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Bifunctional Fluorophosphonium Triflates as Intramolecular Frustrated Lewis Pairs: Reversible CO_2 Sequestration and Binding of Carbonyls, Nitriles and Acetylenes

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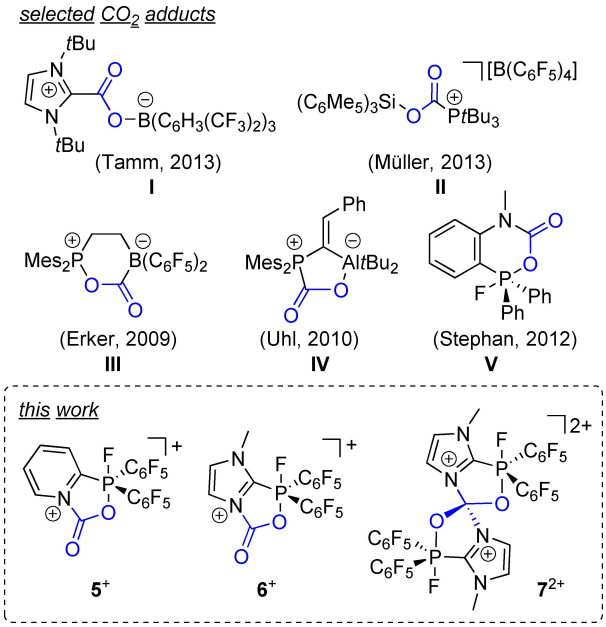
Dedicated to Professor Gerhard Erker on the occasion of his 75th birthday

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 CO_2 (**5**$^+$ and **6**$^+$). An unusual and labile spirocyclic tetrahedral intermediate (**7**$^{2+}$) is observed in CO_2-pressurized (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 (CO_2) and its transformation into value-added chemicals and materials is a challenge of today and success would significantly contribute to decline CO_2 accumulation in the atmosphere.[1] The chemistry of CO_2 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 CO_2 activation approaches.[1a,4] A key-step in the capture-and-release strategies and catalytic conversion, however, is a reversible binding of the CO_2 molecule which needs to be enabled by low-energy and readily-cleavable bonds.[5] Thus, a variety of organic carbon, nitrogen and phosphorus based Lewis bases were developed that are capable of forming adducts with the CO_2 molecule.[6] Notably, a variety of frustrated Lewis pairs (FLPs) have been investigated towards CO_2 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., phosphanes, carbenes, or amines; Scheme 1). However, the key step in a capture-and-release application for the conversion of CO_2[1] is usually hampered by the fact that the majority of FLPs form stable adducts with CO_2.[7a,b,8] Efforts towards binding of CO_2 by highly Lewis acidic amidophosphoranes were reported by the Stephan group (Scheme 1, **V**).[9] 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



Scheme 1. Selected examples of stable CO_2 adducts of inter- and intramolecular FLP systems (**I**–**V**) and CO_2 adducts **5**$^+$, **6**$^+$ and **7**$^{2+}$ derived from bifunctional fluorophosphonium compounds (this work).

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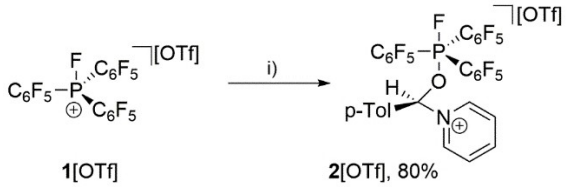
fluorophosphonium salt or designing a fluorophosphonium derivative with an intramolecular Lewis basic site.

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 form labile adducts with CO_2 and bind carbonyls, nitriles and acetylenes by 1,3-dipolar cycloaddition shown by selected examples.

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 CH_2Cl_2 (Scheme 2).[10] The formation of adduct $\mathbf{2}^+$ is indicated by multinuclear NMR spectroscopy and the ^{31}P NMR spectrum displays a doublet resonance at $\delta(P) = -53.2$ ppm ($^1J_{PF} = 644$ 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*-fluorobenzenesulfonimide (NFSI) is added to the corresponding phosphane $(C_6F_5)_2PR$ (R = imidazolyl, pyridyl), followed by the addition of MeOTf (Scheme 3).[10] Triflate salts **3**,**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 CD_2Cl_2 solutions with CO_2 (2 bar). The corresponding ^{31}P and ^{19}F NMR spectra of the solution containing **3**[OTf] reveal no interaction or reaction at ambient temperature indicated by the resonances for cation $\mathbf{3}^+$ ($\delta(^{31}P) = 54.8$ ppm, $\delta(^{19}F) = -114.0$ ppm, $^1J_{PF} = 996$ Hz) in the spectra. However, a VT NMR investigation disclosed the reversible and temperature-dependent binding of CO_2 by **3**[OTf] (Figure 2, left).



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.), CH_2Cl_2, RT, 4 h.

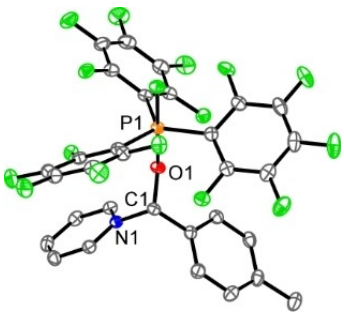
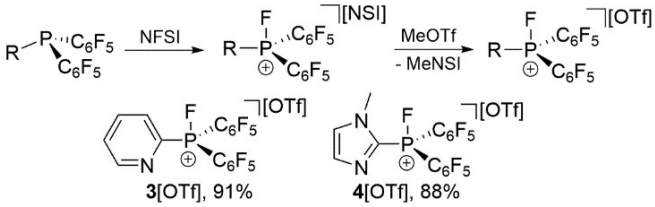


Figure 1. Molecular structure of **2**[OTf]·CH_2Cl_2 (hydrogen atoms, CH_2Cl_2, and non-coordinating anions are omitted for clarity, ellipsoids are set at 50% probability); Selected bond lengths (Å) and angles (°): P1–O1 1.7038(10), O1–C1 1.3974(16), C1–N1 1.5206(17).



Scheme 3. Synthesis of fluorophosphonium triflate salts **3**[OTf] and **4**[OTf]; i) +NFSI (1 equiv.), PhF, RT, 16 h; ii) +MeOTf (1 equiv.), RT, 4 h, −MeNSI; $NSI^- = [N(SO_2Ph)_2]^-$.

The ^{31}P NMR spectrum at 263 K shows, next to the dominant signal of the free cation $\mathbf{3}^+$ (98%), a small high field shifted doublet resonance at $\delta(^{31}P) = -55.5$ ppm (2%, $^1J_{PF} = 769$ Hz), which is well in the region for a penta-coordinate phosphorus atom, thus, indicating the formation of the CO_2 adduct **5**[OTf]. The corresponding resonance in the ^{19}F NMR spectrum is detected as a downfield shifted doublet resonance at $\delta(^{19}F) = -30.0$ 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 CO_2 is observed as a doublet resonance at $\delta(^{13}C) = 141.8$ ppm ($^2J_{PC} = 3$ 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 CD_2Cl_2 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 CO_2 theoretically with two different models (Figure 3). In $\mathbf{3}^+$**-CO$_2$_A**, CO_2 is activated by the incorporation of both the Lewis acidic and the Lewis basic site, whereas in model $\mathbf{3}^+$**-CO$_2$_B** the activation exclusively proceeds through the Lewis acidic P atom. The CO_2 binding energy is slightly stronger for model $\mathbf{3}^+$**-CO$_2$_A** (−20.4 kJ/mol) than model $\mathbf{3}^+$**-CO$_2$_B** (−18.4 kJ/mol). Moreover, the calculated ^{31}P NMR chemical shift change ($\Delta\delta = \delta(\mathbf{3}^+\text{-CO}_2\text{_A}) - \delta(\mathbf{3}^+)$) for model $\mathbf{3}^+$**-CO$_2$_A** ($\Delta\delta(^{31}P) = -124$ ppm) is in the range of the experimental result ($\Delta\delta(^{31}P) = -110.7$ ppm), while the calculated $\Delta\delta(^{31}P)$ for model $\mathbf{3}^+$**-CO$_2$_B** is only shifted by −17 ppm which is not observed in the respective ^{31}P NMR spectrum. Thus, the CO_2 activation is proposed to proceed via the P and pyridyl N atoms, affording **5**[OTf] in the configuration of model $\mathbf{3}^+$**-CO$_2$_A**. As the DFT

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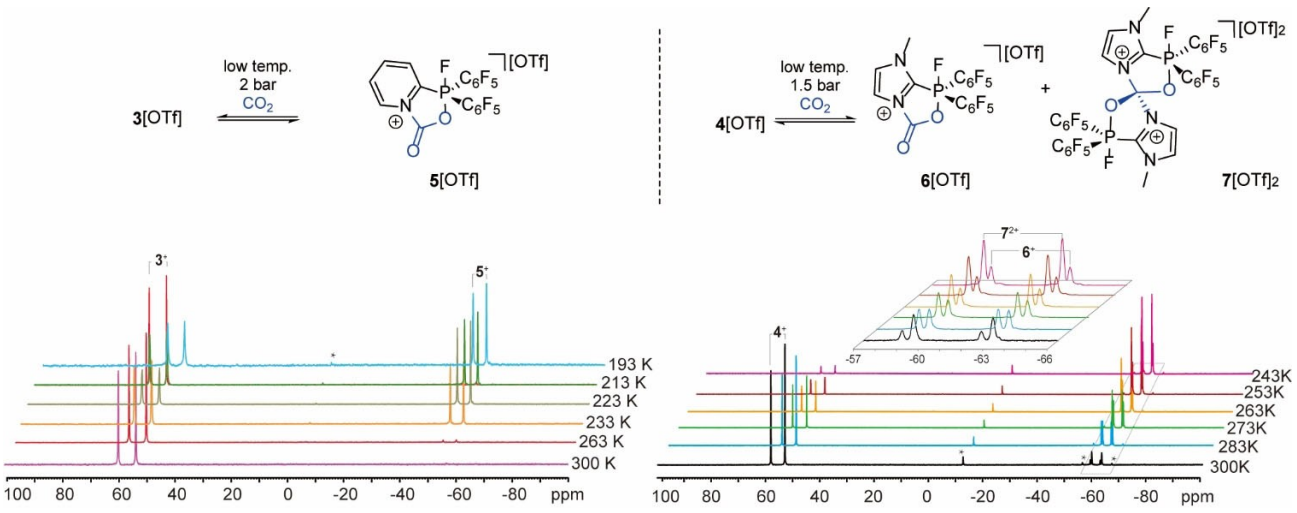

Figure 2. Equilibrium reaction of **3**[OTf] and **4**[OTf] with CO_2 (top); variable-temperature ^{31}P NMR spectra of CO_2 with **3**[OTf] (bottom left, 2 bar in CD_2Cl_2) and **4**[OTf] (bottom right, 1.5 bar in CD_3NO_2). Asterisks indicate small amounts of unidentified compounds.

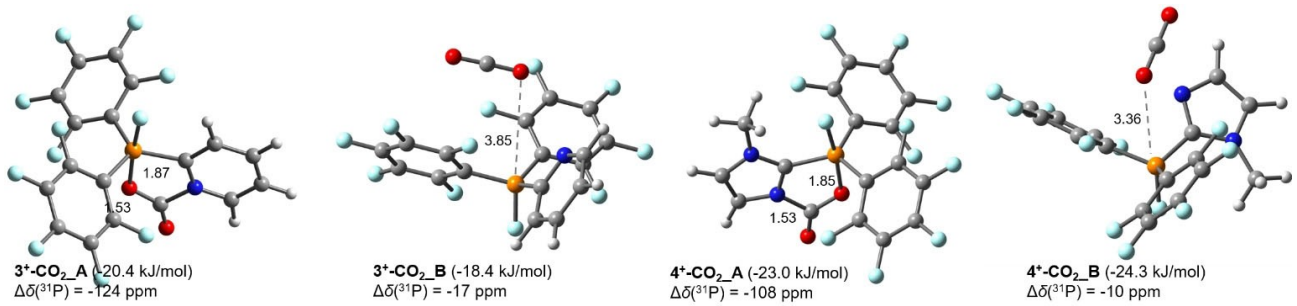

Figure 3. Optimized geometries and free energies of $\mathbf{3}^+$- and $\mathbf{4}^+$-CO_2 complexes (distances in Å, MP2/def2-TZVP level of theory).

calculation reveals a slightly improved CO_2 binding energy (−23.0 kJ/mol) for **4**[OTf], we also investigated the reactivity of **4**[OTf] towards CO_2 (Figure 3). Pressurizing a degassed CH_2Cl_2 solution of **4**[OTf] with CO_2 (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] with CO_2 (1.5 bar) by NMR spectroscopy in degassed CD_3NO_2. The ^{31}P NMR spectrum at ambient temperature shows signals of two different adducts at $\delta(^{31}P) = -60.0$ ppm ($^1J_{PF} = 737$ Hz, 5%) and $\delta(^{31}P) = -61.5$ ppm ($^1J_{PF} = 740$ Hz, 14%) besides the signal of **4**[OTf] ($\delta(^{31}P) = 55.2$ ppm, $\delta(^{19}F) = -111.5$ ppm, $^1J_{PF} = 1045$ Hz, Figure 2, right). The corresponding signals in the ^{19}F spectrum are detected at $\delta(^{19}F) = -8.1$ ppm ($^1J_{FP} = 737$ Hz) and $\delta(^{19}F) = -16.9$ ppm ($^1J_{FP} = 740$ Hz), respectively. Interestingly, the ^{13}C NMR spectrum displays two signals for the bound CO_2 moiety at $\delta(^{13}C) = 139.9$ ppm ($^2J_{PC} = 7$ Hz) as a doublet resonance and at $\delta(^{13}C) = 105.5$ ppm ($^2J_{PC} = 8$ Hz) as a triplet resonance suggesting a coupling to two phosphorus atoms.[13] This strongly indicates the formation of a 1:1 FLP-CO_2 adduct **6**[OTf] ($\delta(^{31}P) = -61.5$ ppm, $\delta(^{19}F) = -16.9$ ppm, $^1J_{PF} = 740$ Hz) and a 2:1 FLP-CO_2 adduct **7**$[OTf]_2$ ($\delta(^{31}P) = -60.0$ ppm, $\delta(^{19}F) = -8.1$ ppm, $^1J_{PF} = 737$ Hz). The ^{31}P NMR chemical shift change of **6**[OTf] ($\Delta\delta = \delta(\mathbf{6}^+) - \delta(\mathbf{4}^+)$, −116.7 ppm) is well in the range of calculated model $\mathbf{4}^+$-**CO_2_A** ($\Delta\delta(^{31}P) = -108$ ppm). Decreasing the temperature stepwise to 243 K, the integral ratio of **7**$[OTf]_2$ 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 CO_2 pressure did not show significant difference on the integral ratio of **6**[OTf] and **7**$[OTf]_2$. 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 CO_2 with **3**[OTf]. This suggests that a certain nucleophilicity of the Lewis basic site is crucial for the formation of the 2:1 FLP-CO_2 adduct **7**$[OTf]_2$.[14]

To our delight, we were able to obtain extremely sensitive but suitable co-crystals containing both cations $\mathbf{6}^+$ and $\mathbf{7}^{2+}$ by vapor diffusion of CH_2Cl_2 into a CH_3NO_2 solution of **4**[OTf] under CO_2 atmosphere (0.5 bar) at −30 °C (Figure 4). Although the double activation of CO_2 has been reported with FLPs based on hafnium (**VI**) and aluminum (**VII**) complexes (Scheme 4),[13,15] the tetrahedral cation $\mathbf{7}^{2+}$ represents the only crystallographically characterized example of a metal-free 2:1 FLP-CO_2 adduct.

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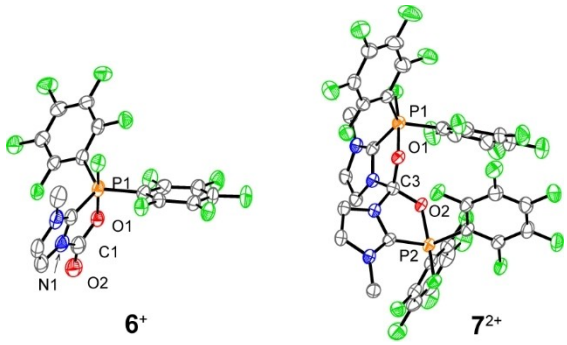
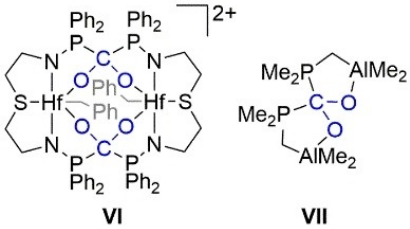
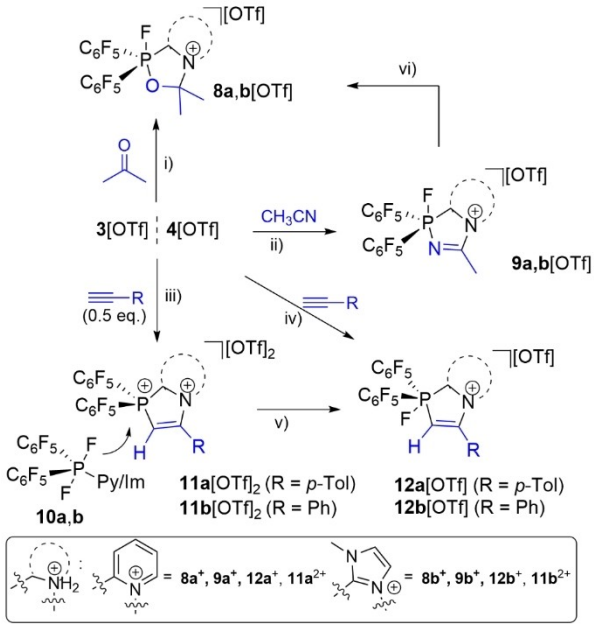


Figure 4. Molecular structure of co-crystal **6**[OTf]·**7**[OTf]$_2$·CH_3NO_2 (hydrogen atoms, CH_3NO_2, and non-coordinating anions are omitted for clarity, ellipsoids are set at 50% probability). Selected bond lengths (Å) and angles (°); for **6**$^+$: P1–O1 1.773(5), O1–C1 1.307(8), C1–N1 1.442(10), C1–O2 1.206(10), O1–C1–O2 128.1(7); for **7**$^{2+}$: P1–O1 1.771(4), P2–O2 1.744(4), O1–C3 1.352(7), O2–C3 1.366(6), O1–C3–O2 114.4(5).



Scheme 4. FLP-CO_2 adducts **VI** and **VII** containing a doubly activated CO_2 molecule.



Scheme 5. Reaction of **3**/**4**[OTf] with unsaturated compounds; i) + Me_2CO (1 equiv.), CH_2Cl_2, RT, 1 h; ii) + MeCN (1 equiv.), CH_2Cl_2, RT, 1 h; iii) + acetylenes (0.5 equiv.), DCE, RT, 4 h; iv) + acetylenes (1 equiv.), DCE, 80 °C, 16 h; v) RT, 2 weeks, or 80 °C, 16 h, −**3**/**4**[OTf]; vi) + Me_2CO (1 equiv.), −MeCN, CH_2Cl_2, RT, 1 h.

The molecular structure of **6**$^+$ which is consistent with the optimized structure **4**$^+$-**CO_2_A**, shows that a CO fragment of the CO_2 is integrated into a five-membered PNC_2O 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 P1–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 bond length of 1.442(10) Å. The C1–O1 (1.307(8) Å) and C1=O2 (1.206(10) Å) bonds in the CO_2 fragment are comparable to other FLP-CO_2 adducts (e.g., C–O 1.33 Å, C=O 1.21 Å).[9a,16] In the case of the 2:1 FLP-CO_2 adduct **7**$^{2+}$, the CO_2 molecule 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–C3 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 carbonyls, nitriles, and acetylenes to the respective heterocycles (Scheme 5). At room temperature, the formation of acetone adducts **8a**,**b**[OTf] (**8a**$^+$/**8b**$^+$: $\delta(^{31}P) = -52.0/-60.0$ ppm, $\delta(^{19}F) = -6.5/9.6$ ppm, $^1J_{PF} = 734/696$ Hz, 97 and 84% isolated yield) and acetonitrile adducts **9a**,**b**[OTf] (**9a**$^+$/**9b**$^+$: $\delta(^{31}P) = -49.3/-65.0$ ppm, $\delta(^{19}F) = 3.0/19.9$ ppm, $^1J_{PF} = 738/702$ 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, $^2J_{CP} = 9/11$ Hz) are significantly shifted to higher field compared to the free acetone ($\delta(^{13}C) = 207$ ppm).[17] The nitrile carbon atoms in **9a**,**b**[OTf] are shifted to lower field (**9a**$^+$/**9b**$^+$: $\delta(^{13}C) = 151.0/150.2$ ppm, $^2J_{CP} = 18/19$ Hz). Interestingly, when compounds **9a**,**b**[OTf] are reacted with acetone at room temperature, the formation of **8a**,**b**[OTf] under release of CH_3CN 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 acetylenes 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

Table 1. Relevant ^{19}F and ^{31}P NMR data of the heterocycles **8**–**12**[OTf].

Compound[a]	Solvent	$\delta(^{19}F)$ (ppm)	$\delta(^{31}P)$ (ppm)	$^1J_{PF}$ (Hz)
8a[OTf]	CD_2Cl_2	−6.5	−52.0	734
8b[OTf]	CD_2Cl_2	9.6	−61.0	696
9a[OTf]	CD_3CN	3.0	−49.3	738
9b[OTf]	CD_3NO_2	19.9	−65.0	702
11a[OTf]$_2$	CD_3CN	–	6.9	–
11a[OTf]$_2$	DCE[a]	–	−15.0	–
12a[OTf]	DCE[a]	34.0	−88.8	707
12b[OTf]	CD_2Cl_2	25.2	−98.8	718

[a] With C_6D_6 capillary.

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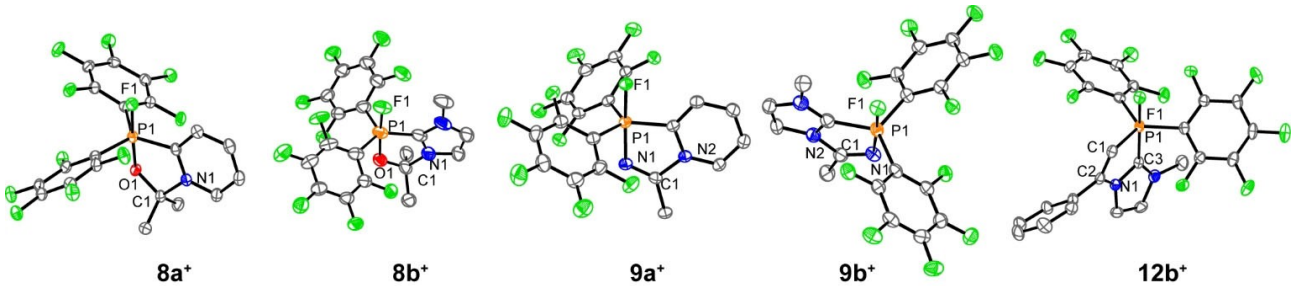

Figure 5. Molecular structures of selected FLP adducts (hydrogen atoms, solvent molecules, and non-coordinating anions are omitted for clarity, ellipsoids are set at 50% probability); selected structural parameters are included in Table 2.

2 weeks (Scheme 5, iii–v). Cation **11a**$^{2+}$(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.[10,18] **11a,b**[OTf]$_2$ are found as singlet resonances in the ^{1}P NMR spectra at $\delta(^{31}P) = 6.9$ and -15.0 ppm, while **12a,b**[OTf] are observed as doublet resonances in the ^{31}P and ^{19}F NMR spectra (**12a**$^{+}$/**12b**$^{+}$: $\delta(^{31}P) = -88.8/-98.8$ ppm, $\delta(^{19}F) = 34.0/25.2$ ppm, $^{1}J_{PF} = 707/718$ Hz, Table 1). We were able to isolate **11a**[OTf]$_2$[19] (78%) and **12b**[OTf] (66%) as pure products for full characterization.

The molecular structures of compounds **8a,b**[OTf], **9a,b**-[OTf] and **12b**[OTf] are confirmed by X-ray analysis of suitable single crystals which were obtained by slow vapor diffusion of *n*-pentane into saturated CH_2Cl_2 solutions at $-30\,°C$ (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(13) Å) are elongated compared to those of the starting materials **3**$^{+}$ and **4**$^{+}$, but comparable to those in difluorophosphoranes (e.g., $(C_6F_5)_3PF_2$: 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).

Table 2. Selected geometrical parameters of the crystallographically characterized FLP adducts.

Compound	P–F (Å)	P–X[a] (Å)	C–X[a] (Å)	N–C (Å)	Angle sum[b] (°)
6[OTf]	1.623(5)	1.773(5)	1.307(8)	1.442(10)	539.7
8a[OTf]	1.673(13)	1.6989(15)	1.398(2)	1.519(3)	536.8
8b[OTf]	1.637(2)	1.695(2)	1.411(5)	1.495(4)	537.2
9a[OTf]	1.6427(16)	1.777(2)	1.250(3)	1.491(3)	540.0
9b[OTf]	1.6426(16)	1.788(2)	1.272(3)	1.458(4)	539.9
12b[OTf]	1.651(3)	1.773(5)	1.330(8)	1.415(6)	539.2

[a] X=O (**6**$^{+}$, **8a,b**$^{+}$), N (**9a,b**$^{+}$), C (**12b**$^{+}$); [b] Angle sum of the newly formed five-membered ring.

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 2061970 (for **4**[OTf]·CH_2Cl_2), 2061971 (for **2**[OTf]), 2061972 (for **3**[OTf]·C_6H_5F), 2061973 (for **6**[OTf]·**7**[OTf]$_2$·CH_3NO_2), 2061974 (for **8a**[OTf]·CH_2Cl_2), 2061975 (for **8b**[OTf]·CH_2Cl_2), 2061976 (for **9a**[OTf]·$(CH_2Cl_2)_2$·CH_3CN), 2061977 (for **9b**[OTf]), 2061978 (for **13**), 2061979 (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**$^{2+}$) 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 adduct formation might provide new applications for in FLP chemistry, which we are currently investigating.

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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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