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Short Communication

Role of pre-organization around the azaphosphatrane catalyst's active site in the conversion of CO_2 to cyclic carbonates

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ABSTRACT

Various N-substituted azaphosphatranes have been prepared and successfully applied to the synthesis of styrene carbonates from CO_2 and epoxides. Enhancement of the catalytic properties of the azaphosphatrane was achieved upon pre-organization of the active site through hydrogen-bonding.

1. Introduction

Conversion of CO_2 to industrially relevant compounds has recently attracted much interest for the development of sustainable and greener alternatives to fossil fuel based resources [1–3]. CO_2 has the advantage of being non-toxic, abundant and is particularly useful as a substitute of phosgene. In this regard, the cycloaddition of CO_2 to epoxides to produce cyclic carbonates is one of the most promising and eco-friendly methodologies to exploit carbon dioxide as a renewable raw material [4–8]. Organic carbonates are important building blocks that have found numerous applications as green solvents, additives to gasoline, thickeners for cosmetics, electrolytes for lithium batteries and as useful intermediates for the production of plastics and fine chemicals [9–12]. Although commercially manufactured for about 50 years [13] using mainly quaternary ammonium or phosphonium salts [14–16] as catalysts, the industrial synthesis of ethylene and propylene carbonates from CO_2 and corresponding epoxides still requires fairly drastic reaction conditions (high temperatures and pressures) and the use of relatively pure CO_2. In the past decades, numerous catalytic systems have been developed to achieve higher performance under milder conditions [17–19]. Recent advances include the use of binary catalysts [7,20] based on the association of a Lewis acid (e.g. Al, Zn, Mn, Cr, Co among others) and a nucleophile (e.g. the counteranion of an onium salt) or the development of one-component systems which contain both functions within a single catalytic site [5,21]. In these systems, the Lewis acid and the nucleophile act cooperatively at the epoxide through oxygen atom coordination and nucleophilic ring-opening, respectively.

Although significant progress has been made, several disadvantages need to be circumvented to produce greener catalysts and the processes: low catalyst stability and reactivity, the need for a cocatalyst and/or cosolvent, the limited scope of substrates and, in most cases, the presence of expensive and toxic metals. In this respect, organocatalysis may represent a powerful tool capable to respond to increasingly stringent regulatory issues concerning metal contamination of pharmaceutical products or consumer chemical feedstocks. In addition to quaternary ammonium and phosphonium salts [22], ionic liquids [23,24], betaine-based structures [25], organic bases among other organocatalysts have been reported to efficiently enable CO_2 fixation into cyclic carbonates. Phenol associated with organic bases such as 4-dimethylaminopyridine (DMAP) was also successfully applied to this transformation [26]. However, unlike metal-mediated catalyzed approaches, elevated temperatures and pressures (90–140 °C, 10–140 bar) were required in most cases to achieve sufficient conversion. More recently, Kleij et al. reported that the combination of phenolic-based compounds such as catechol and/or

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pyrogallol with nBu$_4$NI co-catalyst led to a very efficient catalytic system able to operate under solvent-free and relatively mild reaction conditions (25–45 °C, PCO_2 = 10 bar, 2–5 mol% catalyst), thus fulfilling some of the criteria towards sustainability [4]. The authors attributed this improvement to both synergistic and stabilizing effects provided by the polyphenolic structures through multiple hydrogen-bonding.

In our effort to contribute to the overall trend for clean and effective CO_2 conversion, we have recently described the use of azaphosphatranes (AZAPs), which are the acidic conjugates of the Verkade's superbases [27–29], as efficient single-component, metal-free catalysts for the synthesis of cyclic carbonates from CO_2 and epoxides (Scheme 1) [30]. In that work, we showed that these organocatalysts were able to operate under low CO_2 pressures and relatively mild temperatures (1 bar, 80–100 °C) even at catalyst loadings of 0.1 mol%. We also demonstrated that the presence of bulky substituents on the equatorial nitrogen atoms strongly correlate with higher catalyst activity and stability over several days of reaction. Based on kinetic studies and previous literature precedents [31,32] we proposed a mechanism which involves the insertion of CO_2 into the P–N bond of the AZAP unit as the rate determining step.[1]

In the present contribution, we wish to further explore the different aspects of the catalyst structural dependence through careful adjustment of the substitution patterns around the phosphorus site. As we shall see, the pre-organization of the active site through hydrogen-bonding will lead to the creation of highly reactive pockets with improved performance in the cycloaddition of CO_2 to epoxides.

2. Experimental

Commercial reagents were used without further purifications. ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded on Bruker spectrometers at 500.1, 125.7, 202.4 and 282.2 MHz respectively. Chemical shifts (δ) are referenced with respect to TMS (^{1}H, ^{13}C), H_3PO_4 85% (^{31}P) or TFA (^{19}F). Compounds **1a** and **1c** were synthesized according to literature procedures [33,34]. Yields were estimated during catalytic runs by ^{1}H NMR with a Bruker Avance 300 spectrometer at 300.1 MHz. Mass spectra were performed by the Service Central d'Analyses, CNRS, France. CO_2 of a purity of 99.99% was commercially available and used without further purification.

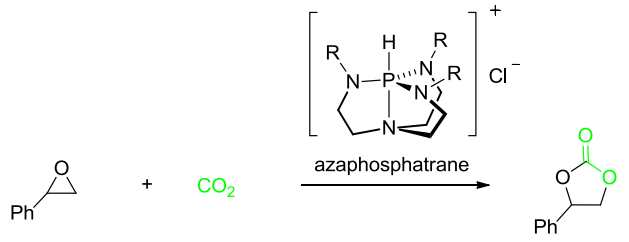
2.1. Syntheses of new compounds

2.1.1. Tris(2,6-difluoro-4-methoxybenzyl)tren

In a round bottom flask, tris(2-aminoethyl)amine (tren) (546 mg, 3.74 mmol) was dissolved in methanol (10 mL) and ice-bath cooled. Then, a solution of 2,6-difluoro-4-methoxybenzaldehyde (2.00 g, 11.60 mmol, 3.1 eq) in a 1:1 (v/v) mixture of chloroform/methanol (10 mL) was added drop-wise. The reaction was slowly warmed up to room temperature and stirred overnight. Methanol (10 mL) was then added. Subsequent portions of $NaBH_4$ (878 mg, 23.20 mmol) were added to the ice-cooled mixture over a thirty-minute period and the mixture was stirred for another hour. Solvents were evaporated. A solution of 10% NaOH in water was added (25 mL), and the resulting mixture was extracted with toluene (3 × 30 mL). The combined organic phases were extracted with HCl 1 M (3 × 50 mL) and the combined aqueous phases were then basified with an aqueous 10% NaOH solution. The solution was then extracted with toluene (3 × 100 mL) and the organic layers were dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure to give a pale yellow oil (1.88 g, 82%).

ESI-HRMS m/z calcd for $C_{30}H_{37}F_6N_4O_3$ (MH^+) 615.2764, found 615.2745.

[1] Note that the participation of the deprotonated AZAP species in the catalytic cycle has been ruled out considering the high pKa value of the AZAP acid–base couple (pKa ~ 33) and the absence of a strong base in the reaction medium.



Scheme 1. Coupling of styrene oxide with CO_2 catalyzed by azaphosphatranes (R = alkyl or aromatic moieties).

^{1}H NMR ($CDCl_3$, 298 K, 500.1 MHz): δ 6.41 (d, $^3J_{H-F}$ = 9.18 Hz, 6H, ArH); 3.76 (s, 9H, $ArOCH_3$); 3.75 (s, 6H, $ArCH_2N$); 2.58 (t, ^3J = 6.01 Hz, 6H, $N(CH_2)_2N$); 2.50 (t, ^3J = 5.80 Hz, 6H, $N(CH_2)_2N$).

^{13}C NMR ($CDCl_3$, 298 K, 125.7 MHz) δ 163.2 (d, J = 12.6 Hz, C_{Ar}); 161.2 (d, J = 12.6 Hz, C_{Ar}); 160.0 (t, J = 14.6 Hz,C_{Ar}); 97.7 (d, J = 30.4 Hz, $C_{Ar}H$); 55.7 (OCH_3); 54.4 ($ArCH_2N$); 46.5 (NCH_2CH_2N); 40.2 (NCH_2CH_2N).

^{19}F NMR ($CDCl_3$, 298 K, 282.2 MHz): δ −115 ppm.

2.1.2. Compound 1b

In an ice-bath cooled round bottom flask, tris(dimethylamino)phosphine (0.410 mL, 2.25 mmol) was dissolved in acetonitrile (15 mL). Phosphorus trichloride (98 μL, 1.12 mmol) was then added drop-wise. The reaction mixture was vigorously stirred at 0 °C for 0.5 h, and a solution of tris(2,6-difluoro-4-methoxybenzyl)tren (1.88 g, 3.06 mmol) in acetonitrile (10 mL) was added drop-wise. The reaction mixture was then stirred overnight at room temperature. The solvent was removed under reduced pressure and the crude compound was chromatographed on silica gel eluting with $CHCl_3$/MeOH 15/1 to give pure **1b** as an off-white powder (1.01 g, 49% yield).

ESI-HRMS m/z calcd for $C_{30}H_{34}F_6N_4O_3P$ (M^+) 643.2267, found 643.2236.

^{1}H NMR ($CDCl_3$, 298 K, 500.1 MHz): δ 6.48 (d, $^3J_{H-F}$ = 9.57 Hz, 6H, ArH), 6.00 (d, $^1J_{P-H}$ = 508 Hz, 1H, P–H); 4.09 (d, $^3J_{P-H}$ = 14.60 Hz, 6H, $ArCH_2N$); 3.79 (s, 9H, $ArOCH_3$); 3.49–3.46 (m, 6H, $N(CH_2)_2N$); 2.97–2.92 (m, 6H, $N(CH_2)_2N$).

^{13}C NMR ($CDCl_3$, 298 K, 125.7 MHz): δ 163.2 (d, J = 11.7 Hz, C_{Ar}); 161.2 (d, J = 11.7 Hz, C_{Ar}); 105.2 (m, C_{Ar}); 98.2 (d, J = 29.06 Hz, $C_{Ar}H$); 55.9 (OCH_3); 46.6 (d, J = 7.09 Hz, $N(CH_2)_2N$); 38.5 (d, J = 6.71 Hz, $N(CH_2)_2N$); 38.1 (d, J = 20.4 Hz, $ArCH_2N$).

^{31}P NMR ($CDCl_3$, 298 K, 202.4 MHz) δ: −14.4 (d, $^1J_{P-H}$ = 508 Hz).

^{19}F NMR ($CDCl_3$, 298 K, 282.2 MHz): δ −114.6 ppm.

2.2. Catalytic procedures

Reactions were carried out in a 5 mL Schlenk tube equipped with a rubber septum. In a typical run, the reactor was charged with 50 mmol of styrene oxide (SO), 0.05 mmol of catalyst (**1a–c**) and 2,4-dibromo-mesitylene used as an internal standard. Carbon dioxide was first bubbled into the solution for 5 min to saturate the liquid phase. A balloon filled with carbon dioxide was then connected to the Schlenk through a needle to maintain a constant atmosphere of carbon dioxide during the course of the reaction. The mixture was placed in a thermostatic oil bath at the required temperature and stirred at a stirring speed of 1000 rounds min^{-1}. After each 24 hour period, the reaction mixture was cooled to room temperature and an aliquot was analyzed by ^{1}H NMR. Based on the SO integrated intensity in the NMR spectrum, additional substrate was added to the mixture to recover the initial substrate to catalyst ratio. Carbon dioxide was bubbled through the solution for 15 min at room temperature, the CO_2 reservoir was connected to the reaction vessel, which was returned to the thermostatic bath. For the catalytic tests run over a course of 24 h, yields were determined by ^{1}H NMR following the same procedure but starting with 5 mmol of styrene oxide and 1 mol% of the catalysts (**1a–c**).

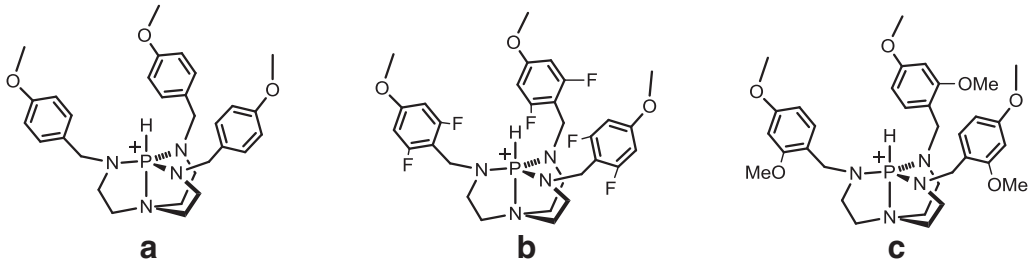


Fig. 1. Targeted azaphosphatranes **1a–c** to probe the structure–activity effects.

2.3. Computational method

Ab initio evaluations were performed using the Gaussian 03 package within a restricted DFT framework. A combination of unrestricted BP86 functional and triple-zeta 6-311G all electron basis sets has proven to be very satisfactory for geometry optimizations [35]. We checked that our results did not suffer from the arbitrariness of the exchange correlation functional using the hybrid B3LYP functional.

3. Results and discussion

Azaphosphatranes possess several remarkable features that make them particularly interesting candidates for the activation of both CO_2 and epoxides. First, these protonated aminophosphines, built from the tris(2-aminoethyl)-amine (tren) scaffold, present a well-defined tricyclic structure around the phosphorus atom which allows for greater stability. The soft organic cation, in which the charge is delocalized around the HPN core, does not strongly associate with hard halide anion. Thus, the anion is more prone to react as nucleophile to initiate the epoxide ring-opening step. Finally, the nature of the lipophilic pocket formed by a ring of amino groups around the central PH unit provides a unique catalytic space to probe the structure/activity effects.

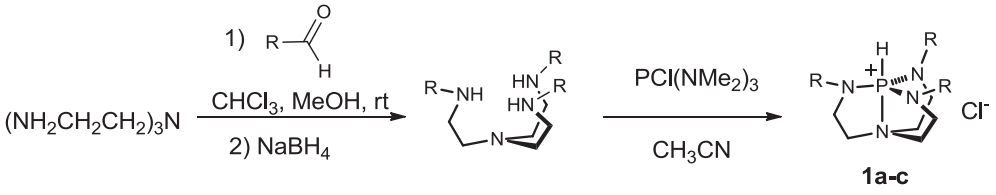
Three N-substituted azaphosphatranes were considered during the course of this study (Fig. 1): AZAP **1a** containing a *p*-methoxybenzyl substituent was chosen as a benchmark structure since the aromatic moiety can provide a versatile platform for fine-tuning of the substitution pattern. AZAPs bearing benzyl rings *ortho*-substituted by fluorine atoms (**1b**) or a methoxy group (**1c**) were also synthesized. We anticipated that these substituents could favor intramolecular hydrogen bonding with the P–H^+ moiety, providing a cavity above the reactive center which may protect it from degradation.

Taking advantage of the high versatility of the AZAP synthesis, catalysts **1a–c** were prepared following a two-step reaction sequence (Scheme 2). The key substituent was introduced in the form of an aldehyde in the triple alkylation of tris(2-aminoethyl)amine (tren) and treatment with $NaBH_4$. Subsequent reaction with $PCl(NMe_2)_2$ led to the desired substituted azaphosphatranes in respectable yields (ca. 50%). ^{31}P NMR spectra of catalysts **1a–c** exhibited a single resonance at −12.4 (**1a**), −14.4 (**1b**) and −10.9 ppm (**1c**) as expected for AZAP derivatives. Full characterization of **1b** has been displayed in Experimental section and Supporting information.

The effect of the catalyst structure on the catalytic performance has been investigated in detail using the coupling of styrene oxide (SO) with CO_2 to produce styrene carbonate (SC) as a model reaction. In coherence with the requirements of highly sustainable green methodologies, we chose to work close to atmospheric pressure (1 bar CO_2) at relatively low temperatures (100 °C) and catalyst loadings (0.1 and 1 mol%). Catalytic tests were first performed over a 24 hour period with a catalyst loading of 1 mol%. All catalysts **1a–c** exhibited good catalytic activities with respectively 73% (**1a**), 86% (**1b**) and 92% (**1c**) yields in styrene carbonate. In order to investigate more accurately the role of these structural changes on catalyst reactivity and stability, a second series of reactions was carried out where the catalyst loading was further decreased to 0.1 mol% and the reaction time extended to 96 h. The progress of the reaction was monitored by ^1H NMR sampling every 24 h (Fig. 2).

At these higher conversions, we can see that the reference organocatalyst **1a** has a limited stability as shown by its steadily decreasing activity over the four-day period. On the contrary, **1b** and **1c** showed nearly constant activity during the course of the experiment. Initial catalytic activities were found to be respectively twice and three times higher with **1b** and **1c** than with **1a** highlighting the key role played by the stereoelectronic properties of the surrounding amino groups on the rate of the reaction. Introduction of specific groups on the benzene ring in **1b** and **1c** also strongly increases the stability of the catalysts: **1b** and **1c** practically maintain their initial activity over the four-day test resulting in much higher TONs (respectively 500 and 800) than for the reference catalyst **1a** (200). This stability enhancement could likely be related to the ability of the fluoro and methoxy Lewis base substituents to create H-bonding with the acidic P–H^+ site. Indeed, Verkade et al. have already reported the occurrence of this type of interactions between the OMe unit and the P–H^+ site in AZAP **1c** [33] and similar interactions are probably effective in **1b**. In our case, we suggest that hydrogen bonding can favor the regeneration of the AZAP core. Moreover, we would like to stress that the Van der Waals radius of hydrogen and fluorine are very close (1.20 and 1.47 Å respectively). Thus, the stability enhancement observed for **1b** with respect to **1a** is likely due to H-bonding between the benzyl substituents and the P–H^+ site.

We thus became interested in investigating further the relative ability of catalysts **1b** and **1c** to achieve intramolecular hydrogen bonding with the P–H^+ site, and addressed this question by means of density functional theory (DFT) calculations. In order to validate our approach, we first decided to compare the X-ray structure of **1a** in the solid state to that obtained in the gas phase by the mean of DFT calculation (Figs. S8 and S9 in the Supporting information) [35]. The optimized bond lengths and valence angles are in good agreement with the



Scheme 2. Synthetic sequence to azaphosphatrane catalysts.

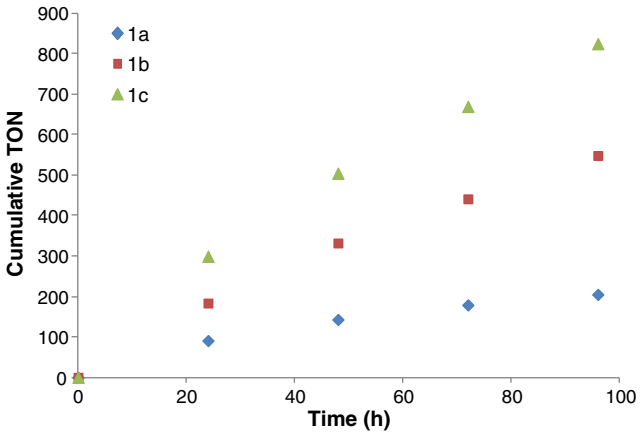


Fig. 2. Influence of the azaphosphatrane substitution on catalyst reactivity. Conditions: styrene oxide (50.0 mmol), catalyst **1a–c** (0.05 mmol), CO_2 (1 bar), 100 °C. TONs were determined by ^1H NMR using 2,4-dibromomesitylene (2.0 mmol) as an internal reference.

X-ray data, thus, the structures of the two other catalysts **1b** and **1c** were optimized with respect to all geometrical parameters, using a BP86/DFT approach leading to global minima (Fig. 3). In their optimized geometry, catalysts **1a–c** displayed some similar features, in particular the distance between the phosphorus and the nitrogen in both equatorial and apical position are characteristic of an azatrane unit (around 2.2 A and 2.3 Å, respectively). Interestingly, intramolecular hydrogen bonding between the $P–H^+$ site and the fluorine or the methoxy groups are likely to occur with both catalysts **1b** and **1c** (the averages of the F…H–P and O…H–P distances are 2.8 Å and 3 Å respectively), whereas such hydrogen bonding is not possible with **1a**. This is consistent with our aforementioned hypothesis concerning the enhanced stability of AZAPs **1b** and **1c** when compared to **1a** during the CO_2 conversion: the presence of intramolecular hydrogen bonds probably protects the active site from degradation. Indeed, the loss of catalytic activity observed for catalyst **1a** may be related to the ring-opening of the AZAP tricyclic structure after CO_2 insertion into the P – N bond [31,32]. Such an intermediate has already been reported to be highly reactive to nucleophilic species, in particular water [31,32]. Thus, intramolecular interactions may reinforce the stability of the catalyst by favoring the regeneration of the polycyclic structure of the azaphosphatrane unit at the end of the catalytic cycle, which is consistent with our proposed mechanism [30]. X-ray structure of **1c** confirms the occurrence of hydrogen bonding between $P–H^+$ and the benzyl substituent ($P–H^+…O–CH_3$ distance of 3.2 Å is observed. See Supporting information).

4. Conclusion

In summary, differently N-substituted azaphosphatranes have been synthesized and successfully applied to the synthesis of styrene carbonate from CO_2 and epoxides. The effects of changes in the local substitution around the central phosphorus site have been evaluated in terms of catalytic activity and stability. We have shown that the introduction of specific substituents at appropriate positions on the aromatic rings led not only to an increased activity but also to more robust catalysts. This improved efficiency has been attributed to the ability of F and OMe Lewis base groups to form H-bonding with the acidic $P–H^+$ inducing larger stabilizing effects. This study demonstrates that by fine design of reactive site structure remarkable reactivity gain can be achieved for organocatalysts.

Acknowledgments

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Appendix A. Supplementary data

NMR data, X-ray and DFT optimized molecular structures of **1a**, X-ray structure of **1c**. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2014.04.004.

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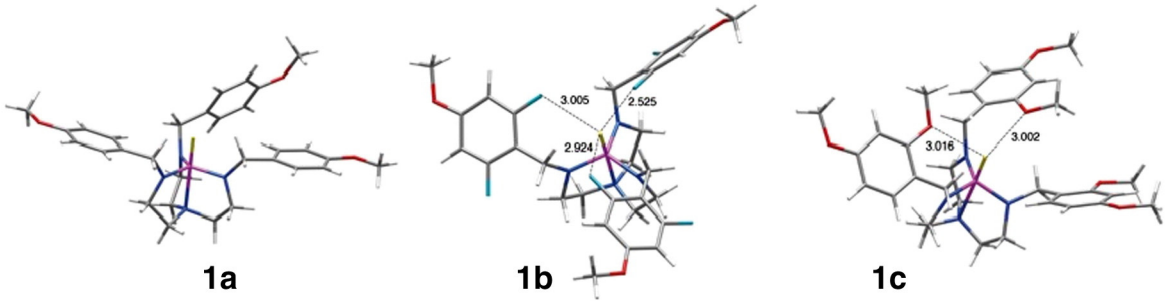

Fig. 3. DFT optimized structures of catalysts **1a**, **1b** and **1c** (typical H-bond lengths (Å) in **1b** and **1c** are displayed).

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