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Cycloaddition of CO₂ to epoxides by highly nucleophilic 4-aminopyridines: establishing a relationship between carbon basicity and catalytic performance by experimental and DFT investigations

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The development of single-component halogen-free organocatalysts in the highly investigated cycloaddition of CO₂ to epoxides is sought-after to enhance the sustainability of the process and reduce costs. In this context, the use of strongly nucleophilic single-component catalysts has been generally restricted to a limited selection of *N*-nucleophiles. In this study, predictive calculations of epoxide-specific carbon basicities suggested that highly nucleophilic 3,4-diaminopyridines possess suitable basicity to serve as active single-component catalysts for the cycloaddition of CO₂ to epoxides. Indeed, experimentally, the most active compounds of this class performed efficiently for the conversion of epoxides to carbonates under atmospheric pressure outperforming the catalytic activity of traditional *N*-nucleophiles. Importantly, the 3,4-diaminopyridino scaffold could be easily supported on polystyrene and used as recyclable heterogeneous catalyst under atmospheric CO₂ pressure. Finally, the mechanism of the cycloaddition reaction catalyzed by several *N*-nucleophiles was investigated highlighting the importance of the 3,4-diaminopyridines nucleophilicity in competently promoting the crucial initial step of epoxide ring-opening without the addition of nucleophiles or hydrogen bond donors.

Introduction

Cyclic organic carbonates are a class of compounds with multiple remarkable applications such as solvents[1-4] and chemical intermediates for the synthesis of fine chemicals[5-7] and polymers.[8-12] Importantly, the synthesis of cyclic carbonates via cycloaddition reaction of CO₂ to epoxides offers the highly sought-after[13-16] opportunity to recycle CO₂ as C1 source for the synthesis of commodity chemicals. ADD here: Bruno Grignard, Sandro Gennen, Christine Jérôme, Arjan W. Kleij, Christophe Detrembleur, Advances in the use of CO2 as a renewable feedstock for the synthesis of polymers. Chem. Soc. Rev., 2019, 48, 4466-4514. DOI:10.1039/C9CS00047J; Lei Song, Yuan-Xu Jiang, Zhen Zhang, Yong-Yuan Gui, Xiao-Yu Zhou, Da-Gang Yu, CO2 = CO + [O]: recent advances in carbonylation of C–H bonds with CO2. Chem. Commun., 2020, 56, 8355-8367. DOI: 10.1039/D0CC00547A; C.-K. Ran, X.-W. Chen, Y.-Y. Gui, J. Liu, L. Song, K. Ren, D.-G. Yu, Recent advances in asymmetric synthesis with CO2. Sci. Chin. Chem. 2020, 63, 1336-1351. DOI:

10.1007/s11426-020-9788-2; Truong, C. C.; Mishra, D. K. Catalyst-free fixation of carbon dioxide into value-added chemicals: a review. Environ. Chem. Lett. 2020, doi: 10.1007/s10311-020-01121-7; V. Aomchad, S. Del Globo, A. Poater, V. D'Elia; "Exploring the potential of Group III salen complexes for the conversion of CO₂ under ambient conditions"; Catal. Today 2020, DOI: 10.1039/c9cy01642b A vast amount of literature has been produced in recent years on the development of efficient catalytic systems for the latter reaction as highlighted in several reviews.[17-23] Current focus on the catalytic synthesis of cyclic carbonates from epoxides has recently strongly diversified to include several environmentally-conscious areas of research such as the carbonation of bio-based epoxides for the valorization of renewable building blocks,[24-27] the use of impure sources of CO₂,[28-30] the conversion of CO₂ to cyclic carbonates under ambient conditions[20, 31-33] ADD: X. Wang, L. Wang, Y. Zhao, K. Kodama, T. Hirose, Efficient and practical organocatalytic system for the synthesis of cyclic carbonates from carbon dioxide and epoxides: 3-hydroxypyridine/tetra-n-butylammonium iodide. Tetrahedron 2017, 73, 1190-1195. DOI: 10.1016/j.tet.2017.01.018 and the development of metal-[34-41] and/or halogen-free catalytic systems.[42-44] ADD: S. Arayachukiat, P. Yingcharoen, S. V. C. Vummaleti, L. Cavallo, A. Poater, V. D'Elia; "Cycloaddition of CO2 to challenging N-tosyl aziridines using a halogen-free niobium complex: Catalytic activity and mechanistic insights"; Mol. Catal. 2017, 443, 280-285. DOI: 10.1016/j.mcat.2017.10.023 Concerning the latter two aspects,

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significant advances have been reported in the development of attractive metal-free catalysts able to efficiently carry out the cycloaddition of CO_2 to carbonates with some catalytic systems employing inexpensive and bio-based hydrogen bond donors (HBDs) such as cellulose,[45] pentaerythritol,[46] ascorbic acid,[26, 47] tannic acid[48] etc.[22, 38] However, the actual sustainability of this catalytic strategy is still limited by the need for halogen-based catalytic components such as ammonium or phosphonium halide salts that serve to provide anions acting as nucleophiles and as leaving groups in different steps of the well-established cycloaddition mechanism.[49, 50] The presence of halides can lead to reactor corrosion;[42, 51] moreover, it is known that the production of halogens is an energy intensive process with a significant carbon footprint.[52] There is, therefore, high interest in developing more sustainable halogen-free organocatalysts. Seminal work on binary catalytic systems employing HBDs in the presence of halogen-free nucleophiles were reported such as DMAP/p-methoxyphenol[53] (DMAP: 4-dimethylaminopyridine), DBU/cellulose[54] (DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene) and DBU-histidine.[55] However, the use of these catalytic systems required relatively harsh reaction conditions (120 °C, 20-36 bar CO_2 pressure) and, often, high loadings (up to 10 mol%) of bases. Moreover, in the prospect of heterogeneous catalysts design, it should be considered that the different components of binary catalytic systems are generally difficult to co-immobilize, making the use of single catalytic moieties more desirable. ADD: C. J. Whiteoak, A. H. Henseler, C. Ayats, A. W. Kleij, M. A. Pericàs, Conversion of oxiranes and CO2 to organic cyclic carbonates using a recyclable, bifunctional polystyrene-supported organocatalyst. Green Chem 2014, 16, 1552-1559. DOI: 10.1039/C3GC41919C
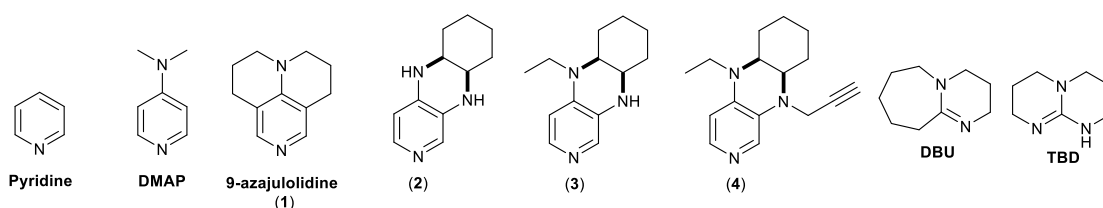
Scheme 1. N-Nucleophiles used as catalysts in this study.

In 2007, Shiels and Jones reported the DMAP-catalyzed synthesis of propylene carbonate from propylene oxide (PO) reaching high PO conversion at 120 °C and 34 bar CO_2.[56] More recently, some single-component halogen- and metal-free homogeneous catalysts were reported to operate under slightly milder conditions (T: 100-120 °C, P_{CO2}: 10-20 bar) based on Schiff bases,[57, 58] tertiary amines,[59-61] ammonium salts[62] and N-heterocyclic compounds (triazoles, azolates, 2-aminopyridines, DBU, adducts of imidazolium compounds).[63-68] Similarly, metal- and halogen-free heterogeneous catalyst were recently reported that operate efficiently in the 120-140 °C temperature range and at CO_2 pressures ≥ 10 bar.[61, 69-71] Therefore, the cycloaddition of CO_2 to epoxides by halide-free homogeneous and heterogeneous organocatalysts under atmospheric pressure remains underreported; Verpoort et al. have very recently reported that nitrogen-rich triazole rings bearing carboxylic acid functionalities were competent halogen-free organocatalysts for atmospheric CO_2 cycloaddition to several epoxides in the 75-100 °C temperature range.[63] However, as a potential drawback, the most active catalyst of this class was a derivative of highly toxic and environmentally hazardous mesitylene (GHS08, GHS09).[72] Whereas all the above-mentioned halogen-free organocatalysts contain nucleophilic and basic nitrogen atoms to assist in the activation and coordination of CO_2, there has been scarce attention at systematically exploring the effect of nitrogen nucleophilicity within a series of comparable compounds with well-known and parameterized nucleophilicity. In this context, 4-aminopyridines are a class of N-nucleophilic catalysts whose nucleophilicity can be strongly enhanced by structural modifications[73-75] and conformational fixation.[76, 77] Their nucleophilicity can be parameterized by using theoretically calculated and experimental descriptors.[78-80] Therefore, with the aim to discover more efficient single-component, halogen-free organocatalysts for the cycloaddition of CO_2 to epoxides able to operate under atmospheric pressure and to provide useful mechanistic insights for the future design of highly nucleophilic catalysts, we investigated the catalytic performance of a selection of aminopyridines of different nucleophilicity displayed in Scheme 1 (DMAP and compounds **1-4**). To this selection we also added pyridine, DBU and TBD as reference compounds. We show here that the catalytic performance of 4-aminopyridines (**1-4**) under ambient pressure surpasses that of traditional N-nucleophiles such as DMAP, DBU and TBD, a result that could be predicted by calculating the carbon basicities of all compounds towards the epoxide substrate.

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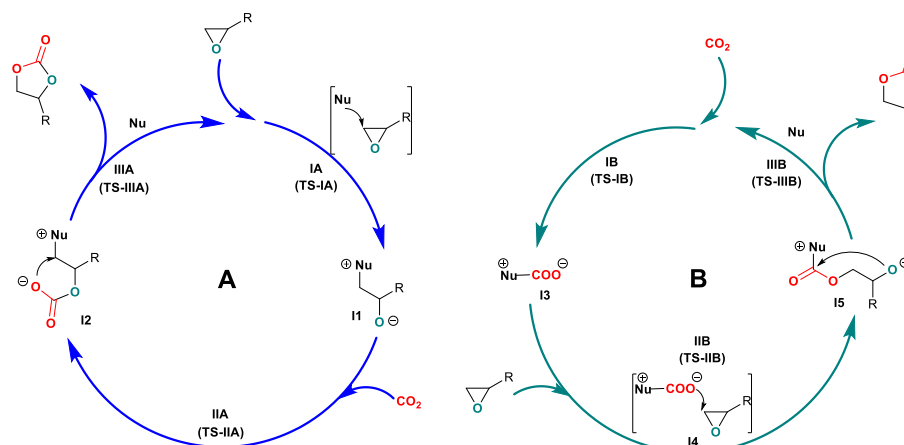
Scheme 2: Possible mechanistic pathways for the cycloaddition of CO_2 to epoxides by single-component nucleophilic catalysts

Additionally, mechanistic experiments and DFT calculations were carried out to gain insight into the possible mechanistic pathways shown in Scheme 2 (each displaying possible reaction intermediates, elementary steps and labels for the expected transition states (TS)) where the nucleophile initially interacts with the epoxide substrate (cycle A) or with CO_2 (cycle B). Finally, the most active aminopyridine catalyst could be readily supported on Merrifield resin via click chemistry leading to a recyclable heterogeneous catalyst able to promote the cycloaddition of CO_2 to epoxides under ambient pressure.

Experimental Section

Materials and methods

Pyridine, DMAP, 9-azajulolidine, DBU and TBD were purchased from commercial sources, stored in a nitrogen glovebox and used as received; compounds **2**, **3**, **4** were synthesized according to previously published procedures.[75, 81]

For a standard catalytic experiment, the epoxide substrate (16.6 mmol) was charged in a 50 mL round bottom Schlenk flask equipped with a magnetic stirrer. The nucleophilic catalyst (0.332 mmol, 2 mol%) was added. A rubber balloon containing CO_2 was connected to the Schlenk flask and part of the CO_2 was used to flush the vessel to replace air. The reaction vessel was well-sealed to prevent losses of CO_2 and stirred at 100°C for 24 h. After this period, the reaction was cooled down and the residual pressure in the Schlenk flask was carefully vented out. An aliquot of the reaction mixture was placed into an NMR tube and diluted with ca. 0.6 mL $CDCl_3$ to determine substrate conversion and selectivity by ^1H NMR spectroscopy. The crude products were

purified by silica-column chromatography using mixtures of ethyl acetate and hexane as eluents.

Further experimental details including computational methods can be found in section S1 of the ESI.

Results and Discussion

For the initial evaluation of the catalytic activity of nucleophilic 4-aminopyridines, and of the dependency of the catalytic performance on nucleophilicity, we selected the compounds in Scheme 1, sorted in order of carbon basicity, according to literature-available MCA (methyl cation affinity) values. The selection includes unfunctionalized pyridine as reference compound, DMAP and its conformationally fixed analogue 9-azajulolidine (**1**) whose nucleophilicity is higher than DMAP.[77] Additionally, we included three 3,4-diaminopyridines (compounds **2-4**) readily accessible via modular synthesis from the coupling of 3,4-diaminopyridine with 1,2-cyclohexanedione followed by reduction and alkylation of the aliphatic nitrogen atoms.[75, 81] Depending also on the pattern of substitution at the latter nitrogen atoms, these compounds generally possess higher nucleophilicity than DMAP due to conformational fixation and inductive effects.[75, 79] Finally, for the sake of comparison, we included in the selection of catalysts two well-established N-nucleophiles (DBU, TBD) previously used in literature as components of catalytic systems for the cycloaddition of CO_2 to epoxides.[54, 82, 83] Computationally-derived parameters defining the carbon basicity of several of the N-nucleophiles in Scheme 1 are available, such as MCAs values[78] or relative acetyl transfer enthalpies.[79] However, in order to make a more meaningful prediction of catalytic performance of the

nucleophiles in Scheme 1 in the cycloaddition of CO_2 to epoxides, it would be more helpful to access a scale of carbon basicities relative to the actual electrophilic carbon atoms where the attack of the nucleophilic catalysts takes place during the formation of cyclic carbonates. To this end we have calculated the affinity of all nucleophiles shown in Scheme 1 towards propylene epoxide (PO) as a small unsymmetrical epoxide substrate. As we are interested here in relative Lewis basicities of various catalysts, we express epoxide affinities here relative to that of pyridine as a comparatively unreactive catalyst. Relative epoxide affinities at a reaction temperature of 373.15 K ($\Delta H_{373}(epox)$) equate to the reaction enthalpies for the formal propylene epoxide transfer from pyridine adduct **pyr-epox** to other catalysts (Figure 1). The 4-amino substituted pyridines DMAP and **1** showed significantly higher epoxide affinities as compared to pyridine, as did the 3,4-diaminopyridine catalysts **2**–**4** (Table 1, entries 1-6). Even higher Lewis basicities were calculated for DBU and TBD (Table 1, entries 7, 8), the latter of which is predicted to be the most basic catalyst in this set. As shown in Fig. 1, the initially formed zwitterionic epoxide adducts can potentially cyclize to 5-membered ring products, which are unable to propagate the catalytic cycle. The reaction enthalpies for this step ($\Delta H_{373}(cyc)$) thus reflect the propensity of various catalysts to undergo this unimolecular deactivation step. From the results shown graphically in Fig. 1 and numerically in Table 1 we can see that cyclization energies are high for pyridine as a system lacking strong electron donor substituents, but also for DBU and TBD. In contrast, the cyclization is comparatively unattractive in the 3,4-diaminopyridine catalysts **2**-**4** and in **1**. We may thus speculate that, for this latter group of compounds, the concentration of zwitterionic epoxide adducts formed by the ring-opening of the substrate (Scheme 2, cycle A) may be particularly high at 100 °C due to their intrinsically high Lewis basicity as well as to their low propensity for intramolecular cyclization.
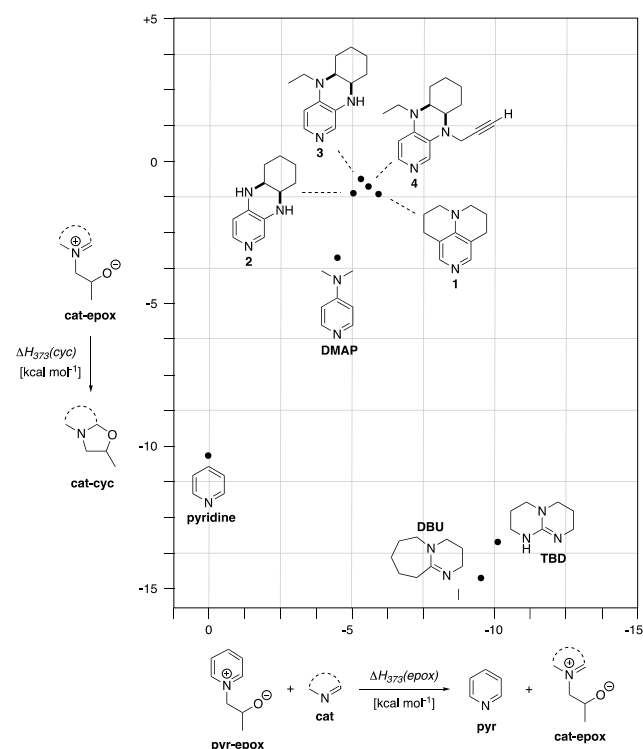

Figure 1. Relative propylene epoxide (PO) affinities ($\Delta H_{373}(epox)$) using pyridine as the reference, and cyclization energies ($\Delta H_{373}(cyc)$) for the initially formed zwitterionic epoxide adducts. All energies have been calculated for a reaction temperature of T = 373.15 K (in kcal mol^{-1}).

Table 1. Relative propylene epoxide (PO) affinities $\Delta H_{373}(epox)$ and cyclization energies $\Delta H_{373}(cyc)$ shown pictorially in Figure 1.

Entry	Nucleophile	$\Delta H_{373}(epox)$ [a] [kJ mol^{-1}]	$\Delta H_{373}(cyc)$ [a] [kJ mol^{-1}]
1	pyridine	0.0	-10.4
2	DMAP	-4.3	-3.3
3	**1**	-5.7	-1.2
4	**2**	-4.9	-1.2
5	**3**	-5.2	-0.6
6	**4**	-5.4	-1.0
7	DBU	-9.5	-14.8
8	TBD	-10.2	-13.2

[a] Calculated at the M06/TZVP PCM(PO) level of theory.

Catalytic testing

The catalytic performance of the 4-aminopyridine nucleophiles and of the reference compounds displayed in Scheme 1 was evaluated versus two different terminal epoxide substrates, i.e. styrene oxide (**5a**) and 1-hexene oxide (**5b**). The results of the latter catalytic investigation are shown in Table 2.

Table 2. Catalytic investigation of *N*-nucleophiles from Scheme 1 for the cycloaddition of CO_2 to epoxides **5a** and **5b** under atmospheric CO_2 pressure.[a]
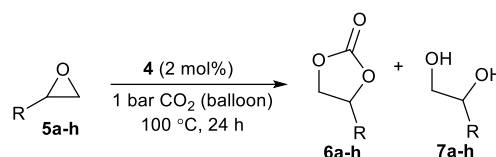

R= Ph (**5a**), Bu (**5b**)
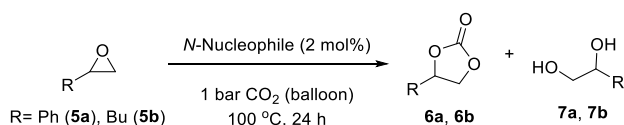
Entry	Nucleophile	Conversion (%)[b]		Selectivity (%)[b,c]	
		5a	5b	5a	5b
1	pyridine	26	3	86	-
2	DMAP	50	16	90	84
3	**1**	66	81	85	95
4	**2**	75	69	93	92
5	**3**	87	70	93	93
6	**4**	93	99	95	95
7	DBU	15	12	78	79
8	TBD	38	15	82	82

[a] Epoxide (16.6 mmol), nucleophile (0.332 mmol, 2 mol%) at 100 °C, 1 bar CO_2 (balloon) for 24 h, solventless. [b] Determined by ^1H NMR (See Section S4 of the ESI and Figures S13-S29). [c] Refers to the selectivity for cyclic carbonates (**6**) versus 1,2-diols (**7**).

It is possible to observe that use of pyridine (Table 2, entry 1) led to only very low epoxide conversion and no carbonate formation; the only observed products were diols (**7**) formed from the decarboxylation of cyclic carbonates under basic conditions due to the presence of traces of moisture.[84] Conversely, 4-aminopyridines displayed a more remarkable catalytic performance with compound **4** affording nearly quantitative epoxide conversion with very high selectivity for cyclic carbonates **6a** and **6b** (Table 2, entry 6).

In general, the catalytic activity of 4-aminopyridines increased in the order DMAP<**2**<**3**<**4**, whereas, the performance of 9-azajulolidine was less predictable and depended on the epoxide substrate used but was generally lower than that of **4** (Table 2, entries 3 and 6). These results are in line with the predicted epoxide-specific carbon basicities of nucleophiles listed in Table 1 (pyridine<<DMAP<**2**<**3**<**4**) whereas the catalytic activity of **1** was slightly lower than expected based on its carbon basicity that was even higher than that of **4** (*Cf.* Table 1, entries 3, 6). Finally, nucleophiles DBU and TBD did not perform well under the applied reaction conditions when compared to most 4-aminopyridine species with low epoxide conversions and relatively low carbonate selectivities. This result is in agreement with the trend displayed in Figure 1, where unimolecular deactivation of the nucleophiles might occur and with previous experimental results where low to moderate epoxide conversions were observed using higher nucleophile loading under identical conditions.[85] Nevertheless, it should also be considered that compounds such as TBD and DBU, known for interacting directly with CO_2,[86] might act as catalysts through a different mechanistic pathway (cycle B of Scheme 2, *vide infra*).[85] Prompted by the promising catalytic activity displayed by **4** in Table 2, we explored the scope of this nucleophile for the conversion of

several terminal epoxide substrates under atmospheric pressure (Table 3).

Table 3. Catalytic performance of nucleophilic catalyst **4** for the conversion of several terminal epoxides under atmospheric pressure.[a]

Entry	Substrate	Conversion(%)[b]/ Selectivity for 6 (%)[b]	Yield (%)[c]
1	**5a** (Ph)	93/95	80
2	**5b** (Bu)	99/95	93
3	**5c** (CH_2Cl)	99/93	86
4	**5d** (CH_2OPh)	>99/97	89
5	**5e** (CH_2OCH_2Ph)	>99/93	78
6	**5f**	>99/97	83
7	**5g**	>99/96	87
8	**5h**	>99/n.d[d].	39

[a] Epoxide (16.6 mmol), **4** (0.332 mmol, 2 mol%) at 100 °C, 1 bar CO_2 (balloon) for 24 h, solventless. [b] Conversion and selectivity determined by ^1H NMR. [c] Isolated yields of carbonate products after column chromatography. [d] The selectivity for **6h** versus **7h** could not be determined because of the presence of additional by-products.

In general, quantitative conversions of the epoxide substrates were observed with high selectivities for carbonate products **6a-g** that could be isolated by column chromatography (See ^{1}H NMR spectra in Figures S48-S73 of the ESI). In the case of epoxide **5h**, despite complete epoxide conversion, the target carbonate **6h** could be isolated in only moderate yields (Table 3, entry 8) because of the formation of several by-products, possibly due to polymerization of the substrate. The ability of nucleophile **4** to promote the cycloaddition of CO_2 to epoxides **5b** and **5d** under several reaction conditions was explored by studying the dependence of epoxide conversion and selectivity on the reaction temperature (Figure 2). It is possible to observe that, at ambient pressure, more reactive epoxide **5d** was partially converted to the target carbonate already at 70-80 °C whereas 1-hexene oxide (**5b**) was not reactive under identical conditions. In both cases a temperature of 100 °C was necessary to achieve quantitative and selective epoxide conversion to the carbonate products. Similarly, when studying the dependence of epoxide conversion at 100 °C and atmospheric CO_2 pressure on reaction time (Figure 3), epoxide **5d** displayed a good degree (77%) of conversion to **6d** after just 6 h, whereas **5b** afforded just moderate conversion in the same period.
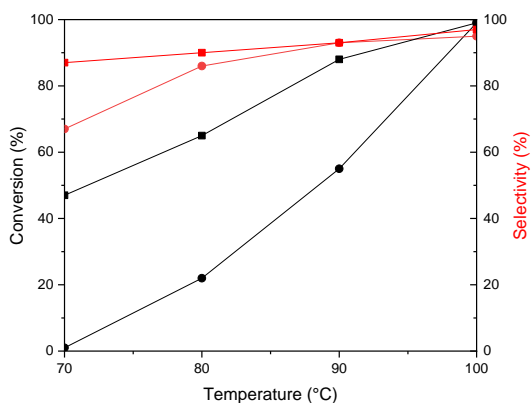

Figure 2. Conversion (black) and selectivity (red) of the cycloaddition reaction of CO_2 to epoxyhexane (**5b**, ●) and glycidyl phenyl ether (**5d**, ■) at different temperatures. (catalyst: **4** (2 mol%); P_{CO2} = 1 bar; 24 h).
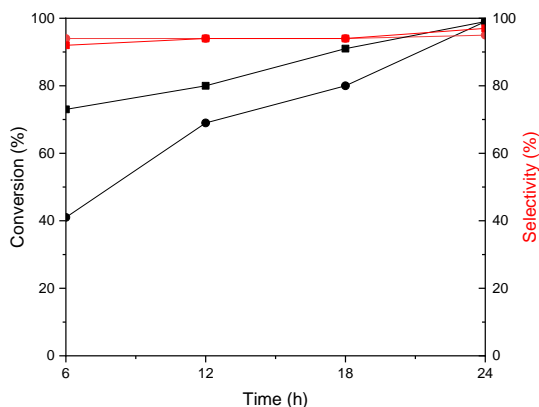

Figure 3. Conversion (black) and selectivity (red) of the cycloaddition of CO_2 to epoxyhexane (**5b**, ●) and glycidyl phenyl ether (**5d**, ■) for different reaction times. (catalyst: **4** (2 mol%); P_{CO2} = 1 bar; 100 °C).

In both cases, a reaction time of 24 h was necessary to afford complete conversion of the epoxide with the selectivity for the carbonate product being only marginally affected by the reaction time. In order to explore the potential of catalyst **4** we attempted the carbonation of internal epoxides such as cyclohexene oxide and epoxidized methyl oleate (EMO, Table S2). In the case of cyclohexene oxide we observed low conversion (<20 %) of the starting material to the carbonate at 100° C under atmospheric CO_2 pressure (Table S2, entry 1). Increasing the CO_2 pressure to 20 bar led to moderate epoxide conversion but the ^{1}H NMR of the reaction mixture displayed the presence of several products (Figure S36) possibly including polymeric material and the desired carbonate was isolated in low yields (Table S2, entry 2). In the case of methyl oleate (Table S2, entries 3, 4), we did not observe any formation of carbonates at atmospheric pressure or at 20 bar. Overall, these data confirm the difficulty of producing internal cyclic carbonates from internal epoxides by using halogen-free single-component organocatalysts.[57-59, 63] Nevertheless, nucleophile **4** could catalyze the synthesis of internal cyclic carbonates from hydroxyl-functionalized internal epoxides and from amino functionalized epoxides (Scheme 3). For instance, the cycloaddition of CO_2 to **5k**[87] using 2 mol% **4** in acetonitrile (Scheme 3A) proceeded with quantitative epoxide conversion (Figure S37) to afford almost exclusively cyclic carbonates **6ka** and **6kb** under relatively mild conditions (60 °C, 20 bar CO_2; the only additional by-product being the decarbonylated form of **6kb**). The higher selectivity for **6kb**, that could be isolated in good yields after column chromatography, indicates the occurrence of a Payne-type rearrangement in which **4** had, principally, the role of a base in shuttling the proton of the initial epoxy alcohol to the product.[67] To the best of our knowledge, a single previous metal- and halogen-free attempt to carry out the synthesis of **6ka** and **6kb** from **5k** and CO_2 was reported.
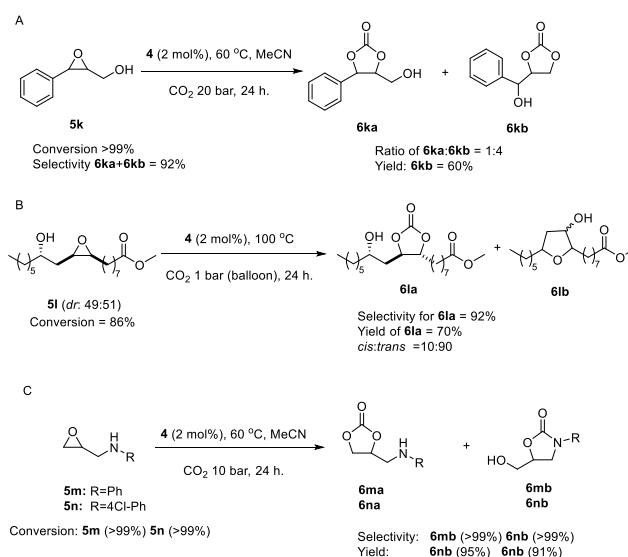
Scheme 3. Cycloaddition of CO_2 to hydroxyl-functionalized internal epoxides and to amino-functionalized epoxides catalyzed by **4**.

Kleij et al. showed that 10 mol% DMAP provided only moderate conversions of **5k** at similar reaction temperature as in our case (45 °C) but higher CO_2 pressure (30 bar) in methyl ethyl ketone albeit with high selectivity for **6kb**.[67] Under identical conditions as DMAP, 10 mol% DBU and TBD provided quantitative conversion of **5k** with TBD being the most selective for **6kb** (**6ka**/**6kb**, 1:9) but with lower overall carbonate selectivity than observed in our case using 2 mol% **4**. As a different epoxy alcohol we considered epoxidized methyl ricinoleate (**5l**, Scheme 3B). Using 2 mol% **4** at 100 °C in a solventless reaction under atmospheric pressure, **5l** could be efficiently converted to carbonate **6la** with the formation of minor amounts of cyclic ether **6lb** from intramolecular cyclization (Figure S38). Importantly, **6la** was obtained mainly as the *trans*-isomer indicating inversion of configuration at one of the epoxide carbon atoms. Given the lack of activity of **4** for the carbonation hydroxyl-free fatty acid EMO, it is expected that the formation of **6la** might proceed with a mechanism comparable to that discussed for the formation of **6kb** with **4** shuttling the proton from the hydroxyl moiety to the product; such process involves a single inversion of configuration by a S_N2 mechanism leading to the *trans*-isomer.[25] Whereas this process should lead to a 6-membered cyclic carbonate, it is expected that such compound might rearrange into the final 5-membered carbonate **6la** by an intramolecular rearrangement as proposed by Kleij et al. when using an aluminum triphenolate complex for the synthesis of **6a**.[25] Interestingly, to the best of our knowledge, our approach to the synthesis of **6la** in scheme 3B is the first to take place under atmospheric CO_2 pressure and by using halogen- and metal-free catalysts. Overall, the reactions in Schemes 3A and 3B show that **4** is a competent catalyst for the synthesis of cyclic carbonates from epoxy alcohols, albeit through a "non-traditional" mechanism of proton shuttling rather than by the usually observed epoxide ring opening.[67] Finally, we turned our attention to the use of epoxy amines **5m** and **5n** that, in the cycloaddition reaction with CO_2 (Scheme 3C), could respectively afford either carbonates **6ma** and **6na** (by the "traditional" cycloaddition mechanism), or carbonates **6mb** and **6nb** by initial coordination of CO_2 to the nitrogen atom and H-transfer to **4**.[87, 88] As in the case of epoxy alcohols **5k** and **5l**, we selectively obtained carbonates **6mb** and **6nb** (Figures S39, S40) under mild conditions (60 °C, 10 bar CO_2 in MeCN) that were isolated in very high yields by using just 2 mol% **4**. As far as we are aware, this was the first organocatalytic (and halogen-free) approach to the reaction in Scheme 3C.

Mechanistic experiments

^{13}C NMR and *in situ* IR experiments were carried out to clarify the reaction mechanism of the cycloaddition reaction catalyzed by **4** with respect to the possible catalytic cycles displayed in Scheme 2. We initially looked into the ^{13}C NMR spectra of reaction mixtures generated by addition of atmospheric CO_2 to CDCl$_3$ solutions of nucleophiles such as DMAP and **4** along with TBD and DBU as reference

compounds (Section S5). When CO_2 was added to solutions of DBU or TBD the formation of white precipitates was observed in both cases in line with previously reported formation of insoluble DBU-CO_2 and TBD-CO_2 adducts.[86] However, when the same experiments were carried out by using DMAP or **4** no precipitates were observed as well as no new signals in the ^{13}C NMR of the solutions apart for a peak at 125 ppm relative to CO_2 dissolved in CDCl$_3$ (Figures S45, 46). These experiments indicate that, differently from the cases of DBU and TBD, there was no strong detectable interaction between pyridine nucleophiles and CO_2 in the solution phase at atmospheric pressure. To gain further insight, *in situ* IR studies were carried out using solutions of **4** in epoxide **5b** at 100 °C (Section S8 of the ESI). The *in situ* IR spectrum of the solution in 1545-1600 cm^{-1} (Figure S47a) initially displayed only a signal at 1585 cm^{-1} attributed to one of the C=C stretching modes of the pyridine ring and observed also in the FT-IR spectrum of pure **4** (Figure S47b).[89] Within 1 h, we observed the appearance of a new strong signal at 1645 cm^{-1} attributed to the C=C ring stretching of a pyridinium moiety[90] as expected for the formation of the adduct of ring-opening of the epoxide by the nucleophilic nitrogen atom (Scheme 1, cycle A and Figure S47c).[91, 92] Additionally, the peak initially centered at 1585 cm^{-1} was replaced by a new signal centered at 1577 cm^{-1}. By addition of CO_2, the formation of cyclic carbonate was observed by a peak at 1814 cm^{-1} (Figure S47d) along with the appearance of a new signal at 1680 cm^{-1} analogous to that observed for the $v_{C=O}$ stretching in metal-coordinated hemicarbonates formed by the reaction of ring-opened epoxides (*i.e.* alkoxides) with CO_2 as expected for step **IIA** of cycle A in Scheme 1.[92] Taken together these observations corroborate a mechanistic picture where **4** acts in carbonation of terminal epoxides according to cycle A of Scheme 1 and not by the initial coordination of CO_2.

Heterogenization of compound 4

Based on the promising catalytic activity of nucleophile **4** in the cycloaddition of CO_2 to terminal epoxides, we immobilized this compound on azide-functionalized Merrifield resin (MR) using the copper-catalyzed alkyne-azide click reaction to afford **4@MR** (See section S2 of the ESI for heterogenization procedure and Figures S1, S2 for characterization of **4@MR**) following a previously developed protocol.[81] The thus synthesized heterogeneous catalyst (**4** loading 0.77 mmol/g according to elemental analysis) was tested for the cycloaddition of CO_2 to several epoxides (**5a**-**5f**) as shown in Table 4. Importantly, by comparing the results in Table 2, entry 1-6 with those in the corresponding entries of Table 3, it is possible to observe that the heterogenization of **4** did not generally lead to a significant drop of catalytic performance when compared to its homogeneous counterpart. Indeed, for almost all epoxides, except **5b** (Table 4, entry 2), the observed conversions obtained for **4@MR** were only slightly lower, if not identical, to those obtained for **4**. In the case of **5b**, quantitative epoxide conversion to carbonate **6b** could be achieved when

increasing the catalyst loading to 4 mol% (Table 4, entry 2b). To note, **4@MR** could be easily recovered from the reaction mixture by filtration and recycled for the cycloaddition of CO_2 to **5b** maintaining almost unchanged catalytic performance at the fourth reaction cycle (Table 4, entry 2). The recyclability of **4@MR** was not affected when using a higher loading of catalyst (Table 4, entry 2b) or a different epoxide (**5d**, Table 3, entry 4).

Table 4. Application of heterogeneous **4@MR** for the cycloaddition of CO_2 to epoxide under atmospheric CO_2 pressure.[a]
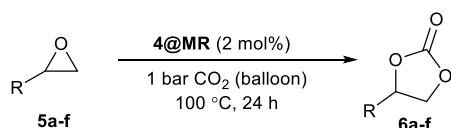
Entry	Substrate	Conversion(%)[b]/ Selectivity for 6 (%)[b]
1	**5a** (Ph)	85/94
2	**5b** (Bu)	Run 1: 64/>99 Run 2: 64/>99 Run 3: 63/>99 Run 4: 63/>99
2b		Run 1: 97/>99[c] Run 2: >99/98[c] Run 3: >99/99[c] Run 4: >99/98[c]
3	**5c** (CH_2Cl)	>99/95
4	**5d** (CH_2OPh)	Run 1: >99/96 Run 2: >99/96 Run 3: >99/95 Run 4: >99/96
5	**5e** (CH_2OCH_2Ph)	95/93
6	**5f**	97/96

[a] Epoxide (4.2 mmol), **4@MR** (107.8 mg, 0.084 mmol **4**, 2 mol%) at 100 °C, 1 bar CO_2 (balloon) for 24 h, solventless. [b] Conversion and selectivity determined by ^1H NMR. [c] Using 215.6 mg **4@MR** (4 mol% **4**).

Overall, these data show that the immobilization of **4** on MR affords a rare example of metal and halogen-free catalyst with the ability to promote the cycloaddition of CO_2 to several epoxides under atmospheric pressure.[93] In this context, the performance of **4@MR** is comparable to that of

other excellent, but halogen-based, single-component heterogeneous organocatalyst recently reported in the literature operating at around 80 °C and in the 1-10 bar pressure range.[94-96]

DFT Investigation of the mechanism of CO_2 cycloaddition to epoxides

Two possible catalytic pathways for single component nucleophilic catalysts (**Nu**), along with expected reaction intermediates (**I1-I5**), are shown in Scheme 2. Each step is expected to proceed through the corresponding transition state (**TS**). In cycle **A**, that is analogous to the cycloaddition mechanism catalyzed by halide anions in the absence of Lewis acids or HBDs,[97, 98] the use of strong nucleophiles could facilitate the often crucial step of epoxide ring opening (**IA**) leading to faster reaction rates under the *caveat* that the leaving group ability of the nucleophilic catalyst would allow the final step of carbonate ring-closure (**IIIA**), located after CO_2 insertion (**IIA**), to proceed with reasonable energy barriers. On the other hand, based on the ability of nucleophilic compounds such as DBU,[99] TBD (triazabicyclodecene),[86] and N-heterocyclic carbenes[100] to activate and coordinate CO_2, an alternative mechanism pathway could be proposed for single-component nucleophilic catalysts involving the initial formation of an adduct between the nucleophile and CO_2 (step **IB**). The latter intermediate would subsequently open the epoxide substrate (step **IIB**) and lead to the final product after cyclization (step **IIIB**).[82, 101-104] Also in the latter pathway, the use of a strong nucleophile could improve the efficiency of the step of CO_2 capture or increase the electron density of the Nu-CO_2 adduct for the attack on the epoxide. In the case of aminopyridines, but limited to the case of DMAP, the mechanism in cycle **A** was found to be favored in the presence of phenols[53] or metal-based Lewis acids.[33, 92, 105] Nevertheless, CO_2 activation by the pyridine nitrogen has also been proposed in some cases.[106] Therefore, DFT Calculations (B3LYP-D3/TZVP(smd)//BP86-D3/TZVP level) were performed on selected nucleophiles to gain further insight into the reaction mechanism of CO_2 cycloaddition and to investigate the reaction barriers for the different nucleophiles. For the sake of simplicity, we used propylene oxide (PO) as the substrate (Figure 4). Calculations on styrene oxide (**5a**, Figure S76) for the step of epoxide ring-opening (**IA**) at the same carbon atom showed no significant differences between PO and **5a**. Our calculations show that the reaction of PO with CO_2 to give the corresponding cyclic carbonate was exergonic by 1.2 kcal/mol. The reaction barriers for the mechanistic pathway relative to cycle A of Scheme 2 starting with epoxide ring opening by the nucleophile are reported in Figure 4. The reaction barriers for the pathway initiated by the interaction of the nucleophile and CO_2 prior to the epoxide opening (cycle B in Scheme 2) are shown in the ESI (Section S10) and compared with the results for cycle A for each nucleophile (Figures S77-S80).
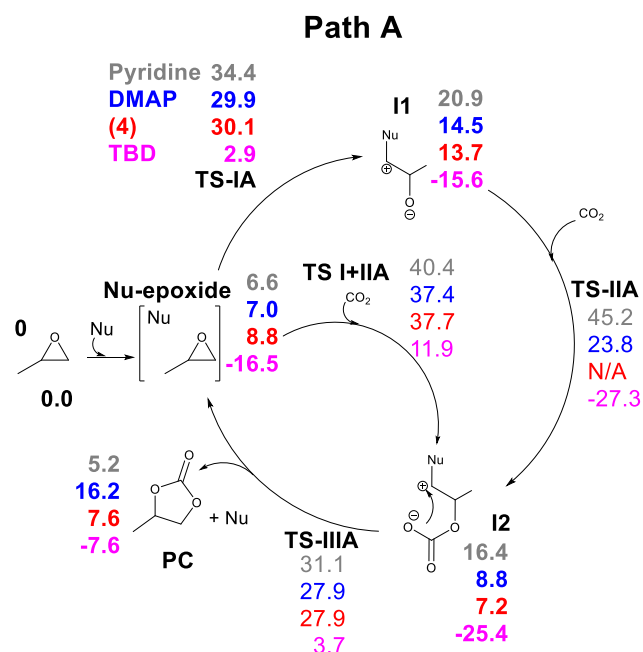
Path A

Pyridine 34.4
DMAP 29.9
(4) 30.1
TBD 2.9
TS-IA

I1 20.9
14.5
13.7
-15.6
Nu

CO$_2$

Nu-epoxide 6.6
7.0
8.8
-16.5

TS I+IIA 40.4
37.4
37.7
11.9
CO$_2$

TS-IIA 45.2
23.8
N/A
-27.3

0
Nu
0.0

Nu

5.2
16.2
7.6
-7.6

PC + Nu

TS-IIIA 31.1
27.9
27.9
3.7

I2 16.4
8.8
7.2
-25.4

Nu

Figure 4. Reaction barriers (kcal/mol) for the cycloaddition of CO$_2$ to PO catalyzed by several nucleophiles; color code: Pyridine grey; DMAP blue; **4** red; TBD pink. Energies shown in kcal/mol. PC: propylene carbonate

The comparison of both pathways shows that the reaction barriers in cycle B were generally always more energy demanding than in cycle A. It was also possible to observe that for all pyridine-based nucleophiles the formation of the adduct of coordination of CO$_2$ (**I3**) was thermodynamically disfavored (by 6.9 kcal/mol for the case of **4**) whereas it was strongly favored by 23.8 kcal/mol for the case of TBD (Figure S80). Structurally, for the case of TBD, we observed the formation of a N–C bond (1.603 Å), whereas for **4** the N···C interaction had a non-covalent character (2.655 Å). These results agree with the fact that a CO$_2$ adduct of **4** and DMAP could not be observed by NMR under atmospheric CO$_2$ pressure whereas, in the case of TBD, direct precipitation of the TBD-CO$_2$ adduct was observed. Based on these data, it is proposed that pyridine and aminopyridines follow the less energy-demanding mechanistic pathway highlighted in cycle A of Scheme 2 whereas TBD, despite milder calculated reaction barriers when acting as catalyst through cycle A, would form a strong adduct with CO$_2$ and proceed through the less kinetically favored cycle B leading to a lower catalytic performance (Table 2, entries 6, 8)

Focusing on the mechanism of the cycloaddition reactions according to cycle A of Scheme 2 for pyridine derivatives in Figure 4 (pyridine, DMAP and **4**), the step of epoxide ring-opening (**IA**) resulted as the rate determining step for DMAP and **4** whereas the step of CO$_2$ activation (**IIA**) by the alkoxide was the most energy demanding for pyridine (45.2 kcal/mol). This result is substantially in agreement with the low catalytic performance of this nucleophile in the cycloaddition of CO$_2$ to epoxides (Table 2). Independent of the epoxide (Figure 2 and Figure S76), pyridine also displayed the highest reaction barrier (34.4 kcal/mol for PO) for

epoxide ring-opening that is in line with its lower carbon basicity (Figure 1 and Table 1). When comparing DMAP and **4**, nearly identical barriers were found for the rate-determining step of epoxide ring opening using PO as the substrate (29.9 kcal/mol for DMAP versus 30.1 kcal/mol for **4**) whereas the ring opening of **5a** (Figure S76) implied a slightly higher barrier for DMAP (32.6 kcal/mol versus 31.9 kcal/mol for **4**); indeed **4** was a more efficient catalyst than DMAP when using **5a** as the substrate (Table 2, entries 2, 6) although the difference in the ring-opening barriers was smaller than expected. To note, the latter nucleophiles displayed moderate reaction barriers for the other steps of the mechanism in Figure 2 with the step of CO$_2$ activation requiring a barrier of 9.3 kcal/mol for DMAP. The analogous transition state (**TS-IIA**) could not be located for **4**, however, the decreasing trend for this barrier with increasing catalyst nucleophilicity (24.3 for pyridine versus 9.3 for DMAP) suggests a moderate CO$_2$ activation barrier for **4**. The final ring closure barrier (step **IIIA**) was 19.1 kcal/mol for DMAP and 20.7 kcal/mol for **4**. We have also analyzed a trimolecular step through transition state **TS-I+IIA** where epoxide ring-opening takes place along with the activation of CO$_2$. However, this process was found to be disfavored by at least 6.0 kcal/mol for all nucleophiles tested and ruled out. The different performance for the pyridine-based nucleophiles could also be rationalized from an electronic point of view. Accordingly, DFT calculations show that pyridine is much less nucleophilic according to the Parr electrophilicity[107, 108] than **4** (0.051 vs 0.030), with DMAP having an intermediate electrophilicity (0.034). Chemical hardness[109,110] can also justify the different catalytic behavior, with values of 0.200, 0.216, and 0.247, for **4**, DMAP, and pyridine, respectively that are in a good qualitative agreement with the experimental conversions reported in Table 2. In addition, it should be noted that the lower performance of DMAP in Table 2 may be motivated by lower solubility than **4**.

Conclusions

In the search for single-component and halogen-free organocatalysts for the cycloaddition of CO$_2$ to epoxides under ambient pressure, we focused on highly nucleophilic 3,4-diaminopyridines that were not previously explored for this reaction. The application of the latter class of catalysts was supported by predictive carbon basicity calculations suggesting higher tendency to ring-open the epoxide substrate than standard pyridine-based nucleophiles such as DMAP. Therefore, we tested 3,4-diaminopyridines, along with other reference *N*-nucleophiles, in the cycloaddition of CO$_2$ to terminal epoxides **5a** and **5b** reporting high catalytic conversions and carbonate selectivities for 3,4-diaminopyridine **4**. The latter compound could be successfully applied to the cycloaddition of CO$_2$ to several other terminal epoxides under atmospheric pressure and also to the selective conversion of hydroxyl- and amino-functionalized internal epoxides to the corresponding

carbonates. Importantly, **4** could be readily heterogenized on modified Merrifield resin (**4@MR**) and applied as recoverable and recyclable catalyst for the carbonation of epoxides with no apparent loss of catalytic performance that was comparable to that of its molecular counterpart. The catalytic mechanism of the cycloaddition reaction of CO_2 to epoxides was studied by a combination of mechanistic experiments and DFT calculations; our results support a pathway where pyridine-based nucleophiles initially interact with the epoxide rather than with CO_2 being this conclusion at variance with what observed for other widely applied *N*-nucleophiles such as DBU and TBD that strongly interact with CO_2. Overall, this work demonstrates that highly nucleophilic aminopyridines hold significant potential as new, efficient halogen-free organocatalysts for the cycloaddition of CO_2 to epoxides and we expect that this work will inspire the design of new homogeneous and heterogeneous halogen-free organocatalysts. In this context, the application of even more nucleophilic,[73, 74] recently developed aminopyridines appears highly promising and is currently under investigation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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