much research has been devoted to the synthesis of organic carbonates starting from CO_2;[9] driven by its potential implications for climate change reduction and the associated economic benefits. The synthesis of cyclic, acyclic and polycarbonates have all been commercialized[6g,10] and the industrially important, non-polymeric, organic carbonates are dimethyl carbonate (DMC), diphenyl carbonate (DPC), ethylene carbonate (EC) and propylene carbonate (PC).

The outstanding impact-resistance and optical transparency of polycarbonates[6e–g] gives them applications in the manufacture of CDs, DVDs, eyeglasses, aircraft windows *etc*. Organic carbonates are important raw materials for polyurethane synthesis (Scheme 1), production of urea derivatives, and as alternatives to phosgene or dimethyl sulfate for methylation reactions.[11] In addition, organic carbonates can be used as green solvents,[12] additives to gasoline,[13] thickeners for cosmetics[6e] and electrolytes for lithium batteries.[6e–g] Diethyl carbonate is also used as an intermediate for phenobarbital synthesis.[14]

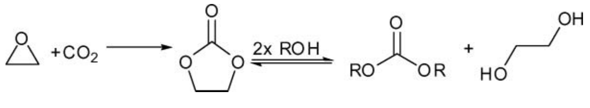


Scheme 1 Synthesis of polyurethanes *via* cyclic carbonates

The annual production of cyclic organic carbonates is still small at only 0.1 Mtons per year, though the use of diphenyl carbonate (DPC) as an intermediate in plastic manufacturing is estimated to be 2 Mtons per year,[6g] and the potential demand for DMC as a fuel additive is greater than 30 Mtons per year,[13] though this would require the cost of production to be reduced by ca 20%.

1.2.1 Acyclic carbonate synthesis. The conventional synthesis of acyclic carbonates is based on a two-step process involving phosgene generation from CO and Cl_2, followed by reaction with alcohols. This transformation gives only moderate yields, and presents several hazards due to the high toxicity of the starting materials and co-produced hydrogen chloride.[15] In 1990, ENIChem developed a single-step process based on oxidative carbonylation of methanol over a CuCl catalyst.[16] At the same time, the Japanese company UBE commercialized a similar transformation based on a Pd-nitric oxide system.[17]

An alternative route to acyclic carbonates involves the reaction of a cyclic carbonate (usually ethylene carbonate) with an alcohol (Scheme 2). In 1986, Texaco investigated the commercialization of this process,[18a–c] despite the disadvantages associated with the multi-step synthesis, generation of ethylene glycol as by-product and the hazards due to the utilization of ethylene oxide as a starting material. The Japanese company



Scheme 2 Synthesis of acyclic carbonates *via* cyclic carbonates

Carl Young

Carl Young was born in Carlisle, England in 1982. In 2000, he began studies in medicinal chemistry at the University of Newcastle upon Tyne and received his MChem in 2004. The following year, he started his doctoral studies under the supervision of Professor Michael North, focusing mainly on the investigation of salen-based catalysts for the asymmetric synthesis of cyanohydrins. He was awarded his PhD in 2009. The co-author of five papers, he is currently working as a postdoctoral researcher in the North group, developing immobilised catalysts for the synthesis of cyclic carbonates from CO_2 *and epoxides under gas-phase continuous flow conditions.*

Asahi Kensai also commercialized the same process several years later.[18d]

Direct formation of dimethyl carbonate (DMC) from CO_2 and methanol is potentially the most straightforward process for the synthesis of organic carbonates.[6b,e,g] The reaction usually requires high temperatures and an organostannane catalyst, though more recently new titanium and tin/acid catalysts have shown enhanced activity.[19] Despite the attempts to improve this process, drawbacks are still related to catalyst decomposition and poor conversions due to product hydrolysis side-reactions. The use of more efficient dehydrating agents such as zeolites, orthoesters, or Mitsunobu reagents[20] has been investigated, and shown significant improvements to the conversions, though the high cost of these dehydrating agents was not practical at an industrial level. At the present time, dehydrative condensation of methanol and CO_2 does appear to be the most efficient system for the synthesis of DMC.[6g] The transformation is carried out at 180 °C and up to 300 atmospheres pressure, using acetals as dehydrating agents, and tin, titanium or zirconium alkoxides catalysts. The process can give 720 kg day^{-1} m^3 of production.

1.2.2 Copolymerization of epoxides and CO_2. In 1969, pioneering work by Inoue[21] demonstrated that CO_2 could be used as a C_1 building block in propylene oxide/CO_2 copolymerization. This was achieved by the use of a heterogeneous catalyst system based on a 1 : 1 Et_2Zn/H_2O mixture, which exhibited a low TOF (0.12 h^{-1}) at 50–60 atmospheres pressure and 80 °C. Comparable results were also obtained with other substrates such as ethylene oxide, epichlorohydrin and styrene oxide.[21a] Different hydroxyl sources including resorcinol and pyrogallol were also investigated,[22] although no significant improvements were found for the Et_2Zn catalyst. The work of Inoue *et al.*[21,22] subsequently prompted increased interest in the development of more efficient catalysts for epoxide/CO_2 copolymerization. Many other catalysts have since been developed for polycarbonate synthesis including zinc-based complexes,[23,24] solid supported zinc catalysts,[25] rare earth metals,[26] metal macrocycles[27] and salen complexes.[28]

2 Cyclic carbonate synthesis

Cyclic carbonates can be obtained through the coupling reaction between CO_2 and strained heterocycles, though harsh reaction conditions and a suitable catalyst are often necessary.[6,29] The reaction between CO_2 and epoxides leads to five-membered ring containing cyclic carbonates, whilst CO_2 and oxetanes produce the corresponding six-membered ring derivatives. This approach benefits from eliminating phosgene as a reagent, and is 100% atom economical, making it a highly desirable transformation.

Cyclic carbonates are valuable synthetic targets; since their commercialization in the mid-1950s, they have found applications as polar aprotic solvents, electrolytes for lithium-ion batteries, and as intermediates in the manufacture of fine chemicals.[6,10,29] Cyclic carbonates are also used as constituents of oils and paints and as raw materials in the synthesis of polycarbonates[6,10] and polyurethanes[6e,13b] (see Scheme 1) since they can undergo ring-opening polymerization.[6] Five-membered ring cyclic carbonates are useful alkylating agents for aromatic amines, phenols and thiols, though high temperatures are required.[6] Thus, ring-opening at either alkylene position in the presence of base, followed by decarboxylation, leads to functionalized primary and secondary alcohols, which can undergo further modification.[30] This process is used for polymer modification, pre-polymer synthesis and the production of super-absorbent polymers.[29,30] Transesterification of cyclic carbonates catalysed by alkali is used for the synthesis of acyclic carbonates (Scheme 2). Thus, transesterification of ethylene carbonate with methanol leads to DMC and dry ethylene glycol. This reaction is an equilibrium, so under appropriate reaction conditions, it can also be used to convert 1,2-diols and acyclic carbonates into the five-membered ring derivatives.[29]

On an industrial scale, the synthesis of cyclic carbonates is usually carried out using Lewis acid or base catalysts, which require high temperatures and pressures. These conditions are a limiting aspect of the process, both in terms of energy and economics. If the utilization of cyclic carbonates is to be substantially increased, then new, commercially viable, catalysts and processes which operate at close to atmospheric pressure and close to room temperature are required to minimize the energy price component of the overall cost of cyclic carbonate production.

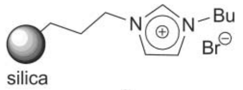
2.1 Catalytic systems for cyclic carbonate synthesis

In view of their potential for reducing CO_2 emissions and because of their economic importance, this review will focus on the synthesis of cyclic carbonates. There is much current interest in developing novel technologies that allow the synthesis of cyclic carbonates from CO_2 and highly reactive heterocycles under more economic conditions, thus reducing both the cost and greenhouse gas emissions. The following sections present a review of the major developments in the area of catalysis of cyclic carbonate synthesis. Alternative routes for the synthesis of cyclic carbonates will be summarized in section 2.3. It is not the intention of this survey to include all of the catalysts that have been reported for cyclic carbonate synthesis, but rather to concentrate on those that have the greatest potential to allow cyclic carbonate synthesis to be carried out under much milder conditions than is currently possible.

The use of traditional solvents is not always effective for the reaction between CO_2 and epoxides due to the low solubility of CO_2 in conventional solvents. In many cases, the reactions are carried out under solvent-free conditions with the epoxide acting as solvent. Alternatively, the cyclic carbonate product can be used as the solvent.[6b] Supercritical CO_2 has also been found to be an appropriate solvent, though this necessitated the use of high-pressure conditions.[31] Another solution is to use an ionic liquid as both solvent and catalyst as discussed in section 2.1.1, exploiting the high solubility of CO_2 in ionic liquids.

2.1.1 Cyclic carbonate synthesis in the presence of ionic liquids. Ionic liquids, or their combination with metal salts have been investigated as catalysts for the synthesis of cyclic carbonates due to the ease of catalyst recovery and product purification.[32,33] Peng and Deng[34] reported the quantitative synthesis of propylene carbonate in the presence of 2.5 mol% of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF_4) **1a**, though the reaction was carried out at 25 atmospheres pressure and 110 °C for six hours with a TOF of 6.6 h^{-1}. A higher TOF

($15\ h^{-1}$) was achieved using 1.5 mol% of **1a**, but under these conditions only 67% conversion was obtained after six hours. In addition, Kim *et al.*[35] investigated the role of Lewis acid species such as $ZnBr_2$ with ionic liquids as catalysts and obtained large improvements in the yields, although high-pressure conditions were still necessary.



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1a: X = BF_4, R = Bu; **1b**: X = Br, R = Bu
1c: X = Cl, R = Bu; **1d**: X = PF_6, R = Bu
1e: X = Cl, R = Oct; **1f**: X = I, R = Bu

Xia *et al.* used a similar system combining zinc salts with [BMIm]X (X = Cl, Br, BF_4, PF_6) **1a–d** for the addition of CO_2 to propylene oxide.[36] The best result in terms of product yield and TOF was the system using $ZnBr_2$ with [BMIm]Br **1b** which gave 98% yield and a TOF of $5580\ h^{-1}$. The use of $ZnCl_2$/[BMIm]Br gave comparable results of 95% yield and a TOF of $5410\ h^{-1}$. Reactions were carried out at 100 °C for one hour using a CO_2 pressure of 15 atmospheres. Other epoxides, including epichlorohydrin, 1,2-epoxybutane and styrene oxide were also tested, giving good results with the exception of cyclohexene oxide which produced a yield of only 34% (TOF $1206\ h^{-1}$). A catalytic cycle was proposed (Fig. 1) which involved activation of the epoxide by zinc and subsequent ring-opening with bromide. CO_2 could then insert into the Zn–O bond with ring-closure giving the cyclic carbonate. Using BF_4 or PF_6 as the ionic liquid counterion (**1a,d**) resulted in minimal catalytic activity, thus proving that the nucleophilic nature of the anion is crucial for the reaction to occur.

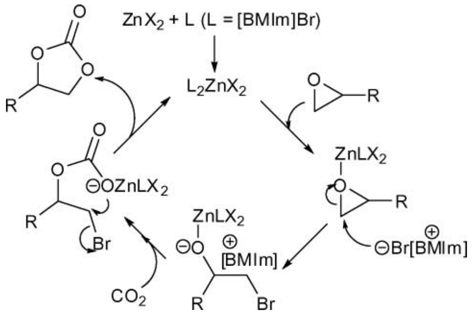
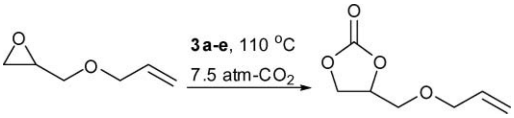


Fig. 1 Catalytic cycle for ZnX_2 facilitated addition of CO_2 to epoxides in the presence of the ionic liquid [BMIm]Br.

In 2006, the same group reported the use of an immobilized catalytic system involving ionic liquid and zinc salts.[37] Silica supported ionic liquid **2** was prepared *via* a sol–gel method and used as a catalyst (with $ZnCl_2$) for the addition of CO_2 to propylene oxide. The reaction parameters were varied within the study and the effect on the reaction was monitored. Standard reaction conditions utilized 10 mL of propylene oxide with CO_2 pressurized to 15 atmospheres and a temperature of 110 °C for one hour. With only zinc chloride as catalyst, no reaction occurred. Using 0.6 g of compound **2** resulted in 59% yield and a TOF of $1684\ h^{-1}$ and these improved further as the amount of compound **2** was increased up to 96% yield and $2741\ h^{-1}$ TOF when using 1.2 g of the immobilized ionic liquid. Reducing the reaction temperature to 90 °C had a significant impact, lowering the yield to just 61% (with a TOF of $1742\ h^{-1}$). Increasing the CO_2 pressure above 20 atmospheres was found to slightly reduce the yield and TOF, whilst reducing the pressure to 5 atmospheres severely retarded the reaction, giving only 19% yield and a TOF of $543\ h^{-1}$.

He *et al.* used a similar solventless catalytic system, but instead of covalently linking the ionic liquid to silica, methylimidazolium derivatives **1a,b,d** were adsorbed onto amorphous silica to form supported ionic liquid catalysts. These were subsequently used for the synthesis of propylene carbonate from propylene oxide in the presence of supercritical CO_2 at 80 atmospheres pressure.[38] The optimal conditions were found to be 160 °C for 4 h using 1.8 mmol% of **1a,b,d**. Under these conditions, catalysts **1a** and **1a**/silica gave excellent yields (>99 and 96% respectively) with >99% selectivity for formation of the cyclic carbonate. It was found that either increasing or decreasing the temperature or pressure away from these optimal values resulted in a reduction in the chemical yield of propylene carbonate. Reducing the catalyst loading to 1 mmol% also resulted in a decrease in the yield to 86% when using catalyst **1a**/silica. Despite the slight reduction in yield when using silica supported *versus* non-supported ionic liquids, the advantage of the supported system was apparent when carrying out a catalyst recycling study. It was found that catalyst **1a**/silica could be extracted from the reaction by filtration and re-used with only a minor loss in activity after four runs. **1a**/Silica was used as a catalyst for the addition of *sc*CO_2 to a selection of other terminal epoxides, which, with the exception of epichlorohydrin, all gave excellent yields (92–98%) and selectivities (94–100%).

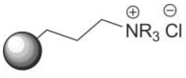
In 2008, Udayakumar *et al.* reported another immobilized ammonium salt based system for the catalytic addition of CO_2 to epoxides.[39] Quaternary ammonium salts were covalently attached *via* an organic linker to MCM-41 to give catalysts **3a–c**. The immobilized salts were then used to promote the reaction of CO_2 with allyl-glycidol (Scheme 3). The best result was 70% conversion, with 89% selectivity for the cyclic carbonate, using 1.0 g of catalyst **3a** in solvent-free conditions at 7.5 atmospheres pressure of CO_2 for 10 h at 110 °C, though the TOF for this reaction was just $6.3\ h^{-1}$. A higher TOF ($19.5\ h^{-1}$) was observed using 0.5 g of catalyst **3b** for 6 h under the same reaction conditions, but in this case the conversion was only 9.3%. When using 0.5 g of catalyst **3c**, 32% conversion (90% selectivity, TOF $8.7\ h^{-1}$) was obtained after 6 h. The use of solvents (dichloromethane or acetonitrile) had a negative impact on the reaction, giving conversions of just 45% and 52% respectively. However, there was a slight improvement in the selectivity for the cyclic carbonate product, particularly with acetonitrile as solvent, which gave 98% selectivity when using catalyst **3a**.



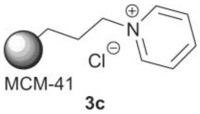
Scheme 3 Reaction of CO_2 with allylglycidol catalysed by immobilized catalysts **3a–e**.

Later,[40] the same group reported the synthesis of allylglycidyl carbonate using immobilized imidazolium-based ionic liquids, with various forms of silica as support. Similarly low TOFs

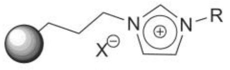
($4.4\ h^{-1}$ to $5.3\ h^{-1}$) were obtained for the addition of CO_2 (at 16.5 atmospheres pressure and 110 °C) to allylglycidyl ether using compounds **3e–g** supported on MCM-41. Using amorphous silica as the support under 17.7 atmospheres CO_2 pressure, better TOFs of $13.0\ h^{-1}$ (for **3d** and **3f**) and $16.2\ h^{-1}$ (**3e**) were achieved. Increasing the CO_2 pressure to 35 atmospheres further improved the results, giving 99% conversion with TOFs of $13.5\ h^{-1}$ (**3d**), $19.9\ h^{-1}$ (**3e**) and $14.5\ h^{-1}$ (**3f**). Use of compound **3e** supported on mesoporous silica gave the highest TOF of $32.6\ h^{-1}$ at 35 atmospheres CO_2 pressure ($15.5\ h^{-1}$ at 8.6 atmospheres).



3a: R = Et
3b: R = Hex

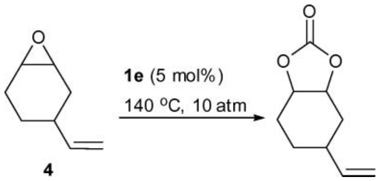


3c



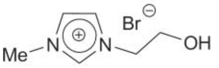
3d) R = ^{n}Bu, X = I
3e) R = ^{n}Bu, X = Br
3f) R = ^{n}Pr, X = Br
3g) R = ^{i}Pr, X = Br

Park *et al.* used similar silica-grafted imidazolium-based ionic liquids for the synthesis of cyclic carbonates from epoxides and CO_2.[41] After a reaction time of three hours, catalyst **3e** gave a 77% yield of allylglycidyl carbonate (Scheme 3) with a TOF of $8\ h^{-1}$ at 110 °C under 7.5 atmospheres CO_2 pressure with no added solvent. The catalytic system was shown to be recyclable up to five times with no apparent loss in activity. Lee *et al.* reported the addition of CO_2 to 4-vinyl-cyclohexene oxide (**4**) in the presence of 1-n-octyl-3-methylimidazolium chloride [OMIm]Cl **1e**, giving the corresponding cyclic carbonate in 62% yield (Scheme 4).[42] The reaction was carried out at 140 °C, and 10 atmospheres pressure and exhibited a TOF of $2.0\ h^{-1}$. Deng *et al.* showed that ionic liquids could also be used for the electrochemical synthesis of cyclic carbonates from CO_2 and epoxides.[32,43] Thus, propylene carbonate was synthesized in 92% conversion in the presence of [BMIm][BF_4] **1a** at room temperature and atmospheric pressure.



Scheme 4 Addition of CO_2 to epoxide **4** catalysed by [OMIm]Cl **1e**

Recent work by Zhang *et al.* resulted in the development of a new series of hydroxyl-functionalized imidazolium-based ionic liquids as highly active catalysts for the synthesis of propylene carbonate.[44a] 1-(2-Hydroxyethyl)-3-methylimidazolium bromide **5** [HeMIm]Br was found to be the most active catalyst, producing propylene carbonate in 99% yield at 125 °C and 20 atmospheres pressure, exhibiting a moderate TOF of $62\ h^{-1}$. An immobilized version (**6**) of the same catalyst system was also developed as a copolymer with styrene.[44b] At a pressure of 25 atmospheres of CO_2 and 120 °C with 1.6 mol% of catalyst **6**, an excellent conversion of 98% was achieved for the synthesis of propylene carbonate from propylene oxide after a reaction time of four hours. Excellent yields were also obtained for the synthesis of cyclic carbonates from a range of terminal epoxides after reaction times of 2.5–6 h at 115–120 °C. Even cyclohexene oxide gave a respectable 80% conversion albeit after 20 h at 125 °C. The results with catalyst **6** were comparable to those with catalyst **5** and had the added advantage of catalyst recyclability, with no apparent loss of activity after six reactions.



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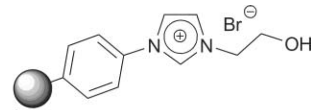

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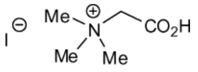
The synthesis of cyclic carbonates can also be accomplished starting from alkenes which are oxidized to epoxides *in situ*. Qiao and Yokoyama demonstrated this process in a multi-step one-pot synthesis starting from styrene under a pressurized CO_2 atmosphere in an ionic liquid medium ([BMIm]BF_4, **1a**) with urea hydrogen peroxide (UHP) as oxidant and methyltrioxorhenium (MTO) as oxidation catalyst.[45] The highest yield of styrene carbonate was 83% (the remainder consisting of styrene oxide), achieved by using 30 atmospheres pressure of CO_2 at 110 °C in the ionic liquid with 2 mol% MTO in the presence of a zinc-based cocatalyst (Zn[EMIm]$_2$$Br_4$) and UHP. The oxidation step was allowed to proceed for two hours, before the CO_2 addition reaction which required a further two hours. At 80 °C, the same procedure gave only a 55% yield of carbonate, and if the reagents for the two steps were all added simultaneously, then only a trace amount of cyclic carbonate could be isolated.

2.1.2 Cyclic carbonate synthesis catalysed by –onium salts or by a metal salt and an –onium salt.

2.1.2.1 Quaternary ammonium and phosphonium salts. Caló *et al.* showed that molten tetrabutylammonium bromide (TBAB) could catalyse the synthesis of styrene carbonate from CO_2 and styrene oxide.[46] The reaction gave styrene carbonate in 83% yield, at 120 °C and atmospheric pressure, with a TOF of $1.3\ h^{-1}$. In 2008, Park *et al.* studied the addition of CO_2 to butyl glycidyl ether in the presence of tetraalkylammonium salts and found that the catalytic activity improved as the length of the alkyl groups increased, though substituents longer than C_8 did not produce any beneficial effect.[47] The effect of the counterion was also investigated, with the chloride derivative being the most active. Thus, tetrahexylammonium chloride (THAC) was found to be the most active catalyst for the addition of CO_2 to butyl glycidyl ether; giving the corresponding cyclic carbonate in 81% conversion at 100 °C and 9 atmospheres pressure, with a TOF of $2.7\ h^{-1}$.[47]

Tetraalkylammonium and phosphonium halides combined with organotin halides were successfully used by Baba *et al.* for the synthesis of cyclic carbonates. Using n-Bu_3SnI with n-Bu_4PI gave excellent yields for a range of cyclic carbonates, the best of which was 100% yield with propylene oxide as substrate after one hour at 40 °C under 49 atmospheres of CO_2 pressure.[48] Tetraalkylammonium and phosphonium halides used alone were less effective catalysts for cyclic carbonate synthesis,[48,49] giving yields of 17–100% for the reaction of CO_2 with phenylglycidol in NMP (100% with 5 mol% benzyltrimethylammonium chloride), corresponding to TOFs of 0.85–$5\ h^{-1}$ at atmospheric pressure and 100 °C.[49c] Pentavalent organoantimony halides such as Ph_4SbBr, Ph_3SbBr_2 and Me_3SbBr_2 were also found to be active catalysts for cyclic carbonate synthesis at 50 atmospheres pressure and 60–120 °C, giving high yields (72–99%) and exhibiting TOFs of 150–700 h^{-1}.[50]

A series of betaine-based solid catalysts synthesized by Han *et al.* showed moderate activity for the addition of CO_2 to epoxides, including disubstituted derivatives such as cyclohexene oxide.[51] Propylene carbonate was obtained in 98% yield in the presence of the betaine hydroiodide catalyst **7** from a reaction carried out at 140 °C and 80 atmospheres pressure with a TOF of 4.9 h^{-1}. Under the same conditions, cyclohexene carbonate was obtained in 85% yield with a TOF of 4.2 h^{-1} and styrene carbonate was prepared in 96% yield (TOF 4.8 h^{-1}).[51]



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A recent paper by Zhang *et al.* reported the use of water as an additive in various systems for the reaction of propylene oxide with CO_2, including some reactions carried out in ionic liquids.[52] During the initial screening of catalytic systems, it was shown that in all cases (except zinc bromide) there was a significant increase in chemical yield when 0.3 equivalents of water were added to the reaction. Excellent isolated yields were obtained using quaternary ammonium salts Bu_4NBr (86%), Bu_4NI (88%), ionic liquids [BMIm]Br **1b** (87%), [BMIm]I **1f** (90%) and phosphonium salts Ph_3PBuBr (88%), Ph_3PBuI (95%), Ph_3PEtBr (85%), $Ph_3PHexBr$ (89%). The reactions were carried out under 20 atmospheres pressure of CO_2 with 0.5 mol% of catalyst at 125 °C for one hour. The highest recorded TOF for a reaction in the presence of water was 194 h^{-1} using Ph_3PBuI. This was four times higher than that obtained for the same catalyst under anhydrous conditions. This phosphonium iodide catalyst was recyclable and retained high activity after being reused ten times. It also gave a good yield of 72% when the CO_2 pressure was reduced to five atmospheres, a result which was nine times higher than the same reaction under anhydrous conditions. The role of the water was proposed to involve initial activation of the epoxide and stabilization of the ring-opened and carbonate intermediates (Fig. 2). Other protic solvents such as phenol and acetic acid also had a beneficial effect on propylene carbonate synthesis, but were not as effective as water. Five other epoxides were used as substrates in the presence of water under the optimized conditions (with Ph_3PBuI as catalyst) and high yields (83–95%) were obtained for terminal aliphatic epoxides and styrene oxide. Cyclohexene oxide gave only a moderate yield of 47%, though this was still much greater than the 6% achieved without adding water.

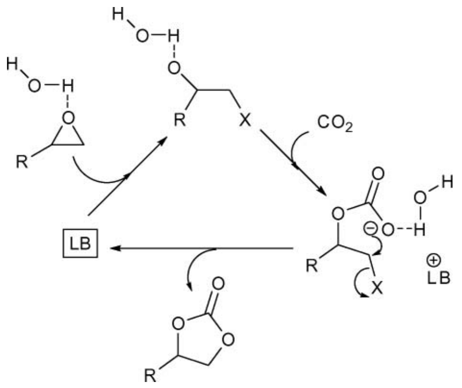
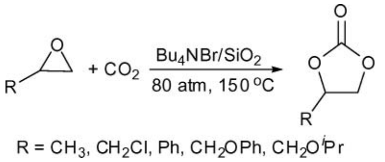


Fig. 2 Proposed catalytic cycle for the addition of CO_2 to epoxides in the presence of water.

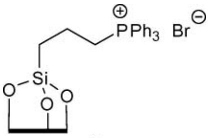
He *et al.* used CO_2 under supercritical conditions with a silica-supported quaternary ammonium salt catalyst for the synthesis of cyclic carbonates from terminal epoxides.[53] Using propylene oxide as substrate, an initial survey was carried out in which a range of unsupported and silica-supported tetra-n-butylammonium halide salts were tested for activity. The reaction conditions used CO_2 at 80 atmospheres pressure with 1 mmol% catalyst at 150 °C for 10 h. All four of the silica supported salts produced high yields with the bromide and iodide salts giving the best results of 97% and 96%. Unsupported TBAB gave an equally good result, but the other halide salts gave marginally lower yields, particularly in the case of the fluoride salt (66%). A similar pattern was found when using epichlorohydrin as the epoxide substrate with silica supported catalysts, but the yields were lower by at least ten percent than with propylene oxide, and in the case of the fluoride salt, the yield was only 50%.

Other quaternary ammonium salts were also investigated including tetra-methyl, ethyl and n-propyl ammonium bromides. Supported on silica, all three of the salts were as active as TBAB, giving excellent yields (≥96%) and selectivity (≥97%) for the cyclic carbonate. The non-supported quaternary ammonium bromide salts, with the exception of tetramethylammonium bromide which gave virtually no reaction, were also equally good catalysts, giving at least 94% yield and 97% selectivity for propylene carbonate. Changing the reaction conditions resulted in variation of the catalyst activity; with 1 mmol% of TBAB on silica, it was found that 8 h was the optimal reaction time and 80 atmospheres the most suitable CO_2 pressure. Any change in the pressure resulted in a reduction of propylene carbonate yield. A temperature of 150 °C was found to be ideal for propylene carbonate formation, whilst using higher or lower temperatures was found to have severely negative effects on the reaction yield. Using the optimized conditions shown in Scheme 5, five terminal epoxide substrates were used to test the scope of the catalyst. Results were very good to excellent for all substrates (89–97% yield, the lowest of which was derived from epichlorohydrin). Selectivity for the cyclic carbonate was also excellent with 95% or above observed in all cases. A recycling experiment showed that over the course of four reactions, there was only a slight reduction in activity of the TBAB/silica catalyst, which could be easily removed by filtration at the end of each reaction.



Scheme 5 Addition of CO_2 to epoxides catalysed by TBAB on silica.

3-(Triethoxysilyl)propyltriphenylphosphonium bromide supported on mesoporous silica (**8**) was prepared by Sakay *et al.* and was found to be a highly active catalyst for the addition of CO_2 to 1,2-epoxyhexane under solvent-free conditions.[54] The cyclic carbonate product was obtained with 99% conversion at 90 °C and 10 atmospheres pressure with a TOF of 8.2 h^{-1}. Recyclability experiments demonstrated that complex **8** could be reused over 10 runs, without a significant loss in activity.[54]



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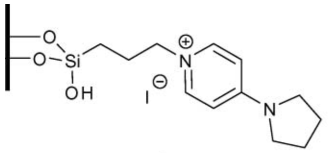
Polystyrene bound onium salts have been used as catalysts for the synthesis of cyclic carbonates. Nishikubo *et al.* reported moderate results for a range of quaternary ammonium or phosphonium salts on a polystyrene (PS) support,[55] the best of which was with (PS)–CH_2–$P^+(Bu)_3Cl^-$ which catalysed the addition of CO_2 to phenylglycidol, producing the corresponding cyclic carbonate in up to 62% yield. Reactions were carried out using 1 mol% of catalyst with atmospheric pressure CO_2 at 60 °C in toluene. Improved yields were obtained by increasing the length of the supporting tether. With seven methylene groups [(PS)–$(CH_2)_7$–$P^+(Bu)_3Cl^-$], yields of 74–86% were obtained under the above conditions and these increased further to 93–100% when the reactions were carried out at 90 °C or with 2 mol% catalyst. Using solvents other than toluene gave lower yields and increasing the amount of catalyst above 6 mol% did not further improve the yield. The catalyst was found to be recyclable over at least seven reactions with little reduction in reactivity. Under the optimal conditions (2 mol% catalyst, 90 °C, 72 h), four other epoxides (n-butylglycidol, vinylglycidol, 2-propenylglycidol and styrene oxide) were used as substrates and all gave yields of 81–91% for the corresponding cyclic carbonate.

A quaternary trimethylammonium iodide supported on chitosan (chitosan-NMe_3I) was found to catalyse the synthesis of propylene carbonate in 100% yield with high selectivity.[56] The reaction was carried out at 140 °C and at 40 atmospheres pressure with a TOF of 9.8 h^{-1}. Syntheses of various cyclic carbonates were carried out in the presence of triphenylphosphonium bromide attached to polyethylene glycol ($Br^-Ph_3P^+$-PEG600-$P^+Ph_3Br^-$) at 100 °C and 27 atmospheres pressure.[57] Styrene carbonate was obtained in 98% yield, but propylene carbonate was obtained in just 60% yield even though the reaction was carried out at 120 °C.

2.1.2.2 Pyridinium salts. Motokura *et al.* reported the use of silica-supported ammonium and aminopyridinium halides as catalysts for the addition of CO_2 to epoxides.[58] Using styrene oxide as substrate with one atmosphere CO_2 at 100 °C, 0.9 mol% of catalysts **9** and **10** produced the best yields of styrene carbonate (both 89%). Catalyst **9** could be reused four times without loss of activity, whereas the chemical yield obtained using catalyst **10** decreased by 20% after just one reuse. By using 3.6 mol% of catalyst **9**, an 86% yield was achieved at 30 °C and one atmosphere pressure after a reaction time of 32 h. Catalyst **9** was used to catalyse the addition of CO_2 to a range of aromatic and aliphatic terminal epoxides, all of which gave yields of 80–89% from reactions carried out at 100 °C.

Polystyrene supported pyridinium salts were also found to catalyse the synthesis of cyclic carbonates from CO_2 and terminal epoxides. After 6 h reaction at 80 °C in *N*-methylpyrrolidone at one atmosphere pressure, poly(4-vinyl-n-butylpyridinium bromide) **11** catalysed the addition of CO_2 to glycidyl phenyl ether (GPE) in quantitative yield.[59] Catalyst **11** was easily recovered from the reaction mixture by centrifugation and reused without significant loss in catalytic activity.



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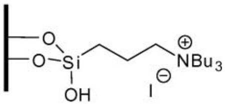

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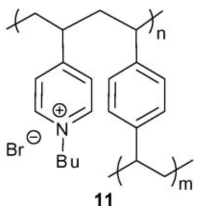


11

2.1.2.3 Zinc-based systems. Many zinc-based catalysts were found to preferentially produce polymers as the product of the reaction between epoxides and CO_2 (see section 1.2.2).[60] This is probably due to multiple metal-site catalysis,[61] though some zinc salts, used alone or with onium species (both homogeneous and heterogeneous) as cocatalysts have been reported to be selective catalysts for cyclic carbonate formation as discussed below.

In 1999, Ree *et al.*[62] modified a Zn-glutarate catalyst previously used for polycarbonate synthesis[60,63] by introducing ZnO as the zinc source. This modified catalyst system was found to promote the synthesis of propylene carbonate with a TOF of just 3.4 h^{-1} even though the reaction was carried out at 60 °C and 25 atmospheres pressure.

Zhang *et al.* reported the use of hexaalkylguanidinium salts as cocatalysts with $ZnBr_2$ for the addition of CO_2 to epoxides.[64] Using propylene oxide with a CO_2 pressure of 40 atmospheres at 100 °C, high TOFs and moderate to excellent yields were obtained after a reaction time of one hour. The best results were obtained using hexabutylguanidinium bromide; when an 8 : 1 ratio of guanidinium salt to $ZnBr_2$ was employed, a 100% yield was obtained with a TOF of 3571 h^{-1}. Notably, the loading of the $ZnBr_2$ catalyst was only 0.03 mol%. A further survey of reaction conditions revealed that the optimal parameters were 130 °C and 30 atmospheres pressure. Using these optimized conditions, with a 6 : 1 ratio of hexabutylguanidinium bromide to $ZnBr_2$, four other epoxides were used as substrates for CO_2 insertion. Excellent TOFs were reported for styrene oxide (6627 h^{-1}), epichlorohydrin (10103 h^{-1}) and phenylglycidol (8120 h^{-1}). Cyclohexene oxide gave a significantly lower TOF of 1958 h^{-1}, but still provided a respectable yield of 65% after just a one hour reaction. Recycling of the catalyst provided consistent results even after five reactions, with only minimal reductions in yield and TOF.

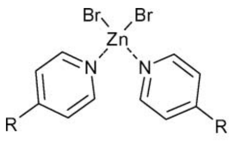
$ZnBr_2$ in conjunction with tetrabutylammonium iodide (TBAI) was also found to be an efficient binary catalyst system for styrene carbonate synthesis[65] (TOF 686 h^{-1}), although the process was carried out in supercritical CO_2. Good results were also obtained when the reaction was carried out in a microwave reactor at 30 atmospheres pressure and 100 °C (yield 72%, TOF 6732 h^{-1}).[66] Kisch *et al.*[67] reported a very efficient $ZnCl_2$-TBAI catalyst for cyclic carbonate synthesis from a wide range of terminal epoxides at room temperature and atmospheric pressure (TOF 143 h^{-1} for propylene carbonate), whereas the catalyst was found to be inactive for di-substituted epoxides. $ZnBr_2$-Ph_4PI mixtures were also found to be highly active (TOF

6272 h^{-1}) and selective for propylene carbonate synthesis at 25 atmospheres pressure and 120 °C.[68]

Zhang *et al.* reported the use of $ZnCl_2$ with a phosphonium halide cocatalyst for the formation of cyclic carbonates from epoxides and CO_2 under supercritical conditions.[69] Several phosphonium salts were screened and the best yield of 98.5% was obtained after a reaction time of one hour using a 1 : 6 ratio of $ZnCl_2/Ph_3PC_{10}H_{21}Br$, for which a TOF of 4841 h^{-1} was obtained for the coupling of CO_2 to propylene oxide under 15 atmospheres pressure at 120 °C. It was noted that the catalytic activity generally increased as the molecular weight of the phosphonium salt increased and phosphonium chlorides were less effective catalysts than the corresponding bromides or iodides. A high selectivity for the cyclic carbonate product was seen in all cases, even for those reactions where the yields were more moderate. Reducing the reaction temperature had a significantly detrimental effect on the reactivity; the yield approached 100% after one hour at 120 °C, but reducing the temperature to 100 °C resulted in approximately 45% yield, with a further reduction to around 27% yield at 80 °C.

High catalyst activity (TOF 1640 h^{-1}) and selectivity for propylene carbonate synthesis has also been reported for phosphine adducts of zinc(II) halides, such as $ZnBr_2(PMePh_2)_2$, though this catalyst system required 25 atmospheres pressure and a temperature of 100 °C.[70] A poly(4-vinylpyridine)/$ZnBr_2$ supported catalyst also showed high activity (TOF 207 h^{-1}) and complete selectivity for ethylene carbonate synthesis, from CO_2 and ethylene oxide at 35 atmospheres pressure and 100 °C.[71]

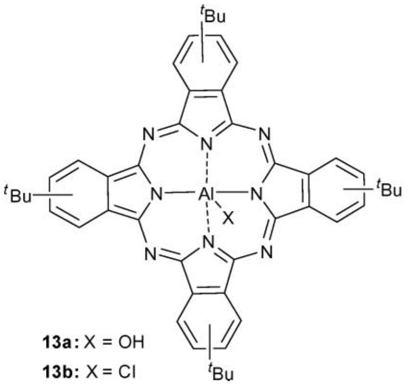
Homogeneous and heterogeneous zinc/pyridine-based catalysts were studied by Baiker *et al.* for the addition of CO_2 to propylene oxide.[72] Starting with zinc salts, pyridine or 4-pyridinecarboxaldehyde was added to give complexes which could then be used directly or be subject to further reactions *via* the aldehyde to form imine linkages to other organic moieties or functionalized silica. The general reaction conditions employed a measured weight (3.4–3.9 equivalents) of CO_2 in a steel autoclave containing the catalyst and propylene oxide, pressurized by heating to 140 °C. Using only 0.02 mol% of catalyst **12a**, a 67% yield of propylene carbonate was obtained after three hours with a TOF of 1125 h^{-1}. This yield was improved to a maximum of 91% by increasing the catalyst loading to 1 mol% and increasing the reaction time to four hours. Significant results were also obtained using catalysts **12b** (38% yield, TOF 657 h^{-1}), **12c** (63% yield, TOF 1055 h^{-1}) and **12d** (42% yield, TOF 660 h^{-1}). As well as the pyridine groups, the nature of the other ligands attached to zinc was found to be extremely important; zinc bromide-based catalysts were found, in all cases, to be many times more active than the corresponding zinc acetate complexes. Heterogeneous catalysts covalently attached to silica were found to be less reactive, a 51% yield was obtained using catalyst **12e** (TOF 331 h^{-1}) which could be improved to 56% (TOF 507 h^{-1}) with the addition of 0.1 mol% of ammonium bromide.



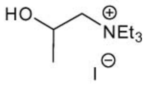
12a: R = H
12b: R = CHO
12c: R = CH=NBu
12d: R = $CH=N(CH_2)_3Si(OEt)_3$
12e: R = $CH=N(CH_2)_3$-silica

Various metal triflate complexes were screened by de Vos *et al.* as catalysts for the synthesis of cyclic carbonates.[73] These complexes were used in conjunction with a cetyltrimethylammonium bromide cocatalyst under 20 atmospheres pressure of CO_2 at 120 °C. With 1,2-epoxyoctane as substrate, after four hours, the best results were obtained using zinc triflate and scandium triflate (98% yield of cyclic carbonate). The high yields appeared to be limited to terminal epoxides, as 1,2-epoxydecane also gave 98% yield whereas cyclohexene oxide gave only 17% yield and 2-methyl-2-vinyloxirane gave just 8% yield. Using immobilized catalysts supported on montmorillonite, excellent yields could also be achieved under the same conditions. Thus, octene carbonate was obtained in 98% yield using the zinc triflate-montmorillonite catalyst, and in 91% yield using the scandium triflate-montmorillonite catalyst

2.1.2.4 Aluminium-based systems. In 1996, Kasuga *et al.* showed that the reaction of CO_2 with propylene oxide could be catalysed by aluminium complex **13a** in the presence of quaternary ammonium iodide **14**.[74] The best result obtained was only 1.3% yield after a reaction time of six hours, but CO_2 was used at atmospheric pressure and ambient temperature with 0.5 mol% of **13a** and 1 mol% of **14**. Other epoxides were tested using 0.2 mol% of the aluminium catalyst and 2 mol% of **14** and it was found that other terminal epoxides gave virtually identical results to propylene oxide, but no reaction occurred with cyclohexene oxide.



13a: X = OH
13b: X = Cl



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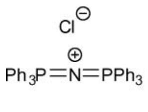
2.1.2.5 Cobalt-based systems. Repo *et al.* used a cobalt catalyst with onium salt cocatalysts for the coupling of CO_2 to epoxides.[75] Initial experiments showed that using 10 atmospheres pressure of CO_2 at 120 °C, $CoCl_2$ was inactive when used alone for the synthesis of propylene carbonate, but gave high TOF's after one hour when used with (*bis*-triphenylphosphoranylidene)-ammonium chloride **15** (2314 h^{-1}), tetra-n-butylammonium chloride (TBACl) (2223 h^{-1}) or 1,3-*bis*-(2,4,6-trimethylphenyl)-imidazolium chloride **16** (2174 h^{-1}). The cobalt catalyst was used at a 0.025 mol% loading with 0.1 mol% of the onium salt in dichloromethane. Other cobalt(II) salts (bromide and acetate) were also active catalysts, but with lower TOFs than $CoCl_2$.

Optimization of the reaction conditions led to further improved TOF values. Using 10 atmospheres pressure of CO_2 with 0.025 mol% $CoCl_2$ and 0.2 mol% of TBACl or **15** resulted in TOFs of 2660 and 2470 h^{-1} respectively for propylene carbonate synthesis. Four other epoxides were also screened using 15 atmospheres pressure of CO_2, 0.05 mol% of $CoCl_2$ and 0.2 mol% of onium salt. Compound **15** was found to be marginally more effective than TBACl and considerably more active than **16** with good TOF values obtained for 1,2-epoxyhexane (1463 h^{-1}), (2-ethylhexyl)glycidol (1450 h^{-1}) and styrene oxide (1238 h^{-1}). However, cyclohexene oxide gave a relatively poor TOF of 156 h^{-1}. The proposed mechanism involved coordination of the epoxide to the cobalt and subsequent ring-opening with a chloride ion. CO_2 then inserts into the cobalt bound alkoxide and ring-closure produces the cyclic carbonate. The onium salt was proposed to be a counterion for the negatively charged cobalt species which could detected by mass spectrometry.


$Ph_3P{=}\overset{\oplus}{N}{=}PPh_3 \quad Cl^{\ominus}$

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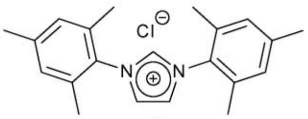

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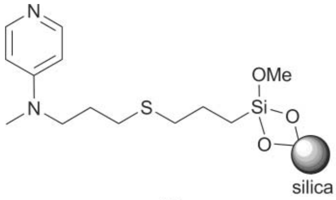
2.1.2.6 Titanium and tin-based systems. Jing *et al.* recently reported the use of titanocene in conjunction with a Lewis base to catalyse the formation of cyclic carbonates.[76] Optimization of the reaction conditions led to the use of 1 mol% of Cp_2TiCl_2 in THF at 150 °C under 12 atmospheres of CO_2 as the standard conditions. The best result obtained with propylene oxide was obtained when using TBAB (1 mol%) as the Lewis base giving a TOF of 392 h^{-1}. Almost all of the Lewis bases studied gave good yields and the second most effective was TBACl which gave a TOF of 149 h^{-1}. Good to excellent yields were achieved using other epoxide substrates although the TOFs were significantly lower than that achieved for propylene oxide. Thus, use of butylene oxide, reduced the TOF to just 75 h^{-1} and with dodecene oxide as substrate, the TOF was further reduced to 28 h^{-1}. Cyclohexene oxide was found to be the least reactive substrate with a TOF of 15 h^{-1} recorded after a five hour reaction.

A $SnCl_4$-DMAP mixture (1 : 5) was found to be an active catalyst system for cyclic carbonate synthesis from terminal epoxides. High TOFs (1388 h^{-1} for propylene carbonate synthesis) were obtained under moderate reaction conditions (75 °C, 3 atmospheres pressure) from reactions which gave high yields (90–100%) of cyclic carbonates in 1–3 h.[77] Cyclohexene oxide was also a substrate, though a 10 h reaction at 100 °C was required to give a 78% yield of cyclohexene carbonate.

2.1.2.7 Mixed metal systems. Sun *et al.* demonstrated the use of a three-component system comprizing a gold/iron hydroxide composite with $ZnBr_2$ and TBAB as a catalyst for the synthesis of styrene carbonate directly from styrene in the presence of *tert*-butylhydroperoxide.[78] The catalyst contained 6.7% gold by weight and was prepared by co-precipitation. Under 40 atmospheres CO_2 pressure at 80 °C, 88% conversion of styrene was observed with a 40% yield of styrene carbonate obtained using 2.5 mol% $ZnBr_2$ and 5 mol% TBAB. The remainder of the product consisted of styrene oxide, benzaldehyde and some oligomers. Using a lower gold loading (4.7%), a slightly better conversion of styrene was observed (91%) with a 43% yield of styrene carbonate obtained. Using hydrogen peroxide as the oxidant had a significantly negative effect on the yield of styrene carbonate, reducing it to just 14%, with a higher proportion of benzaldehyde and other products formed. It was suggested that the gold/iron catalyst was responsible for catalysing the oxidation reaction whereas the $ZnBr_2$/TBAB system facilitated the reaction with CO_2. As an extension to this work, Sun's group also used a gold catalyst supported on R201 resin.[78b] A successful one-pot synthesis of styrene carbonate (51% yield) was achieved after four hours starting from styrene using a 0.01% gold loading on R201 under 40 atmospheres of CO_2 at 150 °C. Reuse of the catalyst was demonstrated with only a small loss in activity.

A double metal cyanide-quaternary ammonium salt catalyst system for the synthesis of cyclic carbonates was developed by Park *et al.*[79] The highest TOF (996 h^{-1}) was obtained using 0.1 mol% of $Zn_3[Co(CN)_6]_2$ with 1 mol% TBAB for six hours at 120 °C under 3.4 atmospheres pressure of CO_2 for the reaction of CO_2 with styrene oxide. Using different ammonium bromide salts as cocatalysts did not greatly affect the reactivity; though reducing the temperature significantly lowered the TOF. Under the optimal conditions, similarly high TOFs were obtained in reactions with other terminal epoxides (propylene oxide 958 h^{-1}, hexene oxide 996 h^{-1}, epichlorohydrin; 963 h^{-1} and phenylpropylene oxide 972 h^{-1}) with a noticeably lower value of 756 h^{-1} obtained when using cyclohexene oxide.

2.1.3 Cyclic carbonate synthesis using organocatalysts. Jones and Shiels reported the use of dimethylaminopyridine (DMAP) as a catalyst for propylene carbonate formation and extended the study to include DMAP derivatives which could be immobilized on silica to give a heterogeneous catalyst.[80] Using 0.4 mol% of DMAP, it was found that a conversion of 85% could be obtained after 4 h at 120 °C under 17 atmospheres of CO_2. This result could be improved to 92% yield by increasing the pressure to 34 atmospheres. Supported DMAP derivative **17** was prepared and used as a catalyst for the addition of CO_2 to propylene oxide, giving a conversion of 81% under the optimized conditions.



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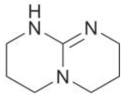

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Tsang *et al.* have recently reported the use of silica supported and non-supported amines for the synthesis of cyclic carbonates.[81] An initial screening of unsupported amines revealed that an excess of 1,5,7-triazabicyclo[4,4,0]-dec-5-ene (TBD) **18** was able to convert propylene oxide into propylene carbonate with 100% yield after 24 h under 50 atmospheres of CO_2 at 150 °C. TBD covalently attached to silica also gave 100% yield under the same conditions. The amine group was suggested to have a role in activating the carbon dioxide in the form of a carbamate which could then attack and ring-open the epoxide.

2.1.4 Cyclic carbonate synthesis catalysed by metal halides. At 50 atmospheres pressure and 120 °C, simple metal salts such as K_2CO_3, KCl, KI, LiBr and NaOH catalysed propylene carbonate formation with quantitative yields,[82] particularly when used in conjunction with crown ethers, although TOFs were only 30 h^{-1}. More recent work carried out by Shi *et al.*[83] reported a moderate TOF of 24 h^{-1} for reactions carried out under 40 atmospheres pressure at 120 °C in the presence of NaI/PPh_3/PhOH. Under the same reaction conditions, a $CaCl_2$/octyl$_3$(Me)NCl catalyst system[84] also exhibited high yields and a moderate TOF of 52 h^{-1} for propylene carbonate synthesis. A catalyst system based on $NiCl_2/PPh_3$ in the presence of TBAB and zinc powder as a reducing agent, produced an excellent yield (>99%) and TOF (3544 h^{-1}) at 25 atmospheres pressure and 120 °C.[85]

Work by González *et al.*[86] demonstrated high catalytic activity for cyclic carbonate formation (TOF 293 h^{-1}), in the presence of solid supported $RuCl_3$ (with SiO_2, or tetraethylammonium bromide as the support), at 80 °C and under supercritical conditions. Conversely, when polyphosphotungstinic acid (HPW) was used as the support, polycarbonate products were obtained with the same TOF.[86] Differences in the solid supports were suggested to influence the relative hardness of the electrophilic ruthenium sites, resulting in the formation of a single- or multi-site catalyst;[61] thus, cyclic carbonate or polycarbonate was formed selectively.[86] Sakakura *et al.*[87] reported the use of samarium oxychloride as a catalyst for the addition of CO_2 to propylene oxide, obtaining quantitative yields in DMF at 200 °C under supercritical conditions.

2.1.5 Cyclic carbonate synthesis catalysed by metal oxides.

The acidic and basic properties of metal oxides allow them to interact with polarizable species such as CO_2. The adsorption of CO_2 onto metal oxides is a known process with several examples reported in the literature,[9,88] including infrared studies on MgO,[88a] CaO,[88a] TiO_2,[88b] ZnO[88c] and BeO.[88d] As a result, activation of CO_2 by metal oxides has been used to catalyse the synthesis of cyclic carbonates from terminal epoxides[89] and the ease of catalyst recovery and product separation has prompted much work on the development of metal oxide catalysts.[90]

MgO[89] was found to convert propylene and styrene oxides into the corresponding cyclic carbonates in 41and 47% yield respectively at 135 °C and 20 atmospheres pressure; exhibiting moderate TOFs of 14 h^{-1} for propylene carbonate synthesis and 15 h^{-1} for styrene carbonate synthesis. In the presence of Mg–Al mixed oxides,[90] propylene carbonate synthesis was accomplished in higher yield (88%) at 120 °C and 3 atmospheres pressure, though no significant improvement was reported for the styrene derivative (38% yield). However, the TOFs were reduced under these conditions, due to the high catalyst loading and the long reaction time employed (TOF < 4 h^{-1}).

Several smectite materials[91] containing Mg–Ni mixtures and alkali metals, such as Na, K and Li, were also investigated for propylene carbonate synthesis, giving high activity (81% yield) and selectivity (94%) at 150 °C and 80 atmospheres pressure. In 2008, Yuan *et al.* found a heterogeneous magnesium-based catalyst system for the addition of CO_2 to terminal epoxides under solvent-free conditions, using a combination of magnesium hydroxychloride [Mg(OH)Cl] and potassium iodide.[92] Propylene carbonate was synthesized in 98% yield at 130 °C and 60 atmospheres pressure, with the catalyst exhibiting a TOF of 17 h^{-1}. Styrene carbonate was obtained in 75% yield with a TOF of 8.0 h^{-1}.

Work carried by Davis *et al.*[93] on ethylene carbonate synthesis investigated various solid catalysts, including modified zeolites and magnesia. Initially, the reaction was carried out at 150 °C and 100 atmospheres pressure in the presence of a Cs-zeolite catalyst, though only 33% of ethylene carbonate could be isolated.[93a] Later results showed that at 80 atmospheres pressure the yield dropped further to 19%.[93b] Conversely, work by Sakakura[94] showed that a caesium-phosphorous-silicon mixed oxide (Cs–P–Si) exhibited quantitative yields for propylene carbonate synthesis at 80 atmospheres pressure and 200 °C. In addition, the Cs–P–Si catalyst also gave greater than 50% yields and complete selectivity for cyclic carbonate formation in a flow reactor.[94]

Titanosilicate molecular sieves[95] have been used as catalysts in conjunction with TBAB or DMAP, and gave high yields (71–85%) of epichlorohydrin carbonate at 120 °C and 7 atmospheres pressure; this catalyst system showed moderate to high TOFs (168–790 h^{-1}). Doskocil[96] reported the use of metal-alkali derivatized titanosilicate ETS-10 for propylene carbonate synthesis at 135 °C and 35 atmospheres pressure, though only 3% yield was obtained after a 24 h reaction. The same group subsequently investigated the role of water in the addition of CO_2 to propylene oxide in the presence of ETS-10 catalyst,[97] though still only a 5% yield of propylene carbonate was obtained. Conversely, mesoporous ordered silicates, such as titanium-MCM-41, exhibited high catalytic activity for propylene carbonate synthesis (yield 90%),[98] although only a moderate TOF (36 h^{-1}) was observed at 120 °C and 7 atmospheres pressure. However, when other terminal epoxides were used, the product selectivity dropped, with the reaction giving a mixture of cyclic carbonate, diols and ethers.

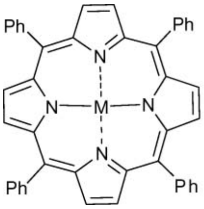
Srinivas also demonstrated the use of titanium incorporated onto an adenine modified SBA-15 silica support for the synthesis of cyclic carbonates and aryl/alkyl carbamates.[99] With 0.5 mol% of catalyst under 7 atmospheres CO_2 pressure and at 120 °C, excellent conversions to cyclic carbonates were achieved using epichlorohydrin (94% after 4 h), propylene oxide (95% after 6 h) and styrene oxide (94% after 8 h). In 2007, Bhanage[100] demonstrated that silica supported-poly(4-vinylpyridine) (SiO_2-PVP) could be used to catalyse the addition of CO_2 to terminal epoxides. Propylene carbonate was synthesized in 93% yield at 150 °C and 54 atmospheres pressure, with a moderate TOF (17 h^{-1}), though this was dependent on the degree of pyridine incorporation into the support.[100] Styrene carbonate and epichlorohydrin carbonate were also obtained with yields greater than 84%.

A zinc-based hydroxyapatite catalyst gave high yields of styrene carbonate (89%), in the presence of DMAP as a cocatalyst;[101] the process was carried out at 100 atmospheres pressure and 100 °C and exhibited a TOF of 308 h^{-1}. Baiker *et al.* investigated the use of zinc-based catalysts supported on silica in conjunction with TBAB as cocatalyst for the synthesis of propylene carbonate under solvent-free conditions.[102] The catalysts were prepared by combining a zinc source with a silica precursor either *via* a sol–gel route or by flame spray pyrolysis. Reactions were carried out at 45 atmospheres pressure and 100 °C and yields of 15.5% and 19.2% were obtained using catalysts derived from flame treated zinc$(acac)_2$/tetraethoxysilane and the sol–gel method respectively. Improved yields were obtained when using zinc oxide catalysts doped with other metal atoms prepared by flame synthesis; the highest yield was 20.3% obtained using 8.6 wt% of barium on zinc oxide. However, due to variations of the surface area for each catalytic system, the best result in terms of yield per $100 m^2 g^{-1}$ was 38.1% from a zinc oxide catalyst doped with 5.5 wt% strontium, even though this system gave the lowest isolated yield of 15.8%. Overall, there was only a 5.1% variation between the lowest and highest results obtained using the range of metal-doped zinc oxide catalysts equating to a 10% difference in yield per unit area. Preformed silica particles with varying amounts of zinc were used to prepare catalysts *via* the flame pyrolysis method and it was found that zinc weight percentages did not significantly affect the yield of propylene carbonate. Between 2.5 wt% and 17 wt% of zinc oxide, the yield increased by just three percent (from 20 to 23%). The yield was however dramatically increased by increasing the amount of catalyst and cocatalyst; using 5 wt% ZnO on silica, the yield increased from 28% to 85% and with 7 wt% ZnO/SiO_2, the yield reached 100% after six hours reaction at 120 °C.

Dai and Au have recently shown that a composite oxide material composed of zinc, aluminium and a third metal could be used for the synthesis of cyclic carbonates from CO_2 and epoxides.[103] The highest yield (89%) for the reaction of CO_2 with propylene oxide was achieved after 12 h using Zn–Mg–Al–O under 25 atmospheres pressure of CO_2 at 120 °C with triethylamine as an additive. This catalyst was reused five times, during which there was no observed reduction in activity. Other metal oxide composites composed of Zn/Al and other group(II) metals gave similarly good results under the same conditions. The method of catalyst preparation (temperature and pH) were found to be important factors for its subsequent activity. It was suggested that the catalyst active sites contain both Lewis acidic (Al) and basic (ZnMg) groups, important for the simultaneous activation of epoxide and carbon dioxide.

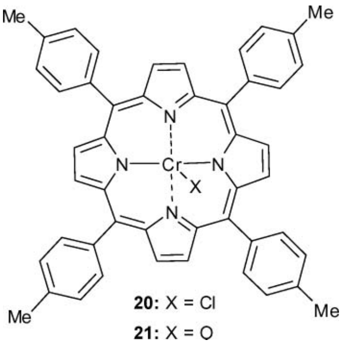
2.1.6 Cyclic carbonate synthesis catalysed by metal porphyrin and related complexes.

2.1.6.1 Aluminium(III) porphyrin and phthalocyanine complexes. In 1978, Inoue *et al.* reported the synthesis of propylene carbonate catalysed by aluminium porphyrinate complex **19a** with *N*-methylimidazole (NMI) as cocatalyst.[104] Low to moderate yields (8–40%) and poor TOFs (0.03 h^{-1}), mainly due to the long reaction time required, were obtained. It is noteworthy, however, that the process was carried out at room temperature, and atmospheric pressure in a dichloromethane solution. In the absence of NMI, a mixture of propylene carbonate and polypropylene carbonate was obtained as the product. Similarly, Kasuga *et al.* reported the aluminium(III) phthalocyanine complexes (**13a,b**), which, in conjunction with NMI, catalysed the addition of CO_2 to propylene oxide at room temperature and atmospheric pressure,[105] leading selectively to propylene carbonate in poor yield and TOF (< 0.02 h^{-1}).



19a: M = Al(OMe)
19b: M = Co(II)
19c: M = Co(III)Cl
19d: M = Co(III)OAc
19e: M = Cu(II)

2.1.6.2 Chromium porphyrin complexes. In contrast to aluminium porphyrinate complexes, chromium(III) and chromium(IV) derivatives[106] (**20** and **21**) produced quantitative yields of cyclic carbonates with moderate TOFs (36–89 h^{-1}), when used in conjunction with NMI or DMAP, with both terminal and disubstituted epoxides. Reactions were carried out at 70–100 °C and 26 atmospheres pressure. Chromium porphyrinate complexes showed high activity even in the presence of dichloromethane as solvent; the introduction of methyl substituents onto the phenyl rings improving the solubility.

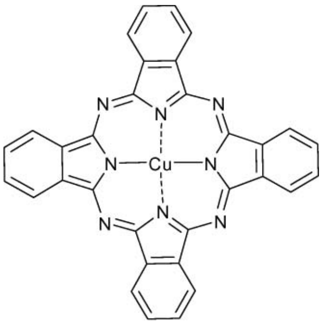


20: X = Cl
21: X = O

2.1.6.3 Cobalt porphyrin complexes. Nguyen *et al.* reported the use of a cobalt porphyrin/DMAP system for the synthesis of cyclic carbonates from CO_2 and epoxides.[107] Tetraphenylporphyrin (TPP) was used as a ligand to chelate cobalt as either Co(II) (**19b**) or Co(III)Cl (**19c**). The reaction conditions involved the use of just 0.038 mol% catalyst under 17 atmospheres pressure of CO_2 at 120 °C. The best result was obtained using complex **19c** with two equivalents of DMAP, for which a TOF of 826 h^{-1} was observed. This was by far the best catalytic system, complex **19b** gave a TOF of only 16 h^{-1}. Using additives other than DMAP also gave much lower TOFs (NMI 80 h^{-1}, triethylamine 85 h^{-1}, pyridine 8 h^{-1}, triphenylphosphine 9 h^{-1}) or no reaction at all (pyridine *N*-oxide, tricyclohexylphosphine oxide). Varying the amount of DMAP away from two equivalents lowered the activity significantly. Similarly, changing the CO_2 pressure away from 17 atmospheres also reduced the activity particularly when using a lower pressure. Under the optimized conditions, a range of epoxides were tested including terminal, 1,1-and 1,2-disubstituted, aromatic, allylic and aliphatic substrates, all of which gave excellent yields although longer reaction times and higher catalyst loadings were sometimes needed, particularly for the more hindered epoxides.

In 2007, Jing's group extended Nguyen's study by investigating cobalt TPP complexes with other counterions and the use of phenyltrimethylammonium tribromide (PTAT) as cocatalyst.[108] Cobalt(III) acetate/TPP complex **19d** gave a TOF of 620 h^{-1} when used as a catalyst for the addition of CO_2 to propylene oxide. Although this was lower in terms of TOF than the best result obtained by Nguyen, the reaction only required 7 atmospheres pressure of CO_2 and could be carried out at 20 °C using 0.1 mol% of catalyst. When a CO_2 pressure of 1 atmosphere was used, the reaction yield was however, significantly reduced to just 20% after four hours reaction time compared with the 90% yield obtained at 7 atmospheres pressure in three hours. Other metal salts were tested instead of cobalt, including manganese, iron and ruthenium, but none of these were particularly effective with TOFs of 33 to 90 h^{-1} being obtained. Yields were also much lower, with the best being 27% obtained using Mn(TPP)Cl with a three hour reaction time compared to Co(TPP)Cl (**19c**) which gave 88% yield in the same time period. A number of other epoxides were used as substrates for CO_2 insertion with mixed results. The best yields were obtained using propylene oxide and phenyl glycidyl ether (93% and 96% respectively after 5 h) whilst the worst result was obtained from styrene oxide which gave only 20% yield after an extended reaction time of ten hours.

2.1.6.3 Copper phthalocyanine complexes. Copper phthalocyanine complex **22** provided the highest TOF (502 h^{-1}) in a study conducted by Srinivas *et al.* of the addition of CO_2 to epichlorohydrin using a series of copper and manganese macrocycles and Schiff base complexes.[109] The reactions were carried out at 120 °C for four hours under 6.9 atmospheres CO_2 pressure using 0.04 mol% of catalyst and DMAP as cocatalyst with dichloromethane as solvent. Copper tetraphenylporphyrin **19e** gave a similar TOF of 489 h^{-1} under the same conditions. All the catalytic systems included in the study provided excellent selectivity for formation of the cyclic carbonate product.



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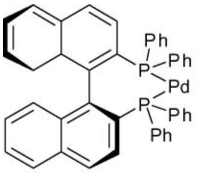
2.1.7 Cyclic carbonate synthesis catalysed by polyoxometalates. Manikandan *et al.* used the zinc-substituted polyoxometalate system $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot 46H_2O$ (Zn-POM), in conjuction with DMAP to catalyse the addition of CO_2 to epoxides.[110] Using epichlorohydrin as substrate, excellent conversions (84–97%) were obtained after only three hours reaction using four atmospheres CO_2 pressure at 140–160 °C. Propylene and butylene oxide were also good substrates, giving conversions of 99% and 96% after reaction times of 12 and 9 h respectively. The reaction worked comparably well (97% conversion) in dichloromethane or with no solvent (99% conversion) using catalyst loadings as low as 4 mmol% along with 12 mmol% of DMAP (for experiments in dichloromethane). The catalyst was also shown to be reusable over three experiments with only minimal loss of activity.

Another metal substituted polyoxometalate system was employed by Sakakura *et al.* for the synthesis of cyclic carbonates.[111] $[(X)_6(\alpha\text{-}SiW_{11}O_{39}M)]$ type complexes were used where X is a tetraalkylammonium salt and M is a metal. From the metals tested in this study (Co, Mn, Ni, Fe, Cu), cobalt and manganese were found to be the most effective as catalysts for the addition of CO_2 to propylene oxide. Using 0.1 mol% of the tetra-n-heptylammonium bromide/cobalt^{II} derived catalyst with 35 atmospheres pressure of CO_2 at 150 °C in DMF, the highest yield obtained was 83% after two hours reaction. Using manganese as the metal gave 73% yield in the same time, whilst all the other metals gave greatly reduced yields of propylene carbonate. With the cobalt catalyst, the system was improved by omitting the DMF and using either ethylene carbonate as solvent (97% yield), or by using supercritical CO_2 at 100 atmospheres (96% yield). Yields were equally high without the use of a solvent (97%). Without the polyoxometalate, using only alkylammonium bromide salts, the yields were extremely poor under solvent-free conditions and only marginally better in DMF.

Zhai and Sun also investigated the use of a polyoxometallate/TBAB catalyst $[(n\text{-}Bu_4N)_9(P_2W_{17}O_{61}Co(\text{II})Br)]$ in conjunction with PEG-400 for the addition of CO_2 to epoxides.[112] Using 0.14 mol% of catalyst with 2.1 mol% of PEG-400 at 2.5 atmospheres of CO_2 pressure, excellent yields (98%) of propylene carbonate were obtained at 120 °C. Reducing the temperature resulted in inferior yields of 82% at 100 °C and 57% at 80 °C, but these yields could be improved to 89% and 64% respectively by increasing the pressure of CO_2 to 20 atmospheres. Catalyst recycling was also possible with only minor losses in activity reported after three runs.

2.1.8 Cyclic carbonate synthesis catalysed by palladium(0) complexes. Palladium(0) complexes and -onium derivatives were found to be active catalysts for the synthesis of cyclic carbonates from CO_2 and epoxides, though this chemistry was applicable only to allylic and vinylic epoxides (Scheme 6). In 1985, Fujinami *et al.* accomplished the synthesis of vinylethylene carbonate (**23**) in 96% yield, in the presence of $(Ph_3P)_4Pd/Ph_3P$ at 0 °C and atmospheric pressure, using THF as solvent.[113] A TOF of 768 h^{-1} was observed. Similarly, Trost *et al.*[114] reported a highly-efficient Pd(0)-catalysed synthesis of cyclic carbonates under mild reaction conditions (room temperature and 3 atmospheres pressure). A series of vinyl epoxides were converted into the corresponding carbonates in moderate to high yield (57%–95%). This process exhibited TOFs between 4.7 h^{-1} and 7.8 h^{-1}.



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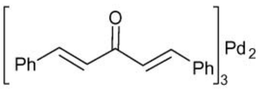

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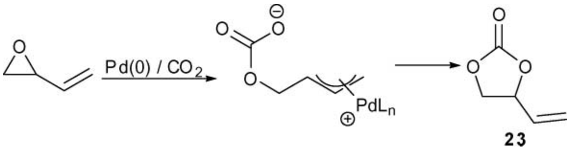
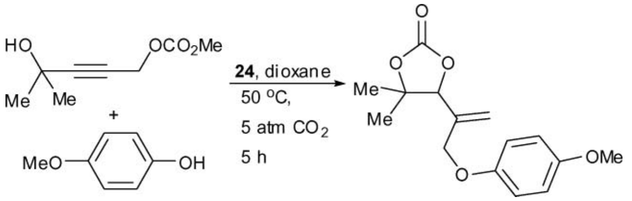
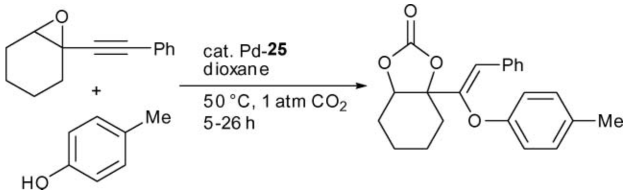


Scheme 6 Synthesis of cyclic carbonates catalysed by a Pd(0) complex

Alternatively, the synthesis of cyclic carbonates was also accomplished through the reaction of propargylic carbonates with phenols in the presence of the [Pd(0)BINAP] complex **24** (Scheme 7).[115a] This process is a straightforward method for the production of enantiomerically pure cyclic carbonates which are useful intermediates in organic synthesis. The reaction was carried out at 50 °C and 5 atmospheres pressure in dioxane as solvent. The products were obtained in low to moderate yield (30–88%). Similarly, in 2007 a three component reaction between propargylic epoxides, phenols and CO_2 was also reported for the synthesis of modified cyclic carbonates in the presence of an *in situ* prepared Pd(dppp) catalyst, obtained from 1,3-bis(diphenylphosphino)propane (dppp) **25** and $Pd_2(dba)_3$ (**26**) (Scheme 8).[115b]



Scheme 7 Palladium-catalysed synthesis of substituted cyclic carbonates from propargylic carbonates and *p*-methoxyphenol

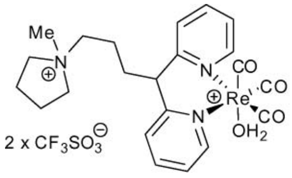


Scheme 8 Palladium-catalysed synthesis of substituted cyclic carbonates from three component systems

2.1.9 Cyclic carbonate synthesis catalysed by rhenium complexes.

In 2005, Hua *et al.* successfully achieved the addition of CO_2 to epichlorohydrin in the presence of a $[Re(CO)_5Br]$ complex.[116] The reaction was carried out in supercritical CO_2, at 110 °C and 54 atmospheres pressure; the product was obtained in 97% yield with a TOF of 40 h^{-1}. Surprisingly, propylene carbonate was obtained in only 46% yield (TOF 11 h^{-1}) under the same conditions.[116]

Similarly, Wong *et al.* showed that Re(I) complex **27** was an effective catalyst for the addition of CO_2 to various epoxides.[117] The reaction was carried out in ionic liquid **28**, at 80 °C and 15 atmospheres pressure. Propylene carbonate was obtained in only 13% yield (TOF 16 h^{-1}), probably due to the harsh conditions which forced a significant amount of the reagent to occupy the headspace of the vessel.[117] Nonetheless, the addition of CO_2 to epichlorohydrin and styrene oxide proceeded in almost quantitative yields, exhibiting TOFs of 124 h^{-1} and 59 h^{-1} respectively.



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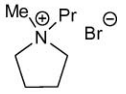

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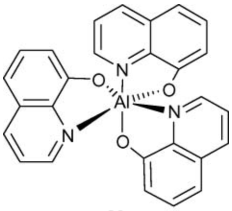
2.1.10 Cyclic carbonate synthesis catalysed by aluminium quinolate complexes.

Aluminium 8-hydroxyquinolate complex **29** was found to catalyse the addition of CO_2 to propylene oxide when used in conjunction with triphenylphosphine oxide.[118] The reaction was carried out at 155 °C and 18 atmospheres pressure, giving propylene carbonate in 92% yield with a TOF of 32 h^{-1}.



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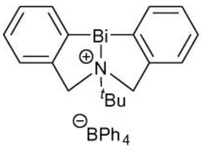
2.1.11 Cyclic carbonate synthesis catalysed by organobismuth complexes.

Organobismuth complex **30** synthesized by Yin *et al.* was found to be highly active for the addition of CO_2 to epoxides in the presence of TBAI as cocatalyst, at 120 °C and 30 atmospheres pressure.[119] Butylene carbonate was obtained in 92% yield, with a TOF of 7384 h^{-1} and it is noteworthy that complex **30** was also able to catalyse the formation of cyclohexene carbonate from cyclohexene oxide in 90% yield, with a high TOF of 2408 h^{-1}.[119] Complex **31** introduced by Shimada *et al.* was found to catalyse the synthesis of propylene carbonate in 91% yield under very mild reaction conditions.[120] The reaction was carried out under solvent-free conditions at room temperature and atmospheric pressure, with NaI as cocatalyst and the catalyst showed a TOF of 31 h^{-1}.



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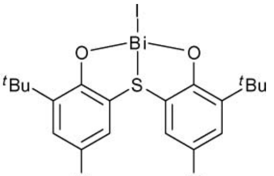

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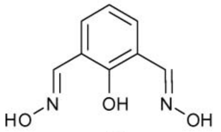
2.1.12 Cyclic carbonate synthesis catalysed by a cobalt(III) isophthaldehyde complex.

The 2-hydroxy-isophthaldehyde-oxime ligand **32** introduced by Tang *et al.* was found to form a dimeric cobalt(III) complex $[Co(III)L_2(C_2H_5OH)_2Cl_2]$ **33** which catalysed the synthesis of cyclic carbonates.[121] Propylene carbonate was formed at room temperature and 7 atmospheres pressure with a TOF of 304 h^{-1}. Complex **33** also promoted the synthesis of styrene carbonate, though the catalyst activity decreased to 5 h^{-1}.



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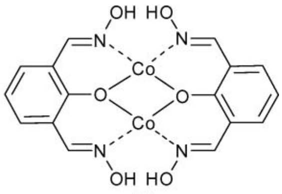

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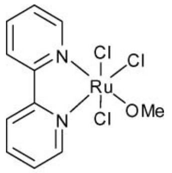
2.1.13 Cyclic carbonate synthesis catalysed by ruthenium complexes.

Ruthenium complex **34** was used by Cao *et al.* for the formation of propylene carbonate using 30 atmospheres pressure of CO_2 at 75 °C.[122] A cocatalyst, cetyltrimethylammonium chloride, (CTAT) was also required and the optimized loadings involved the use of 0.05 mol% of both catalyst **34** and CTAT. A TOF of 1019 h^{-1} and yield of 97% were obtained after a reaction time of 4 h. The effect of changing the temperature and pressure was investigated and it was found that raising the pressure to 40 atmospheres had no effect on the TOF value, but lowering the pressure to 20 or 10 atmospheres lowered the TOF slightly to 996 h^{-1} and 861 h^{-1} respectively. Decreasing the temperature led to a predictable fall in activity with 65% yield and a TOF of 683 h^{-1} obtained at 50 °C. Increasing the temperature to 90 °C resulted in a 98% yield and a TOF of 1029 h^{-1}, only a minor increase compared to the result at 75 °C. The catalyst was also subjected to a recycling experiment where no appreciable loss in activity was observed over at least five runs. A catalytic cycle was proposed to explain the activity in which the metal centre activates the epoxide towards nucleophilic ring-opening by chloride ions with subsequent CO_2 insertion into the intermediate.



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2.1.14 Cyclic carbonate synthesis catalysed by heterobimetallic complexes.

In 2006, Lau, Lin *et al.* developed a heterobimetallic catalyst **37**, prepared by the combination of ruthenium complex **35** and manganese complex **36**, which was active for the coupling of CO_2 to epoxides.[123] A computational study was undertaken to determine a possible mechanism for the reaction and it was proposed that each metal centre has a role in activating the epoxide and CO_2 (Fig. 3). Two catalytic cycles were proposed which had different roles for the manganese group: activating the CO_2 and ring-opening the epoxide respectively.

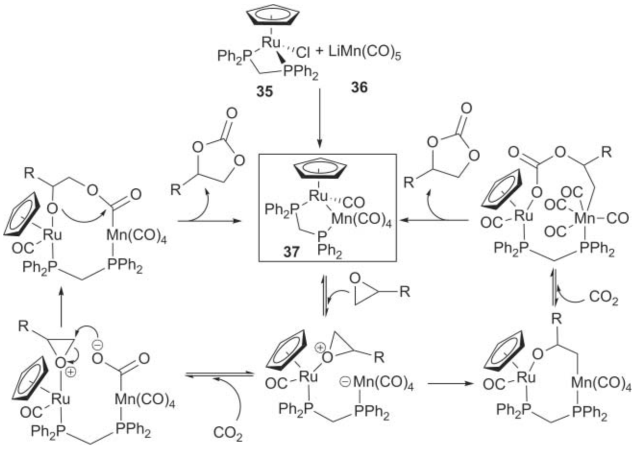


Fig. 3 Proposed catalytic cycle for the addition of CO_2 and epoxides using heterobimetallic catalyst **37**.

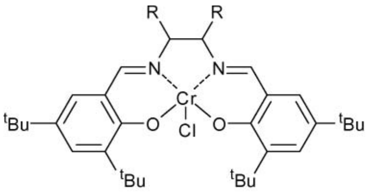
Experimentally, cyclic carbonate synthesis occurred using 40 atmospheres pressure of CO_2 at 100 °C for 45 h with a 9000 : 1 substrate to catalyst ratio. A range of epoxides were used as substrates with the best TOFs obtained when using epifluorohydrin (216 h^{-1}) and epichlorohydrin (200 h^{-1}). Cyclohexene oxide, the only non-terminal epoxide used, gave only trace amounts of product. Although complex **35** alone was shown to be inactive for the coupling of CO_2 to epoxides, manganese complex **36** was found to be active (best results again obtained with epifluorohydrin), but the results were inferior to those obtained using heterobimetallic system **37**. A pentamethylcyclopentadienyl derivative of **35** was also used in the preparation of the corresponding heterobimetallic catalyst and showed moderate activity under the same conditions with TOFs of 176 h^{-1} and 132 h^{-1} for epifluorohydrin and epichlorohydrin respectively.

2.2 Cyclic carbonate synthesis catalysed by metal salen complexes

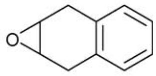
Salen ligands are prepared by the condensation of a salicylaldehyde and a diamine which may be achiral (including aryl diamines) or chiral. Their ease of synthesis and modification has prompted increased interest in salen as a ligand for many different catalytic reactions.[124] The large variety of complexes that salen ligands can form with both transition metals and main-group metals accounts for their widespread use as catalysts for many different reactions. Salen complexes of a number of metals (usually in the +3 oxidation state) have been found to catalyse the addition of CO_2 to epoxides.

2.2.1 Chromium salen complexes.

Driven by Kruper's work on chromium(III) porphyrins[106] (see section 2.1.6.2), Paddock *et al.* investigated use of chromium(III)(salen) complexes for the addition of CO_2 to propylene oxide, obtaining a high TOF of 916 h^{-1} for Cr(III)(salen)Cl complex **38** with DMAP as cocatalyst.[125] The reaction was carried out at 100 °C and 4 atmospheres pressure. Complex **38** was also found to catalyse the synthesis of propylene carbonate at room temperature and 4 atmospheres pressure, though the TOF fell to 3 h^{-1}, due to the long reaction time required to accomplish a satisfactory yield.



38) R = *meso*-Ph
39) R-R = *trans*-$(CH_2)_4$



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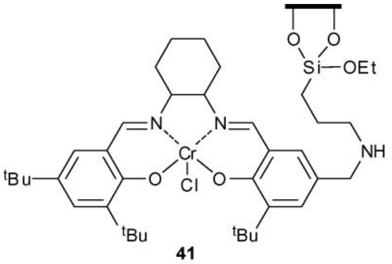
Following on from their work on the development of catalysts for CO_2 and epoxide copolymerization[28c,126] (see section 1.2.2), Darensbourg's group also studied the synthesis of cyclic carbonates in the presence of Cr(III)(salen)Cl complex **39**, under 25 atmospheres pressure at 40 °C and with toluene as solvent.[127a] It was found that, under identical reaction conditions, addition of CO_2 to cyclohexene oxide in the presence of complex **39** gave the alternating copolymer, whereas the addition to propylene oxide led to the cyclic carbonate as the sole product. However, replacing cyclohexene oxide with 2,3-epoxy-1,2,3,4-tetrahydronaphthalene **40** resulted in formation of the corresponding cyclic carbonate as the major product[127b] (20% yield, TOF 1.5 h^{-1}, 80 °C and 55 atmospheres pressure), whereas other catalyst systems were incompatible with this substrate.[128,129]

Solid supported Cr(III)(salen)Cl complex (**41**), used in conjunction with tributylamine or NMI, was found to promote the synthesis of styrene carbonate.[130] The process was carried out at 80 °C and 100 atmospheres pressure, and exhibited a moderate conversion of 74% with a TOF of 73 h^{-1}.

In 2008, Lu *et al.* synthesized a catalyst system based on Cr(III)(pyrrolidine-salen)Cl complex **42**,[131] containing an electrophilic site (the metal centre) and a nucleophilic unit (the strong organic base: 1,5,7-triazabicyclo-[4.4.0]-dec-5-ene, TBD). Complex **42** was found to be an active species for the synthesis of propylene carbonate under 20 atmospheres pressure at 80 °C, displaying a high TOF (1936 h^{-1}). At 5 atmospheres pressure and 25 °C, a TOF of 48 h^{-1} was obtained.[131] Complex **42** was also found to promote cyclic carbonate synthesis from a wide range of terminal epoxides and for the reaction between ethylene oxide and CO_2, a TOF of 3338 h^{-1} was obtained at 80 °C and 20 atmospheres pressure. In 2009, Chen *et al.* reported the synthesis of propylene carbonate in the presence of Cr(III)(salophen)NO_3 complex **43** and DMAP.[132] The reaction was carried out at 40 °C and 15 atmospheres pressure, exhibiting a TOF of 618 h^{-1}. In order to achieve high selectivity for the cyclic product, a 2:1 ratio of complex **43** to DMAP was necessary.



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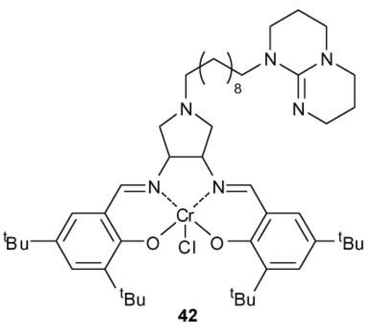

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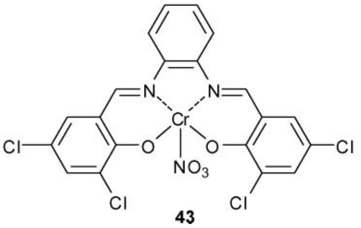
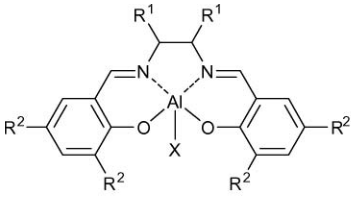


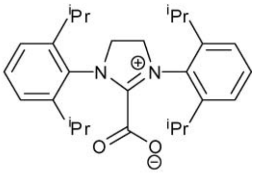
43

2.2.2 Aluminium salen complexes. Work by Darensbourg *et al.* had demonstrated that polymerization of cyclohexene oxide and CO_2 could take place under supercritical conditions in the presence of aluminium(III)(salen) complexes (see section 1.2.2).[28,126,128,129] Conversely, in 2002 He *et al.* reported good results for the synthesis of ethylene carbonate, in the presence of Al(III)(salen)Cl complex **44a** with TBAB as cocatalyst.[133a] The product was obtained in quantitative yield, under 160 atmospheres pressure and at 110 °C, with a TOF of 2220 h^{-1}. Under the same reaction conditions, complex **44a** showed a more moderate activity (TOF 174 h^{-1}) in the absence of -onium cocatalysts.[133a] When the process was carried out at 40 atmospheres pressure, a TOF of 1140 h^{-1} was obtained for complex **44a**-TBAB.[133b]

Similarly, in 2004, Lu *et al.* introduced a catalyst system based on Al(III)(salen)Et complex **44b** and 18-crown-6/KI, which exhibited a moderate TOF of 58 h^{-1} for the synthesis of propylene carbonate, under 6 atmospheres pressure at room temperature.[134a] Use of complex **44b** with TBAI at 35 °C and 6 atmospheres pressure, gave propylene carbonate with a higher TOF of 84 h^{-1}.[134b] Under the same conditions, complex **44a** exhibited comparable results for the addition of CO_2 to propylene oxide (TOF 61 h^{-1}). The use of 18-crown-6/KI with Al(III)(salen) complexes **44c** and **44d** gave TOFs of 10 h^{-1} and 30 h^{-1} respectively. *N*-*N'*-Disubstituted imidazol(in)ium-2-carboxylates **45** have been investigated as efficient CO_2 transfer agents under mild conditions.[135] A binary catalyst system formed from **45** and complex **44b** was found to catalyse the synthesis of propylene carbonate. The process was carried out at 100 °C and 20 atmospheres pressure, though only moderate TOFs of 50 h^{-1} were achieved.[136]



44a) X = Cl, R^1 = H, R^2 = H
44b) X = Et, R^1 = H, R^2 = H
44c) X = Et, R^1 = H, R^2 = ^{t}Bu
44d) X = Cl, R^1-R^1 = *trans*-$(CH_2)_4$, R^2 = ^{t}Bu



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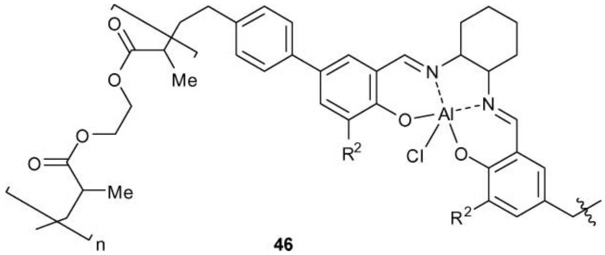
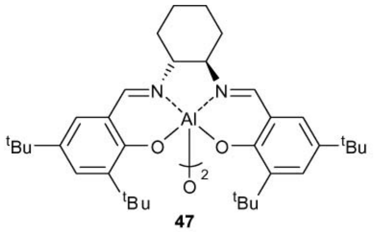
Solid supported Al(III)(salen)Cl complex **46** prepared by García *et al.*[137] was found to be an active catalyst for the synthesis of styrene carbonate in supercritical CO_2 (80 °C and 100 atmospheres pressure). A moderate TOF of 7.8 h^{-1} was reported for complex **46** supported on poly(ethylene glycol *bis*-methacrylate). This catalyst system also showed moderate reusability over 3 reactions, though a significant decrease in activity (to TOF 2.5 h^{-1}) was reported.



46

In 2007, North *et al.* reported the use of dimeric aluminium(salen) complexes for the synthesis of cyclic carbonates from CO_2 and epoxides.[138] Using TBAB as a cocatalyst under solvent-free conditions, this system displayed unique activity as CO_2 could be used at atmospheric pressure and the reaction carried out at 25 °C. When styrene oxide was used as the substrate, 2.5 mol% of catalyst **47** and 2.5 mol% of TBAB catalysed the formation of styrene carbonate with 62% conversion after 3 h and 98% conversion after 24 h. Using just 1 mol% catalyst still gave 86% conversion after 24 h. A number of other terminal epoxides were employed as substrates under the same conditions, thus 3-phenylpropylene oxide, 1,2-hexene oxide and 1,2-decene oxide were transformed into the corresponding cyclic carbonates with yields of 99% (after 24 h), 88% (after 3 h) and 64% (after 3 h) respectively. Propylene oxide was used at 0 °C and gave propylene carbonate in 77% yield after a reaction time of 3 h. Complex **47** could be reused over 60 times without loss of catalytic activity, though periodic readdition of TBAB was necessary.[139]

Kinetic studies of North's system were carried out and showed that the reaction was second order in TBAB as well as being first order in catalyst **47**, styrene oxide and CO_2.[140] In addition, it was shown that the TBAB decomposes to tributylamine under the reaction conditions. On the basis of these results, a catalytic cycle (Fig. 4) was proposed in which the epoxide is first activated by



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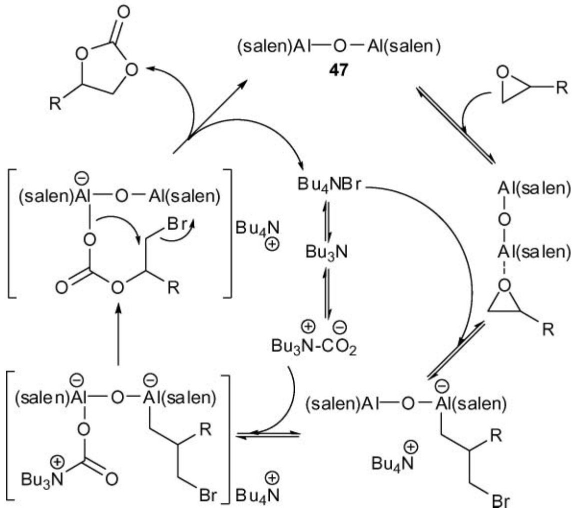
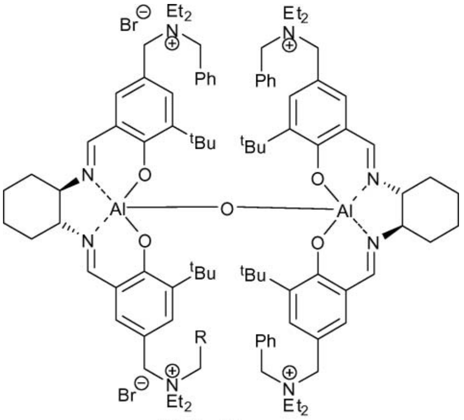


Fig. 4 Catalytic cycle for the addition of CO_2 to epoxides catalysed by complex **47**.

one of the aluminium atoms within the dimeric catalyst and ring-opened by bromide. The CO_2 can form a carbamate salt with the tributylamine and this can coordinate to the other aluminium atom, thus allowing the key reaction between the ring-opened epoxide and CO_2 to occur intramolecularly. Ring-closure and elimination of bromide then forms the cyclic carbonate and regenerates the catalyst. Further support for the involvement of both aluminium atoms in the mechanism came from a finding that monomeric metal(salen) complexes (including aluminium complexes) were inactive for cyclic carbonate synthesis at atmospheric CO_2 pressure and ambient temperature.[139] The involvement of tributylamine in the catalytic cycle was supported by further kinetics experiments carried out in the presence of added tributylamine or butyl bromide, the latter acting as an inhibitor of cyclic carbonate synthesis due to requaternization of the tributylamine. Various quaternary ammonium halide cocatalysts were studied and TBAB was found to be considerably more active (62% conversion) than TBACl (25%), TBAI (15%) or TBAF (trace amount of reaction).[139] This relative reactivity of the halide ions was explained on the basis of a balance between nucleophilicity (epoxide ring-opening) and leaving group ability (ring-closure to cyclic carbonate).

Catalyst **47** has been used as part of an integrated system in which methane was combusted in oxygen to represent the production of CO_2 from an oxyfuel combustion power station.[141] The effluent CO_2 was then passed over the catalyst, TBAB and glycidol (or alternative non-volatile epoxide) at 26 °C to convert the waste CO_2 into cyclic carbonate.

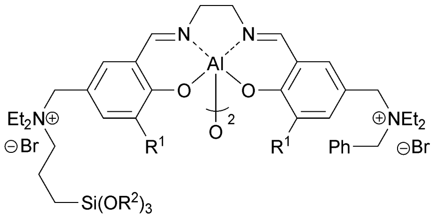
To avoid the need for a cocatalyst, North's group also developed a one-component version of their bimetallic aluminium(salen) system in which quaternary ammonium bromides were covalently attached to the salen ligand.[142] Thus, catalyst **48** was found to convert ten epoxides into cyclic carbonates at ambient temperature and atmospheric pressure CO_2 without the need for TBAB to be added to the reactions. Conversions of 66–100% were achieved with isolated yields of 51–89% after reaction times of 6–24 h. The best yield (89%) was achieved with both styrene oxide and 4-methylstyrene oxide after 24 h reaction. *Para* bromo- and chloro-substituted styrene oxides gave 85% and 83% yields respectively and *para*-thiomethylstyrene oxide gave only a 51% yield of the corresponding cyclic carbonate. 3-Chloropropylene carbonate was obtained in 81% yield after a reaction time of six hours. A Merrifield resin supported version (**49**) of complex **48** was also prepared and found to be active for the addition of CO_2 to styrene oxide, giving a 79% yield of styrene carbonate. Catalyst **49** could be isolated and reused, giving yields of 73, 66 and 60% in three subsequent reactions.



48) R = Ph
49) R = Merrifield resin

Immobilized complexes such as catalyst **49** were designed for use in a flow system and North's group subsequently developed a flow reactor system for the addition of CO_2 to ethylene oxide.[143] Catalysts based on immobilized one-component system **49**, but using silica as the support were prepared and tested both in batch and continuous flow modes. Catalyst **50a** (on amorphous silica) was reused in 32 sequential batch reactions and the catalytic activity was found to decrease over a period of about seven reactions. However, full activity could be restored by treatment of the catalyst with benzyl bromide to requaternize the amino groups. In the flow reactor, N_2 (1 mL min^{-1}) and CO_2 (1 mL min^{-1}) were passed over liquid ethylene oxide contained within a cryogenically cooled stainless-steel reactor vessel, producing an evaporation rate of ethylene oxide of 0.15 mL h^{-1} and giving approximately equal amounts of CO_2 and ethylene oxide in the gas mixture. The mixture of three gases was then passed through a steel tube containing catalyst **50a**. At 20 °C, this system gave a TOF of only 0.15 h^{-1} after 120 h, but this was increased to 7.6 h^{-1} (after six hours) when the temperature of the reactor was increased to 150 °C. Catalyst **50b** (supported on MCM-41) was found to be intrinsically more active, producing TOFs of 21 h^{-1} and 26 h^{-1} at 100 °C and 150 °C respectively. Catalyst **50c** had activity which was intermediate between **50a** and **50b**, and catalyst **50d** was the least active of this series of catalysts.

Complex **50a** was used in the flow reactor continually for up to 168 h. At 150 °C, the percentage of CO_2 converted to ethylene carbonate remained constant at almost 60% for the first 12 h, and reduced to 45% after 18 h, followed by a severe reduction to less than 5% conversion after 24 h. Using the same catalyst at 100 °C resulted in 15% of the CO_2 being converted into cyclic carbonate, but this was only slightly reduced even after 120 h continuous use. Reactivation of the catalyst with benzyl bromide after 144 h restored the catalyst activity to its initial level showing that the supported catalyst did not deactivate even after extended use at 100 °C.



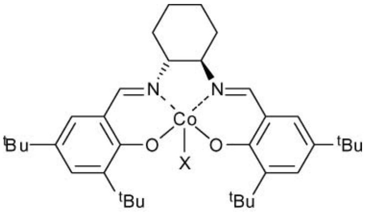
50a) R^1 = ^tBu, R^2 = amorphous silica
50b) R^1 = ^tBu, R^2 = MCM-41
50c) R^1 = ^tBu, R^2 = solgel silica
50d) R^1 = H, R^2 = amorphous silica

2.2.3 Cobalt(salen) complexes.

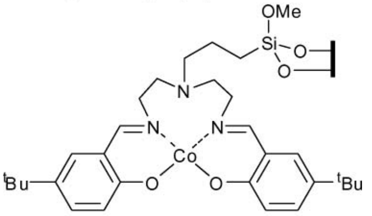
Cobalt(III)(salen) complexes are known to be active catalysts for the stereo-controlled synthesis of polycarbonates from epoxides and CO_2 (see section 1.2.2). However, these complexes were also found to produce cyclic carbonates, although a specific set of reaction conditions was required.[28o–p] Following on from their work on cyclic carbonate synthesis catalysed by Al(III)(salen) complexes[134] (see section 2.2.2), Lu *et al.* used Co(III)(salen) derivatives to accomplish the enantioselective addition of CO_2 to propylene oxide.[144] A binary catalyst system based on chiral $[Co(III)(salen)]O_2CCCl_3$ **51** in conjunction with TBAB exhibited a high TOF of 245 h^{-1} at room temperature and 15 atmospheres pressure and gave the product with 50% enantiomeric excess. Replacing the TBAB with TBACl was found to have a beneficial effect on the enantioselectivity of the reaction, though at the expense of a loss in activity. Thus, when the reaction was carried out at 0 °C in the presence of [Co(III)(salen)]OTs **52**, the cyclic carbonate was formed with 70% enantiomeric excess, but the TOF decreased to 27 h^{-1}.[144]

Jing *et al.* showed that the combination of $[Co(III)(salen)]O_2CCCl_3$ complex **51** and PTAT catalysed the addition of CO_2 to propylene oxide in high yield with a TOF of 706 h^{-1}.[145] The reaction was carried out at room temperature and 4 atmospheres pressure, but exhibited poor enantioselectivity. Reactions carried out at −5 °C in the presence of chiral Co(III)(diphenyl-salen) complexes were also unsuccessful. In 2004, the synthesis of ethylene carbonate in a flow reactor, in the presence of a solid supported MCM-41/[Co(II)(salen)] system **53** was reported.[146] The process was carried out under supercritical CO_2 conditions (110 °C and 123 atmospheres), and ethylene carbonate was obtained with 86% conversion, corresponding to a TOF of 111 h^{-1}.

Paddock *et al.* reported that the combination of [Co(III)(salen)]Cl **54** and DMAP was highly active for the synthesis of propylene carbonate.[147] The reaction exhibited a high TOF of 1200 h^{-1} at 100 °C and 10 atmospheres pressure in dichloromethane. The system showed high activity for a wide range of epoxides, producing cyclic carbonates as the only product. In order to achieve an enantioselective synthesis of propylene carbonate by the kinetic resolution of propylene oxide with CO_2, chiral DMAP* ((*R*)-(+)-4-dimethylaminopyridinyl-(pentaphenylcyclopentadienyl)iron) **55** was used as the cocatalyst, the reaction exhibiting a selectivity factor *s* of 5.6 at 3 °C, though the TOF dropped to 10 h^{-1}.[147]



51) X = O_2CCCl_3
54) X = Cl
65) X = 2-$O_2NC_6H_4O$
52) X = OTs
63) X = OAc



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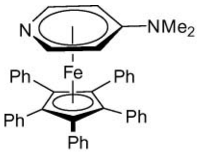

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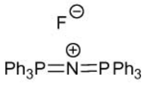
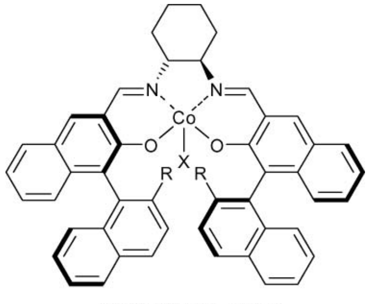


56

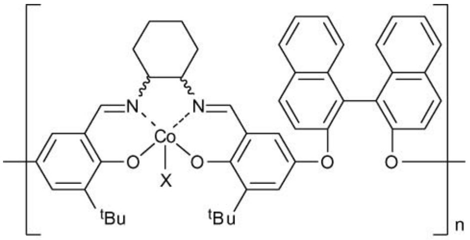
In 2006, Berkessel *et al.* obtained 87% enantiomeric excess for the asymmetric addition of CO_2 to racemic propylene oxide in the presence of a [Co(III)(salen)]OTs **52**/TBACl catalyst system.[148] The reaction was carried out at −50 °C and atmospheric pressure and the product was obtained in 15% yield. The counterion in the [Co(III)(salen)]X complex was found to control the catalyst activity, but to have no influence on the enantioselectivity. Thus, complex **51** in conjunction with (PPN)F **56** gave propylene carbonate with 83% enantiomeric excess in 40% yield, with a moderate TOF of 4.2 h^{-1} at −40 °C and atmospheric pressure.[148]

Cobalt(III)(salen) analogues, such as chiral [Co(III)(binad)]X complexes have also been investigated as catalysts for the asymmetric addition of CO_2 to propylene oxide.[149] In the presence of [Co(III)(binad)]OAc **57**, propylene carbonate was obtained in 25% yield and with 60% enantiomeric excess, with a moderate TOF of 23 h^{-1} at 25 °C and 5 atmospheres pressure. By decreasing the temperature to 0 °C, 87% enantiomeric excess was achieved, though a longer reaction time (72 h) was necessary in order to obtain a 20% yield.[149]



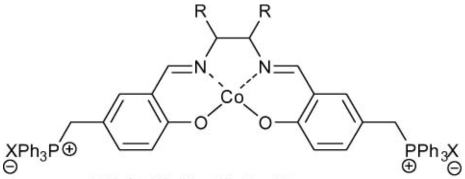
57) X = OAc, R = OMe

In 2009, polymers of BINOL-Co(III)(salen) salts were synthesized and tested as catalysts for the synthesis of enantiomerically enriched propylene carbonate at room temperature and 12 atmospheres pressure.[150] Compound **58**, used in conjunction with PTAT showed a TOF of 244 h^{-1} but exhibited poor enantioselectivity (20%). At 0 °C and 12 atmospheres pressure, the diastereomeric polymer **59** coupled with TBAF catalysed the synthesis of propylene carbonate with 39% conversion, exhibiting a lower TOF of 32 h^{-1}, but a much higher enantioselectivity of 73%.



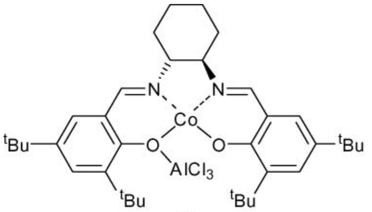
58) (*R*,*R*)-salen; (*R*)-binol
59) (*S*,*S*)-salen; (*R*)-binol

In 2008, He *et al.* reported a bifunctional Co(II)(salen) complex **60** which catalysed the synthesis of propylene carbonate from propylene oxide and CO_2, giving the product in 94% yield and with a moderate TOF of 47 h^{-1} at 100 °C and 40 atmospheres pressure.[151] Complex **60** incorporates quaternary phosphonium chlorides and the anions are proposed to participate in the ring-opening of the epoxide.[151] Thus, complex **60** activates the epoxide with its Lewis acidic cobalt(II), and this is then ring-opened by the nucleophilic species provided by another catalyst molecule. Surprisingly, under the same reaction conditions the [Co(III)(salen)]OAc analogue **61** was not an effective catalyst, since the product was obtained in just 10% yield.[151] Nonetheless, when complex **61** was used in conjunction with DMAP, propylene carbonate was obtained in 99% yield with a TOF of 49 h^{-1}.



60) Co(II), X = Cl, R = H
61) Co(III)OAc, X = Cl, R = H
66) Co(III)OAc, X = Br, R-R = -$(CH_2)_4$-

Building on the work of Lu *et al.*[146] on Co(II)(salen) catalysts, Kim introduced bimetallic cobalt(II) derivative **62** bearing a Lewis-acidic $AlCl_3$ group,[152] and which showed good enantioselectivity for propylene carbonate synthesis. At room temperature and 5 atmospheres pressure, this catalyst system gave product in just 11% yield, but with 81% enantiomeric excess. In an attempt to improve the catalyst activity, various additives were investigated, and the two most effective in terms of TOF were the ionic-liquid [EMIm]OH and TBAI with TOFs of 265 h^{-1} and 322 h^{-1} respectively.[152] Propylene carbonate was obtained in up to 60% yield with low to good enantioselectivities of 27–75% in the presence of quaternary ammonium cocatalysts, the highest enantioselectivity being obtained using tetrabutylammonium hydroxide. Similar yields were achieved in the presence of ionic liquids with an improved enantioselectivity of 83% obtained using [BMIm]OH. In the presence of K_2CO_3 as a cocatalyst, up to 82% enantiomeric excess was obtained when using lower mole ratios of cocatalyst, but this was found to have a negative impact on the chemical yield (22%). The lower reactivity resulted in much lower TOF values of 7–12 h^{-1} for the K_2CO_3 system.



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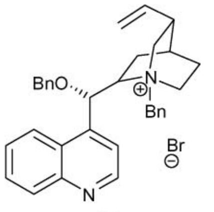

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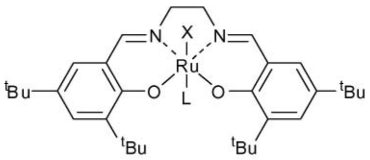
Cai *et al.* showed that the asymmetric addition of CO_2 to epoxides was possible through the use of cobalt(salen) complexes with cinchona alkaloids as cocatalysts.[153] Reactions were carried out at 7 atmospheres CO_2 pressure at 20 °C, using 0.1 mol% of catalyst **63** and 0.2 mol% of cocatalyst. The highest yield of propylene carbonate (40%) was obtained using alkaloid **64** as cocatalyst (although this system did not give the highest enantiomeric excess). The nature of the cobalt catalyst counterion was found to exert a noticeable effect on both the reaction yield and enantiomeric excess. The best yield of 48% was obtained using complex **65** with a 2-nitrophenoxy counterion, this also gave an enantioselectivity of 34% and a TOF of 480 h^{-1}. A range of epoxides were used as substrates, with moderate TOFs (108–227 h^{-1}) recorded for terminal epoxides with the exception of styrene oxide which gave a lower TOF of only 15 h^{-1}. Cyclohexene oxide was also found to be significantly less reactive than the terminal epoxides, giving only 20% yield and a TOF of 25 h^{-1} with complex **65**.

Jing *et al.* used chiral one-component cobalt(III) salen complexes with various quaternary phosphonium and ammonium salts substituted onto the phenyl rings for the asymmetric synthesis of cyclic carbonates.[154] Using propylene oxide as substrate, the highest conversion to propylene carbonate (48% with 42% enantiomeric excess after 20 h) was achieved at ambient temperature using 0.1 mol% of catalyst **66** with CO_2 at 6 atmospheres pressure. The quaternary phosphonium salt counterion was found to be important for the reaction outcome, with the chloride salt equivalent of complex **66** giving propylene carbonate with 77% enantiomeric excess, but with only 24% yield under the same conditions.

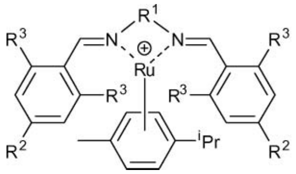
2.2.4 Ruthenium(II) and (III)(salen) complexes.

Continuing from their work on Co(III)(salen) complexes[145] (see section 2.2.3), Jing *et al.* introduced [Ru(III)(salen)]Cl complex **67** as a catalyst for the synthesis of propylene carbonate. In the presence of PTAT as a cocatalyst and at 70 °C and 8 atmospheres pressure in dichloromethane, a TOF of 588 h^{-1} was obtained.[155] Recyclability experiments demonstrated that complex **67** could be reused over 5 runs, although it was necessary to replenish the PTAT and the catalyst activity decreased to 163 h^{-1}.[155] Interestingly, complex **67** in conjunction with PTAT was also found to promote the addition of CO_2 to disubtituted geminal epoxides, such as α-methyl styrene oxide (yield 37%, TOF 9.3 h^{-1}), and vicinal epoxides (yield 31–35%, TOF 7–10 h^{-1}), although cyclohexene oxide was not found to be a substrate for this system.[155] [Ru(II)(salen)]$(PPh_3)_2$ complex **68** used in combination with PTAT was also found to be an active catalyst system for the synthesis of propylene carbonate in dichloromethane at 70 °C and 8 atmospheres pressure, though the product was obtained in only 42% yield after a reaction time of 4.5 h, with complex **68** displaying a TOF of 29 h^{-1}.[155]



67) X = Cl, L = PPh_3
68) X = L = PPh_3

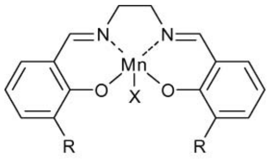
Ulusoy *et al.* recently reported a series of diimine Ru(II) complexes **69a–f** for the synthesis of cyclic carbonates from CO_2, and epoxides.[156] Complex **69c** was found to be the most active species when used with DMAP as a cocatalyst; propylene carbonate was obtained in 67% yield, at 100 °C and 16 atmospheres pressure, with a TOF of 336 h^{-1}. It was observed that both the structure of the diimine ligand and the nature of the epoxide influenced the catalyst activity.



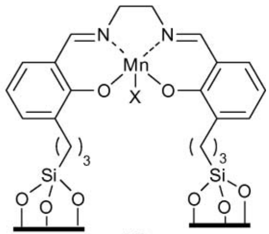
69a) $R_1 = -(CH_2)_2-$, $R^2 = NMe_2$, $R^3 = H$
69b) $R_1 = -(CH_2)_2-$, $R^2 = NMe_2$, $R^3 = H$
69c) $R_1 = -(CH_2)_2-$, $R^2 = NEt_2$, $R^3 = H$
69d) $R_1 = -(CH_2)_2-$, $R^2 = Me$, $R^3 = Me$
69e) $R_1 = -(CH_2)_2-$, $R^2 = Me$, $R^3 = Me$
69f) $R_1 = -(CH_2)_4-$, $R^2 = Me$, $R^3 = Me$

2.2.5 Manganese(III) salen complexes.

In 2008, Baiker *et al.* investigated various homogeneous and immobilized [Mn(III)salen]X complexes as catalysts for the addition of CO_2 to propylene and styrene oxide under supercritical conditions.[157] Complex **70** catalysed the synthesis of propylene carbonate in 91% yield, displaying a TOF of 203 h^{-1} at 140 °C and 200 atmospheres pressure. Complex **70** showed comparable activity (TOF 213 h^{-1}) for the synthesis of styrene carbonate, although the product was obtained in only 31% yield.[157] Under the same reaction conditions, propylene carbonate was obtained in 34% yield in the presence of complex **71**, with a TOF of 233 h^{-1}; the styrene derivative was isolated in 67% yield, with a TOF of 117 h^{-1}.[157] Styrene carbonate was also obtained in the presence of SiO_2-immobilized [Mn(III)salen]Br complex **72**, which gave the product in 96% yield, displaying a TOF of 196 h^{-1}.[157] Recyclability experiments demonstrated that complex **72** could be reused over three reactions, during which time the catalyst activity remained constant (TOF 255 h^{-1} for the 3rd run).[157] Under the same reaction conditions, a kinetics study based on *in situ* FT-IR spectroscopy showed that the nature of the epoxide strongly influenced the reaction rate.[157]



70) X = I, R = H
71) X = Br, R = $CH_2CH{=}CH_2$



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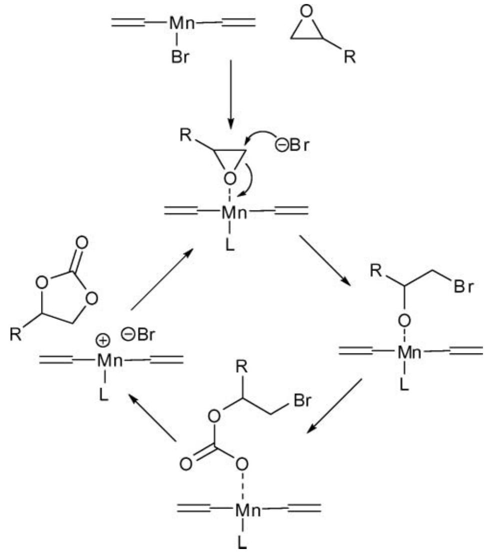
Building on the above work, in 2009 Baiker *et al.* carried out an important mechanistic study of cyclic carbonate synthesis catalysed by Mn(salen) complexes. X-ray absorption spectroscopy was used to probe the reactions and the catalytic cycle shown in Scheme 9 was proposed.[158] This mechanism is similar to the ones previously proposed for Al(III),[159] and Cr(III)[160] salen-based catalyst systems.



Scheme 9 Proposed mechanism of the catalytic cycle based on the data obtained by X-ray absorption spectroscopy by Baiker *et al.*[158]

2.2.6 Tin(IV) salen complexes.

[Sn(IV)(salen)]I_2 complex **73** was prepared by Nguyen *et al.* and used, along with DMAP as a cocatalyst, to catalyse the addition of CO_2 to propylene oxide in quantitative yield. The catalyst exhibited a TOF of 513 h^{-1} in a reaction carried out at 120 °C, and 7 atmospheres pressure in dichloromethane as solvent.[161]

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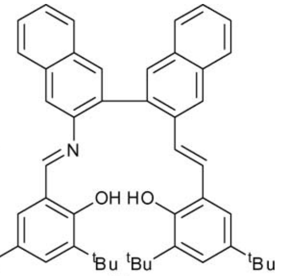

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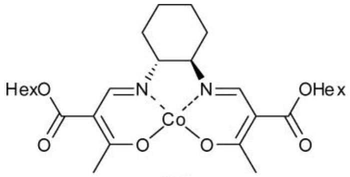
2.2.7 Salen derivatives as organocatalysts for the synthesis of cyclic carbonates.

Work carried by Shen *et al.* reported the first example of cyclic carbonate synthesis catalysed by an organocatalyst.[162] Thus, in the presence of a DMAP cocatalyst, Schiff base **74** was found to catalyse the addition of CO_2 to propylene oxide in quantitative yield, at 120 °C and 35 atmospheres pressure in dichloromethane. Compound **74** exhibited a moderate TOF of 18.5 h^{-1}. On the basis of this successful achievement, the structure of the Schiff base was simplified to just phenol, as it was proposed that the hydroxyl moieties were responsible for the catalytic activity. Under the same reaction conditions, the combination of phenol and DMAP catalysed the synthesis of propylene carbonate in 91% yield, exhibiting a TOF of 4.75 h^{-1}.[162]

2.2.8 Other Schiff base derived complexes for the synthesis of cyclic carbonates. Yamada *et al.* used chiral C_2-symmetric cobalt(acen) complexes to catalyse the addition of CO_2 to epoxides.[163] The catalysis was performed using 2 mol% of catalyst and 1 mol% of an amine cocatalyst under 20 atmospheres pressure of CO_2. With catalyst **75** and *N*-trimethylsilyldiethylamine as cocatalyst, *O*-tritylglycidyl oxide was converted into the corresponding cyclic carbonate in 47% yield with an enantiomeric excess of 68% after a reaction time of three days. A number of other nucleophilic cocatalysts were also investigated and a marginal improvement in yield was noted with the use of diethylamine. Catalyst **75** was also used to screen the addition of CO_2 to a range of glycidol-based epoxides. Yields of 25–49% were achieved, the highest of which was obtained after 36 h reaction time using *p*-methoxyphenylglycidol under the same conditions described above (with 1 mol% diethylamine cocatalyst). Despite this yield, the enantioselectivity achieved with this substrate was one of the lowest recorded (26%), the best enantioselectivity (59%) was obtained with tritylglycidol. Similarly, a series of glycidyl amines were screened in the same way and despite a lack of improvement in terms of yield, much better enantioselectivities were obtained, with the best result achieved using 3-carbazylpropylene oxide **76** which gave 45% yield and 92% enantiomeric excess.



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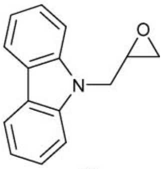

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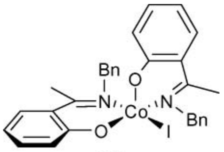
Cobalt Schiff base complexes were used by Repo *et al.* in the presence of Lewis bases to catalyse the addition of CO_2 to epoxides.[164] The best results were achieved using complex **77** (0.01 mol%) with TBAB (0.06 mol%) under 10 atmospheres of CO_2 at 145 °C. Under these conditions, five epoxides were tested as substrates, with the highest TOFs obtained with propylene oxide (900 h^{-1}) and 2-ethylhexylglycidol (910 h^{-1}). A catalytic cycle was proposed in which DMAP replaces the iodine ligand of **77** and participates in the reaction as a ligand. The epoxide coordinates through oxygen to the metal centre and is ring-opened by another molecule of DMAP. Carbon dioxide inserts between the ring-opened epoxide and cobalt after which a ring-closing step forms the cyclic carbonate with elimination of DMAP.



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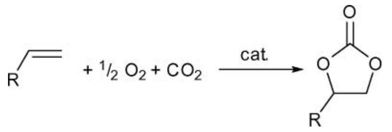
2.3 Alternative routes for the synthesis of cyclic carbonates

2.3.1 Cyclic carbonate synthesis *via* oxidative addition of CO_2 to olefins. Oxidative addition of CO_2 to olefins is an alternative single-step route for the synthesis of cyclic carbonates (Scheme 10). Niobium oxide catalysts in the presence of molecular oxygen showed modest activity for styrene carbonate synthesis, though the process required DMF as the solvent, and the selectivity for the carbonate was quite low. In addition, high pressures and temperatures were necessary (50 atmospheres, 125 °C, 5 h, 27% conversion).[165]

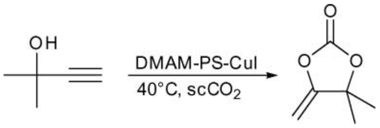


Scheme 10 Oxidative cycloaddition of CO_2 to olefins.

In 2005, Arai *et al.* reported that the oxidative carboxylation of styrene could be carried out in an ionic liquid in the presence of TBAB and *tert*-butyl-hydroperoxide (TBHP) as the oxidizing agent, though pressurized CO_2 and an elevated temperature were still necessary to achieve the transformation (10 atmospheres, 80 °C, 6 h, 38% yield).[32] Arai *et al.* also reported a second system for the direct synthesis of styrene carbonate from styrene without isolation of the intermediate epoxide.[166] By using a one-pot catalytic system consisting of gold on silica, with zinc bromide and TBAB, and TBHP as oxidant, styrene carbonate could be successfully formed in the presence of 80 atmospheres pressure of CO_2 at 80 °C for 4 h. With 2.5 mol% of $ZnBr_2$ and 5 mol% of TBAB, 31–37% of styrene carbonate could be obtained using 1–8 weight% loading of gold on silica. In addition, some styrene oxide and benzaldehyde were formed and made up the remainder of the product. The CO_2 pressure could be reduced to 10 atmospheres, resulting in a similar carbonate yield of 35%. Using cumene hydroperoxide as an alternative oxidant provided better yields of styrene carbonate (up to 45% when 2 equivalents of oxidant were used) under the same conditions with a CO_2 pressure of 10 atmospheres. Increasing the CO_2 pressure from 80 to 150 atmospheres reduced the yield of styrene carbonate to just 18%. At this pressure, the CO_2 was thought to liquefy. Starting from styrene oxide, it was found that the reaction proceeded rapidly to 100% conversion to styrene carbonate, therefore it was established that the limiting process is the oxidation of the alkene to the epoxide.

Earlier work from the same group highlighted the same oxidation/addition process without the zinc salt, using TBHP as oxidant and TBAB as catalyst.[167] A yield of 38% of styrene carbonate was obtained after six hours using 10 atmospheres pressure of CO_2 with 11.6 mol% TBAB at 80 °C. Leaving the reactions for longer time periods did not increase the yields, rather they were lowered slightly, particularly when a higher pressure (15 atmospheres) of CO_2 was used. Using either hydrogen peroxide or oxygen in place of TBHP significantly reduced the amount of styrene carbonate produced and increased the amount of benzaldehyde formed.

2.3.2 Carboxylative cyclization of propargyl alcohol with CO_2. In 2008, Jiang *et al.* reported the use of a solid supported copper iodide catalyst (CuI-[(dimethylamino)methyl-polystyrene; DMAM-PS) for the carboxylative cyclization of propargylic alcohols in supercritical CO_2 (Scheme 11).[168] The product was obtained in 99% yield at 40 °C and 14 atmospheres pressure, with a TOF of 1.4 h^{-1}. Recyclability experiments showed that the supported CuI catalyst could be reused without significant loss of activity over five reactions.

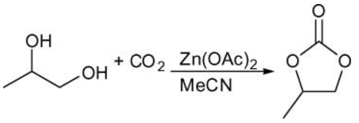


Scheme 11 Synthesis of 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one catalysed by solid-supported (DMAM-PS) CuI catalyst.

2.3.3 Cyclic carbonate synthesis from CO_2 and 1,2-diols.

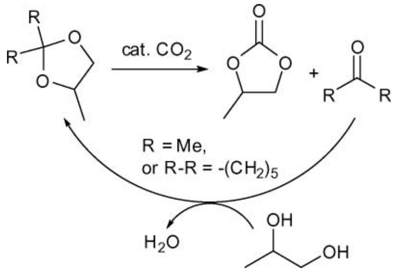
Sun *et al.* demonstrated the synthesis of cyclic carbonates from diols and urea using metal oxides as catalysts.[169] A 93% yield of ethylene carbonate was obtained with zinc oxide as catalyst after three hours at 150 °C under a CO_2 atmosphere. Good results were also obtained starting from other diols with zinc oxide under the same conditions. Extending the reaction time produced higher yields of ethylene carbonate, whilst reduced reaction times gave higher levels of cyclic carbamate which was therefore determined to be an intermediate species in the mechanism.

In 2007, Wei *et al.* reported the synthesis of propylene carbonate from CO_2 and 1,2-propylene glycol in the presence of anhydrous zinc acetate as catalyst (Scheme 12).[170] The process was carried out at 170 °C and 100 atmospheres pressure, using acetonitrile as solvent and exhibited a low TOF of 0.8 h^{-1}. Acetonitrile was used as the reaction solvent and as a dehydrating agent in order to absorb the water formed during the reaction.



Scheme 12 Synthesis of propylene carbonate from CO_2 and propylene glycol.

He *et al.* used tin catalysts in supercritical CO_2 for the synthesis of propylene carbonate directly from propylene glycol (Scheme 13).[171] Using dibutyltin oxide or dibutyltin dimethoxide in the presence of DMF, a low conversion to propylene carbonate could be observed after 12 h at 180 °C under 150 atmospheres pressure of CO_2. The formation of propylene carbonate in this study was generally low (no greater than 2%) with the best result reported for 0.05 mmol% dibutyltin dimethoxide, which gave a TOF of 5.7 h^{-1}. This was achieved from a reaction in which 5 mol% of the acetal derived from cyclohexanone and propylene glycol was added as a dehydrated form of propylene glycol. Scheme 13 shows a proposed catalytic cycle in which the acetal reacts with CO_2 in the presence of the tin catalyst to form the cyclic carbonate and regenerate the ketone which can couple to another propylene glycol molecule.



Scheme 13 Reaction of CO_2 with propylene glycol derived acetals in the presence of tin catalysts

2.3.4 Electrochemical synthesis of cyclic carbonates.

The electrochemical incorporation of CO_2 into epoxides in the presence of $Ni(cyclam)Br_2$ catalyst **78** at room temperature and atmospheric pressure has been reported.[172] The reaction was carried out in a single-compartment electrolysis cell, using DMF as solvent and in the presence of potassium bromide as supporting electrolyte. Catalyst **78** displayed a TOF of 1.3 h^{-1} for the synthesis of styrene carbonate, using a magnesium rod as the anode and stainless-steel for the cathode.[172] Later, $[Ni(bipy)_3]^{2-}(BF_4)_2$ complex **79** was found to give comparable results for the electrochemical addition of CO_2 to *ortho*-halo-substituted styrene oxides under the same reaction conditions.[173] Yuan *et al.* used a 0.05 M solution of TBAB in DMF as electrolyte in a cell at ambient temperature and under 40 atmospheres CO_2 pressure.[174] The best results (using propylene oxide as substrate) were obtained when using an aluminium anode and platinum cathode (98% yield) or a zinc anode with a platinum cathode (95%). Lower, but still reasonable, yields were obtained when using aluminium anodes with either copper, nickel or brass cathodes (67–77%). Other terminal epoxides also provided good yields of cyclic carbonates under the same conditions.

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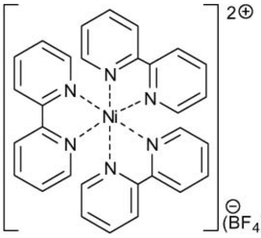

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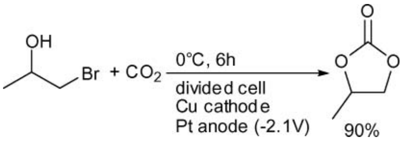
Rossi *et al.* reported the synthesis of cyclic carbonates from primary and secondary alcohols bearing a leaving group in the β-position, using an electrochemical process to activate CO_2 (Scheme 14).[175] Propylene carbonate was synthesized in 90% yield, using a divided cell system with a copper cathode and a palladium anode.



Scheme 14 Synthesis of propylene carbonate using electrochemically activated CO_2.

3 Conclusions

In the previous sections, a review of the most important catalysts for the synthesis of cyclic carbonates has been reported. Only a small number of these catalysts gave satisfactory results under mild reaction conditions (ambient temperature and atmospheric pressure), since cyclic carbonate synthesis usually only proceeds under high temperature and/or high pressure conditions. Table 1 compares the most significant results achieved for the –onium salt, ionic liquid and solid catalysts discussed in this review. In

Table 1 Cyclic carbonate synthesis catalysed by –onium salts, solid catalysts and ionic liquids

Entry	Catalyst	Cocatalyst	Substrate	*P*/atm	*T*/° C	TOF/h^{-1}	Ref.
1	**5**	—	PO	20	125	62	44
2	Tetraalkyl-onium	—	various[a]	50	60	50	48
3	Ph_4SbBr	—	various[a]	50	60–120	150–700	50
4	$ZnBr_2(PMePh)_2$	—	PO	25	100	1640	70
5	Poly(4-vinyl-pyridine) $ZnBr_2$	—	EO	35	100	207	71
6	$ZnBr_2$	TBAI	SO	>80	80	686[b]	65
7	$ZnBr_2$	TBAI	SO	30	100	67[b]	66
8	$ZnCl_2$	TBAI	PO	1.2	25	143	67
9	$ZnBr_2$	Ph_4PI	PO	25	120	6272	68
10	$SnCl_4$	DMAP	PO	3	75	1388	77
11	NaI	PPh_3/PhOH	PO	Mild	170	24	83
12	$NiCl_2/PPh_3$	TBAB	PO	25	120	3544	85
13	Supported $RuCl_3$	—	PO	>80	80	293[b]	86
14	HPW	—	PO	25	80	297[b]	86
15	MgO	—	PO, SO	20	135	14	90
16	Ti–Si molecular sieves	TBAB/DMAP	ECH	7	120	168–790	95
17	Ti–MCM-41	—	PO	7	120	36	98
18	Zn–HAP	DMAP	SO	10	100	308	101
19	$(Ph_3P)_4Pd$	Ph_3P	PO	15	0	768	113

[a] Ethylene oxide (EO), propylene oxide (PO), epichlorohydrin (ECH) and styrene oxide (SO) were used as substrates. [b] Reaction carried out in $scCO_2$.

Table 2 Cyclic carbonate synthesis catalysed by metal complexes

Entry	Catalyst	Cocatalyst	Substrate	*P*/atm	*T*/°C	TOF/h^{-1}	Ref.
1	**20–21**	NMI/DMAP	Various[a]	26	100	38–39	106
2	**27**	**28**	PO	15	80	124	117
3	**30**	TBAI	Butylene oxide	30	120	7384	119
4	**33**	—	PO	7	25	304	121
5	**41**	Bu_3N/NMI	SO	100	80	73	130
6	**42**	—	PO	20	80	1936	131
7	**42**	—	EO	20	80	3338	131
8	**44a**	TBAB	EO	160	110	2220[b]	133a
9	**44a**	—	EO	160	110	174[b]	133a
10	**44a**	TBAB	EO	40	110	1140[b]	133a
11	**44b**	18-crown-6-KI	PO	6	25	48	134a
12	**44b**	TBAI	PO	6	35	84	134b
13	**44a**	—	PO	6	35	60	134b
14	**44d**	TBAI	PO	6	35	30	134b
15	**44b**	**45**	PO	20	100	50	136
16	**51**	TBAB	PO	15	25	245	144[c]
17	**52**	TBAC	PO	15	0	27	144[d]
18	**53**-MCM-41	—	EO	123	110	111[b]	146
19	**54**	DMAP	PO	10	100	1200	147[e]
20	**54**	DMAP[f]	PO	10	3	10	147[e]
21	**51**	PTAT	PO	4	25	706	145
22	**57**	—	PO	5	25	23	149[g]
23	**58**	PTAT	PO	12	25	244	150[h]
24	**62**	TBAI	PO	5	25	309	152[i]
25	**67**	PTAT	PO	8	70	588	155[e]
26	**69c**	DMAP	PO	16	100	336	156
27	**70**	—	PO	200	140	203	157
28	**70**	—	SO	200	140	213	157
29	**71**	—	PO	200	140	233	157
30	**72**	—	SO	200	140	196	157
31	**73**	DMAP	PO	7	120	513	161[e]
32	**74**	DMAP	PO	35	120	18	161[e]

[a] Ethylene oxide (EO), propylene oxide (PO), epichlorohydrin and styrene oxide (SO) were used as substrates. [b] Reaction carried out in $scCO_2$. [c] PC was obtained with 50% enantiomeric excess. [d] PC was obtained with 70% enantiomeric excess. [e] Reaction was carried out in CH_2Cl_2. [f] Reaction was carried out in the presence of chiral DMAP **55**, and showed a selectivity factor s of 5.6. [g] The product was obtained in 25% yield and with 60% enantiomeric excess. [h] The product had 20% enantiomeric excess. [i] The product was obtained in less than 50% yield, although in the presence of K_2CO_3 it was obtained with 82% enantiomeric excess.

general, the catalytic systems reported were found to be very active, but required the use of harsh reaction conditions. In addition, these catalysts were generally found to promote the addition of CO_2 to only terminal epoxides. Incorporation of halide anions either as part of the solid catalyst (Entries 1–5) or within the cocatalyst (Entries 6–12, 16, 18–19) was often found to be necessary to obtain a catalytically active species.

The highest catalyst activity was observed for the $ZnBr_2/Ph_4PI$ catalyst system[68] (Entry 9), with a TOF of 6272 h^{-1} for the synthesis of propylene carbonate at 120 °C and 25 atmospheres pressure. Under the same reaction conditions, the $NiCl_2/PPh_3$ system[85] displayed a TOF of 3544 h^{-1} in the presence of TBAB (Entry 12). High catalyst activity was also observed for the $SnCl_4$/DMAP system, which promoted the synthesis of propylene carbonate at 75 °C and 3 atmospheres pressure, with a TOF of 1338 h^{-1} (Entry 10).[77] The $ZnCl_2$/TBAI system[67] showed a TOF of 143 h^{-1} at room temperature and 1.2 atmospheres pressure, which is the most successful propylene carbonate synthesis carried out under mild reaction conditions (Entry 8) using the catalysts included in Table 1.

Table 2 summarizes the most significant results achieved for cyclic carbonate synthesis using metal complexes as the catalyst species. Generally, metal complex-based catalysts also required high temperatures and pressures to exhibit high activity, although moderate results were also observed at lower CO_2 pressures (Entries 2, 4, 11–25, 30, 31). However, low to moderate temperatures were reported to be effective for the synthesis of enantiomerically pure propylene carbonate, though the catalyst activity decreased significantly (Entries 16, 17, 20, 22, 23).

Lewis base additives were usually necessary to accomplish high catalyst activity, with tetraalkylammonium halides being the most effective. It is known that tetraalkylammonium salts are able to catalyse cyclic carbonate formation by epoxide ring-opening by the halide anion, followed by CO_2 insertion into the alkoxide.[8b,46] Metal(III) complexes incorporating nucleophilic halides at the Lewis-acid centre, were found to catalyse cyclic carbonate formation in the absence of any additive. However, the catalyst activity significantly decreased in the absence of a halide additive, as observed for catalyst **44a**, in which the TOF dropped from 2220 h^{-1} to 174 h^{-1} (Entries 8, 9).[133]

Notably [Cr(III)(salen)]X complexes **54** were found to catalyse both polycarbonate[28c–f] and cyclic carbonate synthesis,[127] under comparable reaction conditions. In general, the same trend was observed for cobalt[28k–s,144–145,151,152] and aluminium[28a–b,133–137] salen complexes, though differences in Lewis acidity due to changes in the counterion may be responsible for the differing catalytic activities. Work by Coates,[28o] Darensbourg[28a–g,127] and Lu[131,134,144,146] showed that aliphatic terminal epoxides such as propylene oxide or styrene oxide preferentially form cyclic carbonates, whilst disubstituted epoxides, such as cyclohexene oxide, undergo polymer formation. Thus, the relative efficiency of polymerization and cyclic carbonate formation with a particular catalyst system can also depend on the nature of the epoxide.

In summary, the current industrial production of cyclic carbonates requires the use of high temperatures and high pressures, along with the use of highly purified CO_2. However, the development of new catalysts for this reaction continues to be a fruitful area of research and recent breakthroughs such as the development of bimetallic aluminium(salen) complexes have the potential to allow this industrial process to be transformed into one which can be achieved at or near room temperature and pressure, potentially even exploiting waste CO_2 from a power station or other major fixed site producer through the use of immobilized catalysts in a gas phase flow reactor. A detailed understanding of the reaction mechanism and catalytic cycles is essential to allow catalyst structures to be optimized and again major breakthroughs have recently been made in this area. It is now recognised that the most effective catalysts combine a Lewis-acid to activate the epoxide with a nucleophile to ring-open the epoxide and subsequently act as a leaving group and a Lewis- or Brønsted-base to activate the CO_2. In view of the global industrial and academic interest in this reaction and the recently achieved level of mechanistic understanding, it is likely that further significant developments in catalyst and process design will occur in the next few years, thus allowing cyclic carbonate synthesis to take its place as one of the technologies which can be used to help to limit global CO_2 emissions.

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