Bifunctional Fluorophosphonium Triflates as Intramolecular Frustrated Lewis Pairs: Reversible CO₂ Sequestration and Binding of Carbonyls, Nitriles and Acetylenes

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Dedicated to Professor Gerhard Erker on the occasion of his 75th birthday

Abstract: Electrophilic fluorophosphonium triflates bearing pyridyl (3[OTf]) or imidazolyl (4[OTf])-substituents act as intramolecular frustrated Lewis pairs (FLPs) and reversibly form 1:1 adducts with CO₂ (5⁻ and 6⁻). An unusual and labile spirocyclic tetrahedral intermediate (7⁺) is observed in CO₂-weekpressurized (0.5–2.0 bar) solutions of cation 4⁺ at low temperatures, as demonstrated by variable-temperature NMR studies, which were confirmed crystallographically. In addition, cations 3⁻ and 4⁺ actively bind carbonyls, nitriles and acetylenes by 1,3-dipolar cycloaddition, as shown by selected examples.

The selective, reversible binding of carbon dioxide (CO₂) and its transformation into value-added chemicals and materials is a challenge of today and success would significantly contribute to decline CO₂ accumulation in the atmosphere.[1] The chemistry of CO₂ binding and transformation receives tremendous attention as it is regarded as an important heat-trapping (greenhouse) gas[2] but at the same time considered as readily available, abundant, nontoxic, and renewable C₁ synthon in synthesis.[3] In this context, generous efforts continue to be devoted to the development of efficient physical or chemical CO₂ activation approaches.[1a,4] A key-step in the capture-and-release application for the conversion of CO₂[5] is usually hampered by the fact that the majority of FLPs form stable adducts with CO₂.[1a,6] Efforts towards binding of CO₂ by highly Lewis acidic amidophosphoranes were reported by the Stephan group (Scheme 1, V).[8] Although phosphonium cations have been extensively studied for their electrophilic properties, their application as Lewis acid in FLP chemistry is scarcely investigated so far. In thought of using fluorophosphonium cations in FLP chemistry, where in contrast to known systems the P atom is the Lewis acidic site, two different strategies are feasible: either the addition of a Lewis base to the Lewis bases were developed that are capable of forming adducts with the CO₂ molecule.[6] Notably, a variety of frustrated Lewis pairs (FLPs) have been investigated towards CO₂ sequestration including inter- (I, II)[7] and intramolecular (III,IV)[8] FLPs derived from different combinations of electrophiles (e.g., borane-, aluminum-, or silylium-based) and nucleophiles (e.g., phosphines, carbenes, or amines; Scheme 1). However, the key step in a capture-and-release application for the conversion of CO₂[5] is usually hampered by the fact that the majority of FLPs form stable adducts with CO₂[1a,6] Efforts towards binding of CO₂ by highly Lewis acidic amidophosphoranes were reported by the Stephan group (Scheme 1, V).[8] Although phosphonium cations have been extensively studied for their electrophilic properties, their application as Lewis acid in FLP chemistry is scarcely investigated so far. In thought of using fluorophosphonium cations in FLP chemistry, where in contrast to known systems the P atom is the Lewis acidic site, two different strategies are feasible: either the addition of a Lewis base to the Lewis bases were developed that are capable of forming adducts with the CO₂ molecule.[6] Notably, a variety of frustrated Lewis pairs (FLPs) have been investigated towards CO₂ sequestration including inter- (I, II)[7] and intramolecular (III,IV)[8] FLPs derived from different combinations of electrophiles (e.g., borane-, aluminum-, or silylium-based) and nucleophiles (e.g., phosphines, carbenes, or amines; Scheme 1). However, the key step in a capture-and-release application for the conversion of CO₂[5] is usually hampered by the fact that the majority of FLPs form stable adducts with CO₂[1a,6] Efforts towards binding of CO₂ by highly Lewis acidic amidophosphoranes were reported by the Stephan group (Scheme 1, V).[8] Although phosphonium cations have been extensively studied for their electrophilic properties, their application as Lewis acid in FLP chemistry is scarcely investigated so far. In thought of using fluorophosphonium cations in FLP chemistry, where in contrast to known systems the P atom is the Lewis acidic site, two different strategies are feasible: either the addition of a Lewis base to the Lewis bases were developed that are capable of forming adducts with the CO₂ molecule.[6] Notably, a variety of frustrated Lewis pairs (FLPs) have been investigated towards CO₂ sequestration including inter- (I, II)[7] and intramolecular (III,IV)[8] FLPs derived from different combinations of electrophiles (e.g., borane-, aluminum-, or silylium-based) and nucleophiles (e.g., phosphines, carbenes, or amines; Scheme 1). However, the key step in a capture-and-release application for the conversion of CO₂[5] is usually hampered by the fact that the majority of FLPs form stable adducts with CO₂[1a,6] Efforts towards binding of CO₂ by highly Lewis acidic amidophosphoranes were reported by the Stephan group (Scheme 1, V).[8] Although phosphonium cations have been extensively studied for their electrophilic properties, their application as Lewis acid in FLP chemistry is scarcely investigated so far. In thought of using fluorophosphonium cations in FLP chemistry, where in contrast to known systems the P atom is the Lewis acidic site, two different strategies are feasible: either the addition of a Lewis base to the
fluorophosphonium salt or designing a fluorophosphonium derivative with an intramolecular Lewis basic site.

Herein, we present the synthesis of pyridyl- and imidazolyl-substituted fluorophosphonium triflate salts and their application as intramolecular N/P FLP systems. Both compounds readily substituited fluorophosphonium triflate salts and their application as intramolecular N/P FLP systems. Both compounds readily
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To illustrate our approach, we first reacted fluorophosphonium salt 1[OTf][10] as a very strong Lewis acid in combination with pyridine as a Lewis base and p-tolylaldehyde in CH₂Cl₂ (Scheme 2).[10] The formation of adduct 2⁺ is indicated by multinuclear NMR spectroscopy and the ³¹P NMR spectrum displays a doublet resonance at δ(P) = -53.2 ppm (Jₚν = 644 Hz) being well in the range for penta-coordinate P atoms. X-ray analysis of 2[OTf] confirms that the Lewis acidic P atom of the fluorophosphonium cation and Lewis basic N atom of the pyridine act cooperatively acts as an intermolecular FLP system activating the carbonyl group of the aldehyde (Figure 1). The corresponding P1–O₁ and C₁–N₁ distances are 1.7038(10) Å and 1.5206(17) Å, respectively. The C₁–O₁ distance of 1.3974(16) Å is about 0.2 Å longer compared to the C–O double bond in free aldehydes.[11] However, the application of this intermolecular FLP system is limited as we observed the decomposition of 1[OTf] in the presence of pyridine without a suitable substrate.

We therefore targeted the synthesis of bifunctional fluorophosphonium salts such as 3[OTf] and 4[OTf] which contain a pyridyl- or imidazolyl-substituent, respectively. The synthesis follows our recently reported one-pot procedure, where N-

![Image](image-url)

**Scheme 2.** Adduct formation of 2[OTf] from the reaction of 1[OTf] with pyridine and p-tolylaldehyde: i) pyridine (1 equiv.), p-tolCHO (1 equiv.), CH₂Cl₂, RT, 4 h.

**Figure 1.** Molecular structure of 2[OTf]: CH₂Cl₂ (hydrogen atoms, CH₂Cl₂ and non-coordinating anions are omitted for clarity, ellipsoids are set at 50% probability); Selected bond lengths (Å) and angles (°): P1–O1 1.7038(10), O1–C1 1.3974(16), C1–N1 1.5206(17).

fluorobenzensulfonylimide (NFSI) is added to the corresponding phosphane (C₆F₅)₃PR (R = imidazolyl, pyridyl), followed by the addition of MeOTf (Scheme 3).[11] Triflate salts 3[OTf], 4[OTf] are isolated as colorless, air- and moisture-sensitive salts in very good yields of >88%.[12] We started to investigate the cooperative properties of these salts by pressurizing degassed CD₃Cl solutions with CO₂ (2 bar). The corresponding ³¹P and ¹⁹F NMR spectra of the solution containing 3[OTf] reveal no interaction or reaction at ambient temperature indicated by the resonances for cation 3⁺ (δ(P) = 54.8 ppm, δ(F) = -114.0 ppm, Jₚν = 966 Hz) in the spectra. However, a VT NMR investigation disclosed the reversible and temperature-dependent binding of CO₂ by 3[OTf] (Figure 2, left).

The ³¹P NMR spectrum at 263 K shows, next to the dominant signal of the free cation 3⁺ (98%), a small high field shifted doublet resonance at δ(³¹P) = -55.5 ppm (2 %, Jₚν = 769 Hz), which is well in the region for a penta-coordinate phosphorus atom, thus, indicating the formation of the CO₂ adduct 5[OTf]. The corresponding resonance in the ¹⁹F NMR spectrum is detected as a downfield shifted doublet resonance at δ(¹⁹F) = -30.0 ppm. When the temperature is further decreased to 213 K the integral ratio of 5[OTf] increases to 41:59. The carbon atom of the bound CO₂ is observed as a doublet resonance at δ(C₂) = 141.8 ppm (J₁₂ = 3 Hz). Further decrease of the temperature to 193 K leads to the separation of a colorless precipitate, suggesting that 5[OTf] exhibits a reduced solubility in CD₃Cl at low temperature. Accordingly, gradually increase to RT leads to the dissolution of 5[OTf] and its disappearance in the NMR spectrum. This process is reversible without decomposition of 3[OTf]. We investigate this interaction of 3[OTf] with CO₂ theoretically with two different models (Figure 3). In 3⁻⁻CO₂A, CO₂ is activated by the incorporation of both the Lewis acidic and the Lewis basic site, whereas in model 3⁻⁻CO₂B the activation exclusively proceeds through the Lewis acidic P atom. The CO₂ binding energy is slightly stronger for model 3⁻⁻CO₂A (−20.4 kJ/mol) than model 3⁻⁻CO₂B (−18.4 kJ/mol). Moreover, the calculated ³¹P NMR chemical shift change (Δδ(³¹P) = 124 ppm) is in the range of the experimental result (Δδ(³¹P) = −110.7 ppm), while the calculated Δδ(¹⁹F) for model 3⁻⁻CO₂B is only shifted by −17 ppm which is not observed in the respective ³¹P NMR spectrum. Thus, the CO₂ activation is proposed to proceed via the P and pyridyl N atoms, affording 5[OTf] in the configuration of model 3⁻⁻CO₂B. As the DFT
calculation reveals a slightly improved CO₂ binding energy (−23.0 kJ/mol) for 4[OTf], we also investigated the reactivity of 4[OTf] towards CO₂ (Figure 3). Pressurizing a degassed CH₃Cl₂ solution of 4[OTf] with CO₂ (0.5 bar) at ambient temperature results in the immediate formation of a colorless solid. However, the solid re-dissolves immediately after releasing the pressure and all our separation attempts ended up with the recovery of 4[OTf]. We therefore monitored the reaction of 4[OTf] towards CO₂ (2.0 bar CO₂ pressure did not show significant difference on the calculated binding energy). The reaction of 4[OTf] with CO₂ (1.5 bar) by NMR spectroscopy in degassed CD₃NO₂ solution at ambient temperature shows signals of two different adducts at δ₁³P = −60.0 ppm (Jₚ &= 737 Hz, 5 %) and δ₁³P = −61.5 ppm (Jₚ &= 740 Hz, 14 %) besides the signal of 4[OTf] (δ₁³P = 55.2 ppm, δ₁³F = −111.5 ppm, Jₚ &= 1045 Hz, Figure 2, right). The corresponding signals in the ¹³C NMR spectrum are detected at δ₁³C = −8.1 ppm (Jₚ &= 737 Hz) and δ₁³C = −16.9 ppm (Jₚ &= 740 Hz), respectively. Interestingly, the ¹³C NMR spectrum displays two signals for the bound CO₂ moiety at δ₁³C = −139.9 ppm (Jₚ &= 7 Hz) as a doublet resonance and at δ₁³C = −105.5 ppm (Jₚ &= 8 Hz) as a triplet resonance suggesting a coupling to two phosphorus atoms.¹³ This strongly indicates the formation of a 1:1 FLP-CO₂ adduct 6[OTf] (δ₁³P = −61.5 ppm, δ₁³F = −16.9 ppm, Jₚ &= 740 Hz) and a 2:1 FLP-CO₂ adduct 7[OTf] (δ₁³P = −60.0 ppm, δ₁³F = −8.1 ppm, Jₚ &= 737 Hz). The ¹³P NMR chemical shift change of 6[OTf] (Δδ₁³P = −6(4°)−δ(6°), −116.7 ppm) is well in the range of calculated model 4° -CO₂ - A (Δδ₁³P = −108 ppm). Decreasing the temperature stepwise to 243 K, the integral ratio of 7[OTf] gradually increases to 66 %, while the integral ratio of 6[OTf] increases to 28 %. Variable-temperature NMR studies at 0.5 or 2.0 bar CO₂ pressure did not show significant difference on the integral ratio of 6[OTf] and 7[OTf]. Although the calculated electrophilicities are similar for 3[OTf] (GEI = 3.164 eV, FIA = 748.0 kJ/mol) and 4[OTf] (GEI = 3.121 eV, FIA = 743.8 kJ/mol),¹⁰ in no case do we observe a double activation of CO₂ with 3[OTf]. This suggests that a certain nucleophilicity of the Lewis basic site is crucial for the formation of the 2:1 FLP-CO₂ adduct 7[OTf].¹⁴ To our delight, we were able to obtain extremely sensitive but suitable co-crystals containing both cations 6° and 7°⁺ by vapor diffusion of CH₃Cl₂ into a CH₃NO₂ solution of 4[OTf] under CO₂ atmosphere (0.5 bar) at −30 °C (Figure 4). Although the double activation of CO₂ has been reported with FLPs based on hafnium (VI) and aluminum (VII) complexes (Scheme 4),¹³¹⁵ the tetrahedral cation 7°⁺ represents the only crystallographically characterized example of a metal-free 2:1 FLP-CO₂ adduct.
The molecular structure of $6^+$ which is consistent with the optimized structure $4^+\cdot CO_2^-$, A, shows that a CO fragment of the CO$_2$ is integrated into a five-membered PNC heterocycle while the other O atom is exocyclic. The CO$_2$ moiety is bent, giving an O1–C1–O2 angle of 128.1(7). One oxygen is bound by the Lewis acidic P atom with a P–O1 bond length of 1.773(5) Å and the carbon atom is stabilized by the Lewis basic N atom to give a N1–C1–O2 bond length of 1.442(10) Å. The C1–O1 (1.307(8) Å) and C1–O2 (1.206(10) Å) bond lengths in the CO$_2$ fragment are comparable to other FLP-CO$_2$= (P) = 1.21 Å). When P–O1 bond lengths (P1–O1 1.21 Å), $6^+$ is captured by two cations 4$^+$ resulting in a distorted tetrahedral geometry of the central carbon atom. The P–O bond lengths (P1–O1 1.771(4) Å, P2–O2 1.744(4) Å) are similar to those of $6^+$. The C–O bonds (O1–C1 1.352(7) Å, O2–C3 1.366(6) Å) are both significantly longer than those in $6^+$, but comparable to those reported for the hafnium based FLP-CO$_2$ adduct VI (1.383 and 1.369 Å, Figure 4).[15]

Inspired by these results, further studies concerned the 1,3-dipolar cycloaddition of salts 3,4(OTf) with carboxyls, nitriles, and acetylenes to the respective heterocycles (Scheme 5). At room temperature, the formation of acetone adducts 8a,b(OTf) ($8a^+/8b^+$: $\delta^{13}$P$= -52.0$–$-60.0$ ppm, $\delta^{13}$F$= -6.5/9.6$ ppm, $\nu_{PF}= 734/696$ Hz, 97 and 84% isolated yield) and acetonitrile adducts 9a,b(OTf) ($9a^+/9b^+$: $\delta^{13}$P = $-49.3$–$-65.0$ ppm, $\delta^{13}$F = $3.0/19.9$ ppm, $\nu_{PF}= 738/702$ Hz, 71 and 95% isolated yield) are indicated by multinuclear NMR spectroscopy (Table 1) and are isolated in good to excellent yields after workup. The carbonyl carbon atoms in 8a,b(OTf) ($8a^+/8b^+$: $\delta^{13}$C$= 101.8$–$96.7$ ppm, $\nu_{CO}= 99/111$ Hz) are significantly shifted to higher field compared to the free acetone (C$= 207$ ppm). The nitrile carbon atoms in 9a,b(OTf) are shifted to lower field (9a$^+/9b^+$: $\delta^{13}$C = 151.0/150.2 ppm, $\nu_{CN}= 18/19$ Hz). Interestingly, when compounds 9a,b(OTf) are reacted with acetonitrile at room temperature, the formation of 8a,b(OTf) under release of CH$_2$CN is observed after a reaction time of 1 h (Scheme 5, ii). The quantitative exchange is indicated by the clean shift of the corresponding doublet resonance in the $^{31}$P NMR spectrum of the reaction mixture.

When 3,4(OTf) are reacted with acetonitrile in dichloroethane (DCE) at room temperature for 4 h, the formation of 10a,b and 11a,b(OTf)$_2$ is observed, while 12a,b(OTf) are cleanly formed by fluoride abstraction from 10a,b to 11a,b$^{2+}$ after reacting at 80 °C overnight or at ambient temperature for
2 weeks (Scheme 5, iii–v). Cation 11a+ ([GEI] = 7.408 eV, FIA = 1066.9 kJ/mol) is more Lewis acidic than 3+ ([GEI] = 3.164 eV, FIA = 748.0 kJ/mol), thus, low reaction tendency from 11a.b to 12a,b seems to be influenced by solvent effects, which significantly decrease the Lewis acidity compared to the gas phase calculations.\(^{[15,16]}\) 11a.b[OTf] are found as singlet resonances in the \(^1\)P NMR spectra at \(\Delta (^{19}\)P) = 6.9 and \(-15.0\) ppm, while 12a,b[OTf] are observed as doublet resonances in the \(^3\)P and \(^{19}\)F NMR spectra (12a+/12b+ : \(\Delta (^{19}\)P) = \(-88.8/-98.8\) ppm, \(\Delta (^{19}\)F) = 34.0/25.2 ppm, \(\nu_{\text{as}} = 707/718\) Hz, Table 1). We were able to isolate 11a[OTf][\(\nu\)] (78%) and 12b[OTf] (66%) as pure products for full characterization.

The molecular structures of compounds 8a,b,9a,b-[OTf] and 12b[OTf] are confirmed by X-ray analyses of suitable single crystals which were obtained by slow vapor diffusion of n-pentane into saturated CHCl\(_3\) solutions at \(-30\, ^\circ\text{C}\) (Figure 5). All obtained structures show a distorted trigonal-bipyramidal bonding environment at the P atom and display the expected five-membered heterocycles with angle sum ranging from 536.8° to 540.0° (Table 2). In the structures of 8a,b+ and 9a,b+, the heteroatoms (O, N) and the fluorine atoms occupy the axial position. The P–F bonds (1.637(2)–1.673(3) Å) are elongated compared to those of the starting materials \(^3\) and \(^4\)+, but comparable to those in difluorophosphoranes (e.g., C\(_3\)F\(_3\))PF\(_2\): 1.638(2) Å.\(^{[20]}\) The resulting P-heteroatom distances in the acetone adducts (8a+/8b+ : 1.695(2)/1.695(3) Å) are significantly shorter compared to the acetonitrile adducts (9a+/9b+ : 1.777(2)/1.788(2) Å) while the C–N bonds are around 0.15 Å longer (8a+/8b+ : 1.495(4) Å/1.411(5) Å, 9a+/9b+ : 1.250(3)/1.272(3) Å, Table 2).

The C–O bond lengths of the carbonyl moiety 8a+/8b+ : 1.495(4)/1.411(5) Å and the C–N distances of the nitrile moiety (9a+/9b+ : 1.250(3)/1.272(3) Å) are typical for C–O single bonds and C–N double bonds, respectively.\(^{[11]}\) The structure of 12b+ shows that the pyridyl moiety is in the axial position, opposite to the fluorine atom (Figure 5). Thus, the terminal carbon atom of the alkyne occupies one of the equatorial positions adopting the minimum energy configuration due to steric restraints. The newly formed P1–C1 bond distance (1.790(6) Å) and the N1–C2 bond distance (1.414(6) Å) are comparable to those in the acetonitrile adduct 9b+ (Table 2). The C1–C2 bond length (1.330(8) Å) is well in the range of a typical C=C double bond.\(^{[11]}\)

Deposition Numbers 2061971 (for 4[OTf]·CH\(_2\)Cl\(_2\)), 2061971 (for 2[OTf]), 2061972 (for 3[OTf]·CH\(_2\)F\(_2\)), 2061973 (for 6[OTf]·7[OTf]·CH\(_3\)NO\(_2\)), 2061974 (for 8a[OTf]·CH\(_2\)Cl\(_2\)), 2061975 (for 8b[OTf]·CH\(_2\)Cl\(_2\)), 2061976 (for 9a[OTf]·(CH\(_2\)Cl\(_2\))·CH\(_2\)CN), 2061977 (for 9b[OTf]), 2061978 (for 12b[OTf]), and 2061980 (for 14) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

In summary, electrophilic fluorophosphonium compounds bearing pyridyl (3[OTf]) or imidazolyl (4[OTf]) substituents, thus an additional Lewis basic site, represent a new type of intramolecular FLP that reacts with small molecules in a cooperative manner. The cyclizations of 3[OTf] and 4[OTf] with the 1,2-dipolar compounds acetone, acetonitrile and acetylenes gave rise to the formation of the corresponding heterocyclic compounds, thus illustrating the cooperative reactivity of the new FLP derivatives. This is additionally demonstrated by the reversible formation of adducts with CO\(_2\) (5+ and 6+) at low temperature, which was investigated by variable-temperature NMR studies and X-ray analysis. Surprisingly, the bifunctional phosphonium cation 4+ forms an adduct with CO\(_2\) (7+) comprising one molecule of CO\(_2\) and two molecules of 4+, resulting in a spirocyclic geometry at the central carbon atom, which is hitherto unreported for an N/P FLP system. These novel bifunctional phosphonium cations extend the diverse library of FLP systems, and the reversible CO\(_2\) adduction formation might provide new applications for in FLP chemistry, which we are currently investigating.

![Figure 5. Molecular structures of selected FLP adducts (hydrogen atoms, solvent molecules, and non-coordinating anions are omitted for clarity, ellipsoids are set at 50% probability); selected structural parameters are included in Table 2.](Image)
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Conflict of Interest

The authors declare no conflict of interest.

Keywords: carbon dioxide · frustrated Lewis pairs · fluorophosphonium cations · small-molecule activation

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