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Homogeneous and heterogenised masked N-heterocyclic carbenes for bio-based cyclic carbonate synthesis†

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(Multifunctional) cyclic carbonates are generating much interest, with bio-based bis-cyclic compounds attracting attention from the polymer sector as potential renewable monomers for systems such as non-isocyanate polyurethanes. Here, the efficient synthesis of one such substrate, diglycerol dicarbonate, utilising CO_2-masked N-heterocyclic carbene (NHC) organocatalysts is demonstrated. The 1,3-dialkylimidazole-2-carboxylate pre-catalyst, which can be produced both *in* and *ex situ*, yields the desired cyclic product, expressing full conversion within 3 h when using the *ex situ* synthesised pre-catalyst with 5 mol% loading, but can also operate with 1 mol% loading efficiently. Substituted derivatives of the imidazole-based organocatalyst have also been investigated to gauge the sensitivity of the system. A number of bio-based diols are also investigated, with 1,2-, 2,3- and 1,3-diols yielding five- and six-membered cyclic products, respectively; 1,3-diols are significantly more reluctant to cyclisation, yielding both 1- and 3-monocarbonates, dicarbonates and the cyclic products. A more in depth study was also carried out on glycerol as a substrate, both in its pure a crude form, providing insight into how impurities impact on the activity of the carbene catalyst. Through ^{13}C-labelled reagent experiments, a mechanism is proposed for the conversion of diols to their cyclic carbonate analogues. Finally, the organocatalyst was immobilized on siliceous mesostructured cellular foam (MCF). Using an alternative activation procedure, a supported, masked NHC catalyst is achieved and characterised with DRIFTS, TGA and ^{13}C solid-state NMR. This heterogenised catalyst can be easily recovered and reused up to three times expressing its original activity if properly regenerated by a simple ion exchange procedure. Of important note, this system can also successfully convert crude glycerol with high selectivity observed for the cyclic product.

Introduction

The multitude of applications of cyclic carbonates include their use as aprotic solvents, precursors to polymeric materials, electrolytes and as intermediates for a number of fine chemicals to name but a few. Cyclic compounds are typically synthesised from either the diol or epoxide precursor, with both pathways having received ample interest over the past decade and most studies concentrating on short-chain, terminally functionalised substrates.[1–5] One substrate that has received considerable attention in this respect is glycerol. Glycerol is a renewable raw material derived from triglycerides and is industrially produced *via* saponification, hydrolysis and transesterification. Glycerol itself can be converted into a number of useful chemicals, with routes explored including glyceric acid by oxidation, propylene glycol and 1,3-propanediol by hydrogenolysis and acrolein by acid-catalysed dehydration.[6–8] In addition, extensive research efforts have focussed on glycerol carbonate (GC) production from glycerol.[9] Indeed, GC has highly desirable physical and chemical properties. It is biodegradable, water-soluble, non-toxic and non-flammable and can be utilised in a number of ways, from solvents and beauty product component to building eco-composites and as a carrier in lithium batteries.[10,11] Phosgene has previously been used for the synthesis of GC from glycerol,[12] but its highly toxic nature has led to research into more environmentally friendly processes. A number of different catalytic systems have been developed for this process, making use of a

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range of "CO" sources including CO_2, CO and O_2, urea, ethylene carbonate and dimethyl or diethyl carbonate (DMC, DEC), of which each can be considered renewable.[9,13]

The different CO sources have been tested in combination with numerous homogeneous, heterogeneous and biological catalysts for the synthesis of GC.[9] Focussing on those examples that make use of the alkyl carbonates, it can be seen that di(m)ethyl carbonate typically gives higher conversions and selectivities (95+%) than ethylene carbonate. Systems explored include Mg–Al hydrotalcites,[14] Mg–Al mixed oxides,[15] Mg–Al–Zr mixed oxides,[16] calcium oxide[17,18] and calcium hydroxide[19] for DMC/DEC, compared with zeolites and basic resins,[20] Mg-mixed oxides,[3] immobilised ionic liquids[21] and Li-hydrotalcites[3] that use ethylene carbonate. Lipases have also yielded good catalytic results, with up to 100% yields being reported, albeit after long reaction times.[22,23]

Organocatalysts have recently also been reported for GC formation in particular and cyclic carbonate formation in general. Sakai *et al.*, for instance, employed organocatalysts with an ammonium betaine framework for the conversion of various epoxides to cyclic carbonates, including the conversion of glycidol to GC.[24] Lu *et al.* showed that CO_2 adducts of N-heterocyclic olefins and alkoxide-functionalised imidazolium betaines are highly active for the carboxylative cyclisation of propargylic alcohols under mild CO_2 pressures.[25,26]

Naik *et al.* in turn used DMC as the CO source with 1,3-dialkyl-substituted imidazolium-2-carboxylate catalysts for the conversion of glycerol to glycerol carbonate.[27] The catalyst could also be obtained *in situ* by methylation and carboxylation of the appropriate 1-alkylimidazole precursor with DMC. The authors tentatively suggest that in solution, this (pre-)catalyst undergoes decarboxylation to yield the active N-heterocyclic carbene (NHC), although do not evidence this. Such imidazole-based betaines, which have also been used as (pre-)catalysts for other reactions[26,28,29] and as precursors for N-heterocyclic carbene transfer agents, can be synthesised *via* a number of routes as demonstrated by Crabtree *et al.*[30] It has been shown that such imidazole-2-carboxylates perform as "masked" NHCs, in which the carboxylate actually acts as a protecting group for the active carbene, with decarboxylation in solution preceding the catalytic reaction.[31–34] Relatedly, Palencia *et al.* recently demonstrated the NHC-catalysed synthesis of glycerol carbonate from glycerol and DMC. In this study, the NHC is generated *in situ* from the imidazolium halide by the addition of potassium *tert*-butoxide.[35]

Naik *et al.* furthermore found the alkyl chain length on the 1-position of the imidazole to influence catalyst activity, with a butyl chain being optimal.[27] The organocatalyst system was significantly faster than the benchmark catalyst K_2CO_3,[36] and, in contrast to K_2CO_3, proved effective for the conversion of a crude glycerol. The substrate scope of the imidazolium-2-carboxylates studies was limited to glycerol, however. It is clearly of interest to see how such readily accessible organocatalysts would perform with other diol substrates, such as ethylene diol, 1,2- and 1,3-propanediol and 1,2-, 2,3- and 1,3-butanediol as well as diglycerol.[2,37–39]

Dicyclics synthesis is also of considerable interest, for instance to the polymer sector. In particular, ring-opening of cyclic carbonates by amines provides an interesting, non-isocyanate-based alternative to the current production routes to polyurethanes.[9,11,40] Indeed, the current use of isocyanates for polyurethane production is associated with environmental concerns, not only because the isocyanates are highly toxic themselves, but also because they are produced from the highly toxic compound, phosgene. To mitigate these toxicity concerns, a number of dicyclic monomers have been highlighted to replace isocyanates for the production of non-isocyanate polyurethanes (NIPUs). Examples include limonene dicarbonate,[41] fatty acid-based bis-cyclic carbonates,[42,43] di(glycerol (di)carbonate)s[11,44] and others.[40] Diglycerol thus is an attractive substrate for cyclocarbonation, given its potential as precursor to NIPU monomers. To date, there is only one reported catalytic synthesis of diglycerol dicarbonate (DGDC) from diglycerol, utilising Mg–Al hydrotalcites.[39]

In this paper, the synthesis of DGDC is explored further utilising analogues of the imidazole-derived organocatalysts reported by Naik *et al.*[27] A number of other renewable diol substrates (Fig. 1(b)) are also used to explore the general applicability and efficiency of this system as well as its use for the conversion of an industrial crude glycerol. Reactions performed with ^{13}C-labelled dimethyl carbonate furthermore provided insight into the mechanism of cyclic carbonate formation. Based on this system, a heterogeneous, silica-supported imidazole-based catalyst is prepared and tested and its reuse demonstrated.

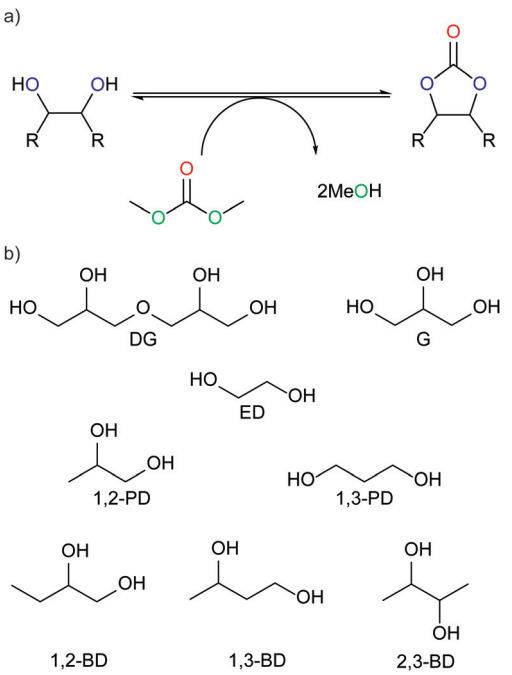

Fig. 1 (a) Reaction overview, (b) renewable diols used as substrates in this research. DG – diglycerol, G – (crude) glycerol, ED – ethylene diol, PD – propanediol, BD – butanediol.

Results and discussion

Homogeneous NHCs

Building on the example reported by Naik *et al.* of glycerol carbonate synthesis using 1-butyl-3-methylimidazolium-2-carboxylates, we investigated a range of 1-*n*-alkyl-3-methylimidazolium-2-carboxylates and their precursors for cyclic carbonate synthesis utilising DMC, concentrating first on the synthesis of DGDC from DG under mild, solvent-free conditions. The three stages of the imidazole-based catalyst are defined in Fig. 2, and will be referred to throughout this study as stated.

The results show that DGDC can also be synthesised efficiently with these organocatalysts (Fig. 3). For example, 1-butylimidazole gave a DGDC yield of 65%, with 80% selectivity after 18 h at 74 °C. A dimethyl carbonate to glycerol ratio of 6 : 1 is used to both aid with the higher viscosity of DG and to take into account the fact that it contains two hydroxyl pairs per molecule. K_2CO_3 was also tested as benchmark catalyst, yielding 10% diglycerol dicarbonate and 32% diglycerol monocarbonate (DGMC) at 44% conversion, under the same conditions. The pre-catalyst is formed *in situ* by reaction of the relevant 1-alkylsubstituted imidazole precursor with the excess of dimethyl carbonate. This activation process has previously been studied computationally and was suggested to first involve a rate-determining methyl transfer from DMC to the alkylimidazole, which results in an ion pair. Proton transfer then induces C–O bond cleavage to give an N-heterocyclic carbene (NHC), CO_2 and MeOH. The third and final step is nucleophilic attack of CO_2 by the NHC forming the new C–C bond.[30]

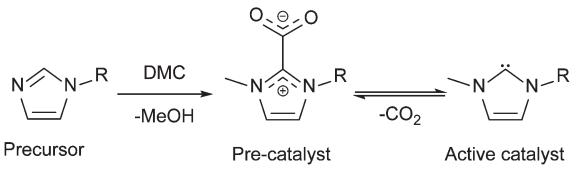

Fig. 2 The three stages of the imidazole-based catalyst (R = alkyl chain).

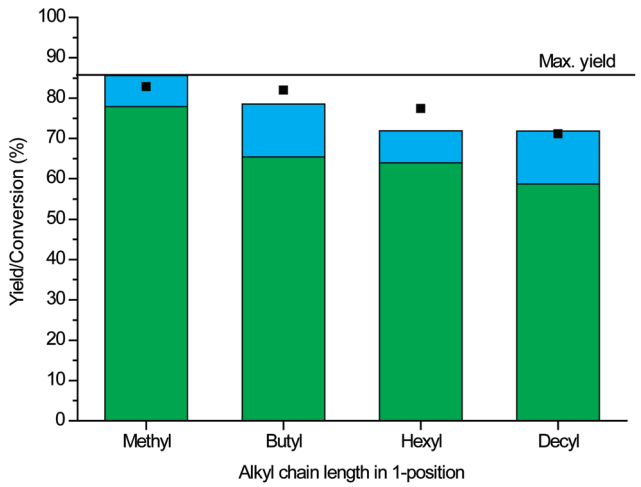

Fig. 3 Influence of alkyl chain length on conversion of DG (squares) and yield of DGDC (green) and DGMC (blue), utilising 5 mol% 1-alkyl-3-methylimidazolium-2-carboxylate synthesised *in situ* from its 1-alkyl-substituted imidazole precursor. Conditions: DG : DMC 6 : 1, 74 °C, 18 h. Max. yield is the theoretical maximum yield of DGDC due to the purity of feedstock, see ESI.†

As previously observed by Naik *et al.*, variation of the 1-alkyl chain length influenced the catalytic activity of the active carbene form, with activity decreasing with an increase in alkyl chain length, Fig. 3. This could be the result of (a combination of) two factors; namely the longer induction period required to generate the carboxylate form and the stability of the formed carboxylate w.r.t. to the formation of the active carbene. As generation of the carboxylate actually proceeds *via* the active carbene, the relative stability of the carbene and the carboxylate thus plays a pivotal role in the expressed activity. Each of the 1-alkylimidazoles produced DGDC within 18 h with a 5 mol% loading, with the 1-methyl-substituted catalysts expressing the highest yield (78% with 94% selectivity). This yield is close to the maximum that can be obtained as the purity of the starting diglycerol is only 86% (see ESI† for definitions), with no by-products being observed, except for small amounts of the intermediate DGMC. The largest impurity in the starting material is glycerol, and glycerol carbonate is indeed observed in the reaction mixture. With the inclusion of glycerol carbonate, the carbon balance amounts to 95% for the reaction with 1-methylimidazole. The longer hexyl and decyl alkyl chains gave yields of 64 and 59% of the dicarbonate, respectively (both with 83% selectivity). The optimal chain length for DGDC is thus different from the butyl one found by Naik *et al.* for GC. They attributed the influence of the chain length to a balance between the stability of the pre-catalyst, the methyl-substituted carboxylate being too stable, and the rate at which the carboxylate form is made, *i.e.* longer alkyl chains decreasing the rate of formation.[27] The stability of the carboxylate can be gauged from the torsional angle the carboxylate makes with the imidazolium ring; for 1,3-dimethylimidazolium-2-carboxylate, this angle is 29.03°, which still allows for a certain degree of π-orbital overlap and hence stabilisation. As alkyl chain length increases, the torsional angle increases, decreasing the π-orbital overlap and allowing for more facile decarboxylation.[45] Thus, the decrease in activity that we observed with increasing chain length may be a combination of lower activity of the carbene catalyst and lower amounts of the pre-catalyst being formed from the precursor due to slower kinetics. The fact that Naik *et al.* observed that butyl was optimal for glycerol conversion can be associated with steric hindrance of the larger chain approaching the substrate being more apparent for the diglycerol substrate.[27] It should also be noted that imidazole as catalyst precursor gave a DGDC yield of only 4%. Variation of the molar ratio of DMC : substrate for the best catalyst to either of 3 and 9 : 1 resulted in a drop in activity to 64 and 63%, respectively (Table S1†).

This observation is attributed to the necessity to overcome the viscosity of the substrate and a balance between the system becoming diluted when too large an excess of reagent is added. Equilibrium considerations will also play a role.

1-Methylimidazoles with various electron-donating and withdrawing substituents in the 2- or 5-position, depicted in Fig. S1,† were also tested. These substitutions proved to have a rather dramatic effect on activity, as each of the 5-substituted precursors tested gave no diglycerol dicarbonate, with only low amounts of diglycerol monocarbonate being detected (Table S2†). This reduction in activity can be attributed to two factors; electron-withdrawing groups are thought to influence the formation of the carboxylate pre-catalyst detrimentally, affecting the rate-determining methylation of the imidazole.[46] The introduction of electron-donating groups on the other hand stabilise the pre-catalyst carboxylate, and hence reduce the extent to which the active carbene is formed.[45] As discussed in more detail below, the 4-carboxylate isomer can also form when reactions are run at higher temperatures. 1,2-Dimethylimidazole, *i.e.* a precursor for which the 2-carboxylate cannot be formed and any reaction has to go through the 4-carboxylate and the resulting mesoionic carbene,[47] was also tested. Although significantly less active, it did show the highest conversion (29%) of all the substituted 1-methylimidazoles. It was also the only derivative tested that was able to produce the desired dicyclic product, although in very low yields (3%).

The results discussed thus far were achieved using the 1-alkylimidazole precursor rather than the (substituted) 1,3-dialkylimidazolium carboxylate pre-catalyst, which is generated *in situ.* The pre-catalyst, however, can also be synthesised and isolated in its crystalline form and used as such.[30] In fact, it has already been noted that the pre-catalyst synthesis conditions are similar to those of the reaction; indeed, the choice of reaction temperature might have consequences if the pre-catalyst has to be formed *in situ*, as syntheses carried out below 95 °C predominantly yield the 2-carboxylate, while above this temperature the formation of the 4-carboxylate becomes increasingly favoured, and dominates above 120 °C.[27,30] As already shown above and further detailed below, the mesoionic carbene obtained from the 4-carboxylate is less active than the one obtained from the 2-carboxylate.[47] The use of the as-synthesised 1,3-dimethylimidazolium-2-carboxylate (**1**) pre-catalyst has a significant impact on the reaction rate, as can be clearly seen from Fig. 4; the induction period seen for the precursor is absent when the pre-catalyst is used. This induction period is in line with separate synthesis times of 2 h required to achieve quantitative conversion of the precursor to the active catalyst *ex situ*.[30] Reaction times are now decreased significantly with the pre-catalyst, with a yield of 71% already being achieved after 3 h, with a maximum yield of 75% after 6 h; in contrast, the reaction with the precursor required 18 h to get to a similar yield of 78%. This finding is also significant, as our previously reported method for catalytic synthesis of DGDC requires 6 h to achieve high yields utilising 30 wt% of Mg–Al hydrotalcites under less mild conditions.[39]

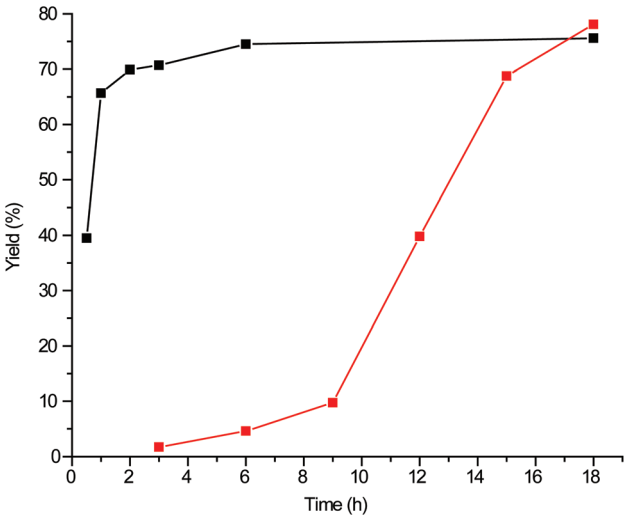

Fig. 4 Yield of DGDC against time for reactions starting with the precursor (red) or pre-catalyst (black). Conditions: 5 mol% 1-methyl-substituted pre-catalyst or catalyst precursor, 74 °C, DMC : DG 6 : 1 molar ratio.

Reactions with a 1 mol% loading of the pre-catalyst were also investigated, achieving a yield of 55% within 18 h, with 20% of the monocarbonate being observed as an intermediate product. Three other carboxylate derivatives were also synthesised, isolated and tested (**2–4**, Fig. 5). **2** expressed higher activity than **1** when compared using 1 mol% loading reaching full conversion and expressing 91% selectivity towards the dicyclic product in 18 h, Table 1. These results indicate that **1** is the most active form for this reaction when starting with the precursor, as formation of the carboxylate is more facile with small substituents in the 1- and 3-positions. However, larger substituents destabilise the pre-catalyst, and thus, the 1-butyl form shows higher activity when the as-synthesised pre-catalysts are compared.[35]

The 4-carboxylate pre-catalysts **3** and **4** were considerably less active than **1** and **2**. The lower activity can be associated with 4-carboxylates being thermodynamically more stable than the 2-carboxylates. As exemplified by the torsion angles of the carboxylates with the imidazolium ring,[47] the carboxylate group is more weakly bound in the 2-carboxylate, thus leading to the active carbene species more easily. The addition of an extra methyl group in the 2-position, (**3**), did have a drastic effect on activity, compared to **4**. The latter exhibited only 15%

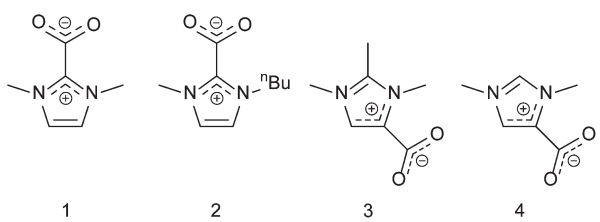

Fig. 5 Synthesised pre-catalysts for cyclocarbonation reactions.

Table 1 Activity of the isolated 2- and 4-carboxylate pre-catalysts for the conversion of diglycerol

Pre-catalyst	Catalyst loading (mol%)	Conversion (%)	Dicyclic yield (%)	Dicyclic selectivity (%)	Mono-cyclic carbonate yield (%)	Mono-cyclic carbonate selectivity (%)	C-balance (%)
1	5	100	72	83	16	18	102
1	1	93	55	69	20	25	94
2	1	100	79	91	9	11	102
3	5	76	50	77	15	23	100
4	5	15	0	—	8	60	94

Conditions: 0.5 g DG, 18 h, 6 : 1 DMC : DG, 74 °C, mol% pre-catalyst loading with respect to DG.

conversion (no dicarbonate, 8% monocarbonate), whereas the trimethyl derivative was able to express 76% conversion, with 50% yield of DGDC compared to just 8% monocarbonate after 18 h for the **4**. This can be attributed to the electron-donating effect of the extra methyl group in the 2-position, decreasing the stability of the carboxylate and increasing the nucleophilicity (σ-donating ability) of the resulting carbene species.[48] Under our conditions, **4** may indeed be too stable and not yield the active carbene.[47]

Substrate scope. Cyclic carbonate formation from 1,2-diols, 1,3-diols and 2,3-diols has been shown in literature, with varying degrees of success.[49] The groups of Munshi and Huang showed conversion of 1,2- and 1,3-diols using dibutyltin(IV) oxide and metal acetate systems with CO_2 in organic solvents, respectively.[2,37] 1,3-Diols expressed a significantly reduced conversion rate, yet similar selectivities towards the cyclic product of around 60%.[2] Recently Selva *et al.* studied a broad range of substrates for the synthesis of five- and six-membered cyclic carbonates in the presence of methyl trioctylphosphonium alkyl carbonate salts with dialkyl carbonates. Selectivity to the desired cyclic carbonate strongly depended on the nature of the diol. The efficiency of the conversion was, expectedly, found to strongly depend on the ring size of the cyclic carbonate formed. Indeed, the 1,2-diols yielded the five-membered cyclic carbonates with high selectivity and only very small amounts of open mono and dicarbonate by-products. In contrast, 1,3-diols led to an abundance of these mono- and dicarbonates, with the six-membered cyclic carbonate only being obtained as a minor product. Only 2-methyl-2,4-pentadiol exhibited high yields of the six-membered product, with very small amounts of monocarbonate formed by transesterification of the secondary hydroxyl group detected. No monocarbonate species involving the tertiary hydroxyl group could be detected, though.[38]

Cyclocarbonation of various 1,2-diols, 1,3-diols and 2,3-diols was tested with **1** (Table 2), allowing for a comparison of the activity of terminal *versus* internal, primary *versus* secondary alcohols and five- or six-membered ring formation. Cyclic carbonate products were achieved for all the substrates tested, with the highest yield of 83% achieved for glycerol when using a DMC : substrate ratio of 3 : 1 after 3 h with 1 mol% **1**. Yields of the cyclic product were found to increase with increasing alkyl chain length of the substrate. Ethylene diol was converted to give the cyclic carbonate in 55% yield, while 1,2-propanediol and 1,2-butanediol showed improved yields of 74 and 79% and high selectivities of 96 and 99%, respectively.

The products from the 1,3-diol reactions could not be identified unambiguously from the crowded standard ^{1}H NMR spectra (Fig. S3 and S5†), but could from their 2D NMR spectra (Fig. S4, S6 (both ^{1}H–^{1}H TOCSY) and S7 (^{1}H–^{1}H COSY)†). In Table 2, products **17** and **18** are presented together due to the fact that their spectra are indistinguishable in the NMR

Table 2 Conversion of various diols with pre-catalyst 1,3-dimethylimidazolium-2-carboxylate (**1**)

Substrate	DMC molar ratio	Conversion (%)	Cyclic product yield (%)	Cyclic product selectivity (%)	Mono-cyclic carbonate yield (%)	**13**/**16** yield (%)	**14**/**17** + **18** yield (%)	C-balance (%)
Glycerol	6	79	72	93	—	—	—	95
Glycerol	3	88	83	94	—	—	—	95
Diglycerol	6	58	21	37	32	—	—	95
ED	3	61	55	90	—	—	—	94
1,2-PD	3	76	74	96	—	—	—	97
1,3-PD	3	49	2	3	—	36 (**13**)	7 (**14**)	96
1,2-BD	3	80	79	99	—	—	—	100
1,3-BD	3	40	2	4	—	26 (**16**)	**13** (**17** + **18**)	101
2,3-BD	3	51	41	80	—	—	—	90

Conditions: 0.5 g substrate, 1 mol% **1** was utilised as the pre-catalyst for 3 h at 74 °C with DMC as "CO" source. Products are denoted as: **12** – propane 1,3-carbonate, **13** – 3-methoxycarbonyloxypropan-1-ol, **14** – propane-1,3-diyl dimethyl dicarbonate, **15** – butane 1,3-carbonate, **16** – 3-methoxycarbonyloxybutan-1-ol, **17** – 3-methoxycarbonyloxybutan-3-ol, **18** – butane-1,3-diyl dimethyl dicarbonate.

spectra. As expected, much less cyclic carbonate formation is observed for 1,3-butanediol and 1,3-propanediol (2% in both cases), with six-membered rings being less favourable than the five-membered ones formed from their 1,2-counterparts. The conversion of these 1,3-diols was still relatively high, however, and in agreement with Selva *et al.*,[38] open carbonates were detected instead (Fig. S2†).

For 1,3-propanediol yields, 36% and 7%, of the open mono- (**13**) and dicarbonate (**14**) were formed. For 1,3-butanediol, the yield of the open carbonate of the primary alcohol (**16**, 26%) was significantly higher than the combination of the **17** and **18**, *i.e.* those carbonates involving the secondary alcohol (13%). Comparing the results of the three butanediols tested, both 1,2- and 2,3-butanediol can be converted to their respective five-membered cyclic carbonates, however the yield of the internal cyclic carbonate is lower than of the terminal counterpart. For 1,3-butanediol the yield of the six-membered cyclic carbonate is very small, with the open carbonates being favoured.

The conversion of ethylene diol, 1,3-propanediol and 2,3-butanediol was also studied over time, Table 3. The reaction appears to be equilibrium-limited, with its position dependent on the substrate. For example, ethylene diol yielded 32% (100% selectivity) of the cyclic carbonate after 20 min, however only produced a yield of 58% after 6 h, with similar trends observed with different substrates. Indeed, addition of the equivalent amount of methanol that would be produced upon full conversion, from the start to a reaction of glycerol and 1 mol% **1** at 74 °C for 3 h led to a 13% reduction in both conversion and yield, but with the very high selectivity (99%) maintained. A reaction run in methanol as solvent yielded only 11% after 3 h compared with 83% without added methanol. 1,3-Propanediol was initially converted to the open carbonate, with yields of the cyclic product being only 2% after 1 h. However, as the reaction progressed, the yield of the open dicarbonate (**14**) increased from 4% after 1 h to 11% after 6 h, whilst still maintaining high selectivity (70–75%) towards the 1-mono open product (**13**), Table 3. This again highlights the higher reactivity of the diol substrate compared to the open monocarbonate product and that the open carbonates are favoured over cyclic carbonates for 1,3-diols. Without catalyst, only starting material is recovered for both 1,3-butanediol and 1,3-propanediol under standard reaction conditions. The fact that no open products are observed for substrates that yield the five-membered cyclic products indicated that under our conditions, the ring closing reaction is fast and driven by the stability of the product.[38]

Results reported thus far have been for reactions carried out at 74 °C. Increasing the temperature to 90 °C for reactions with a few selected substrates, did lead to higher activity, Table 3. Glycerol reached 95% conversion within 3 h, which is a slight increase of 7% compared with the reaction run at 74 °C. Diglycerol saw its yield double to 45%, with an increase in selectivity towards the dicyclic product, 60% compared with 37% at 74 °C, with less mono-cyclic product yielded. 1,3-Butanediol did not show a significant change in the amount of cyclic product yielded at the higher reaction temperature, however an increase in the products involving the secondary alcohol (**17** and **18**) was noted. For the internal diol of 2,3-butanediol, yield of cyclic product increased by 28% at the increased temperature. Care must be taken with further increasing the temperature, as above 95 °C the formation of the less active 4-carboxylate becomes favoured over the 2-carboxylate.

Crude glycerol conversion. The crude glycerol tested was obtained from an industrial source and contained 83.3% gly-

Table 3 Influence of time and temperature on conversion of bio-based diols utilising as-synthesised **1** as pre-catalyst

Substrate	Time (h)	Temp. (°C)	Conversion (%)	1-Open mono-carbonate yield (%)	DGMC yield (%)	**14**/**18** and **17** yield (%)	Cyclic carbonate yield (%)	Cyclic carbonate selectivity (%)	C-balance (%)
ED	0.33	74	32	—	—	—	32	100	100
ED	1	74	59	—	—	—	54	91	95
ED	3	74	61	—	—	—	55	90	94
ED	6	74	63	—	—	—	58	92	95
1,3-PD	1	74	35	25	—	4	2	6	96
1,3-PD	3	74	49	36	—	7	1	3	96
1,3-PD	6	74	58	43	—	11	10	2	97
2,3-BD	1	74	33	—	—	—	28	83	95
2,3-BD	3	74	51	—	—	—	41	80	90
2,3-BD	6	74	56	—	—	—	50	88	93
G	3	90	95	0	—	—	98	103	103
DG[a]	3	90	74	—	21	—	45	60	92
1,3-BD	3	90	69	41	—	26	3	4	101
2,3-BD	3	90	67	—	—	—	69	103	102

Conditions: 0.5 g substrate, stirred under argon for the indicated reaction time at indicated temperature. 1 mol% **1** was utilised as the pre-catalyst with 3 : 1 DMC : substrate ratio. Products are denoted as: **12** – propane 1,3-carbonate, **13** – 3-methoxycarbonyloxypropan-1-ol, **14** – propane-1,3-diyl dimethyl dicarbonate, **15** – butane 1,3-carbonate, **16** – 3-methoxycarbonyloxybutan-1-ol, **17** – 3-methoxycarbonyloxybutan-3-ol, **18** – butane-1,3-diyl dimethyl dicarbonate. [a] DG : DMC ratio was 6 : 1.

cerol, with the remaining being made up of soaps, water and esters and had a neutral pH in water. Cyclic carbonate formation was investigated with 1 mol% **1** with respect to glycerol and yield was monitored against time, Fig. 6. For an initial 4 h period, glycerol carbonate is produced at a steady, yet reduced rate compared with reactions on pure glycerol. When reactions are run for prolonged periods of 18 h, there is only a 10% difference in yield achieved. The impurities in crude glycerol thus reduce the rate of reaction, but do not deactivate the catalyst irreversibly. While the exact cause for the drop in rate is not yet known, the water present in the crude glycerol, which could be associated with deactivating the carbene by protonation, was not found to be the major reason for the observed lower rate; introduction of a known amount of water or sodium nitrate after 1 h to reactions were run with pure glycerol and allowing the reaction to proceed for a further 5 h showed only a small drop in yield (84% and 82% for water and sodium nitrate, respectively, compared to 96% in their absence). Sodium nitrate was tested as sodium compounds are known impurities in crude glycerol.

Mechanistic study. A number of mechanisms have been proposed for the synthesis of cyclic carbonates, in particular glycerol carbonate, depending on the catalytic system used. Simple bases such as K_2CO_3 are thought to first deprotonate the primary alcohol of glycerol, followed by nucleophilic attack of the formed alkoxide on the carbonyl of the dialkyl carbonate. The base again deprotonates the secondary alcohol to allow nucleophilic attack again of the carbonate to give the cyclic carbonate.[9] For the methyltrioctylphosphonium methyl carbonate system utilised by Selva *et al.* electrophilic activation of the carboxylic oxygen of the dialkyl carbonate by the tetraalkylphosphonium cation was proposed, combined with nucleophile activation due to an acid–base reaction between the alcohol and basic anion of the catalyst to facilitate the transesterification reaction.[38] While the reaction with the 1-alkylimidazolium-2-carboxylate catalyst has previously been suggested to involve decarboxylation of the pre-catalyst to give the NHC,[27,31] further details are unknown. Such NHCs promote the transesterification between alcohols and organic esters[50] and have been investigated for ring opening polymerisation, in which the NHC is generated and has been shown to proceed *via* nucleophilic attack.[51] For the cyclocarbonation reaction, reactions with $^{13}C_3$-labelled DMC and **1** in a 1.5 : 1 molar ratio run in DMSO-d_6 provided more insight into the mechanism of reaction. ^{1}H, ^{13}C and HMBC 2D NMR experiments allowed the identification of a ^{13}C-labelled methyl ester group attached to the imidazolium compound and a signal attributed to ^{13}C-labelled methanol (Fig. 7(a), S8 and S9†). The HMBC NMR spectra confirmed that the ^{13}C-labelled ester group was indeed attached to the imidazole ring, through multiple bond correlation. The detection of the labelled carbonyl carbon and methyl ester carbon attached to the imidazole framework indicates that decarboxylation of the unlabelled CO_2 had occurred, followed by attack of the carbonyl carbon of the $^{13}C_3$-DMC, with subsequent loss of one ^{13}C-labelled methoxy group. The observation of such a labelled ester species allowed other mechanisms, such as one in which the carboxylate itself acts as a base to deprotonate the alcohol group of the substrate, to be ruled out and suggests that an NHC species is indeed involved in the catalytic cycle. The formation of ^{13}C-labelled methanol is thought to be the result of the methoxy anion reacting with trace amounts of water in the NMR solvent, and hence the counter ion is a hydroxyl group in this experiment.

As the NHC attacks the carbonate and is not protonated by the water present, this suggests that the NHC itself does not deprotonate the alcohol either, but that is the role of the methoxy group generated following the nucleophilic attack of the NHC on the carbonyl group of DMC. Taking into account previous literature and the reaction run with $^{13}C_3$-DMC, we propose the mechanism shown in Fig. 7(b), in which the *in situ* generated carbene attacks the carbon of the carbonyl group of DMC. In doing so, one methoxy anion is cleaved, and in turn deprotonates the primary alcohol group of the substrate. The substrate alkoxide can then attack the carbonyl group attached to the imidazole complex and the other methoxy anion is lost. This free anion can then deprotonate the secondary alcohol group, which can then attack the carbonyl carbon of the imidazole complex regenerating the active carbene species. Based solely on literature evidence,[47,48] Palencia *et al.* have recently proposed a similar mechanism starting from 1-(2,6-dimethylphenyl)-3-hexadecylimidazolium bromide, which requires the addition of a base to yield the carbene *in situ*.[35]

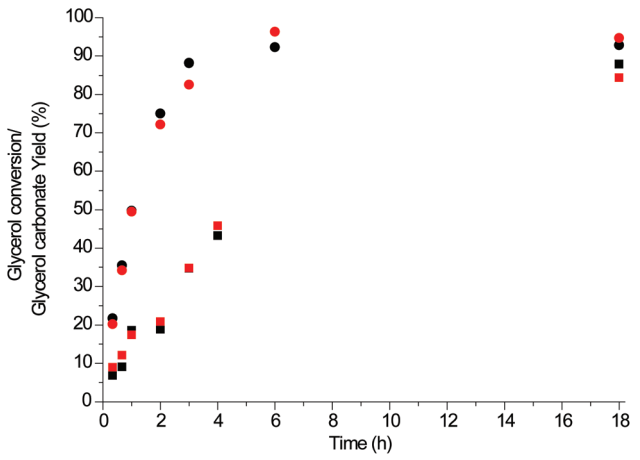

Fig. 6 Glycerol conversion (black symbols) and glycerol carbonate yield (red symbols) against time for the conversion of pure (circles) and crude (squares) glycerol with **1**. Conditions: 1 mol% loading of pre-catalyst, 3 : 1 DMC : (crude) glycerol, 74 °C.

Catalyst immobilisation

To allow for facile separation and potential reuse the organocatalyst was immobilised on a support. Carbene-based catalysts and their masked forms, including the 2-carboxylates, have been integrated into a number of polymer systems for a variety of reactions using different approaches.[52–54] Notably, it has been shown that a differently masked NHC, *i.e.* the hydrogen

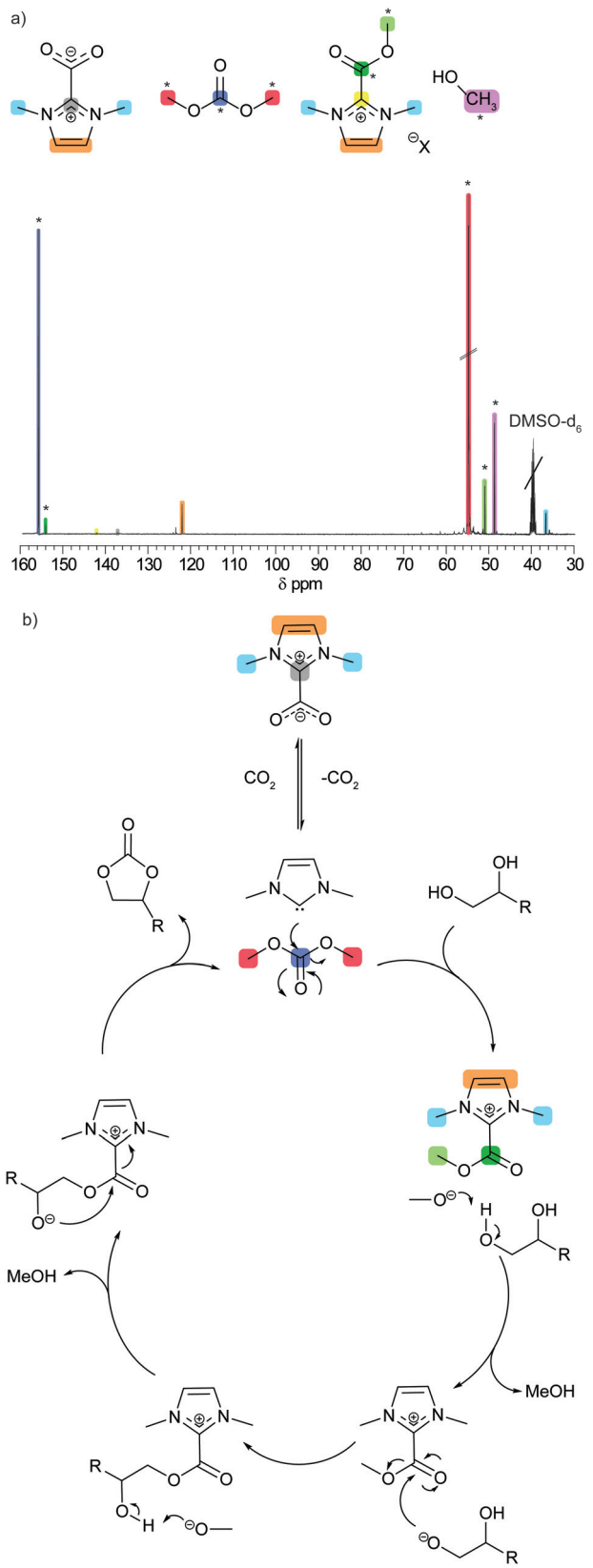

Fig. 7 (a) ^{13}C-NMR of reaction between $^{13}C_3$-DMC and 1,3-dimethylimidazolium-2-carboxylate (**1**) at 74 °C for 18 h, in DMSO-d_6, X representing OH. * represents ^{13}C-labelled carbon atoms. (b) Proposed mechanism for the conversion of vicinal diol substrates to cyclic carbonates.

carbonate protected form ((H)HCO_3^-), allows facile handling and this system can be easily recovered and reused, maintaining high activity.[31,55,56] A silica-supported hydrogen carbonate masked NHC catalyst was, for example, used in the epoxidation of olefins with H_2O_2.[57] For these reasons we have attempted to synthesise such protected NHCs on silica for the purpose of cyclic carbonate formation. Based on the results detailed above and previous studies in which the active carbene catalyst is protected by either CO_2 or (H)HCO_3^- to allow facile handling of the catalyst,[52,55] 1-methyl-3-(3-triethoxysilylpropyl) imidazolium chloride was immobilised on self-synthesised mesostructured cellular foam (MCF) silica (**IL1**). **IL1** was subsequently converted to generate two differently masked supported-NHCs; either the supported CO_2-masked NHC (**IL2**) *via* deprotonation and treatment with CO_2 or (H)HCO_3-masked NHC (**IL3**), *via* ion exchange with $KHCO_3$. 1-Methyl-3-(3-triethoxysilylpropyl) imidazolium chloride was chosen for grafting as it can allow a route to both **IL2** and **IL3** and due to the fact that initial attempts to activate supported 1-propylimidazole with DMC, as with the organocatalyst system, proved unsuccessful. Siliceous MCF was chosen due to its large surface area and pore volume as well as the fact that imidazolium halide compounds had previously been successfully grafted to it.[58]

Characterisation of MCF-supported catalyst

Degree of functionalisation and textual properties. The MCF used was characterised by a high surface area (738 $m^2\ g^{-1}$) and average pore size of 12.1 nm. **IL1** was prepared by grafting 0.93 mmol g^{-1} of 1-methyl-3-(3-triethoxysilylpropyl) imidazolium chloride (as determined by TGA) on the MCF support, which was accompanied by a reduction in surface area and pore volume, in accordance with literature.[59–62] Conversion of **IL1** to **IL2** and **IL3** resulted in functionalisations of 0.59 and 0.34 mmol g^{-1}, respectively. The results presented in Table 4, show that pore volume of **IL2** is similar to that of **IL1**, but increases upon converting **IL1** to **IL3**, which can be attributed to the partial loss of functionalisation that occurs. The same trend is observed when comparing surface area, which is similar for **IL1** and **IL2**, but increases for **IL3**. This could be associated with the lower degree of functionalisation, with higher degrees of functionalisation known to decrease surface area.[62] This trend is similar to the one observed by Park *et al.*[59]

The degrees of functionalisation of **IL1**, **IL2** and **IL3** were analysed both with TGA and elemental analysis (EA), Fig. S11† and Table 4. For **IL1**, TGA measurements showed a loss of 17.5% above 180 °C, with distinct weight losses at 247 °C, and 494 °C, which are associated with the loss of ethoxy groups left on the silica tether and the imidazole group, respectively.[63] For **IL2** and **IL3** the weight losses above 180 °C were 11.6% and 8.3% respectively, which equates to loadings of 0.59 mmol g^{-1} and 0.34 mmol g^{-1}. The weight loss at higher temperatures for **IL2** is less sharp, and can be associated with partial hydrolysis of the ethoxy group of the tether during functionalisation. The loss in this region for **IL3** comes at a higher temperature than the other functionalised samples, which is attributed to full hydrolysis of the ethoxy groups of the tether due to the

Table 4 Textual properties of pristine and functionalised MCF

Catalyst	BET surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Average pore size (nm)	Functionalisation[a] (mmol g^{-1})	Functionalisation[b] (mmol g^{-1})
MCF	738	2.23	12.1	—	—
IL1	300	1.21	13.6	0.93	1.40
IL2	273	1.29	15.7	0.59	0.96
IL3	439	1.68	14.8	0.34	0.53

[a] Determined by TGA. [b] Determined by EA.

exposure to water during the synthesis route.[63] The degree of functionalisation obtained by elemental analysis and TGA differed considerably, with EA giving higher values of 1.40, 0.96, and 0.53 mmol g^{-1} for **IL1**, **IL2** and **IL3**, respectively. For parity, catalyst loading was calculated using the TGA data. Elemental analysis also indicated that around 80% of the inactive chloride was exchanged for hydrogen carbonate in the ion exchange step for the synthesis of **IL3**. The significantly lower degree of functionalisation seen for **IL3** can be attributed to the use of methanol and water in each of the procedures respectively. It has been observed that the Si–O bond is labile when in the presence of water and alcohols.[64] When **IL1** is stirred in water to yield **IL3** the loss of functionalisation is more extreme than when **IL2** is washed with methanol.

DRIFTS and solid-state NMR analysis. **IL1**, **IL2**, **IL3** and pristine MCF were analysed by means of DRIFTS, as shown in Fig. S12.† **IL1** exhibited the characteristic bands of aromatic C–H stretching (2930, 2960, 3100 and 3150 cm^{-1}), ring stretching of the imidazolium group (1575, 1525 and 1460 cm^{-1}) and the C–Si stretching (620 cm^{-1}) vibrations, indicating, in accordance with literature, successful grafting had taken place.[59] As well as the additional signals attributed to C–H, C–C and C–N bonds, functionalisation was also indicated by a reduction in the free silanol signal at 3740 cm^{-1}.[65] **IL2** and **IL3** also contain the characteristic signals of the organic stretching vibrations as in **IL1**, indicating that functionalisation remains after their respective treatments. The band at 1312 cm^{-1} in the spectra of **IL3** can be tentatively assigned to the symmetrical stretching vibration of the hydrogen carbonate counter ion,[66] however due to the strong absorption bands of the silica support, the carboxylate and (H)HCO_3 forms of the supported system could not be confirmed using DRIFTS analysis. ^{13}C MAS-NMR measurements of the **IL1**, **IL2** with and without methanol washing and **IL3** (Fig. 8) confirmed the nature of the groups tethered to the MCF silica. In the NMR spectra, all the signals of the molecule are accounted for and in accordance with literature, with the addition of some residual signals attributed to unreacted ethoxy groups at 59 and 16 ppm.[59,63,67,68] To enhance the signal of the quaternary carboxylate carbon, **IL2** was prepared using ^{13}C-labelled CO_2.

The initial measurement of a sample of **IL2** (Fig. 8(c)) prepared as described in the ESI† with a final methanol washing step, to remove the potassium chloride salt, did not show the anticipated carboxylate signal at around 160 ppm. This could either be due to unsuccessful carboxylation or be the result of carboxylate loss due to reaction with moisture in the methanol, hence forming the hydrogen carbonate derivative.[45,69] The latter is in accordance with literature that demonstrated the interchange of the carboxylate and hydrogen carbonate forms in wet solvents.[56,69] For the **IL2** sample that was not washed with methanol (Fig. 8(b)), a signal at 162 ppm was indeed seen, corresponding to the carbon of the carboxylate.[51] Further ^{1}H–^{13}C cross-polarisation experiments varying the Hartmann–Hahn contact time, Fig. S13,† show this peak to indeed belong to a quaternary carbon, and thus that the carboxylation was successful. In fact, the NMR spectrum of the methanol-washed **IL2** sample is very similar to the one of **IL3**, which contains a hydrogen carbonate counter ion, further evidencing that the carboxylate had formed and reacted with trace amounts of water. The signal of hydrogen carbonate expected around 160 ppm is not observed in the spectra, however this signal is often weak compared to the other carbons of the imidazolium compound in solution NMR and given the relatively low loading, the HCO_3 carbon was not resolved.[31,55,56] Signals attributed to the ethoxy group of the silicon tether are reduced in those samples exposed to wet conditions (Fig. 8(c) and (d)). The peak seen around −1 ppm in each of the **IL2** samples was identified as being quaternary, but its origin is not clear. These NMR findings thus indicate that for catalytic testing **IL2** and **IL3** can in fact be considered to be the same (H)HCO_3 protected carbenes, which differ in the degree of functionalisation.

Catalyst testing

Synthesis of glycerol carbonate. The supported hydrogen carbonate-masked NHCs were studied for the conversion of glycerol to glycerol carbonate. Reaction temperature and DMC : substrate ratio were assessed and results are presented in Table 5. A reaction temperature of 90 °C gave the highest yield (37%) and selectivity (104%) when run with a DMC : substrate ratio of 5 for 6 h. This temperature is just below the point at which the 4-carboxylate begins to be favoured over the 2-carboxylate, as shown for the homogeneous system earlier. The 5 : 1 ratio yielded the highest amount of product, 37%, compared to ratios of 2.5 : 1, 7.5 : 1 and 10 : 1, which yielded 29%, 30% and 22%, respectively, under the same conditions. The DMC : substrate ratio thus had a significant effect on the activity of the catalyst, as was also observed for the homogeneous system. The lower activity observed for the reaction run with **IL2** at 110 °C may be associated with the formation of

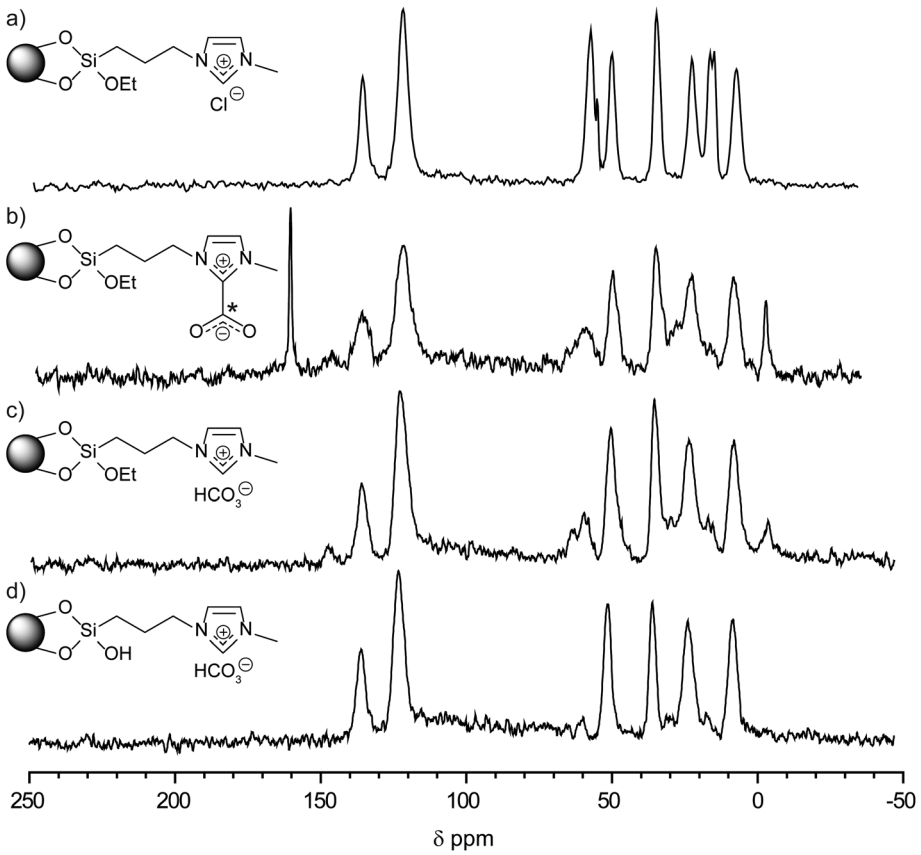

Fig. 8 ^{13}C MAS-NMR of (a) **IL1**, (b) **IL2** without washing, (c) **IL2** washed with methanol (d) **IL3**. **IL2** was prepared with ^{13}C-labelled CO_2 to enhance the signal of the quaternary carbon of the carboxylate. * represents ^{13}C-labelled carbon atoms.

Table 5 Effect of temperature, DMC : glycerol ratio and reaction time on the synthesis of glycerol carbonate

Catalyst	DMC molar ratio	Temp. (°C)	Time (h)	Conversion (%)	Cyclic yield (%)	Cyclic selectivity (%)	C-balance (%)
—	5	90	6	0	0	0	101
MCF	5	90	6	0	0	0	99
IL1	5	90	6	0	0	0	103
IL2	5	90	6	35	37	104	101
IL2	5	74	6	19	17	90	98
IL2	5	110	6	27	21	79	94
IL2	2.5	90	6	32	29	90	97
IL2	7.5	90	6	37	30	81	93
IL2	10	90	6	22	22	98	100
IL2	5	90	24	83	75	91	92

Conditions: 0.25 g glycerol with 1 mol% loading of **IL2**.

the inactive 4-carboxylate form. Reactions without any catalyst, with only pristine MCF or with the catalyst precursor **IL1** showed no conversion under these conditions (Table 5).

Monitoring conversion and selectivity against time for both **IL2** and **IL3** at the same (tethered) catalyst loading (Fig. 9), showed both systems to efficiently convert glycerol to glycerol carbonate at the same rate, once the active carbene is formed, with TOFs of 4.2 for both **IL2** and **IL3**. This further confirms the NMR results, which indicated **IL2** and **IL3** essentially to be the same, only differing in the degree of functionalisation. The activity of the supported carbene studied here is significantly lower than the homogeneous imidazolium-carboxylates described above and by Naik *et al.*[27] The homogeneous organocatalyst does not allow for facile recovery and reuse of the

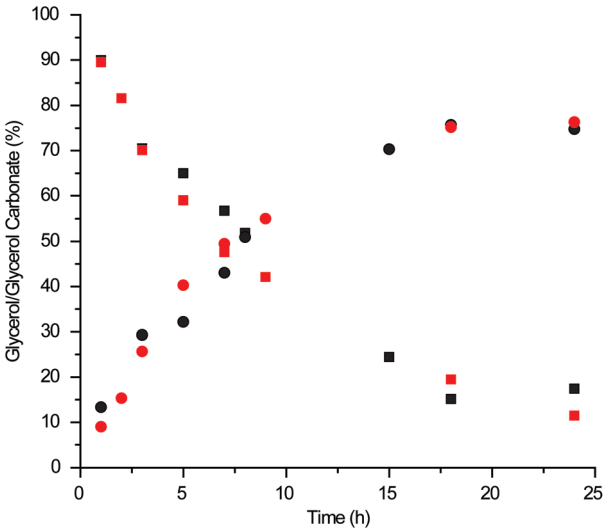

Fig. 9 Comparison of **IL2** (black) and **IL3** (red) for the conversion of glycerol (squares) to glycerol carbonate (circles) over time.

catalyst, however. This supported imidazolium system under study can be easily recovered, and as shown below, recycled. Having established that **IL2** and **IL3** are the same species, further experiments were run using **IL3** only.

Catalyst recycling. Recycling experiments, shown in Fig. 10, were run using recovered **IL3**, which was washed with methanol and dried at 60 °C under vacuum between reactions. A loss of activity is seen for each recycle, to give an overall 50% loss of activity after three runs. Such loss in activity could be due to deactivation during the reaction or loss of functionalisation during the washing step or the reaction itself. A hot filtration experiment was carried out using 1,2-butanediol as the substrate rather than glycerol, as the viscosity of the latter meant facile catalyst separation could not be achieved without washing with an additional solvent. The yield of 1,2-butylene carbonate was 13% after 3 h using **IL3** and 12% for a reaction run for 3 h and then filtered and run for a further 3 h. This result indicated that no significant leaching, if any, took place during reaction. Of particular note, when a sample of spent **IL3** underwent an ion exchange procedure, by stirring it in distilled water with 1.02 eq. $KHCO_3$ before reuse,[57] this regenerated **IL3** catalyst expressed its original activity, presented in Fig. 10 as "Regen". This would indicate that the deactivation observed in runs 1–3, is due to unfavourable ion pair formation, which blocks or inhibits the facile release of the carbene under these conditions. Indeed, EA of the spent **IL3** gave degrees of functionalisation of 0.53, 0.51, 0.51 and 0.51 mmol g^{-1} recorded for fresh and spent catalyst after run 1, 2 and 3, respectively. This supports that the loss of activity is not due to loss in functionalisation but to unfavourable ion pair formation during the reaction. The results thus highlight the advantage of the hydrogen carbonate system over the carboxylate derivative; the hydrogen carbonate system not only allows for facile handling and an easy route to the active carbene, but also offers a straightforward strategy for reactivation.

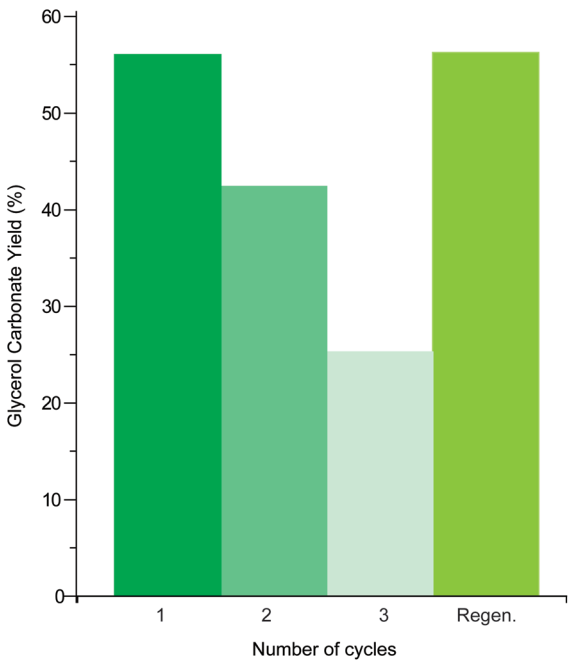

Fig. 10 Recycling experiments of **IL3**. Conditions: 1 mol% loading of catalyst, 90 °C, 8 h, DMC : glycerol ratio of 5. Spent **IL3** was washed with $KHCO_3$ before reuse for Regen. result. For all other results, the spent catalyst was used without further treatment.

Spent **IL3** for run 1 was analysed using DRIFTS and TGA. TGA of **IL3**, Fig. S14(b),† indicated an increase in weight loss of just 2% compared to the fresh catalyst and signals attributed to glycerol carbonate were detected in DRIFTS (Fig. S14(a)†). However, the high mass balance together with the results of both the DRIFTS and TGA results show that little organics are deposited on the solid.

Substrate scope. Having demonstrated the efficiency of this system for glycerol; diglycerol, 1,2-butanediol, 2,3-butanediol and crude glycerol were investigated. For each of the substrates tested, all expressed lower conversion and yields than the homogeneous system, although selectivities remained similar. As shown in Table 6, terminal diols could be converted to their cyclic carbonate products efficiently, but a distinct drop in activity was seen for internal diols as in 2,3-butanediol. DG could also be successfully converted to its dicyclic product; long reaction times were required to achieve high yields, however. Reactions with DG were again run at a higher DMC : diglycerol ratio of 10.[39] The low selectivity towards the dicyclic product observed at shorter reaction times is due to the fact that the DGMC is formed first, as was the case for the hydrotalcite system[39] and the homogeneous NHC catalysts described above. The catalytic activity of **IL3** towards diglycerol is considerably lower than that observed for the homogeneous 1,3-imidazolium-2-carboxylate (**1**) and expresses turnover numbers around one tenth of the only other known heterogeneous catalyst for diglycerol conversion, around 152 compared with 1887.[39] Of particular note is that the catalytic system also

Table 6 Conversion of bio-based diols by **IL3**

Substrate	DMC: substrate ratio	Time (h)	Conversion (%)	Cyclic yield (%)	Cyclic selectivity (%)	DGMC yield (%)	C-balance (%)
DG	10	6	51	8	15	38	95
DG	10	24	83	68	82	16	101
1,2-BD	5	6	48	48	101	—	100
2,3-BD	5	6	15	15	98	—	100
Crude G	5	6	52	44	85	—	92

Conditions: 1 mol% **IL3**, at 90 °C with DMC as "CO" source.

efficiently converts crude glycerol, Table 6. Similar yields and selectivities were achieved for both the pure and crude glycerol, and similar yields as that of the homogeneous system, although obtained at a slightly more elevated temperature. This is in contrast with the results of the homogeneous system, which expressed reduced activity when converting the same crude glycerol.

Conclusions

Imidazolium carboxylates and hydrogen carbonates were studied as masked NHCs and found to successfully catalyse the synthesis of cyclic carbonates from their respective diols. The organocatalyst system expressed high activity for the conversion of diglycerol to diglycerol dicarbonate, with loadings as low as 1 mol%, operating under solvent-free and mild conditions. The substrate scope of this system was extended to different renewable diol-substrates, containing both terminal and internal diols. Cyclic carbonate products were yielded in high amounts with good selectivity for systems that contain vicinal diols, however the 1,3-diol systems we investigated favoured open carbonates over the six-membered cyclic product. Notably, the system is able to efficiently convert crude glycerol, expressing high selectivity towards glycerol carbonate, albeit at a reduced rate compared to reactions with pure glycerol. Structural variation of the organocatalyst illustrated the sensitivity of the system to the introduction of either electron-withdrawing or donating groups, affecting either the initial methylation of the precursor or the relative stability of the carbene catalyst *vs.* the carboxylate pre-catalyst. A mechanism for this system was furthermore postulated based on studies with ^{13}C-labelled dimethyl carbonate, demonstrating that the system indeed involves a carbene as active catalyst.

The masked NHC system has also been heterogenised on siliceous MCF, protecting the NHC with hydrogen carbonate. This heterogeneous catalyst could efficiently convert both pure and crude glycerol feedstocks, as well as a number of other vicinal diols under mild conditions and without the use of an additional solvent. Catalyst recycling studies with glycerol as substrate showed that the catalyst can be easily recovered and reused if properly reactivated by a straightforward ion-exchange procedure between runs.

Experimental

Details of materials, instrumentation, substituted imidazole synthesis, MCF synthesis and product analysis can be found in the ESI.†

Typical homogeneous NHC testing

Diglycerol dicarbonate synthesis. In a 25 mL round bottom flask was charged 1 g (6.02 mmol) diglycerol, 8.4 mg (0.06 mmol) 1,3-dimethyl-imidazolium-2-carboxylate and 3 mL (35.6 mmol) dimethyl carbonate. The reaction flask was then sealed and heated to either 74 °C or 90 °C. The reaction was stirred for 3 h, after which it was cooled and the excess dimethyl carbonate and the formed methanol were removed under vacuum. 0.5 mL anisole as internal standard was added and the reaction products were solvated in DMSO-d_6 for analysis by ^{1}H NMR. Due to the purity of the starting material, stated yields represent the amount of product as if the starting material was 100% pure, selectivity takes into account the impurity, so maximum yield is 86%, which would represent 100% selectivity and 100% conversion.

Typical conditions for reactions with other diols. To a 12 mL vial was added 0.5 g of substrate and the required amount of 1,3-dimethyl-imidazolium-2-carboxylate, either 1 or 5 mol%. Dimethyl carbonate was subsequently added to obtain a 3 : 1 molar ratio of dimethyl carbonate to diol. The vials were placed under argon and stirred under heating for the assigned time.

Typical heterogenised NHC testing

Glycerol carbonate synthesis. 12 mL vial was charged with 0.25 g (2.7 mmol) glycerol, 1 mol% of activated functionalised silica with respect to substrate and 1.15 ml (13.6 mmol) dimethyl carbonate. The reaction flask was placed under argon, sealed and heated to 90 °C unless stated otherwise. The reaction was stirred for 6 h, after which it was cooled and either silylated as described in ESI† or filtered and washed with methanol. The excess dimethyl carbonate and methanol were removed under vacuum. 0.5 mL anisole as internal standard was added and the reaction products were solvated in DMSO-d_6 for analysis by ^{1}H-NMR.

Typical conditions for reactions with other vicinal diols. In a 12 mL vial 0.25 g substrate was charged. To this 1 mol% of

catalyst was added followed by a 5 : 1 molar ratio of dimethyl carbonate. The vials were placed under argon, sealed and stirred under heating for the assigned time.

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