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Synthesis, Characterizations and Applications of Fluoroazaphosphatranes

Anne-Doriane Manick,^[a] Jean-Pierre Dutasta,^[b] Paola Nava,^[a] Véronique Dufaud,^[c] Guohua Gao,^{*[d]} Bastien Chatelet,^{*[a]} and Alexandre Martinez^{*[a]}

Abstract: Haloazaphosphatranes are the halogenated parents of proazaphosphatranes, also known as Verkade's superbases. While the synthesis of iodo-, bromo- and chloroazaphosphatranes was reported more than thirty years ago by J. G. Verkade, the first synthesis of fluoroazaphosphatranes was only described in 2018 by Stephan et al. Currently, no common and versatile procedure exists to access fluoroazaphosphatranes platform with different structural characteristics. In this report, a new and simple synthesis of this class of compounds was developed based on the nucleophilic attack of the fluoride anion on chloroazaphosphatrane derivatives with good to high isolated yields for the corresponding fluoroazaphosphatranes (70–92%). The scope

of the reaction was widened to fluoroazaphosphatranes bearing various substituents and X-ray molecular structures of two of them are reported. The stability of fluoroazaphosphatranes toward nucleophilic solvents like water has been investigated. As they revealed much more robust cations than their chloroazaphosphatrane parents, their chloride salts were tested as organocatalysts for the formation of cyclic carbonates from epoxides and CO₂. Fluoroazaphosphatranes proved to be both efficient and stable catalytic systems for CO₂ conversion with catalytic activities similar to those of azaphosphatranes, and no decomposition of the cation was observed at the end of reaction.

Introduction

Proazaphosphatranes, also named Verkade's superbases,^[1] are non-ionic highly basic phosphorus derivatives (**1**; Figure 1). Compared to phosphazenes, their protonation occurs on the phosphorus atom leading to the formation of highly stable azaphosphatranes.^[2] Verkade's superbases have found numerous applications from basic and nucleophilic catalysts or stoichiometric reagents,^[3] ligands for transition metals,^[4] to Lewis bases in frustrated Lewis pair (FLP) systems.^[5] Moreover, their confinement in molecular cavities strongly affects the thermodynamics and kinetics of the proton transfer and leads to supramolecular catalysts displaying improved catalytic activities or selectivities.^[6,7] Their conjugated acids, the azaphosphatranes (**2**; Figure 1), have been also used as organocatalysts, for instance in the Strecker or the ring-opening polymerization

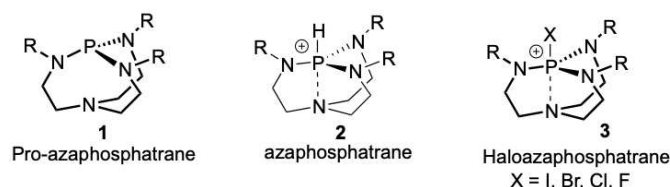


Figure 1. Structures of proazaphosphatrane Verkade's superbases (**1**), azaphosphatranes (**2**) and haloazaphosphatranes (**3**; X=I, Br, Cl or F) cations.

(ROP) reactions and CO₂ conversion.^[8,9,10] Moreover, once included in self-assembled cages, this motif is capable of anions recognition and extraction in water.^[11] Haloazaphosphatranes are the halogenated version of the azaphosphatranes where the hydrogen atom has been replaced by a halogen one (**3**; Figure 1). Although their first synthesis was reported by J. G. Verkade in 1989, they were much less studied than their proazaphosphatrane or azaphosphatrane counterparts.^[12] They have only very recently aroused growing interest, with, for example, the report of the first application of chloroazaphosphatranes as an original motif for halogen bonding of anions in solution.^[13] Unlike iodo-, bromo- and chloroazaphosphatranes, the first synthesis of a fluoroazaphosphatrane derivative bearing a methyl group on the equatorial nitrogen atoms was described only in 2018 by Stephan et al. by using an original FLP strategy.^[14] Indeed, all the synthesis attempts to obtain the fluoroazaphosphatranes by an approach similar to those used for other haloazaphosphatranes have proved unsuccessful because the oxidation in the presence of XeF₂ led to a mixture of products, including the PF₆⁻ anion. However, when isopropyl units are grafted on these equatorial nitrogen atoms, Johnson et al. reported in 2019 that the use of XeF₂ allowed achieving

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the synthesis of the corresponding fluoroazaphosphatrane.^[12d] The 30-year delay between the first reported synthesis of an iodoazaphosphatrane and that of a fluoride analogue also demonstrates how difficult access to this class of compounds is.

Herein, we report on the development of a simple and convenient route to readily access to various fluoroazaphosphatrane derivatives (Figure 2). We shall see that a nucleophilic substitution by the fluoride anion on the chloroazaphosphatrane counterparts could lead to the corresponding fluoroazaphosphatrane compounds in good to high isolated yields. These cations were found to be more stable toward nucleophilic solvents than other haloazaphosphatranes and proved to be efficient organocatalysts for CO₂ fixation into cyclic carbonates.

Results and Discussion

Preliminary evidence of the formation of fluoroazaphosphatranes through titration experiments

We previously reported that chloroazaphosphatranes were able of selective recognition of anions in solution.^[13] Our set of experiments supported that the chlorine atom of chloroazaphosphatrane interacts with anions via halogen bonding. Among the halide anions used as guests, chloride displayed the higher binding constant in agreement with its higher basicity that induces a better ability to interact with the σ -hole of the chloroazaphosphatranes. We thus wondered whether higher binding constant could be attained when using fluoride anion as guest. ¹H NMR titration experiments were first performed in CD₃CN at 298 K using chloroazaphosphatrane **3 a-Cl⁺.PF₆⁻** as receptor. However, as shown in Figure 3a, no change in chemical shifts was noticed upon increasing addition of tetrabutylammonium fluoride salt (TBAF). Instead, a new set of signals appeared on the NMR spectra leading to full disappearance of the signal of **3 a-Cl⁺.PF₆⁻** at 4.67 ppm after addition of around 10 equivalents of TBAF. The ³¹P NMR spectrum (Figure 3b) reveals, in addition to the signal corresponding to the PF₆⁻ anion at -144.60 ppm and that of **3 a-Cl⁺.PF₆⁻** at -19.48 ppm, the presence of a doublet at -43.16 ppm with a

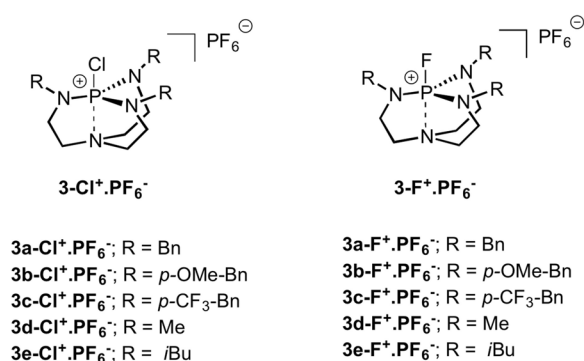


Figure 2. Structures of the starting chloroazaphosphatranes (left) and synthesized fluoroazaphosphatranes (right).

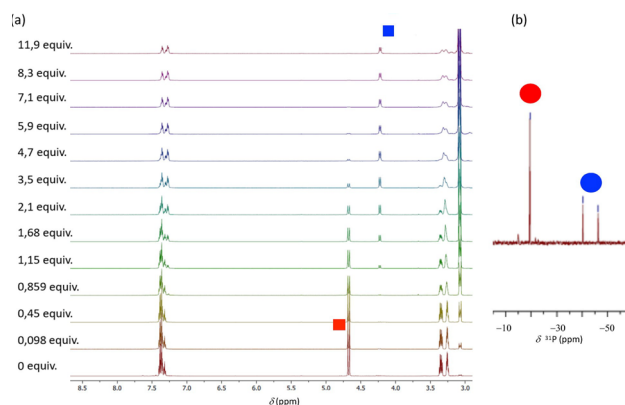


Figure 3. (a) ¹H NMR spectra of the titration of **3 a-Cl⁺.PF₆⁻** (5 mM) upon progressive addition of F⁻ (as a 50 mM solution of TBAF salt) in CD₃CN (600 MHz). N-CH₂-Ph signal of **3 a-Cl⁺**; N-CH₂-Ph signal of **3 a-F⁺**. (b) ³¹P NMR spectrum after the addition of 4 equivalents of TBAF in CD₃CN (121 MHz), phosphorus signal of **3 a-Cl⁺** (red); phosphorus signal of **3 a-F⁺** (blue).

coupling constant $J^{\text{PF}} = 733.3$ Hz, corresponding to the formation of the fluoroazaphosphatrane **3 a-F⁺.PF₆⁻** salt. The ¹⁹F NMR spectrum also displayed a doublet at -70.65 ppm with a coupling constant of 736.0 Hz, attributed to the **3 a-F⁺** cation (Figure S4). The mass spectrum also supports the formation of this species, with the expected exact mass of 463.5 for the **3 a-F⁺** cation (figure S60). Indeed, a small nucleophilic ion can attack the electrophilic P centre of the five-coordinate azaphosphatrane as previously proposed by J. G. Verkade, D. Stephan and our group.^[7,14,15,16] The resulting six-coordinate transition state or intermediate can then give rise to the fluoroazaphosphatrane derivative. These results demonstrate the formation of the **3 a-F⁺.PF₆⁻** salt during the titration experiment. Interestingly, no degradation of the **3 a-F⁺** cation was evidenced during these titration experiments, although the formation of PF₆⁻ anion by decomposition of this cation could not be fully ruled out because of its presence in the initial mixture. The same set of experiments were performed using **3 d-Cl⁺.PF₆⁻** as receptor, also corroborating the formation of the **3 d-F⁺** cation during the titration experiments (Figures S56 and S57). Thus, fluoroazaphosphatranes could be readily obtained by a nucleophilic attack of the fluoride anion on the phosphorus atom of **3 a-Cl⁺** cation. Therefore, the optimization of the reaction conditions was then carried out to provide a clean access to pure fluoroazaphosphatranes.

Optimization of the synthetic procedure and scope of the reaction

We first used the conditions close to those described above for the titration experiments. Six equiv. of TBAF were added to a solution of **3 a-Cl⁺.PF₆⁻** salt in acetonitrile and stirred for 3 h at room temperature. The ¹H and ³¹P NMR spectra of the crude mixture showed a total conversion and high selectivity since no other byproducts can be detected. However, the resulting **3 a-F⁺.PF₆⁻** was difficult to isolate from the mixture, possibly

because the excess of TBAF added and the TBACl formed were difficult to remove. Thus, NaF salt was chosen as fluoride source, but under the same conditions, no reaction was observed and the starting material was fully recovered. To solve the solubility issue of the NaF salt that was possibly responsible for this lack of reactivity, CsF salt was used instead. However, only traces of the expected **3 a-F⁺.PF₆⁻** were observed in the ¹H and ³¹P NMR spectra. Thus, to increase both the reaction rate and the solubility of the fluoride source, the reaction was heated to reflux (82 °C). After 3 h, a partial conversion of 18% was reached, which could be significantly improved by extending the reaction time to 18 h. Thus, under these reaction conditions (18 h, 82 °C, 6 equiv. CsF), full conversion of the chloroazaphosphatranes **3 a-Cl⁺.PF₆⁻** was obtained, affording pure **3 a-F⁺.PF₆⁻** in 92% isolated yield.

With this procedure in hand, we decided to investigate the scope of this reaction. Thus, this reaction was tested on chloroazaphosphatranes bearing benzyl substituents with electron-donating or -withdrawing groups in para position in order to address the electronic effect on the reactivity of the phosphorus center (Table 1). The introduction of a methoxy group led to a drop-in yield (70%, entry 2, Table 1), probably because it decreases the electrophilicity of the cationic phosphorus. On the other hand, with a CF₃ unit on the benzyl, an improvement in the yield was reached (98%, entry 3, table 1), the increased electrophilicity of the phosphorus center making the nucleophilic attack of the fluoride anion easier. We then investigated whether fluoroazaphosphatranes could be obtained by this way when alkyl substituents were grafted onto the equatorial nitrogen instead of benzyl ones. Compound **3 d-F⁺.PF₆⁻**, with methyl substituents, was synthesized in good yield (87%, entry 4, table 1). However, a decrease of the yield

was obtained when **3 e-Cl⁺.PF₆⁻** with iso-butyl groups on the equatorial nitrogen atoms was used as substrate (57%, entry 5, table 1) and the formation of phosphine oxide could be observed in the ³¹P NMR spectrum of the crude mixture at δ ³¹P = 20.99 ppm (Figure S19). The steric hindrance of this functional group could account for this change in the reactivity: the formation of the fluoroazaphosphatranes derivative is probably more difficult, and side reactions could not be avoided. Thus, the present method allowed for the synthesis of fluoroazaphosphatranes with various substituents, providing three new fluoroazaphosphatranes in addition to those previously reported. Full characterization of compounds **3 a-e-F⁺.PF₆⁻** by NMR (¹H, ¹³C, ³¹P, ¹⁹F) and HRMS analyses are displayed in Supporting Information.

Characterizations

The ³¹P and ¹⁹F NMR spectra of the fluoroazaphosphatranes display δ ³¹P between - 41.8 and - 43.5 ppm and δ ¹⁹F between - 72.9 and - 69.7 ppm, respectively. Thus, these chemical shifts appear weakly sensitive to the nature of the substituents linked to the equatorial nitrogen atoms as previously observed for the chloroazaphosphatranes derivatives.^[13] This suggests that they probably display similar structure around the phosphorus atom, with close values of P- F, P-N_{eq} and P-N_{ax} bond lengths and the C-N_{ax}-P-N_{eq} dihedral angles.

Crystals of **3 a-F⁺.PF₆⁻** and **3 c-F⁺.PF₆⁻** suitable for X-ray crystallography analysis were obtained by crystallization in a mixture of Et₂O/CH₂Cl₂. The corresponding structures are shown in Figure 4 and details are given in Supporting Information. As observed previously in the structures of aza- and chloroazaphosphatranes, the apical nitrogen adopts a pseudo-pyramidal geometry whereas the phosphorus atom presents a pseudo-trigonal bipyramidal one (Table 2). Moreover, these structures display similar P- F, P- N_{ax} and P- N_{eq} bond lengths (1.59–1.60 Å;

Table 1. Substrate scope of the synthesis of fluoroazaphosphatranes				
Entry	Substrate	R	Product	Yield ^[a]
1	3 a-Cl⁺.PF₆⁻	Bn	3 a-F⁺.PF₆⁻	92%
2	3 b-Cl⁺.PF₆⁻	<i>p</i> -OMe-Bn	3 b-F⁺.PF₆⁻	70%
3	3 c-Cl⁺.PF₆⁻	<i>p</i> -CF ₃ -Bn	3 c-F⁺.PF₆⁻	98%
4	3 d-Cl⁺.PF₆⁻	Me	3 d-F⁺.PF₆⁻	87%
5	3 e-Cl⁺.PF₆⁻	<i>i</i> -Bu	3 e-F⁺.PF₆⁻	57%

[a] Isolated yield.

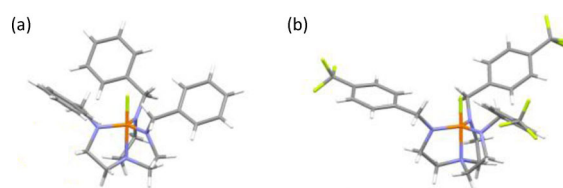


Figure 4. X-ray molecular structures of **3 a-F⁺** (a) and **3 c-F⁺** (b) cations.

Table 2. Selected crystallographic parameters for 3 a-F⁺ , 3 c-F⁺ and 3 d-Cl⁺ cations.						
	<i>d</i> _{Pf} [Å]	<i>d</i> _{PN_{ax}} [Å]	<i>d</i> _{PN_{eq}} [Å]	∑ Neq - P - Neq [deg]	∑ C - N _{ax} - C [deg]	dihedral angle C-N _{ax} -P-N _{eq} [deg]
3 a-F⁺ ^[a]	1.594(2)	1.921(3)	1.662(3)	359.1(2)	336.1	29.3(3)
3 c-F⁺ ^[a]	1.592(3)	1.918(5)	1.663(4)	359.2(2)	339.8	27.7(4)
3 d-F⁺ ^{[14] [b]}	1.601	1.932	1.658	359.3	336.0	23.4
3 e-F⁺ ^{[12] [c]}	1.600	1.920	1.660	359.3	337.5	27.9
3 c-Cl⁺ ^[13]	2.112 ^[d]	1.960	1.662	358.3	339.6	32.8

[a] PF₆⁻ as counterion; [b] FBPh₃⁻ as counterion; [c] HF₂⁻ as counterion; [d] *d*_{P-Cl} (Å).

1.92–1.93 Å and 1.66 Å respectively, Table 2). Furthermore, the three five-membered-rings of the fluoroazaphosphatranes exhibit a propeller arrangement in both structures with $C-N_{ax}-P-N_{eq}$ dihedral angles between 23.4° and 29.9° . It can be underlined that these structural features are closed to those observed for haloazaphosphatranes (except for the $P-X$ bond),^[13,14] showing that the halide as a weak influence on the geometric structure of the azatrane unit.

Reactivity of fluoroazaphosphatranes

With this convenient access to fluoroazaphosphatranes in hand we decided to investigate the properties of this class of compounds as reactant or catalyst. We have previously observed that iodo- and bromo-azaphosphatranes are more sensitive to nucleophilic solvent, like water or alcohol, than chloroazaphosphatranes.^[13] We hypothesized that fluoroazaphosphatranes might be more robust cations than their chlorinated parents, therefore **3 a-F⁺.PF₆⁻** and **3 a-Cl⁺.PF₆⁻** salts were dissolved in 0.4 mL of deuterated acetonitrile and 10 drops of water were added at room temperature. After 3 hours, new signals, that can be probably assigned to azaphosphatrane **2 a-H⁺.PF₆⁻** and **1 a=O** species,^[17] appeared in the ³¹P NMR spectrum of **3 a-Cl⁺.PF₆⁻** at respectively - 0.16 and 19.42 ppm (Figure 5 and Figure S64). In contrast, the ³¹P NMR spectrum of **3 a-F⁺.PF₆⁻** remained unchanged under the same conditions (Figures 5 and S62) supporting that no decomposition of this

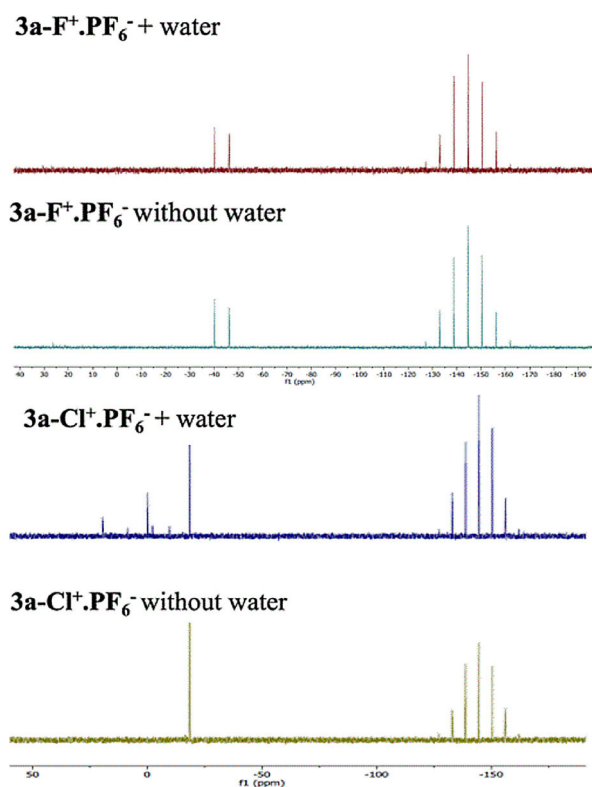


Figure 5. ³¹P NMR spectra of chloro- and fluoro-azaphosphatranes with or without water.

cation occurred. Thus, fluoroazaphosphatranes appear more robust cations than other haloazaphosphatranes. This prompted us to examine the potential catalytic behavior of this class of compound.

We have previously demonstrated that azaphosphatranes are efficient single component, metal-free catalysts for the conversion of CO₂ into cyclic carbonates in the presence of epoxides.^[10] Detailed kinetic studies allowed us to propose a mechanism involving the activation of epoxide and CO₂ by hydrogen bonding and insertion into the P–N bond of the azaphosphatrane molecule respectively.^[10] Although the hydrogen bonding with the phosphonium cation is not possible with fluoroazaphosphatranes, an activation pathway of both the CO₂, through its insertion into the P–N bond, and the epoxide, via electrostatic interactions or Lewis adduct formation, could occur.

Indeed, in the case of fluoroazaphosphatranes, the phosphorus atom could act as a Lewis acid site to activate the epoxide. The Lewis acidity of the phosphorus atom in **3 a-F⁺.PF₆⁻** was therefore determined using the Gutmann-Beckett method (see Supporting Information for details).^[18] The change in the ³¹P NMR chemical shift of triethylphosphine oxide (TEPO) in the presence of **3 a-F⁺.PF₆⁻** allowed calculating a Gutmann acceptor number of 21.72, showing the modest acidity of this compound to activate the epoxide by formation of a Lewis adduct. Then, we tested the activity of fluoroazaphosphatranes as organocatalysts using the coupling of CO₂ with styrene oxide as a model reaction. Chloride anion was chosen as counterion instead of PF₆⁻ because of its key role in the reaction mechanism, i.e., the nucleophilic attack of the chloride at the secondary carbon of the epoxide. The synthesis and full characterization of **3 a-eF⁺.Cl⁻** analogues by NMR (¹H, ¹³C, ³¹P, ¹⁹F) and HRMS analyses are given in Supporting Information. The reactions were carried out at 100 °C under solvent-free conditions, using 0.5 mol% of catalyst. Azaphosphatrane catalysts were also tested under the same conditions allowing for a direct comparison between the two systems. Table 3 shows the turnover number (TON) obtained after 24 hours. Fluoroazaphosphatranes exhibit catalytic activity in the same range of values as those of azaphosphatranes (TON between 35 and 131 for

Table 3. Compared catalytic activity of fluoroazaphosphatranes and azaphosphatranes.^[a]

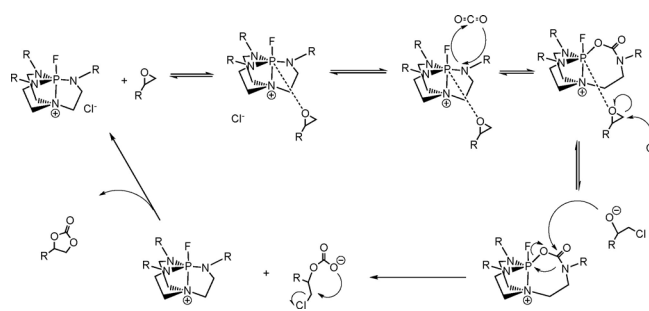
Entry	Catalyst	R	TON ^[b]
1	3 a-F⁺.Cl⁻	Bn	131 (120) ^[c]
2	2 a-H⁺.Cl⁻	Bn	168
3	3 b-F⁺.Cl⁻	<i>p</i> -OMe-Bn	98 (82) ^[c]
4	2 b-H⁺.Cl⁻	<i>p</i> -OMe-Bn	81
5	3 c-F⁺.Cl⁻	<i>p</i> -CF ₃ -Bn	62 (59) ^[c]
6	2 c-H⁺.Cl⁻	<i>p</i> -CF ₃ -Bn	56
7	3 d-F⁺.Cl⁻	Me	90 (81) ^[c]
8	2 d-H⁺.Cl⁻	Me	153
9	3 e-F⁺.Cl⁻	<i>i</i> -Bu	35 (34) ^[c]
10	2 e-H⁺.Cl⁻	<i>i</i> -Bu	100

[a] Conditions: Styrene oxide (2.0 mmol), catalyst (0.01 mmol), CO₂ (1 atm), T = 100 °C. [b] TON were determined by ¹H NMR spectroscopy using 2,4-dibromomesitylene (0.2 mmol) as an internal standard. [c] TON based on isolated cyclic carbonate.

fluoroazaphosphatranes and between 56 and 168 for corresponding azaphosphatranes). This is consistent with the previously proposed mechanism, where the insertion of CO₂ into the P–N bond is probably the rate determining step for both systems, hence leading to similar catalytic performance. The effect of the steric and electronic properties of the fluoroazaphosphatranes on their catalytic properties has then a TON of 131 (entry 1, Table 3). Introduction of either electron-withdrawing or -donating groups in the para position of the benzyl groups led to a decrease of the TON (TON=62 and 98 respectively, entries 5 and 3, Table 3). It can be noted that a similar trend was observed with azaphosphatrane derivatives (entries 4 and 6, Table 3). With bulky isobutyl substituents on the equatorial nitrogen atoms, the catalytic activity of **3 e-F⁺.Cl⁻** dropped with a TON of 35 (entry 9, Table 3) whereas that of **2 e-H⁺.Cl⁻** remained high (TON=100, entry 10, Table 3). The steric hindrance around the phosphorous center could account for this experimental result. Indeed, the X-ray molecular structures of fluoroazaphosphatranes revealed hydrogen bonding between the CH₂ linked to the N_{eq} atoms and the fluorine atom. Such intramolecular interactions are not present in the solid state of the azaphosphatrane parents. This specific arrangement of the linkers might be retained in solution, inducing a bulkier environment around the reactive center that probably limits the CO₂ insertion into the P–N bond. The formation of di(phenylethanol)ether as the major byproduct of this reaction arose from the condensation of two molecules of epoxide, supporting that the CO₂ was not well activated by this fluoroazaphosphatrane bearing isobutyl substituents. The increase in the catalytic activity using **3 d-F⁺.Cl⁻** with less bulky methyl substituents supports this assumption (TON=90, entry 7, Table 3).

In order to get more information on the activation of the epoxide by the fluoroazaphosphatrane, the calculation of the electrostatic potential of **3 d-F⁺** was carried out and shows that the phosphorus atom exhibits a high positive charge (Figure S69). The determination of the frontier orbitals of **3 d-F⁺** shows that the LUMO is accessible and highly developed on the phosphorus atom. In the light of these elements, we propose a mechanism where the activation of the epoxide mainly occurs via coordination of the oxygen atom to the phosphorus atom through both orbital and electrostatic interactions. The hydrogens of the C–H bonds of the NCH₂CH₂N linkers also exhibit partial positive charges and can be also involved in the activation process. Then, the activated epoxide is opened by nucleophilic attack of the chloride anion leading to the formation of an alcoholate. It can then react with CO₂ yielding the anionic carbonate which is then cyclized with regeneration of the catalyst (Scheme 1).

Furthermore, ³¹P and ¹⁹F NMR spectra of the crude mixtures were performed at the end of the reactions in order to address the stability of the fluoroazaphosphatranes. Only the signals corresponding to **3 a-F⁺.Cl⁻** could be observed in the NMR spectra; in particular no peaks arising from other phosphorus species could be detected, demonstrating the high stability of this fluoroazaphosphatrane-based organocatalysis under these conditions (figures S66 and S67). In addition, this also evidences



Scheme 1. Proposed mechanism for the synthesis of cyclic carbonates

that the catalytic activity is not related to the formation of azaphosphatrane derivatives which could be obtained by the in-situ decomposition of the fluoroazaphosphatranes.

Conclusion

In conclusion, we have described a new and straightforward method to obtain fluoroazaphosphatranes directly from the chloroazaphosphatranes by nucleophilic substitution with CsF. The substrate scope of this synthetic route has been investigated, and fluoroazaphosphatranes with various substituents have been obtained. X-ray structures of fluoroazaphosphatranes displayed similar features than those of their chloroazaphosphatrane parents. Additionally, fluoroazaphosphatranes were shown to be more robust cations than their chlorinated counterparts, allowing them to be used as organocatalysts for the conversion of CO₂ into cyclic carbonates. Fluoroazaphosphatranes exhibit catalytic activities for this reaction similar to those of azaphosphatranes, but more importantly appeared as more stable catalytic systems since no decomposition of the spent catalyst was observed. This new methodology opens up new way for other development of applications of this class of compounds, that are under study in our laboratory.

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