which is homogeneously nucleated,[32] some other zeolites are nucleated inhomogeneously.[33]

The materials prepared in this study could offer applications such as controlled access of molecules with selected size and shape to a sensor surface, membranes for catalysis and for separations with true molecular selectivity, and orientation of molecules for nonlinear optical applications.

Experimental Section

The seed crystals of LTA-type zeolite were prepared from an aqueous mixture of $NaAlO_2$, $Na_2SiO_3\cdot 9H_2O$, and $N(C_2H_4OH)_3$ by hydrothermal treatment. Before mixing the starting materials, the aqueous solution of $NaAlO_2$ was filtered through a membrane filter with pore size of 0.2 µm to remove impurities such as $Fe(OH)_3$. The other reagents were used as received. The composition of the aqueous mixture was adjusted to Na_2O:Al_2O_3:SiO_2:TEA:H_2O = 1.88:1:0.88:8:106. During mixing, precipitates formed. The resulting suspension was transferred to a teflon-lined stainless steel autoclave and heated at 110 °C under autogenous pressure for one week. The product was filtered, washed with 1000 mL of distilled water, and dried at 70°C in air for 12 h.

The chemical composition of the solid component in the starting suspension was derived from that of the liquid component and the initial composition. The chemical composition of the liquid component was determined by ICP analysis (JICP-PS-1000UV·AT, Leeman Labs). The samples were diluted with milli-Q water.

The crystalline phase and the orientation in the specimens were examined by X-ray diffraction measurements (Rigaku Geigerflex) with graphite-monochromated $Cu_{K\alpha}$ radiation at a scan rate of $2^\circ\,min^{-1}$ in the range $5 < 2\theta < 70^\circ$.

The microstructure of the membranes was observed by SEM (Philips XL30) at an acceleration voltage of 10 kV after deposition of a carbon layer with a thickness of about 15 nm on the specimen.

The formation of complexes from Al compounds and alkanolamines was examined by ^1H, ^{13}C, ^{23}Na, ^{27}Al, and ^{29}Si NMR spectroscopy (JEOL α400) at 20 °C and 9.4 T.

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Nickel-Assisted Carbon–Fluorine Bond Activation of 2,4,6-Trifluoropyrimidine: Synthesis of New Pyrimidine and Pyrimidinone Derivatives[**]

Thomas Braun, Simon P. Foxon, Robin N. Perutz,[*] and Paul H. Walton

Several methods have been described for the activation of carbon–fluorine bonds of fluoroaromatic and fluoroaliphatic compounds by reaction at transition metal centers.[1–3] One of the most striking is the fast oxidative addition of pentafluoropyridine at a nickel center to give *trans*-[$NiF(2\text{-}C_5F_4N)(PEt_3)_2$].[3] Here we report 1) the activation of a carbon–fluorine bond of 2,4,6-trifluoropyrimidine by a nickel center under mild conditions, 2) the conversion of the nickel fluoride compound into a bifluoride complex, and 3) the selective substitution of the 4-fluoro substituent of 2,4,6-trifluoropyrimidine by a hydroxyl group through reaction at nickel.

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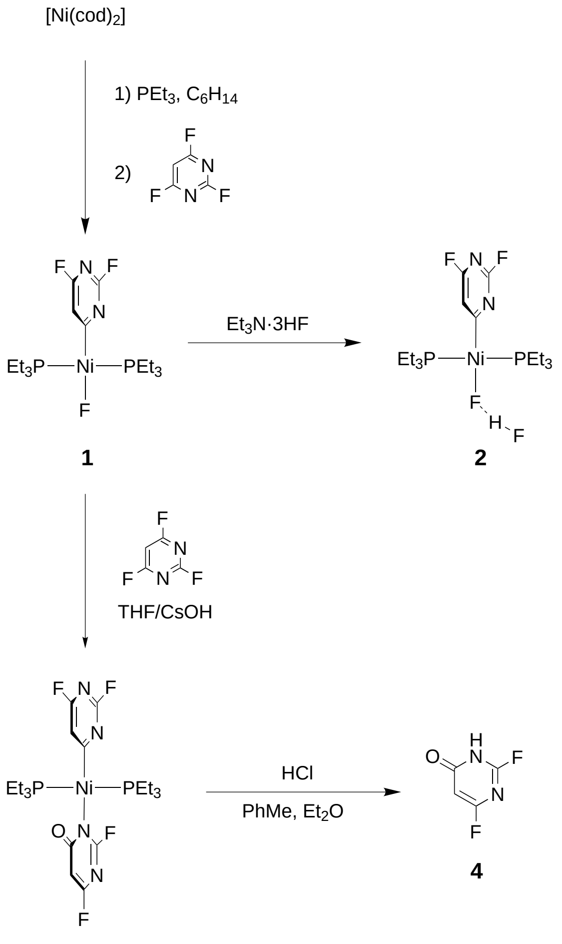
We show that nickel-supported C–F activation provides an unusual opportunity for the functionalization of fluorinated heterocyclic compounds.

The stepwise treatment of [Ni(cod)$_2$] (cod = 1,5-cyclooctadiene) with PEt$_3$ and 2,4,6-trifluoropyrimidine in hexane results in the fast and regioselective formation of the C–F activation product **1** (Scheme 1). The proposed structure is supported by ^{1}H, ^{31}P, ^{19}F, and ^{13}C NMR spectroscopic data (Table 1). The ^{31}P NMR spectrum displays a doublet at $\delta = 13.6$ ($J = 47.6$ Hz) for the two equivalent phosphorus nuclei coupled to the metal-bound fluorine nucleus. The ^{19}F NMR spectrum shows a signal at $\delta = -361.66$ for the nickel fluoride ligand.[3] Two other resonances ($\delta = -46.31, -73.10$) indicate the presence of the pyrimidyl ligand.



Scheme 1. Synthesis and reactions of **1**.

Addition of Et$_3$N · 3HF to **1** at room temperature gave the bifluoride complex **2** (Scheme 1). This reagent was recently employed as a mild source of HF for the synthesis of ruthenium and palladium bifluoride complexes from hydride and hydroxide precursors, respectively.[4, 5] Few other stable adducts of metal fluorides and HF have been reported, and none for a first-row transition metal.[4, 6, 7] The presence of a bifluoride unit in **2** is revealed by two signals in the ^{19}F NMR spectrum at 233 K at $\delta = -180.35$ (br d, $^1J_{F,H} \approx 390$ Hz, Ni-F-H-*F*) and -332.61 (br s, 1 F, NiF), and a broad doublet in the ^{1}H NMR spectrum at $\delta = 11.36$ ($^1J_{F,H} \approx 430$ Hz). The ^{31}P NMR spectrum displays a doublet at $\delta = 13.2$ ($^2J_{P,F} = 43.2$ Hz).

Treatment with CsOH · H$_2$O converted **2** into **1** and a second compound **3** (Scheme 1), which has four inequivalent fluorine atoms according to its ^{19}F NMR spectrum. The reaction was incomplete, and the ^{31}P NMR spectrum of the crude solution also revealed the presence of free phosphane. Attempts to separate the products by fractional crystallization led to the isolation of single crystals that contain **2** and **3** as independent molecules in the unit cell (Figures 1 and 2).[8] Both compounds exhibit a square-planar geometry with two *trans* phosphane ligands. The Ni–F bond length of 1.908(3) Å in **2** is significantly longer and the Ni–C bond length of 1.844(3) Å is shorter than the corresponding distances in *trans*-[NiF(2-C$_5$NF$_3$H)(PEt$_3$)$_2$] (1.856(2) and 1.869(4) Å, re-

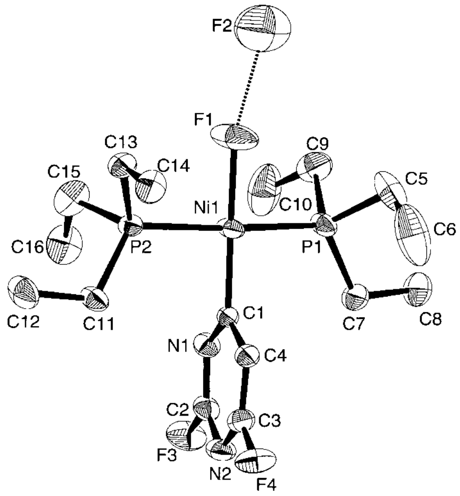


Figure 1. Molecular structure of **2** (ORTEP plot) in the crystal. Selected distances [Å] and angles [°]: Ni1–C1 1.844(4), Ni1–F1 1.908(3), F1 ··· F2 2.400(6); C1-Ni1-F1 177.63(18), P1-Ni1-P2 171.82(5), Ni1-F1-F2 156.7(2).

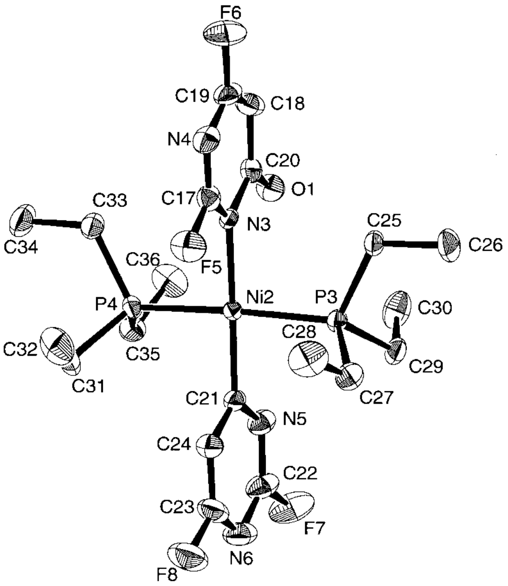


Figure 2. Molecular structure of **3** (ORTEP plot) in the crystal. Selected bond distances [Å] and angles [°]: Ni2–C21 1.877(3), Ni2–N3 1.949(3), O1–C20 1.241(4), N3–C17 1.322(4), N3–C20 1.407(4), N4–C17 1.303(5), N4–C19 1.352(5), C18–C19 1.348(6), C18–C20 1.435(5); C21-Ni2-N3 175.83(14), P4-Ni2-P3 173.27(4).

spectively).[3] The F$\cdots$F distance of 2.400(6) Å is clearly longer than that of 2.276(8) Å in *trans*-[RuH(FHF)(dmpe)$_2$][4] or in bifluoride salts MHF$_2$ (M = Na, K, NH$_4$),[9] but it is comparable to that of 2.389(6) Å in [WF(H)$_2$(FHF)](PMe$_3$)$_4$].[7] The interaction in **2** is best described, therefore, as a hydrogen bond between the NiF moiety and HF.[7] Complex **3** contains an N(3)-metalated pyrimidin-4-one unit *trans* to a 2-pyrimidyl ligand (Scheme 1, Figure 2).

Treatment of **1** or **2** with CsOH$\cdot$H$_2$O in the presence of excess 2,4,6-trifluoropyrimidine in THF resulted solely in the regioselective formation of **3** (NaOH may be used instead of CsOH). The NMR data for **3** (Table 1) are consistent with the crystal structure. Assignments are based partly on ^{13}C–^{1}H and ^{13}C–^{19}F COSY spectra. The most characteristic features in the ^{13}C NMR spectra are the signals for the nickel-bound carbon atom at $\delta = 215.8$ and for the C=O group at $\delta = 174.6$ (t, J = 11.5 Hz).

Table 1. Selected spectroscopic data for **1**–**5**.[a]

1: ^{1}H NMR (C$_6$D$_6$): $\delta = 7.04$ (br s, 1H, CH); ^{19}F NMR (C$_6$D$_6$): $\delta = -46.31$ (br s, 1F, CF), -73.10 (br s, 1F, CF), -361.66 (br, 1F, NiF); ^{31}P NMR (C$_6$D$_6$): $\delta = 13.6$ (d, $^{2}J_{P,F} = 47.6$ Hz)

2: ^{1}H NMR ([D$_8$]toluene, 223 K): $\delta = 11.36$ (br d, $^{1}J_{F,H} \approx 427$, 1H, FHF), 6.96 (br s, 1H, CH); ^{19}F NMR ([D$_8$]toluene, 223 K): $\delta = -44.43$ (s, 1F, CF), -76.62 (s, 1F, CF), -180.35 (br d, $^{1}J_{F,H} \approx 392$ Hz, 1F, FHF), -332.61 (br, 1F, NiF); ^{31}P NMR ([D$_8$]toluene, 223 K): $\delta = 13.2$ (d, $^{2}J_{P,F} = 43.2$ Hz)

3: IR (Nujol) $\tilde{\nu} = 1644$ cm^{-1} (C=O); ^{1}H NMR (C$_6$D$_6$): $\delta = 7.57$ (br s, 1H, CH of R^{C}), 5.69 (d, $J_{F,H} = 2.5$ Hz, 1H, CH of R^{N}); ^{19}F NMR (C$_6$D$_6$): $\delta = -45.41$ (s, 1F, CF), -45.50 (s, 1F, CF), -70.46 (s, 1F, CF), -70.82 (s, 1F, CF); ^{13}C NMR (C$_6$D$_6$): $\delta = 215.8$ (m, *ipso*-C of R^{C}), 174.6 (t, 11.5 Hz, CO), 173.2 (dd, $^{1}J_{C,F} = 247.8$, $^{3}J_{C,F} = 22.5$ Hz, CF of R^{N}), 166.3 (dd, $^{1}J_{C,F} = 260.4$ Hz, $^{3}J_{C,F} = 35.0$ Hz, CF of R^{C}), 161.3 (dd, $^{1}J_{C,F} = 220.2$ Hz, $^{3}J_{C,F} = 28.9$ Hz, CF of R^{N}), 158.2 (dd, $^{1}J_{C,F} = 222.7$ Hz, $^{3}J_{C,F} = 15.7$ Hz, CF of R^{C}), 111.3 (d, $J_{C,F}$ = 20.5 Hz, CH of R^{C}), 88.2 (dd, $J_{C,F} = 27.6$, $J_{C,F} = 8.2$ Hz, CH of R^{N}); ^{31}P NMR (C$_6$D$_6$): $\delta = 9.9$ (s)

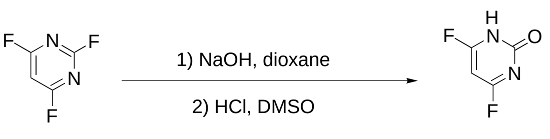
4: ^{1}H NMR (C$_6$D$_6$): $\delta = 13.5$ (br s, 1H, NH), 5.87 (d, $^{3}J_{F,H} = 2.5$ Hz, 1H, CH); ^{19}F NMR (C$_6$D$_6$): $\delta = -45.47$ (s, 1F, CF), -61.89 (s, 1F, CF); MS (EI): m/z (%): 132 (53.8) [M^{+}]

5: ^{1}H NMR (C$_6$D$_6$): $\delta = 10.47$ (br s, 1H, NH), 5.03 (t, $J_{F,H} = 1.3$ Hz, 1H, CH); ^{19}F NMR (C$_6$D$_6$): $\delta = -56.61$ (s, CF); ^{13}C NMR (C$_6$D$_6$): $\delta = 173.14$ (AXX′ system; apparent coupling constants: $J = 260$, $J = 21$ Hz, CF), 164.77 (t, $^{3}J_{C,F} = 23.4$ Hz, CO), 84.58 (t, $^{2}J_{C,F} = 35.7$ Hz, CH)

[a] R^{C} = C$_4$N$_2$F$_2$H, R^{N} = C$_4$N$_2$F$_2$HO; ^{1}H 500 MHz, ^{19}F 470.4 MHz, ^{31}P 202.4 MHz, ^{13}C 125.8 MHz.

Treatment of **3** with a solution of HCl in diethyl ether resulted in cleavage of the Ni–N bond and formation of *trans*-[NiCl(C$_4$N$_2$F$_2$H)(PEt$_3$)$_2$] and the previously unknown pyrimidin-4-one **4** (Scheme 1). The two compounds can be separated by sublimation of **4**. The ^{19}F NMR spectrum of **4** displays two signals at $\delta = -75.47$ and -61.89 for the two inequivalent fluorine atoms. The ^{1}H NMR spectrum has one signal in the nonaromatic region at $\delta = 5.90$, assigned to the ring proton, and a broad singlet at $\delta \approx 13.5$ for the nitrogen-bound proton.[10]

In contrast, the reaction of 2,4,6-trifluoropyrimidine with NaOH and then HCl afforded the pyrimidin-2-one **5**, an isomer of **4** (Scheme 2). The ^{1}H NMR spectrum of **5** shows one resonance in the nonaromatic region at $\delta = 5.03$ but only one ^{19}F signal at $\delta = -55.52$ for the fluorine atoms, which are equivalent on the NMR time scale.[10b] We also treated 2,4,6-trifluoropyrimidine with CsOH$\cdot$H$_2$O and showed that the cesium salts of **4** and **5** are formed in a 1:3 ratio. Fluorinated pyrimidinones are of general interest as building blocks in agrochemicals and because of their antitumor activity.[11]



5

Scheme 2. Synthesis of **5**.

Experimental Section

1: A suspension of [Ni(cod)$_2$] (120 mg, 0.36 mmol) in hexane (5 mL) was treated with PEt$_3$ (142 µL, 9.60 mmol). The solution was stirred for 5 min at room temperature until the color changed from red-purple to yellow. After addition of 2,4,6-trifluoropyrimidine (58 µL, 0.65 mmol), the solution was stirred for 10 min, and the volatile components were removed under vacuum. The orange residue was dissolved in hexane (5 mL), and the resulting yellow solution filtered and concentrated to about 1 mL. Complex **1** was crystallized as a yellow solid on cooling overnight at −20 °C. Yield 135 mg (72 %).

2: A solution of **1** (68 mg, 0.15 mmol) in hexane (5 mL) was treated with a solution of Et$_3$N$\cdot$3HF in THF (98 µL, 0.10 mmol). After stirring for 5 min at room temperature, the solvents were removed under vacuum. The residue was dissolved in hexane (3 mL), and the suspension was filtered. Orange crystals of **2** precipitated at −20 °C. Yield 44 mg (62 %).

3: A solution of **2** (120 mg, 0.27 mmol) in THF (20 mL) was treated with CsOH$\cdot$H$_2$O (100 mg, 0.60 mmol) and 2,4,6-trifluoropyrimidine (500 µL, 5.59 mmol). After stirring for 20 h at room temperature, the volatile components were removed under vacuum. The residue was extracted with hexane (20 mL), the extract was filtered, and the filtrate was concentrated to about 3 mL in vacuo. Complex **3** precipitated as a yellow powder. Yield 97 mg (67 %).

4: A solution of **3** (220 mg, 0.41 mmol) in toluene (5 mL) was treated with a solution of HCl in diethyl ether (430 µL, 0.43 mmol). After stirring for 1 min, the volatile components were removed under vacuum. Sublimation of the residue at 2.6×10^{-3} mbar and 50 °C afforded **4** as a white solid. Yield 11 mg (20 %; not optimized).

5: A solution of NaOH in water (339 mg, 8.47 mmol) was added to a solution of 2,4,6-trifluoropyrimidine (1.1 g, 8.20 mmol) in 1,4-dioxane (50 mL). After stirring for 4 h, the solution was concentrated to 2 mL under vacuum. The product was recrystallised from boiling water. The white product was collected by filtration, dried over anhydrous silica, and dissolved in DMSO. After treatment of the solution with a solution of HCl (4.50 mL, 4.40 mmol) in diethyl ether, the volatile components were removed under vacuum. The residue was extracted with benzene (20 mL), the extract filtered, and the solvent removed in vacuo to give **5** as a white powder. Yield 325 mg (30 %; not optimized)

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[8] Crystal data for **2** + **3**: $C_{36}H_{64}F_8N_6Ni_2OP_4$ ($M_r = 990.2$): crystal dimensions 0.8 × 0.4 × 0.4 mm; triclinic; space group $P\bar{1}$; $a = 14.682(7)$, $b = 18.359(5)$, $c = 9.197(5)$ Å, $\alpha = 100.90(3)$, $\beta = 101.37(4)$, $\gamma = 78.32(3)°$, $Z = 2$, $V = 2351.2(19)$ Å^3, $\rho_{calcd} = 1.817$ g cm^{-3}; $T = 150(2)$ K; $\theta_{max} = 27.99°$; of 11450 reflections collected, 11013 were unique ($R_{int} = 0.0279$); Rigaku AFC6S diffractometer; graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å); Lorentz and empirical absorption corrections (ψ scan, min. transmission 84.9%). The structure was solved by direct methods (DIRDIF) and refined by full-matrix least-squares methods on F^2; $R_1 = 0.0443$, $wR_2 = 0.1109$ (for 7642 reflections with $I > 2\sigma(I)$); GOF on F^2 1.070; data-to-parameter ratio 20.9; max./min. residual electron density $+1.387/-0.924$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplemantary publication no. CCDC-122712. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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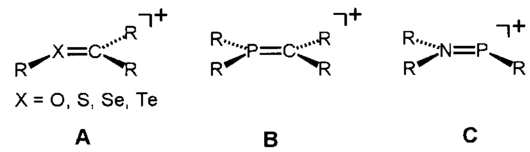
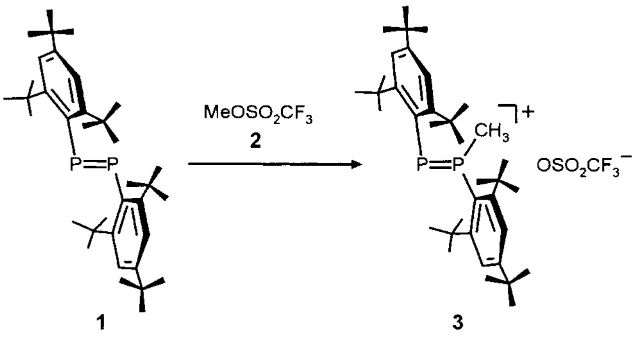
Strong P=P π Bonds: The First Synthesis of a Stable Phosphanyl Phosphenium Ion**

Sandra Loss, Christoph Widauer, and
Hansjörg Grützmacher*

Dedicated to Professor Hans Bock
on the occasion of his 71st birthday

α-Heteroatom-substituted carbenium ions **A** (X = S, Se, Te),[1] methylene phosphonium ions **B**,[2] and amino phosphenium ions **C**[3] can be formally described as donor – acceptor π-bond systems. In context with our investigations on these quite polar bond systems (i.e., $(X,P)^{\delta+},C^{\delta-}$ in **A**, **B**; $N^{\delta-},P^{\delta+}$ in **C**), we became interested in an ion analogous to **C** in which only third-row elements are involved in π bonding. The plan for the synthesis appeared simple: Protonation or alkylation of a diphosphene, R–P=P–R, should give a phosphanyl phosphenium ion, $[R_2P{=}PR]^+$, in which a phosphanyl group, R_2P, serves as π-electron donor towards an electron-deficient phosphenium unit, PR^+.[4] Others have attempted this approach in condensed phase; however, these ions have never been detected.[5] In the gas phase these species are observed as fragmentation products of $[R_2P{-}PR_2]^{\cdot+}$ radical cations.[6] Calculations show the planar $[H_2P{=}PH]^+$ ion to be the global minimum on the $[H_3,P_2]^+$ singlet potential energy surfaces.[7] Our own efforts to obtain $[Mes^*MeP{=}PMes^*]^+$ (**3**; Mes* = 2,4,6-tBu$_3$C$_6$H$_2$) were initially frustrating since no reaction occurred when diphosphene **1**[8] was treated with stoichiometric amounts of methyl trifluoromethanesulfonate (methyl triflate, **2**) in CH_2Cl_2. However, in the presence of a 35-fold excess of **2**, the methylated cation **3** was formed quantitatively (Scheme 1).





Scheme 1. Synthesis of phosphanyl phosphenium ion **3**.

Only two doublets at $\delta = 237$ (Mes*MeP) and 332.2 (Mes*P; $^1J_{PP} = 633$ Hz) were observed in the ^{31}P NMR spectrum. Note that the creation of a positive charge causes a considerable low-frequency shift of both ^{31}P NMR resonances ($\Delta\delta(P1) = 258$; $\Delta\delta(P2) = 163$) when compared to neutral **1** ($\delta(^{31}P) = 495$). The n → π* ($\lambda = 364$ nm) and π → π* transitions ($\lambda = 249$ nm) of the P=P chromophore are shifted to shorter wavelengths by 98 and 92 nm, respectively.

Since **3** proved to be particularly unstable in nonpolar organic solvents, crystals suitable for an X-ray analysis were grown within five minutes by diffusion of diethyl ether into a solution of **3** in CH_2Cl_2 under a microscope. A rapidly formed small yellow platelet was selected and mounted on the diffractometer, and the resulting stucture of **3** is shown in Figure 1.[9]

The phosphorus center P1 in **3** is trigonal-planar coordinated. The O2 center of the triflate anion is in line with the P=P vector and has a long contact with the two-coordinate phosphorus atom P2 (P2–O2 3.148(3) Å; P1-P2-O2 175.6°), without causing a structural perturbation. There is no twist around the P=P bond; the central skeleton of the cation is

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