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^{19}F and ^{31}P NMR Evidence for Silver Hexafluorophosphate Hydrolysis in Solution. New Palladium Difluorophosphate Complexes and X-ray Structure Determination of $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(PO_2F_2)(PCy_3)]$

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Introduction

In spite of the rich chemistry of electrophilic palladium compounds as $[Pd(CH_3CN)_4](BF_4)_2$ toward functionalization of alkanes and arenes or isomerization and polymerization of olefins,[1] the electrophilic chemistry of allylic palladium fragments has not yet been extensively explored. In contrast there has been detailed study of the nucleophilic chemistry of the unsaturated ligand.[2] We have tried to generate the unsaturated fragment $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)]^+$ by means of the reaction of $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(\mu\text{-}Cl)]_2$ with $AgPF_6$ in a noncoordinating solvent as CH_2Cl_2 but the final product of the reaction has been found to be $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(\mu\text{-}PO_2F_2)]_3$. We have demonstrated that the group $PO_2F_2^-$ must have been generated from the partial hydrolysis, catalyzed by Ag^+, of the hexafluorophosphate ion, due to the presence of adventitious water probably derived from the $AgPF_6$ or the solvent. The $PO_2F_2^-$ ion has been shown to be present in an X-ray structure determination of the complex $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(PO_2F_2)(PCy_3)]$, generated from the trimer species and PCy_3.

Examples of the partial hydrolysis to $PO_2F_2^-$ are known in cases where a PF_6^- ion is acting as a counterion in rhodium,[3] manganese,[4] and rhenium[5] complexes or is bonded to an iridium center.[6] The presence of $PO_2F_2^-$ ion in an old and moist sample of $AgPF_6$ may also explain its presence in ruthenium difluorophosphate[7] and rhodium–silver[8] complexes .

Our studies have shown that $AgPF_6$ undergoes hydrolysis in solutions of methylene chloride even in the absence of the palladium complex. To our knowledge, this is the first time that a study of the hydrolysis of $AgPF_6$ in an organic solvent has been evaluated. This has allowed us to detect several intermediates and to demonstrate a clear solvent dependence.

Some reactivity of the new palladium–PO_2F_2 complex has also been explored.

Experimental Section

All reactions were performed by using standard Schlenk techniques under an atmosphere of dry, oxygen-free nitrogen or argon. Solvents were distilled from appropriate drying agents and degassed before use.

Elemental analyses were performed with a Perkin-Elmer 2400/ microanalyzer. NMR spectra were recorded on a Varian Unity.FT-300 spectrometer. ^{1}H (300 MHz), ^{13}C (75 MHz), ^{19}F (282 MHz), and ^{31}P-(121 MHz) are recorded as δ from $SiMe_4$ (for ^{1}H and ^{13}C), $CFCl_3$, and H_3PO_4 (85%), respectively. IR spectra were recorded as KBr pellets in the region 4000–200 cm^{-1} with a Perkin-Elmer PE 883 IR spectrometer. Mass spectra were recorded on a VG Autospec instrument using FAB technique and NBA as matrix. $AgPF_6$, PPh_3, and PCy_3 were purchased from Aldrich, and $P(p\text{-tolyl})_3$ was purchased from Fluka. $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(\mu\text{-}Cl)]_2$ and $[Cu(CH_3CN)_4]PF_6$ were prepared according to literature.[9,10]

Synthesis of $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(\mu\text{-}PO_2F_2)]_3$, 2. To a yellow solution of $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(\mu\text{-}Cl)]_2$ (1.000 g, 2.54 mmol) in 25 mL of CH_2Cl_2 was added water (0.108 mL, 6 mmol) and 1.310 g (5.08 mmol) of $AgPF_6$, 98%. The solution was stirred, and immediately a white precipitate of AgCl was formed with the liberation of HF. Special care must be taken in this reaction because of this gas emission. After 18 h, the resulting solution was filtered and concentrated, diethyl ether was added, and the solution was cooled to give a yellow, non-air sensitive, slightly thermally unstable solid of complex **2**, which was filtered and dried under vacuum (0.733–0.933 g). Yield: 55–70%. Anal. Calcd for $C_4H_7F_2O_2PPd$: C, 18.30; H, 2.68. Found: C,17.91; H, 2.35. IR (cm^{-1}): 1312, 1152 [ν(PO)], 853, 833 [ν(PF)]. ^{1}H NMR ($CDCl_3$): 2.20 (s, 3H, CH_3), 2.76 (s, 2H, H_{anti}), 3.82 (s, 2H, H_{syn}); ^{13}C{^{1}H} ($CDCl_3$): 22.21 (s, CH_3), 56.41 (s, CH_2), 127.30 (s, C_{quat}). ^{13}C [$(CD_3)_2CO$]: 21.96 (c, CH_3), 57.1 (t, CH_2), 128.86 (s, C_{quat}). ^{31}P{^{1}H} NMR [$(CD_3)_2CO$]: −10.41 (t, $^1J_{P-F}$ = 955 Hz). ^{19}F NMR [$(CD_3)_2CO)$]: −82.57 (d, PO_2F_2). Mass spectrum: m/z 686, ($M^+ - PO_2F_2$).

Synthesis of $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(\mu\text{-}PO_2F_2)(PR_3)]$, 3-5. To a solution of **2** (0.200 g, 0.25 mmol) in 15 mL of CH_2Cl_2 was added PCy_3, 97% (0.213 g, 0.75 mmol), PPh_3, 99% (0.198 g, 0.75 mmol), or $P(p\text{-tolyl})_3$, 97% (0.235 g, 0.75 mmol). The reaction mixture was allowed to stir at room temperature, and after 4 h the solvent was removed in vacuo. Dry hexane was added to triturate the white oil. The resulting off-white, non-air-sensitive solid was isolated via filtration and crystallized from CH_2Cl_2 layered with hexane. Data for **3** are as follows. Yield: 60% (0.244 g). Anal. Calcd for $C_{22}H_{40}F_2O_2P_2Pd$: C, 48.60; H, 7.42. Found: C, 49.20; H, 7.33. IR (cm^{-1}): 1311, 1152 [ν(PO)], 852, 836 [ν(PF)]. ^{1}H NMR ($CDCl_3$):[11] 1.98 (s, 3H, CH_3), 2.37 (s, 1H, H_{2anti}), 2.92 (d, 1H, H_{2syn}), $J_{H1syn-H2syn}$ = 3 Hz), 3.65 (d, 1H, H_{1anti}, $J_{H1anti-P1}$ = 8.4 Hz), 4.66 (dd, 1H, H_{1syn}, $J_{H1syn-P1}$ = 5.8 Hz), 1.2–1.9 (m, 33H, PCy_3). ^{13}C{^{1}H} ($CDCl_3$): allyl group, 22.76 (s, CH_3), 45.08 (s, C(2)-H_2), 81.62 (d, C(1)H_2, J_{C-P} = 26.7 Hz), 131.21 (s,C_{quat}); phosphine (C^{cy}(1)H is the C atom bonded to P and so on), 25.99 (s, C^{cy}(4)H_2), 27.17 (d, C^{cy}(3,5)H_2, J_{C-P} = 11.1 Hz), 29.82 (d, C^{cy}(2,6)H_2, J_{C-P} = 13.1 Hz), 33.15 (d, C^{cy}(1)H, J_{C-P} = 18.6 Hz). ^{31}P{^{1}H} NMR [$(CD_3)_2CO$]: -10.40 (t, PO_2F_2, $^1J_{P-F}$ = 955 Hz), 44.50 (s, PCy_3). ^{19}F NMR [$(CD_3)_2CO$]: −82.40 (d, PO_2F_2). Data for **4** are as follows. Yield: 65% (0.255 g). Anal. Calcd for $C_{22}H_{22}F_2O_2P_2Pd$): C, 50.35; H, 4.22. Found: C, 50.20; H, 4.26. IR (cm^{-1}): 1306, 1152 [ν(PO)], 847, 837 [ν(PF)]. ^{1}H NMR ($CDCl_3$):[11] 2.05 (s, 3H,CH_3), 2.60 (s, 1H, H_{2anti}), 2.73 (d, 1H, H_{2syn}, $J_{H2syn-H1syn}$ = 2.9 Hz), 3.80 (d, 1H, H_{1anti}, $J_{H1anti-P1}$ = 9.1 Hz), 4.80 (dd, 1H, H_{1syn}, $J_{H1syn-P1}$ = 6 Hz), 7.1–7.6 (m, 15H, PPh_3). ^{13}C{^{1}H} ($CDCl_3$): allyl group, 23.09 (s, CH_3), 54.65 (s, C(2)H_2), 81.33 (d, C(1)-H_2, J_{C-P} = 28.64 Hz), 131.4 (s, C_{quat}); phosphine, 128.80 (d, C_{meta}, J_{C-P} = 10.56), 130.78 (d, C_{para}, J_{C-P} = 2.26 Hz), 133.70 (d, C_{ortho}, J_{C-P} = 13.57 Hz), 134.53 (d, C_{ipso}, J_{C-P} = 6.03 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): −12.83 (t, $PO_2F_2^-$ J_{P-F} = 964 Hz,), 23.63 (s, PPh_3). ^{19}F NMR ($CDCl_3$): −85.77 (d, $PO_2F_2^-$). Data for **5** are as follows. Yield: 85%. (0.365 g).

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Table 1. Crystallographic Data for 3

chem formula: $C_{22}H_{40}F_2O_2P_2Pd$	fw = 542.90
$a = 24.053(9)$ Å	space group: monoclinic, $P2_1/c$
$b = 10.157(3)$ Å	$T = 295$ K
$c = 21.045(6)$ Å	$\lambda = 1.541\,838$ Å
$\beta = 100.31(2)°$	$\rho_{calc} = 1.426$ g cm^{-3}
$V = 5058(3)$ Å^3	μ(Cu Kα) = 75.33 cm^{-1}
$Z = 8$	R^a = 0.0400
$F(000) = 2256$	R$_w{}^b$ = 0.0505

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ with $w = 1.0000[\sigma^2(F_o) + 0.00323F_o{}^2]^{-1}$.

Anal. Calcd for $C_{25}H_{28}F_2O_2P_2Pd$: C, 52.9; H, 5.51. Found: C, 52.20; H, 4.90. IR (cm^{-1}); 1309, 1155 [ν(PO)], 839, br [ν(PF)]. ^{1}H NMR ($CDCl_3$):[11] 2.04 (s, 3H, allyl CH_3), 2.36 (s, 9H, *p*-tolyl CH_3), 2.59 (s, 1H, H_{2anti}), 2.72 (br s, 1H, H_{2syn}), 3.81 (d, 1H, H_{1anti}, $J_{H1anti-P1} = 9.6$ Hz), 4.78 (dd, 1H, H_{1syn}, $J_{H1syn-P1} = 5.7$ Hz), 7.19–7.37 (m, 12H, P(*p*-tolyl)$_3$). ^{13}C{^{1}H} ($CDCl_3$): allyl group, 22.74 (s, CH_3), 54.06 (s, C(2)-H_2), 80.70 (d, C(1)H_2, $J_{C-P} = 28.7$ Hz), C_{quat} is not seen; phosphine, 21.07 (s, CH_3) 129.20 (d, C_{meta}, $J_{C-P} = 10.60$ Hz), 133.28 (d, C_{ortho}, $J_{C-P} = 13.10$ Hz), 134.04 (d, C_{ipso}, $J_{C-P} = 4.60$ Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): −12.8 (t, $PO_2F_2^-$, $J_{P-F} = 961$ Hz), 21.0 (s, P(*p*-tolyl)$_3$). ^{19}F NMR ($CDCl_3$): −81.69 (d, $PO_2F_2^-$).

Reaction of 2 with [Cu(CH_3CN)$_4$]PF_6. Synthesis of [Pd(η^3-2-Me-C_3H_4)(CH_3CN)$_2$]PF_6. To a solution of **2** (0.20 g, 0.25 mmol) in CH_2Cl_2 (15 mL) was added [Cu(CH_3CN)$_4$]PF_6 (0.28 g, 0.76 mmol), and the mixture was stirred for 3 h. The suspension was filtered and partially evaporated. Addition of diethyl ether gave a solid which after filtration and washing with CH_2Cl_2 allowed the isolation of $CuPO_2F_2$. IR (cm^{-1}) 1316 , 1150 [ν(PO)], 854, 833 [ν(PF)]. ^{31}P{^{1}H} NMR (D_2O): −6.6 (t, $PO_2F_2^-$, $J_{P-F} = 958$ Hz). ^{19}F NMR (D_2O): −81.57 (d, $PO_2F_2^-$). Partial evaporation of the CH_2Cl_2 filtrate, addition of diethyl ether, and filtration gave a white solid of [Pd(η^3-2-Me-C_3H_4)(CH_3CN)$_2$]PF_6. Yield: 63%. Anal. Calcd for $C_8H_{13}F_6N_2PPd$: C, 24.73; H, 3.37; N, 7.21. Found: C, 25.15; H, 3.38; N, 7.30. IR (cm^{-1}): 843, 559 [ν(PF)]. ^{1}H NMR ($CDCl_3$): 2.13 (s, 3H, allylic CH_3), 2.32 (s, 6H, CH_3CN), 2.99 (s, 2H, H_{anti}), 4.11 (s, 2H, H_{syn}). ^{13}C{^{1}H} ($CDCl_3$): 2.13 (s, $\mathit{C}H_3CN$), 22.30 (s, allylic CH_3), 62.54 (s, CH_2), 121.48 $CH_3\mathit{C}N$, 134.04 (C_{quat}).

X-ray Structure Determination. Crystallographic data for **3** are presented in Table 1 An off-white crystal was mounted on a fine glass capillary under nitrogen. The cell parameters were determined by least-squares refinement of diffractometer angles for 30 automatically centered reflections, $\lambda = 1.541\,838$ Å. Crystal dimensions were 0.18 × 0.25 × 0.35 mm. A Siemens AED diffractometer was used, with a θ–2θ scan mode, scan width $1.20 + 0.142 \tan\theta$, scan speed 3–12° min^{-1}, Ni-filtered Cu Kα radiation. A total of 9634 unique reflections (±*hkl*) ($3 \le \theta \le 70°$) were observed, 5007 with $I \ge 2\sigma(I)$ [merging $R = 0.0140$ after absorption correction (maximum and mininimum transmission factors = 1.1490, 0.8892)]. The Patterson method (Pd, P atoms) was used followed by normal procedures. Full-matrix least-squares techniques with isotropic thermal parameters and then blocked full-matrix least-squares techniques with anisotropic thermal parameters in the last cycles for all non-hydrogen atoms were used; hydrogen atoms of the Cy rings were placed at their geometrically calculated positions (C–H = 1.00 Å) and refined "riding" on the corresponding carbon atoms with one, overall, refined U_{iso} for each of the two independent molecules [0.090(5), 0.075(4) Å^2], and hydrogen atoms of the 2-methylallyl ligands were located in difference maps and refined isotropically with one, overall, refined U_{iso} for each of the two independent molecules [0.084(9), 0.098(9) Å^2] giving a total of 569 refined parameters. An absorption correction was performed according to the literature.[15] Calculations were performed using SHELXS-86 and SHELX-76 programs.[19]

Results and Discussion

$AgPF_6$ Hydrolysis. When 1 mol of [Pd(η^3-2-Me-C_3H_4)(μ-Cl]$_2$, **1**, was treated with 2 mol of $AgPF_6$ in CH_2Cl_2, an immediate precipitate of AgCl and emission of HF gas was observed. After appropriate workup, the complex [Pd(μ-PO_2F_2)(η^3-2-Me-C_3H_4)]$_3$, **2**, was isolated. The $PO_2F_2^-$ group can only arise from the partial hydrolysis of the PF_6^- ion. ^{19}F and ^{31}P NMR spectra of freshly prepared solutions of the $AgPF_6$ reagent were obtained which showed that the amount of $PO_2F_2^-$ present in the solid $AgPF_6$ was negligible and that partial hydrolysis occurs during the reaction. The overall process follows

$$[Pd(\eta^3\text{-}C_4H_7)(\mu\text{-}Cl)]_2 + 2AgPF_6 + 4H_2O \rightarrow 2AgCl + 8HF + {}^2/_3[Pd(\mu\text{-}PO_2F_2)(\eta^3\text{-}C_4H_7)]_3 \quad (1)$$

The water necessary to initiate the hydrolysis process must arise from both the $AgPF_6$ reagent (demonstrated by IR spectroscopy and elemental analysis) and traces in the solvent. It has not been possible to completely eliminate the water from $AgPF_6$ even after drying under P_2O_5 and a vacuum higher than 10^{-2} mmHg during 5 days. (Similar results have been reported[5] elsewhere). Probably all the water required for the hydrolysis process is not necessary initially. At the first stages of the hydrolysis HF is produced (see, for example, eq 2). HF reacts with glass in a cyclical reaction to produce H_2O (eq 3), which reacts with a fluoride to produce HF (reverse of eqs 3 and 6). This HF reacts with SiO_2 to produce H_2O and so on. A small amount of H_2O can therefore hydrolyze a large quantity of fluoride.

$$H_2O + PF_6^- \rightarrow POF_4^- + 2HF \quad (2)$$

$$SiO_2 + 4HF \rightleftharpoons SiF_4 + 2H_2O \quad (3)$$

$$SiF_4 + F^- \rightarrow SiF_5^- \quad (4)$$

$$SiF_4 + 2F^- \rightarrow SiF_6^{2-} \quad (5)$$

$$POF_4^- + H_2O \rightarrow PO_2F_2^- + 2HF \quad (6)$$

The species POF_4^-, SiF_4 and SiF_6^{2-} have been detected (see below).

The amount of water present in the reaction medium was critical for the yield of **2**. In fact, this yield was dramatically diminished when the process was carried out under extreme conditions of dryness and also when an excess of water was present (H_2O/$AgPF_6$ ≫ 2:1) (vide infra).

To determine if the silver cation was involved in the hydrolysis, the reaction of **1** with $TlPF_6$ in CH_2Cl_2 has been carried out. In this case, no gas emission was observed and the PF_6^- anion remained unchanged. We conclude that the presence of the silver cation is necessary for the hydrolysis to occur. Furthermore, we have observed by NMR that solutions of $AgPF_6$ in CD_2Cl_2 were hydrolyzed with time in the absence of the palladium complex.

We propose that the role of the silver center is to promote a cationic activation of the water molecule. In support we note that heterolytic activation of H_2O promoted by $AgPF_6$ in presence of niobium complexes has been observed. $Cp'_2NbHP(OMe)_3$, ($Cp' = C_5H_4SiMe_3$) was protonated to [$Cp'_2NbH_2P(OMe)_3$]$^+$, in presence of acids or $AgPF_6$.[13] Some examples of fluorinations of phosphites[14] and phosphines[15] by HBF_4 have also been described.

An attempt has been made to detect intermediates of the hydrolysis of $AgPF_6$ in CD_2Cl_2 by use of ^{19}F and ^{31}P NMR, with and without the presence of the palladium complex **1** at room temperature. Obviously, the detection of intermediates was limited by the relevant equilibrium constants, solubilities, and the time scale of the NMR experiment. At the beginning of the reaction and in the absence of the palladium complex **1**,[16] the major signals are due to PF_6^- (^{19}F, −72, d, $^1J_{P-F} = 717$ Hz; ^{31}P-

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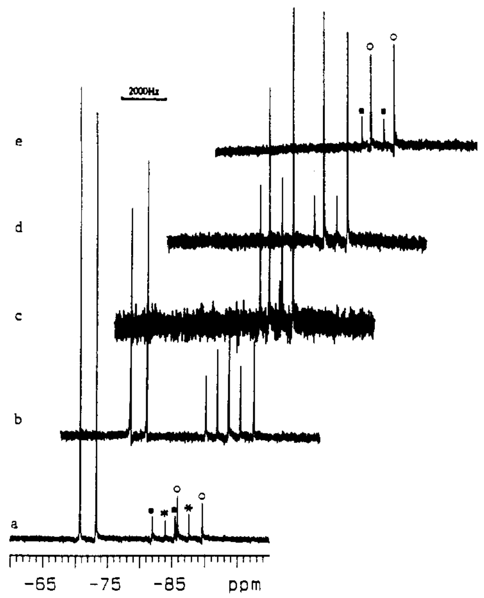
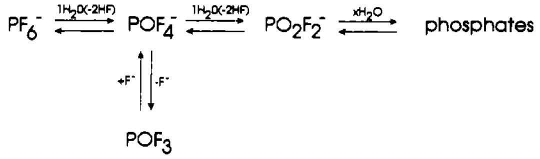


Figure 1. ^{19}F NMR monitoring of the $AgPF_6$ hydrolysis in the $PO_xF_y^{z-}$ region (solvent CD_2Cl_2, room temperature): (a) 5 min; (b) 12 min; (c) 22 min; (d) 45 min; (e) 16 h. The doublet at low field corresponds to PF_6^-. Peaks marked correspond as follows: (*) POF_4^-; (■) POF_3; (○) $PO_2F_2^-$.

Scheme 1. Proposed Diagram for the $AgPF_6$ Hydrolysis Showing the Different Intermediates Detected by ^{19}F and ^{31}P NMR



{^1H} −142.1, m). Also detectable in this solution was a species which showed a doublet in the ^{19}F spectra (−85.8, $^1J_{P-F}$ = 1016 Hz), and three peaks (−2.4, −10.9, −19.2) with relative intensities characteristic of a quintet, rather than a triplet in the ^{31}P spectra (it is likely that it is not possible to fully resolve the quintet at this dilution). These signals disappeared as the reaction proceeded. We assign these signals to the POF_4^- ion (see Scheme 1). Early in the reaction, and throughout the experiment, signals (^{19}F, −87.7, d, $^1J_{P-F}$ = 1071 Hz; $^{31}P\{^1H\}$, −26.3, q) assigned to POF_3[17] were detected. Throughout the reaction, and until nearly the final stage of the hydrolysis, a signal (^{19}F, −84.0, d, $^1J_{P-F}$ = 976 Hz; $^{31}P\{^1H\}$ −14.7, t) was observed which must be unambiguously assigned to the $PO_2F_2^-$ ion. After several hours of reaction, species containing both P and F were almost nonexistent; the ^{31}P spectra showed a complex signal at −16 to +14 which is due to a mixture of phosphates, and the ^{19}F spectra showed several single peaks from −165 to −125. Two peaks at −126 and −162 in ^{19}F NMR were assigned to the species SiF_6^{2-} and SiF_4, respectively. These single peaks are also detected in earlier stages of the hydrolysis. Figure 1 shows an example of the progress of the hydrolysis followed by ^{19}F NMR.

It was not been possible to conduct a detailed kinetic study because of the difficulty in controlling the amount of water present and the low solubility of $AgPF_6$ in CD_2Cl_2. In addition, solubility properties of the detected intermediates are not known.

If the NMR study of $AgPF_6$ hydrolysis is carried out in the presence of complex **1** ($AgPF_6$/**1** = 2/1) the hydrolysis stops at the $PO_2F_2^-$ stage, probably due to the coordination of the $PO_2F_2^-$ ion to the palladium center. In this case, and at the end of the reaction, we detected small amounts of a species (^{19}F, −76.2, d, $^1J_{P-F}$ = 930 Hz; $^{31}P\{^1H\}$, −12.9, d) which was not unambigously assigned.

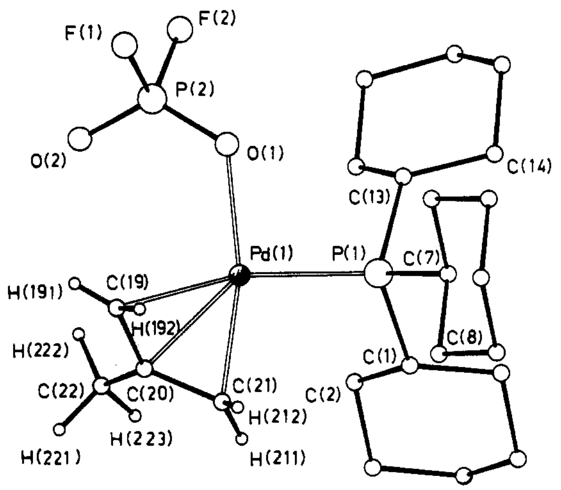


Figure 2. Perspective view of complex **3**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for complex **3** (Values in Brackets Refer to the Second Independent Molecule)

Pd(1)–P(1)	2.317(2) [2.314(2)]
Pd(1)–O(1)	2.314(6) [2.126(5)]
Pd(1)–C(19)	2.208(8) [2.210(7)]
Pd(1)–C(20)	2.150(7) [2.161(7)]
Pd(1)–C(21)	2.085(8) [2.095(8)]
P(2)–O(1)	1.471(5) [1.455(5)]
P(2)–O(2)	1.468(8) [1.441(8)]
F(1)–P(2)–F(2)	97.2(5) [96.0(4)]
O(1)–P(2)–O(2)	123.3(4) [122.1(4)]
P(1)–Pd(1)–O(1)	94.3(2) [94.6(2)]
Pd(1)–O(1)–P(2)	125.4(3) [124.7(3)]
Pd(1)–C(20)–C(22)	118.3(5) [119.4(6)]

An acceleration of the hydrolysis after addition of an excess of water (e.g. $H_2O/AgPF_6$ = 3.5) was observed, and in this case, the presence of the corresponding amount of **1** did not prevent the total hydrolysis. This total hydrolysis of the PF_6^- anion to phosphates after addition of water might explain the decrease in the yield of **2** when a large amount of water was previously added to the reaction mixture (vide supra).

When **1** and $AgPF_6$ were mixed in CD_2Cl_2 and the AgCl was filtered off after 15 min of stirring, the initial spectra of the solution showed both PF_6^- and significant amounts of $PO_2F_2^-$. Upon standing, the former disappeared completely while the latter increased. Thus a small amount of silver in solution was able to catalytically hydrolyze all the PF_6^- to $PO_2F_2^-$ under these experimental conditions.

The facile hydrolysis of $AgPF_6$ in methylene chloride prompted its study in other solvents. Similar behavior was observed in chloroform and benzene. However, acetone, acetonitrile, and tetrahydrofuran solvents gave no observable hydrolysis after several days and even after addition of water. The coordinating ability of the solvent toward the silver cation seems to exert decisive control over the promotion of the hydrolysis process. Coincidently, in reported cases wherein $PO_2F_2^-$ is formed in the presence of $AgPF_6$, the corresponding reactions have been carried out in methylene chloride[5] or in benzene[8].

PO_2F_2–Palladium Complexes. Complex **2** was obtained according to eq 1. We propose for this complex a composition with three palladium centers and three $PO_2F_2^-$ ligands. This is because in the higher mass range of the FAB mass spectrum, the major peak observed (*m/z* = 686) can be assigned to a fragment which has lost a $PO_2F_2^-$ ligand from the parent ion of the proposed trimer species. However, an alternative composition with a different nuclearity, for example a polymer species can not be completely excluded. It has not been possible to obtain suitable crystals for an X-ray structure determination of complex **2**.

The complex **2** is a precursor to a range of complexes containing the $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(PO_2F_2)]$ fragment. **2** reacts with PR_3

(R = Ph, Cy, *p*-tolyl) (molar ratio 1:3) to give pale yellow solutions from which the complexes $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(PO_2F_2)(PR_3)]$ are isolated (eq 7). Before recrystallization, small amounts of the $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(PR_3)_2]PO_2F_2$ complexes are detected.

$$[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(\mu\text{-}PO_2F_2)]_3 + 3PR_3 \rightarrow 3[Pd(PO_2F_2)(\eta^3\text{-}2\text{-}MeC_3H_4)(PR_3)] \quad (7)$$

$$R = Cy, \mathbf{3};\ Ph, \mathbf{4};\ 4\text{-}MePh, \mathbf{5}$$

A single-crystal X-ray structure determination was carried out on complex **3**. In the unit cell there are two crystallographically independent, but essentially identical, molecules. The structure of one of them is depicted in Figure 2. Selected bond distances and angles are reported in Table 2.

The stereochemistry around palladium is approximately square planar with a coordination site occupied by a P atom from a PCy_3, two sites occupied by C atoms from the 2-methylallyl ligand, and the last site occupied by an oxygen atom from the $PO_2F_2^-$ anion. In both molecules the coordination bond distances are normal and the significantly different Pd–C bond lengths are in agreement with the larger trans effect of the P atom with respect to the O atom. The $PO_2F_2^-$ anion shows normal geometry with the largest bond angle between the oxygen atoms and the smallest between the fluorine atoms.

Complex **2** does not react with CH_3CN, even when its solution is refluxed. However, the complex $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(CH_3CN)_2]PF_6$[18] is obtained from **2** and $[Cu(CH_3CN)_4]PF_6$. It is most likely that the simultaneous formation of $CuPO_2F_2$ allows the displacement of the PO_2F_2 group by the CH_3CN ligand on the palladium center (eq 8).

$$[Pd(\eta^3\text{-}C_4H_7)(PO_2F_2)]_3 + [Cu(CH_3CN)_4]PF_6 \rightarrow [Pd(\eta^3\text{-}C_4H_7)(CH_3CN)_2]PF_6 + CuPO_2F_2 \quad (8)$$

Conclusions

To our knowledge, this is the first time that intermediates of the PF_6^- hydrolysis have been detected. Also an important conclusion of our work is that much care must be taken in working with $AgPF_6$ in noncoordinating solvents like CH_2Cl_2, $CHCl_3$, or benzene, especially when long reaction times, several hours, are involved. It may be helpful to reconsider previous work carried out by others using $AgPF_6$ in these solvents. The other solvent systems studied in this work exhibit no anomalous behaviour when used with this silver salt.

As far as we know, the present work describes the first example as well as the first structure determination of a palladium difluorophosphate complex. The availability of these compounds provides the opportunity for seeking new data on their reactivity.

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Supplementary Material Available: Complete tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, least-squares planes, and crystallographic data (14 pages). Ordering information is given on any current masthead page.

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