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Polymeric frustrated Lewis pairs in CO_2/cyclic ether coupling catalysis†

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Frustrated Lewis pairs (FLPs) are now ubiquitous as metal-free catalysts in an array of different chemical transformations. In this paper we show that this reactivity can be transferred to a polymeric system, offering advantageous opportunities at the interface between catalysis and stimuli-responsive materials. Formation of cyclic carbonates from cyclic ethers using CO_2 as a C_1 feedstock continues to be dominated by metal-based systems. When paired with a suitable nucleophile, discrete aryl or alkyl boranes have shown significant promise as metal-free Lewis acidic alternatives, although catalyst reuse remains illusive. Herein, we leverage the reactivity of FLPs in a polymeric system to promote CO_2/cyclic ether coupling catalysis that can be tuned for the desired epoxide or oxetane substrate. Moreover, these macromolecular FLPs can be reused across multiple reaction cycles, further increasing their appeal over analogous small molecule systems.

Introduction

Valorisation of CO_2 as a renewable carbon feedstock is desirable in the pursuit of a sustainable, carbon-neutral society. Current efforts to use this typically unreactive substrate rely either on designer gas-capture systems and subsequent reactions, or combining CO_2 directly with suitably reactive substrates.[1] Epoxides are one such reactive substrate that has been extensively explored, where insertion of CO_2 yields the corresponding cyclic or polycarbonate products.[2] While the majority of early research efforts in this area have employed expensive or non-abundant metal-based systems, the use of metal-free catalysts to facilitate these transformations has expanded in recent years.[3]

Frustrated Lewis pairs (FLPs) are ubiquitous as metal-free catalysts for a myriad of chemical transformations.[4–7] The frustration induced by sterically hindered Lewis acid (LA) and base (LB) centres permits cooperative action of, and catalysis with, a multitude of substrates including carbon dioxide, dihydrogen and cyclic ethers.[8–15] In 2017, our group demonstrated that FLP reactivity is maintained when incorporated into a polymeric system, revealing a new class of stimuli-responsive materials that exploit FLP-mediated small molecule activation.[16,17] Inspired by these systems, Yan *et al.* later reported similar macromolecular FLPs capable of activating CO_2 and catalysing amine formylation.[18] Polymeric FLPs have also been reported in C–H functionalisation, amination and hydrogenation catalysis with demonstrated potential for catalyst recovery and reuse.[19–22]

Recently, we reported the successful crosslinking of highly Lewis acidic styrenic copolymers with a corresponding Lewis basic copolymer, *via* ring-opening of cyclic ether substrates.[23,24] Given these results, we wondered whether our systems would enable effective catalytic insertion of CO_2 into the ring-opened cyclic ether substrates. Aryl and alkyl boranes have previously been applied successfully in the formation of both cyclic and polycarbonates when paired with a phosphonium or ammonium salt partner.[25–31] More recently, superbasic phosphazenes have also proved active under mild conditions.[32] The use of a phosphine LB in these reactions is however, to our knowledge, previously unreported. Herein, we report the first use of both conventional small molecule and polymeric FLPs to catalyse the insertion of CO_2 into cyclic ether substrates with high selectivity towards the cyclic product (Fig. 1).

Results and discussion

Screening of LA/LB copolymer catalysts

Having previously reported three boron-containing copolymers of varying Lewis acidity (**B1–3**) we first sought to optimise the LA component of our proposed system (Fig. 2). Propylene oxide (**PO**) was selected as a model substrate. A readily synthesised triphenylphosphine functionalised copolymer, **P1**, was selected as the Lewis basic co-catalyst. For the **PO**/**P1**/**B2** system, conversion to propylene carbonate was observed but remained low, as the catalysis promoted reverse hydroboration to decouple the catalytic site from the polymer backbone (Fig. S5 and S6†). We know that the addition of epoxides affords stable

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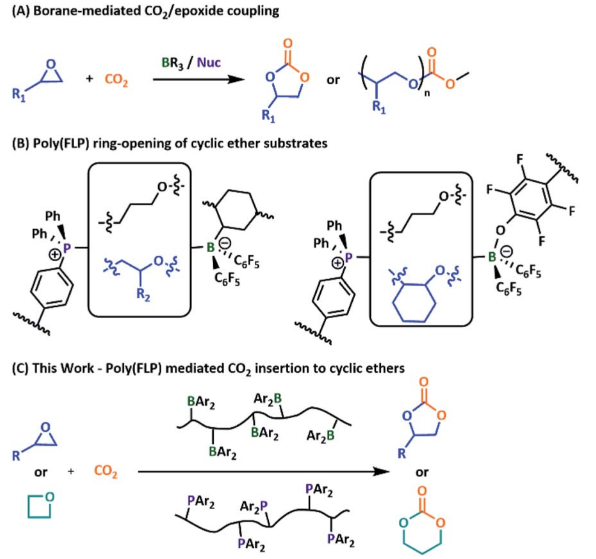


Fig. 1 (A) Previously reported borane-mediated CO_2 insertion catalysts. (B) Cyclic ether triggered poly(FLP) networks. (C) Poly(FLP) catalysed cyclic carbonate formation.

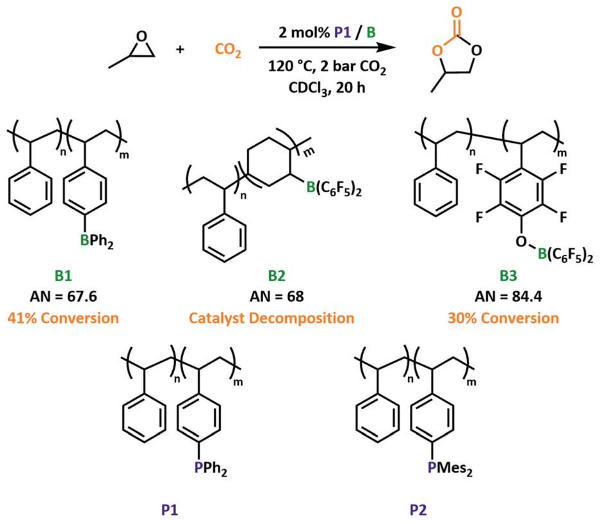


Fig. 2 Performance of polymeric LAs for CO_2 insertion to **PO** when paired with **P1**. Structure of **P2** to be used in later reaction screening. AN = acceptor number calculated using the Gutmann–Beckett method.

networks, suggesting that the addition of CO_2 promotes decomposition after the first turnover. Decomposition occurs at both moderate and elevated temperatures and mimics reversible reactions commonly associated with polymeric alkyl boranes,[33] therefore preventing further catalytic testing using **B2**.

Aryl-boron-containing polymers have a higher thermal stability.[21] This was proven when pairing a polymeric LB with **B1** and **B3**. While the capacity of **B3** to ring-open cyclic ethers was already established,[24] we anticipated **B1** would also facilitate this reaction based on previous small-molecule systems.[15,27] Previous studies into small molecule borane catalysed formation of cyclic carbonates reported a reactivity decrease when using stronger LAs as a result of adduct stability.[27] Indeed, the same trend can be observed within our polymeric systems when considering estimations of Lewis acidity by the Gutmann–Beckett method.[34,35] Reactions employing **B3** (acceptor number, AN = 84.4) were notably slower than those with the less Lewis acidic **B1** (AN = 67.6) under the same optimised conditions (Fig. 2 and S5†). Given its superior performance, we selected **B1** as the Lewis acidic component for the rest of this study.

With catalytic conversions using **B1** remaining low, optimisation of the system was essential. We hypothesised that catalyst decomposition was occurring, as extended reaction times did not increase product formation. Analysis of the reaction mixture by ^{31}P NMR spectroscopy revealed the presence of a new oxidised phosphine species, a commonly encountered off-cycle product during phosphine-promoted catalysis.[36] As direct CO_2 activation is not observed with this FLP system under the mild conditions used in catalysis, the mechanism likely proceeds *via* ring-opening of the epoxide substrate, followed by CO_2 insertion as reported with other aryl borane-containing systems.[27] Triphenylphosphine oxidation was not observed in the absence of epoxide, meaning that an on-cycle decomposition process involving **PO** must be occurring. Deoxygenation could potentially form propene, however analysis of the crude reaction mixture by ^1H NMR spectroscopy revealed no obvious side products, potentially due to their gaseous nature.

As we previously noted that ring-opening of styrene oxide (**SO**) by poly(FLP) systems was rapid,[23] we hoped to use this substrate to better understand this catalytic system. Under the same conditions, only 19% conversion from **SO** to styrene carbonate was observed. However, the system showed increased phosphine oxidation and the concomitant formation of styrene as confirmed by the presence of vinyl peaks at 5.3 ppm and 5.8 ppm in ^1H NMR spectra (Fig. S7 and S9†). Inspired by this finding, we re-attempted the reaction with **PO** under milder conditions and preventing gaseous product release, and indeed observed propene *in situ* (Fig. S8†).

Evidence of alkene formation prompted us to consider the possible routes to epoxide deoxygenation that would result in phosphine oxidation. Previous work had shown ring-opening of epoxides by tertiary phosphines results in Wittig-like reactivity,[37] while heating an FLP activated N_2O complex releases N_2 gas, forming a P=O–B linked species.[38] Ring-opening of episulfides, the sulfuric analogue of epoxides, also leads to formation of similar linkages.[15] It is thus hypothesised that, at elevated temperatures, CO_2 insertion is competitive with alkene

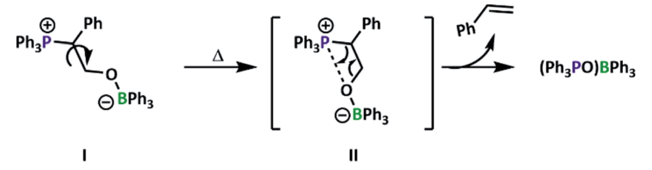


Fig. 3 Proposed route of catalyst deactivation for **P1**, represented using small-molecule model compounds.

elimination and phosphine oxidation, gradually leading to catalyst decomposition (Fig. 3).

Catalyst activity could thus be renewed through the addition of disiloxane reducing agents[36,39–42] used to regenerate the phosphine. Indeed, we found that addition of 1,3-diphenyldisiloxane (**DPDS**) to our **PO**/**B1**/**P1**/CO_2 reaction mixture allowed for >99% conversion of **PO** (Fig. S10†). Although **DPDS** addition increased catalytic performance, the mix of desired carbonate products and alkene side products obtained when using **SO** both rendered the reaction less green and made product separation more difficult.

From this understanding, we sought to design a system to preclude this decomposition pathway. In N_2O systems, elimination of N_2 occurred when the phosphorus and boron components were oriented in the less energetically favourable *cis* conformation.[38] If the same conformational requirements are present, as previous small molecule studies suggested the *cis* configuration is preferred for **PO** activation by a BPh_3/P*t*Bu_2Me FLP pair,[15] a bulkier polyphosphine may be preferred, especially as PPh_3 has a lower cone angle than P*t*Bu_2Me.[43] This doesn't preclude decomposition from the *trans* configurations as attack of the phosphine copolymer on **SO** occurs at the more hindered carbon of the epoxide ring (*i.e.* adjacent to the phenyl ring) as assigned by ^{31}P–^{13}C coupling constants (44.5 Hz, Fig. 4A). With this mode of attack, rotation from conformations **I** to **II** (Fig. 3) affords the undesired conformation, with decomposition encouraged by the enthalpic driving force of conjugated product formation (styrene).

The switch to our previously reported mesityl-substitute **P2** (ref. 16) would increase both steric bulk (favouring the *trans* attack and precluding rotation) and increase Lewis basicity to enhance its reactivity. The impact of this increased steric bulk from the mesityl groups was readily observable using small molecule model compounds, with a 7 : 1 preference for ring-opening at the less hindered carbon observed for **SO** (Fig. 4B). Under the same reaction conditions, the **P2**/**B1** catalyst combination led to >99% conversion of **SO** to styrene carbonate. Notably, no vinyl peaks were observed in the reaction mixture by ^1H NMR spectroscopy (Fig. S13†), with minimal phosphine oxidation observed by ^{31}P NMR spectroscopy. Taken together, the mesityl groups and polymer backbone bulk mitigate unproductive alkene elimination.

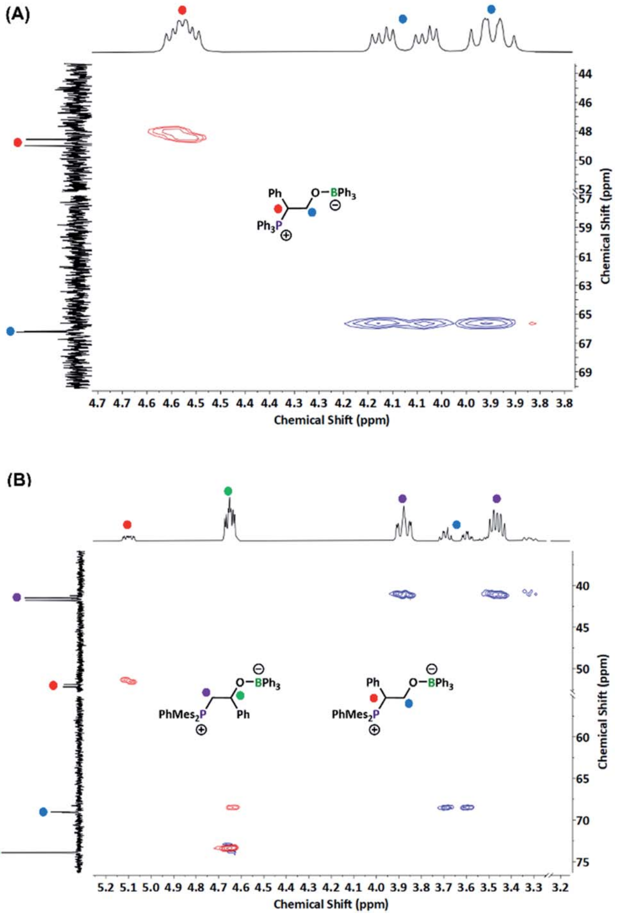


Fig. 4 HSQC analysis demonstrating the influence of phosphine steric bulk on mode of **SO** ring-opening. Red = CH/CH_3, blue = CH_2. (A) **P1**/**B1** system, attack of phosphine LB observed exclusively at more hindered carbon. (B) **P2**/**B1** catalytic system, attack of phosphine LB at least hindered carbon is preferred by a factor of 7. Solvent peaks omitted for clarity.

Substrate scope

With an optimised system in hand, we investigated the substrate scope and overall reactivity of the **P2**/**B1** system. Conversion of **PO** to propylene carbonate reaches >99% conversion in just 7 hours, dramatically outperforming the less Lewis basic **P1**. Realising that CO_2/epoxide catalysis with small molecule FLPs is also unreported, we compared our macromolecular catalysts to their small molecule equivalents, BPh_3 and $PMes_2Ph$. These conventional FLPs, under the same reaction conditions, gave >99% conversion of **PO** within just 6 hours (Fig. S27†), the first example of conventional FLP use in CO_2 insertion to epoxides. Use of a B/P system therefore significantly outperforms previously reported organocatalytic systems which typically require higher catalyst loadings.[3,44] Use of a phosphine LB also allows for milder conditions than ammonium salt systems,[29] while maintaining the same selectivity, although phosphonium systems are substantially more active.[27]

A variety of substrates were screened for **P2**/**B1** using similar reaction conditions (Fig. 5). All terminal epoxide substrates were quantitatively converted in under 24 hours, although their rates differed markedly depending on sterics and electronics. 3-Chloropropylene oxide (**CPO**) outperformed all other tested substrates, consistent with trends reported for other systems.[27,45] While the electron withdrawing chlorine promotes rapid turnover, the sterically similar methyl group (butylene oxide, **BO**) shows decreased conversion. The role of steric bulk was also apparent for internal epoxides. While ring-opening of cyclohexene oxide (**CHO**) is possible using both **P2**/**B1** and our previously reported poly(FLP) systems,[23,24] productive conversion into product is not observed. Previous attempts to use conventional FLPs in the copolymerisation of **CHO** and carbonyl sulfide were also unsuccessful,[26] although borane/phosphonium salts do form polycarbonates.[27,28] To check if

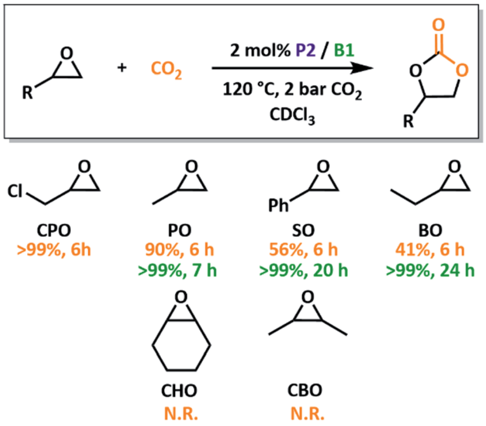


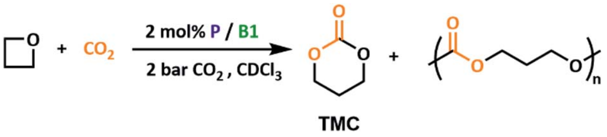
Fig. 5 Screening of cyclic ether substrates for CO_2 insertion to obtain cyclic carbonate products. Conversions calculated by ^1H NMR spectroscopy after 6 h are shown in orange (N.R. = no reaction) and the times required for >99% conversion are shown in green. Reactions were carried out in a sealed ampoule on a 0.8 mmol scale using 2 bar CO_2 pressure and catalyst **P2/B1** (2 mol% as calculated from the number of expected active functional groups).

this was due to the strain induced during CO_2 insertion preventing cyclohexyl rearrangements, *cis*-2,3-butylene oxide, **CBO**, was trialled. With no conversion for this derivative, it is likely down to steric clashes during ring-closure that prevent product formation.

Reactivity with oxetane substrates

Notably, oxetane (**OX**) can also be successfully ring-opened by **P2/B1**. Conversion to trimethylene carbonate (**TMC**) was slower due to the lower ring strain of **OX** relative to epoxide substrates,[46,47] as well as the relatively high strength of the intermediate crosslinked networks formed as reported in our previous work.[23] Attempts to expand the **OX** substrate scope with both 3-bromooxetane and 3,3-dimethyloxetane were unsuccessful. Although a change in chemical shift was observed in ^{11}B NMR spectra, indicating LA coordination, no change was observed by ^{31}P NMR spectroscopy for the LB counterpart, suggesting steric clashes prevent nucleophilic attack. Selectivity for cyclic 6-membered carbonates over their polymeric counterparts is often cited as problematic when using a CO_2 insertion synthetic route.[48] With epoxide substrates, high selectivity for the cyclic product is achieved at all temperatures screened. However, if the high temperatures optimised for epoxide ring opening are used (120 °C) with oxetane, only 61% preference for the cyclic product **TMC** (Table 1, entry 1) is observed. Lowering the temperature to 100 °C gives a significant improvement in selectivity, although longer reaction times are required to achieve high conversions (Table 1, entry 2 and 3). This additionally supports the formation of the polycarbonate product directly, rather than *via* **TMC** polymerisation. Interestingly, while better leaving groups have been proposed as routes to improve cyclic product selectivity in small molecule catalysts,[29] the opposite trend is observed herein where the better **P1** leaving group gave less selectivity (Table 1, entry 4).

Table 1 Effect of temperature and LB on oxetane/CO_2 coupling conversion and selectivity



Entry	LB	T (°C)	Time (h)	Con.[a] (%)	% **TMC**[a]
1	**P2**	120	24	57	61
2	**P2**	100	24	32	76
3	**P2**	100	72	83	81
4	**P1**	120	24	26	31

[a] Conversion determined using ^1H NMR spectroscopy (ESI Fig. S31–S34).

Catalyst recyclability

Polymer-supported catalysts have also shown potential for facile reuse or incorporation into flow reactors as an enabler for green manufacturing.[49,50] Previous polymeric Lewis bases have been synthesised in pursuit of multiple use cycles but require more forcing conditions and suffer from limited substrate scopes.[51,52] We thus decided to explore the catalytic performance of **P2/B1** across multiple reaction cycles (Fig. 6) using a precipitation-recovery strategy (Section 6, ESI†), comparing it to the spiking of the reaction mixture with fresh substrate. This more rigorous recovery procedure is a true stress test of catalyst reuse using **P2/B1**.

As can be seen in Fig. 6, and for either reuse methodology, catalytic performance decreases significantly for **P2/B1** after the first reaction cycle. Smaller rate decreases are observed over subsequent cycles. Gradual phosphine oxidation can be observed (Fig. S40†), although attempted regeneration using **DPDS** did not substantially increase reaction rates, as the

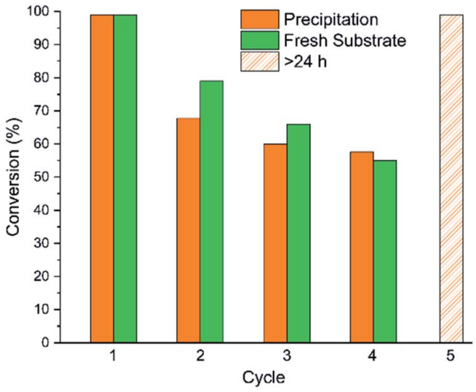


Fig. 6 Conversions obtained in consecutive reaction cycles for CO_2 insertion to **PO**, as calculated by ^1H NMR spectroscopy, using 1,3,5-trimethoxybenzene as an internal standard. Reaction conditions as stated in Fig. 5. The data shown in green was obtained by adding fresh substrate at the end of each cycle (*i.e.* without purification and catalyst recovery). The recovered **P2/B1** catalysts remain active after 4 cycles, achieving >99% conversion with extended reaction times (cycle 5).

additional steric bulk from the mesityl groups could prohibit silane attack.[39] It is important to note that this is a reduction in rate only, as extending the reaction time gives quantitative conversion (Fig. 6, cycle 5 and S39†).

It is important to highlight that these macromolecular catalysts are generated *in situ*, with the addition of substrate triggering gelation. This means that the accessibility of the catalyst active site is a key factor in reuse efficiency. Post-reaction, we observed that the catalyst resting state was present in its gelated, cross-linked form, supported by ^{31}P and ^{11}B NMR spectroscopy, and GPC measurements of hydrodynamic volume (Fig. S43 and S44†). Precipitation thus forms a superstructure that does not dissolve, but instead swells (Fig. S42†), creating a physical constraint on substrate access to catalytic sites.[20] In our case, crosslinking occurs at the active components, limiting polymer chain segmental motions in the vicinity of the FLP and likely suppressing the rate of epoxide capture and CO_2 insertion. This hypothesis is consistent with the observation that a significant decrease in activity is only observed after the first cycle. Future work in the team directed at incorporating these metal-free catalysts into flow reactors is an important step in overcoming these practical constraints.

Conclusions

In summary, we report the first use of both conventional and polymeric FLPs in the formation of carbonates from cyclic ethers using CO_2, with high selectivity for the cyclic carbonate product. The synthesised macromolecular catalysts displayed good reactivity for a variety of terminal epoxide substrates and are also active catalysts for the formation of trimethylene carbonate from oxetane and CO_2. Post-reaction, the poly(FLPs) used can be easily recovered and reused, with gradual decreases in catalyst efficiency attributed to partial phosphine oxidation as well as increased crosslinking. Further tuning of both the catalytic system and reaction conditions is expected to offer a more diverse substrate scope with higher selectivity for oxetane substrates. Further development of intermolecular poly(FLPs) for catalysis is expected to instead utilise the effects seen from crosslinking to enhance reactivity with other substrates *via* compartmentalisation.

Author contributions

Thomas A. R. Horton and Meng Wang: investigation, methodology and manuscript writing. Michael P. Shaver: conceptualisation, manuscript writing – review and editing, supervision and funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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