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New studies on the reactivity of allyl difluorophosphate palladium complexes: synthesis of the first difluorophosphate metallocene derivatives

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Abstract

The reaction of $[Pd(\eta^3\text{-}2Me\text{-}C_3H_4)(\mu\text{-}PO_2F_2)]_3$ **1**, previously synthesized by us, with P- or S-donor ligands leads to the new derivatives $[Pd(\eta^3\text{-}2Me\text{-}C_3H_4)(PO_2F_2)L]$ (L = $PMePh_2$; $P(OR)_3$, R = Me, Et, Ph; $SPPh_3$) and $[Pd(\eta^3\text{-}2Me\text{-}C_3H_4)L_2]PO_2F_2$ (L = $SPPh_3$). The neutral and ionic derivatives with L = tetrahydrothiophene, were detected by ^{1}H-NMR. The fluxional behavior of $SPPh_3$ complexes has been analyzed and a dissociation of $SPPh_3$ ligand evidenced. When **1** is made to react with $M(\eta^5\text{-}C_5R_5)_2Cl_2$ (M = Ti, R = H, Me; M = Mo, R = H) the new metallocene derivatives $M(\eta^5\text{-}C_5R_5)_2(PO_2F_2)_2$ are obtained. Using $M(PPh_3)PF_6$ (M = Ag, Cu) the complex $[Pd(\eta^3\text{-}2Me\text{-}C_3H_4)(PPh_3)_2]PF_6$ and $M(PO_2F_2)_x$ (M = Ag, $x = 1$; M = Cu; $x = 2$) are formed. A similar reaction takes place between $[Pd(\eta^3\text{-}2Me\text{-}C_3H_4)(PO_2F_2)(PPh_3)]$ and $Ag(ClO_4)PPh_3$. With $AuPPh_3PF_6$ and **1** no reaction is observed. The derivatives *trans*-$[PdCl(\mu\text{-}Cl)(PR_3)]_2$ (R = Ph, Cy) and $[Pd(\eta^3\text{-}2Me\text{-}C_3H_4)(PhCN)_2]PO_2F_2$ are formed after the reaction of $[Pd(\eta^3\text{-}2Me\text{-}C_3H_4)(PO_2F_2)(PR_3)]$ and $PdCl_2(PhCN)_2$. **1** or $[Pd(\eta^3\text{-}2Me\text{-}C_3H_4)(PO_2F_2)(PPh_3)]$, **2**, does not react with weak acids However, HCl gives rise to $[Pd(\eta^3\text{-}2Me\text{-}C_3H_4)Cl(PPh_3)]$ after the reaction with **2**. HBF_4 also reacts with **1** or **2** and by means of ^{19}F-NMR studies at low temperatures BF_4^- coordination has been observed when a non-coordinating solvent is used.

Keywords: Pd-, Ti- and Mo-complexes; Difluorophosphate; Fluxional behavior; BF_4^- coordination

1. Introduction

Recently we described [1] the first study of the hydrolysis process of $AgPF_6$ in organic solvents. Before our work, examples of the partial hydrolysis to $PF_2O_2^-$ of a PF_6^- ion acting as a counterion [2–6] or ligand [7] in several complexes had been described. Also the presence of $AgPO_2F_2$ in old samples had been postulated [8] to account for the formation of PO_2F_2 complexes. Recently, other cases of PF_6^- hydrolysis have been reported [9].

Our ^{19}F- and ^{31}P-NMR studies of the PF_6^- hydrolysis process in organic solution allowed us to state the catalytic role of the silver cation and a clear solvent influence. Also intermediates as POF_4^- or POF_3 were detected in solution. Interestingly, Cotton et al. [10] described the structure of a ruthenium complex containing a POF_4 ligand, proposed to be formed by partial hydrolysis of the PF_6^- ion over the long period of time required to obtain the crystalline product. We also described [1] the reaction between $[Pd(\eta^3\text{-}2Me\text{-}C_3H_4)Cl]_2$ and $AgPF_6$ in dichloromethane solution which led to $[Pd(\eta^3\text{-}2Me\text{-}C_3H_4)(\mu\text{-}PO_2F_2)]_3$, **1**, the first palladium difluorophosphate complex. Some reactivity of this derivative was initially explored. Its reaction with PR_3 ligands (molar ratio 1:3) allowed the isolation

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Table 1
^{1}H-NMR data for **5–15** and **19**[a]

Complex	η^3-2-Methylallyl group					P- or S-donor ligand
	–CH_3	$H_{1_{anti}}$	$H_{2_{anti}}$	$H_{1_{syn}}$	$H_{2_{syn}}$	
5	2.02 (s)	3.76 (d), $J_{HP}=9.3$	2.51 (s)	4.74 (d), $J_{HP}=6.3$	2.91 (s)	1.99 (d, Me), $J_{HP}=9.3$, 7.4–7.5 (m, Ph)
6	2.00 (s)	3.73 (d), $J_{HP}=13.9$	2.11 (s)	4.69 (d), $J_{HP}=9.8$	2.64 (s)	3.66 (d, Me), $J_{HP}=12.4$
6[b]	2.08 (s)	3.87 (d), $J_{HP}=14.0$	2.17 (s)	4.74 (d), $J_{HP}=9.8$	2.68 (s)	3.75 (d, Me), $J_{HP}=12.5$
7	2.04 (s)	3.74 (d), $J_{HP}=14.0$	2.17 (s)	4.72 (d), $J_{HP}=9.8$	2.71 (s)	1.31 (t, CH_3), $J_{HH}=7.1$, 4.08 (m, CH_2), $J_{HP}=9.1$, 7.1–7.6 (m, Ph)
8	1.4 (s)	3.71 (d), $J_{HP}=13.9$	1.84 (s)	4.75 (d), $J_{HP}=10.5$	2.93 (s)	
9	1.82 (s)	3.27 (pst), $J^*_{HP}=9.3$	3.27 (pst), $J^*_{HP}=9.3$	4.51 (pst, br), $J^*_{HP}=4.5$	4.51 (pst, br), $J^*_{HP}=4.5$	3.67 (pst, br, Me)
10	1.85 (s)	3.38 (pst), $J^*_{HP}=9.3$	3.38 (pst), $J^*_{HP}=9.3$	4.44 (pst, br)	4.44 (pst, br)	1.33 (t, CH_3), $J_{HH}=7.1$, 4.06 (m, CH_2)
11	1.84 (s)	3.34 (pst), $J^*_{HP}=9.0$	3.34 (pst), $J^*_{HP}=9.0$	4.02 (pst, br)	4.02 (pst, br)	7.1–7.6 (m, Ph)
12	1.96 (s)	2.30 (bs)	2.30 (bs)	3.79 (s)	3.79 (s)	1.92 (bs, CH_2), 2.98 (bs, CH_2–S)
13	1.98 (s)	3.17 (bs)	3.17 (bs)	3.84 (s)	3.84 (s)	1.93 (bs, CH_2), 2.98 (bs, CH_2–S)
14	1.86 (s)	2.60 (bs)	2.60 (bs)	3.72 (s)	3.72 (s)	7.5–7.8 (m, Ph)
14[b]	1.85 (s)	2.62 (bs)	2.62 (bs)	3.64 (s)	3.64 (s)	7.6–7.9 (m, Ph)
15	1.63 (s)	2.41 (bs)	2.41 (bs)	3.45 (s)	3.45 (s)	7.5–7.8 (m, Ph)
15[b]	1.63 (s)	2.62 (bs)	2.62 (bs)	3.51 (s)	3.51 (s)	7.6–7.9 (m, Ph)
19	2.14 (s)	2.89 (s)	2.89 (s)	3.93 (s)	3.93 (s)	7.5–7.9 (m, Ph)

[a] When two different ligands are present the subscript 1 refers to the allylic protons *cis* to the $PO_2F_2^-$ group. In $CDCl_3$ unless specified. Coupling constants in Hz. *J**, apparent coupling constant; pst, pseudotriplet; bs, broad singlet.
[b] $(CD_3)_2CO$.

of the complexes $[Pd(\eta^3\text{-}2Me\text{-}C_3H_4)(PO_2F_2)(PR_3)]$ (R = Ph, **2**; Cy, **3**; *p*-tolyl, **4**) while it did not react with CH_3CN. However, the complex $[Pd(\eta^3\text{-}2Me\text{-}C_3H_4)(CH_3CN)_2]PF_6$ was obtained from the trimer species **1** and $[Cu(CH_3CN)_4]PF_6$ with the concomitant formation of $CuPO_2F_2$.

We report here on the results of the reactivity studies we have pursued with **1** and its PR_3 derivatives, **2** and **3**, which include reactions with (i) other ligands, (ii) early and late transition metal complexes and (iii) acids. The aim of the work was to explore the behavior of complexes containing this unusual anion in a broad range of processes.

2. Results and discussion

2.1. Reactions with ligands

We carried out the reaction between the trimer complex **1** and other ligands as $PMePh_2$, phosphites, ($P(OR)_3$, R = methyl, ethyl, phenyl) and also the S-donor ligands tetrahydrothiophene (tht) or triphenylphosphine sulfide.

The P-donor ligands reacted with **1** in a ratio Pd:L = 1 and the complexes$[Pd(\eta^3\text{-}2Me\text{-}C_3H_4)(PO_2F_2)L]$, were obtained (Eq. (1)).

$$[Pd(\eta^3\text{-}C_4H_7)(\mu\text{-}PO_2F_2)]_3 + 3L \rightarrow 3[Pd(\eta^3\text{-}C_4H_7)(PO_2F_2)L]$$
$$L = PMePh_2,\ \mathbf{5};\ P(OMe)_3,\ \mathbf{6};\ P(OEt)_3,\ \mathbf{7};\ P(OPh)_3,\ \mathbf{8} \quad (1)$$

When phosphites were used as ligands the ionic derivatives $[Pd(\eta^3\text{-}C_4H_7)L_2]PO_2F_2$, (L = ($P(OMe)_3$), **9**; ($P(OEt)_3$), **10**; ($P(OPh)_3$), **11**), were also formed as minor components in a mixture with the neutral derivatives. It was not possible, even after several crystallization attempts, to separate the two complexes from the oily mixture (see Section 4) and they were identified by the ^{1}H- and $^{13}C\{^1H\}$-NMR signals in solution.

The ^{1}H- and $^{13}C\{^1H\}$-NMR data for the new complexes are collected in Tables 1 and 2, respectively. In the ^{1}H-NMR spectra of all the neutral complexes (**5–8**) an asymmetric allyl group is seen with two H_{syn} and two H_{anti} signals. The protons situated *trans* to phosphorus appear at higher chemical shift and exhibit the corresponding coupling constant (higher for the H_{anti} than for the H_{syn}). The signals of the phosphine or phosphite groups are also observed. For the determination of the corresponding coupling constants INDOR and heteronuclear decoupling experiments were made. The $^{13}C\{^1H\}$-NMR data confirmed the asymmetric nature of the allyl groups showing two different signals

Table 2
$^{13}C\{^1H\}$-NMR in $CDCl_3$ data for **6–11** and **14, 15**[a]

Complex	η^3-2- Methylallyl group				P- or S-donor ligand
	CH_3	C_1	C_2	C_3	
6	23.1 (s)	83.2 (d, $J_{CP} = 43.8$)	52.2 (s)	125.9 (s)	49.6 (s, CH_3)
7	23.9 (s)	83.2 (d, $J_{CP} = 43.9$)	51.0 (s)	136.1 (s)	16.7 (s, CH_3). 62.1 (bs, CH_2)
8	21.9 (s)	84.1 (d, $J_{CP} = 44.1$)	50.2 (s)	126.6 (s)	120.1 (d, $J_{CP} = 5.6$, C_{ortho}), 125.7 (s, C_{para}), 130.0 (s, C_{meta}), 150.2 (d, $J_{CP} = 4.6$, C_{ipso})
9	23.9 (s)	71.6 (pst, $J^*_{CP} = 23.0$)	71.6 (pst, $J^*_{CP} = 23.0$)	[b]	52.0 (pst, Me)
10	24.2 (s)	71.7 (pst, $J^*_{CP} = 24.0$)	71.7 (pst, $J^*_{CP} = 24.0$)	135.9 (s)	16.9 (s, CH_3). 62.6 (bs, CH_2)
11	[b]	73.2 (pst, br)	73.2 (pst, br)	[b]	136.3 (d, $J_{CP} = 8.6$, C_{ortho}), 120.3 (s, C_{para}), 130.6 (s, C_{meta}), 149.7 (s, C_{ipso})
14	22.3 (s)	62.8 (bs)	62.8 (bs)	127.9 (s)	129.0 (d, $J_{CP} = 17.5$, C_{ortho}), 133.0 (d, $J_{CP} = 4.5$, C_{para}), 132.7 (d, $J_{CP} = 14.7$, C_{meta}), C_{ipso} [b]
15	22.2 (s)	66.1 (bs)	66.1 (bs)	128.4 (s)	136.3 (d, $J_{CP} = 13.0$, C_{ortho}), 133.1 (bs, C_{para}), 132.1 (d, $J_{CP} = 11.0$, C_{meta}), C_{ipso} [b]

[a] C_1 and C_2 refers to the carbons *cis* or *trans* to the $PO_2F_2^-$ group, respectively. C_3, central carbon; J^*, pseudocoupling constant; pst, pseudotriplet; bs, broad singlet.
[b] Not observed.

for the terminal carbons with a chemical shift at lower field for those situated *trans* to phosphorus. This result is in accordance with the higher trans influence of the phosphine or phosphite ligands [11] as compared to the $PO_2F_2^-$ group.

In the ^{31}P-NMR spectra a singlet is observed for the neutral ligands while the difluorophosphate gives rise to a triplet ($J_{PF} = 953–963$ Hz). The corresponding doublet is observed in the ^{19}F-NMR spectra for this group.

When the reaction of **1** with three equivalents of tht (tht = tetrahydrothiophene) was monitored in a NMR tube ($CDCl_3$ solution) the formation of a new complex **12**, as well as the complete disappearance of **1**, was observed. Apparently the allyl group is symmetric although the broad appearance of the H_{anti} and H_{syn} signals might be indicative of a fluxional process. The addition of another equivalent of tht per palladium center gave rise to a different derivative, **13**, with unique and narrow signals for the H_{anti} and H_{syn} shifted to lower field with respect to **12**. In both cases, the corresponding signals of the tht group were observed. The sequence of reactions reflected in ref. Eq. (2) could account the NMR data.

When the reaction was made in a Schlenk to isolate the corresponding complexes, only the derivative **1** is obtained. Probably when vacuum is applied to the solid, the tht group that must be slightly bonded, is replaced by the $PO_2F_2^-$ group. This can be easily understood if we consider the numerous examples of late transition metal complexes where this ligand is easily replaced by other groups [12].

A different behavior was observed when **1** was made to react with other S-donor ligand as $SPPh_3$. In this case, and using a ratio L:Pd = 1 or 2, the new complexes $[Pd(\eta^3\text{-}C_4H_7)(PO_2F_2)(SPPh_3)]$, **14**, and $[Pd(\eta^3\text{-}C_4H_7)(SPPh_3)_2]PO_2F_2$, **15,** respectively, were easily obtained.

$$1/3[Pd(\eta^3\text{-}C_4H_7)(\mu\text{-}PO_2F_2)]_3 + L \rightarrow [Pd(\eta^3\text{-}C_4H_7)(PO_2F_2)L] \text{ (12, 14)} \rightarrow [Pd(\eta^3\text{-}C_4H_7)L_2](PO_2F_2) \text{ (13, 15)} \quad (2)$$

L = tht (**12, 13**); $SPPh_3$ (**14, 15**)

The ^1H-NMR spectrum of **14**, besides the signals of the phenyl and methyl groups, show only two resonances, one for each type of allylic proton (H_{syn} and H_{anti}). This is not in accordance with the expected asymmetric environment of the allyl group in this complex. A similar observation has been made for the corresponding tht complex and it contrasts with the four signals obtained for the *syn* and *anti* protons in case of phosphine or phosphite complexes of similar stoichiometry (for complex **3** an increase in the temperature up to 55°C, does not affect the chemical shift of these four signals). In the $^{13}C\{^1H\}$-NMR spectrum of **14** also a unique, although broad, signal is obtained for the terminal allylic carbons. All these data indicate that a fluxional process that interconverts both ends of the allylic group (*syn–syn*, *anti–anti* interconversion) is taking place (see below for discussion). The ^1H- and $^{13}C\{^1H\}$-NMR spectra of **15** exhibit the expected resonances considering the symmetry of the allyl group. However, the signals corresponding to the H_{anti}, H_{syn}

and terminal allylic carbons are broad which also point to a possible dynamic behavior.

Several mechanisms have been proposed to account for the *syn–syn*, *anti–anti* interconversion. Although the simple rotation of the allyl ligand is a mechanism often proposed to explain some isomerizations in complexes of metals as Mo, W and Fe [13], it is not widely accepted for square-planar palladium complexes and orbital considerations suggest a high activation barrier in square-planar geometries [14]. This rotation is apparently a more facile process via a possible pentacoordinate intermediate [14]. Dissociative pathways, via tricoordinate palladium intermediates, with monodentate ligands such as CO [15], $SnCl_3$ [16], amines [17], macrocycles [18], polyenes [19], and also N-donor chelate ligands [20] have been proposed to explain the dynamic behavior in asymmetric allyl palladium complexes. A η^3-η^1-η^3 mechanism is not considered in our case because it would lead to a different interchange (*syn–anti*). Besides, when the temperature is increased, a change in the H_{syn}, H_{anti} chemical shifts is not observed.

We carried out several experiments in order to study the possible fluxional behavior of **14** and **15**. An ^{1}H-NMR variable temperature study of **14** in CD_2Cl_2 was carried out with the aim of splitting the H_{anti} and H_{syn} resonances and observe the corresponding coalescences. Lowering the temperature these signals are broadened and split in a very complex way without being possible to measure any clear coalescence temperature. Also the methyl resonance is split and at least three different methyl groups are observed. Obviously, this implies that different allylic groups coexist in solution at low temperature.

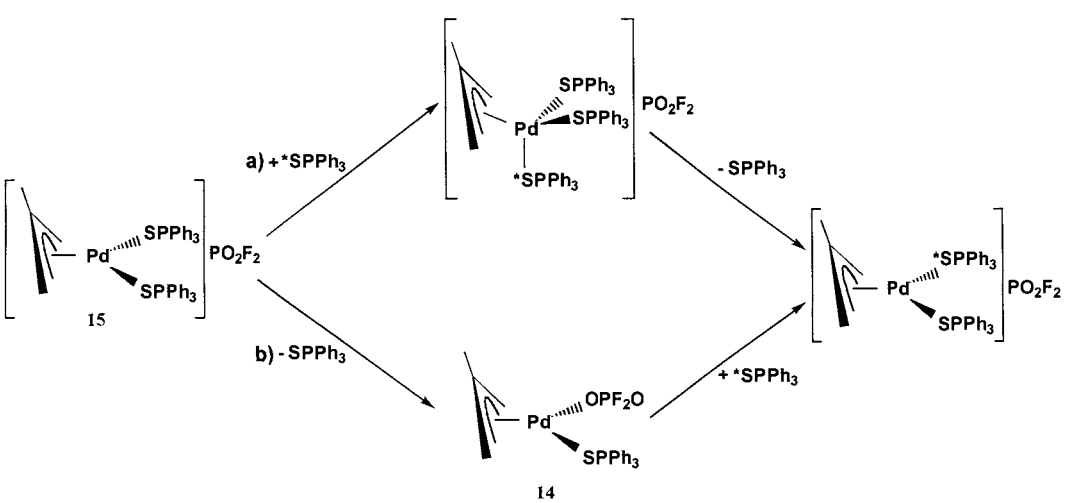
Considering that the $PO_2F_2^-$ group is also present in the phosphine or phosphite complexes which do not exhibit fluxional behavior and that the dynamic processes are observed in complexes with S-donor ligands, we decided to explore the possibility of the dissociation of the $SPPh_3$ group as the origin of the observed behavior of **14** and **15.**

A ^{31}P-NMR variable temperature study of a mixture of **15** and free $SPPh_3$ in acetone-d^6 was undertaken. At room temperature (r.t.) only one signal was seen (besides the triplet of the $PO_2F_2^-$ group) while at low temperature two clearly separated peaks, corresponding to **15** and free $SPPh_3$, were observed. The coalescence temperature was -34°C and the calculated free energy of activation 43.0 kJ mol^{-1}. Consequently, for complex **15** an interchange between free and coordinated $SPPh_3$ is taking place. From this experiment it is not possible to conclude if the interchange occurs via a previous coordination of the free ligand and formation of a pentacoordinate intermediate (path a, Scheme 1) or via a spontaneous dissociation of $SPPh_3$ (path b, Scheme 1) and the participation of **14** as a possible intermediate.

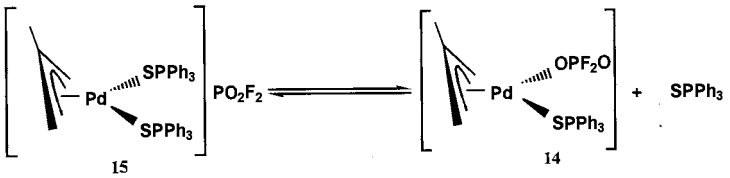
In order to test the possible spontaneous dissociation of $SPPh_3$ in **15** in the absence of free ligand, we have made to react **15** with **1** in a NMR tube ($CDCl_3$). A ^{31}P-NMR made instantaneously shows that **14** is the only palladium complex present (Eq. (3)).

$$[Pd(\eta^3\text{-}C_4H_7)(SPPh_3)_2]PO_2F_2\ (\mathbf{15}) + 1/3[Pd(\eta^3\text{-}C_4H_7)(\mu\text{-}PO_2F_2)]_3\ (\mathbf{1}) \rightarrow 2[Pd(\eta^3\text{-}C_4H_7)(PO_2F_2)(SPPh_3)]\ (\mathbf{14}) \quad (3)$$

Consequently, complex **15** is capable of dissociating $SPPh_3$ in the absence of free ligand. The $PO_2F_2^-$ group may enter the coordination sphere of the palladium center to occupy the position of an $SPPh_3$ ligand that is lost and the equilibrium, probably shifted to the left, reflected in Scheme 2 may be established. The existence of this equilibrium might explain the broad appearance of the ^{1}H- and ^{13}C-NMR resonances.



Scheme 1.



15 14

Scheme 2.

Supposing that, like **15**, **14** may also dissociate $SPPh_3$, the intermediate thus formed could be stabilized by a chelate coordination of the $PO_2F_2^-$ group or via the formation of oligomeric species with the $PO_2F_2^-$ ligands acting as bridges between two metal centers (see Scheme 3). The opening of a Pd–O bond and recoordination of the $SPPh_3$ ligand in a different position complete the process that makes equivalent the two halves of the allylic group. The existence of different species acting as intermediates may explain the complexity of the spectrum of **14** at low temperature.

The possibility of formation of a pentacoordinate intermediate without dissociation of a $SPPh_3$ group and via coordination of an oxygen atom of another molecule can not be fully excluded. In this intermediate the rotation of the allyl group should be more facile and this would account for the r.t. ^{1}H- and $^{13}C\{^1H\}$-NMR spectra. However, this mechanism is less appropriate to explain the low temperature ^{1}H-NMR spectrum.

2.2. Reactions with early and late transition metal complexes

Some reactions of **1** or its phosphine derivatives **2** and **3** with early and late transition metal complexes were explored. The high oxophilicity of the first type of metals would probably lead to a transfer of the $PO_2F_2^-$ group and, consequently, to the generation of new complexes. The second type of metals having a not very different oxophilicity from palladium could give rise to new derivatives with a bridging $PO_2F_2^-$ group. The ability of this ligand to act as a bridge not only in homonuclear but also in heteronuclear complexes is well established [21].

Derivatives of the type $MCp^R_2Cl_2$ where chosen to react with **1** for two reasons: (i) the high stability of the 'MCp^R_2' fragment and (ii) the presence of the chloride groups that could favor the transfer process by the formation of the highly stable palladium dimer $[Pd(\eta^3\text{-}C_4H_7)Cl]_2$. According to our proposal, the reaction of $M(\eta^5\text{-}C_5R_5)_2Cl_2$ (M = Ti, R = H, Me; Mo, R = H) with **1** leads to the formation of the new derivatives **16–18**, as is shown in Scheme 4.

Complexes **16–18** exhibit solubility properties very similar to those of $[Pd(\eta^3\text{-}C_4H_7)Cl]_2$. Consequently, it was not possible to achieve proper separation of the two products that are obtained in the corresponding reaction. After careful crystallization small amounts of the pure products were obtained which allowed their complete characterization (an alumina chromatographic column made to separate **16** and $[Pd(\eta^3\text{-}C_4H_7)Cl]_2$ led to decomposition of the titanium complex).

Only one resonance is seen in the ^{1}H-NMR spectra of **16–18** showing the equivalence of the two cyclopentadienyl groups. According with that, complexes **16** and **18** give rise to a unique signal in the corresponding $^{13}C\{^1H\}$–NMR spectra while **17** exhibits the two signals of the methyl and cyclopentadienyl carbons. In the ^{31}P- and ^{19}F-NMR spectra, the resonances corresponding to the $PO_2F_2^-$ groups are observed.

The similar reaction of **1** with $ZrCp^R_2Cl_2$ {$Cp^R = C_5H_5$ ([22]a), $C_5H_4(SiMe_3)$, $C_5H_3(SiMe_3)_2$ ([22]b)} also led to the formation of $[Pd(\eta^3\text{-}C_4H_7)Cl]_2$ which is indicative of a $PO_2F_2^-$ transfer process. However, the expected zirconium complex $ZrCp^R_2(PO_2F_2)_2$ can not be isolated and a very insoluble white solid was obtained which was not fully characterized.

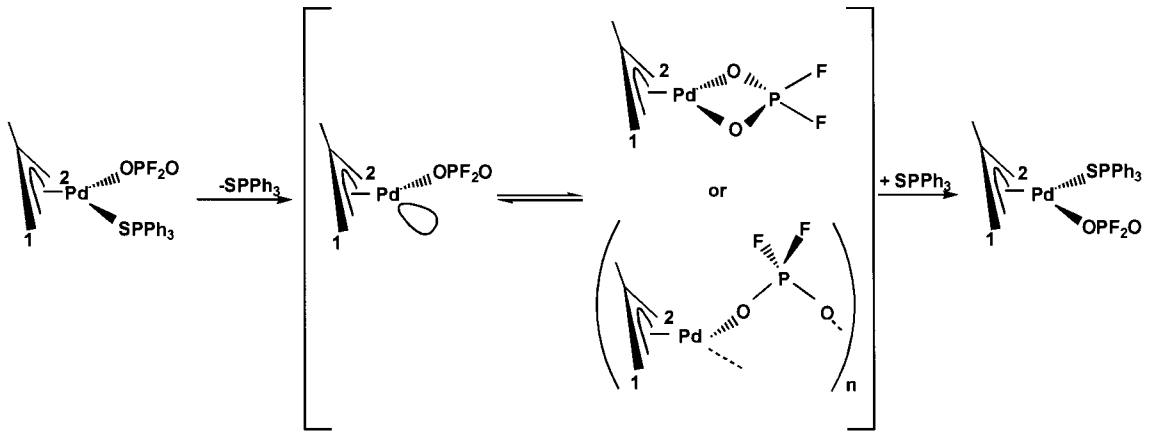
To our knowledge complexes **16–18** are the first described metallocene derivatives containing the difluorophosphate group. Although some difluorophosphate titanium derivatives as $TiCl_2(PO_2F_2)_2$ have been described [23], **16** and **17** are the first organometallic complexes of titanium containing this group. As far as we know, difluorophosphate molybdenum derivatives have not been previously reported.

The reaction of **1** with $[MPPh_3]PF_6$ (M = Cu, Ag), freshly prepared in THF solution from $AgClPPh_3$ [24] or $[CuClPPh_3]_4$ [25] and $TlPF_6$, did not give the expected heteronuclear $PO_2F_2^-$ bridged complexes but the known derivative $[Pd(\eta^3\text{-}C_4H_7)(PPh_3)_2]PF_6$. When $M = Ag^+$, $AgPO_2F_2$ was also obtained and for M = Cu the species $CuPO_2F_2$ that could be initially formed must disproportionate and Cu(0) and $Cu(PO_2F_2)_2$ were obtained. According with the stoichiometry the solvato complex $[Pd(\eta^3\text{-}C_4H_7)(S)_2]PF_6$ could remain in solution but it decomposes when the solution is evaporated to dryness (see Eq. (4)).

$$2\,[Pd(\eta^3\text{-}C_4H_7)(PO_2F_2)]_3 + 6\,[M(PPh_3)]PF_6 \xrightarrow{THF} 3\,[Pd(\eta^3\text{-}C_4H_7)(PPh_3)_2]PF_6 + 6\,M(PO_2F_2) + 3\,[Pd(\eta^3\text{-}C_4H_7)(S)_2]PF_6$$

$$\downarrow M=Cu$$

$$3\,Cu(PO_2F_2)_2 + 3Cu \qquad (4)$$



Scheme 3.

In order to prevent the formation of the solvato derivative, the complex $[Pd(\eta^3\text{-}C_3H_7)(PO_2F_2)(PPh_3)]$ was used as starting product. The silver derivative utilized was $Ag(ClO_4)PPh_3$ [24b]. The reaction led clearly to the formation of $[Pd(\eta^3\text{-}C_4H_7)(PPh_3)_2]PF_6$ and $AgPO_2F_2$ (Eq. (5)).

$$[Pd(\eta^3\text{-}C_4H_7)(PO_2F_2)(PPh_3)] + Ag(ClO_4)PPh_3 \rightarrow [Pd(\eta^3\text{-}C_4H_7)(PPh_3)_2]ClO_4 + AgPO_2F_2 \quad (5)$$

The behavior of **1** against a THF solution of $[AuPPh_3]PF_6$ [26] was different. The transfer of PPh_3 and $PO_2F_2^-$ did not take place and **1** was recovered unaltered even after long reaction times.

Complexes **2** and **3** reacted instantaneously with $PdCl_2(PhCN)_2$ [27], a bright red color appearing in the solution. After appropriate work up, two products were separated from the reaction mixture: *trans*-$[PdCl(\mu\text{-}Cl)(PR_3)]_2$ [28], R = Ph, Cy and $[Pd(\eta^3\text{-}C_4H_7)(PhCN)_2]PO_2F_2$ (**19**) (see Scheme 5)

Consequently, a mutual transfer of PR_3 and PhCN ligands between the '$PdCl_2$' and '$Pd(\eta^3\text{-}C_4H_7)$' fragments takes place. The previously described dimer complexes [29] exhibit in the stretching M–Cl region of the corresponding IR spectra, the expected three normal vibration modes characteristic of C_{2h} square-planar complexes of the type *trans*-MX_4L_2 [30]. A single resonance is observed in their ^{31}P-NMR spectra.

In the mass spectrum of *trans*-$[PdCl_2(PCy_3)]_2$ peaks are observed at m/z 915 $[M^+]$, 881 $[M-Cl]^+$, 527 $[M-3Cl-PCy_3]^+$ and 421 $[PdCl(PCy_3)]^+$.

Although the cation of complex **19** has already been described [31], the complex with the difluorophosphate anion has not been previously reported. The existence of a symmetric allyl group is deduced from the ^{1}H-NMR spectrum (one type of H_{anti} and H_{syn}) where the corresponding resonances of the PhCN group are also observed. In the ^{31}P- and ^{19}F-NMR spectra the expected signals for the $PO_2F_2^-$ are seen.

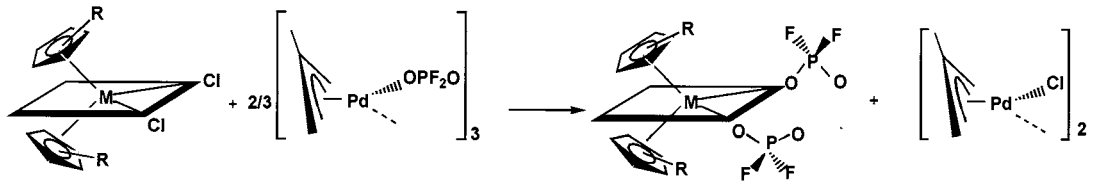
2.3. Reaction with acids

In the process of formation of **1** that implies the hydrolysis of the PF_6^- anion, HF is simultaneously formed [1]. Under the reaction conditions, **1** does not react with this acid. However, we decided to find out if changes in the strength of the acid or in the coordinating ability of the anion could lead to the protonation of the difluorophosphate group in **1** or in its derivative **3** that contains a monodentate $PO_2F_2^-$ group.

When **1** is made to react, in a 1:3 molar ratio, with acetylacetone or CF_3COOH, both with conjugated bases anions of good coordinating ability, no reaction was observed after 6 h in $CDCl_3$ at r.t. However, when the reaction of **1** with $HBF_4 \cdot Et_2O$, (1:3 ratio), a stronger acid but with a weak coordinating anion, was monitored by ^{1}H-NMR (acetone-d_6) an instantaneous reaction was detected. A product with a symmetric allyl group, different to **1**, was observed. A broad signal at 11.72 ppm was also seen. The complex $[Pd(\eta^3\text{-}C_4H_7)\{(CD_3)_2CO\}_2]BF_4$, already described with non deuterated acetone [31], is probably formed as it is reflected in Eq. (6).

$$[Pd(\eta^3\text{-}C_4H_7)(\mu\text{-}PO_2F_2)]_3 + 3HBF_4 \rightarrow 3[Pd(\eta^3\text{-}C_4H_7)\{(CD_3)_2CO\}_2]BF_4 + 3HPO_2F_2 \quad (6)$$

Considering these results, and looking for a coordination of the tetrafluoroborate anion, the same reaction was performed in a non coordinating solvent as $CDCl_3$. Signals corresponding to a symmetric allyl group, different to **1**, and a broad singlet at 8.43 ppm, were observed. The triplet and the quartet of the Et_2O molecule appeared at 3.8 and 1.4 ppm, shifted to lower field with respect to the expected signals of free Et_2O in this solvent, pointing out to a coordination of the molecule to the palladium center. In the ^{19}F-NMR a complex signal was observed in the BF_4^- region at r.t. and, consequently, a variable temperature NMR study was undertaken. In Fig. 1 the appearance of the region



M= Ti; R= H (**16**), Me (**17**)
M= Mo; R= H (**18**)

Scheme 4.

at selected temperatures is collected. The four signals (two thin and two slightly broad) seen at −75°C were transformed into two thin singlets at −60°C. When the temperature was increased, two effects were observed: (i) a coalescence of the two signals at ca. 40°C and (ii) the appearance of a third singlet whose intensity increased with temperature.

Although the BF_4^- anion is considered to be of very weak coordinating ability (see [32] for a comparative study of different anions), several examples of BF_4^- coordination have been described. The coordination has been proposed from IR spectra [33] or unambigously seen by X-ray diffraction studies [34]. ^{19}F-NMR [35] has also been used to find some of the M–FBF_3 interactions. With metals such as Mo, W [36], or Fe [37] two signals at very different chemical shifts (usually a quartet and doublet) have been found for the two types of fluorine atoms, but in other cases a singlet, as a consequence of fluorine interchange, has been observed for a coordinated BF_4^- [35,38]. Also equilibria between free and coordinated groups have been described [33a] with the amount of the former usually increasing with temperature [35]. Considering these ideas we propose that in our case at −75°C the less intense signals that appear at −147.9 and −148.2 ppm correspond to two types of fluorine atoms (three for the broad signal) of a coordinated BF_4^- group. The same must apply for the two intense signals that appear at −151.0 and −151.2 ppm for another type of BF_4^-, also coordinated. An increase in temperature leads to a rapid interchange of the two types of fluorine atoms of each group. Further increasing of temperature finally leads to interchange between these two groups. The new central signal may be due to free BF_4^- whose ratio reasonably increases with temperature. The possible coalescence between the ^{19}F-NMR signals of free and coordinated groups can not be seen perhaps due to the limit of the solvent boiling point.

Before proposing the possible species that could coexist in solution the $PO_2F_2^-$ region of the ^{19}F-NMR spectra must be considered (see Fig. 2). At low temperature two doublets with a similar J_{PF} of 973–976 Hz and 7:3 ratio are observed. After increasing the temperature both are broadened until the coalescence is reached at 20°C. At 60°C a unique thin doublet is observed. The corresponding triplets are observed in the ^{31}P-NMR spectra. The coupling constants are higher than those observed for complexes with the difluorophosphate group and similar to that described for the difluorophosphoric acid, 974 Hz [39] (other authors have reported a J_{PF} of 992 Hz for this acid [40]). As a consequence two types of HPO_2F_2 must be present in solution.

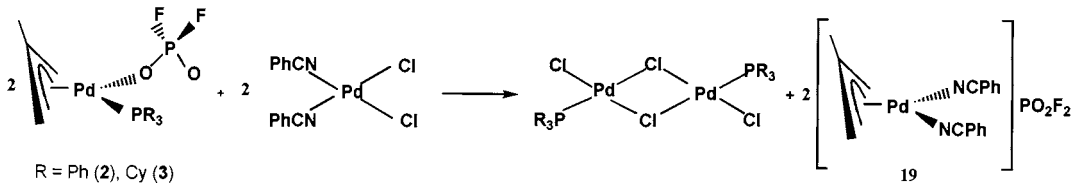
Considering all these data, we propose the existence of an equilibrium between species A, B and C as shown in Scheme 6. The formation of a hydrogen bond with the BF_4^- group might favor the coordination of the acid in A. This group will be in equilibrium with free acid HPO_2F_2.

At low temperature only one type of allyl is seen in the ^{1}H-NMR spectrum. Perhaps the chemical shift differences between the different signals are not big enough to give rise to separate signals at low temperature.

We have also explored the reactivity of complex **2** with acids. No reaction was observed with CF_3COOH. When **2** was made to react with a HCl solution in Et_2O, a complex is obtained whose analytical and spectroscopic data correspond with the known complex $[Pd(\eta^3\text{-}C_4H_7)Cl(PPh_3)]$ [41] (see Eq. (7)). A broad singlet in the ^{1}H-NMR spectrum may correspond to HPO_2F_2.

$$[Pd(\eta^3\text{-}C_4H_7)(PO_2F_2)(PPh_3)]\ (\mathbf{2}) + HCl \cdot Et_2O \rightarrow [Pd(\eta^3\text{-}C_4H_7)Cl(PPh_3)] + HPO_2F_2 \quad (7)$$

The reaction of **2** with $HBF_4 \cdot Et_2O$ in $(CD_3)_2CO$ in an NMR tube was analyzed by ^{1}H-, ^{19}F- and ^{31}P-NMR. After 10 min three types of allyl groups, two symmetric and one asymmetric, were seen in the ^{1}H-NMR. One product was unambiguously identified as $[Pd(\eta^3\text{-}C_4H_7)(PPh_3)_2]BF_4$ [31]. Two doublets were seen in the difluorophosphate region of the ^{19}F-NMR ($J_{PF} = 973.6$ and 964.4 Hz) that may correspond to the acid and the anion. In the BF_4^- region three singlets (one minor) are observed. In the ^{31}P-NMR spectrum, besides the two expected triplets, two singlets corresponding to two different PPh_3 groups were seen. Considering all this data, we cannot propose specific formulations for the



Scheme 5.

unknown complexes. They must be adducts where coordination of PPh_3, $(CD_3)_2CO$, $PO_2F_2^-$ (or the acid) and BF_4^- to the allyl fragment is possible. We have also recorded the corresponding spectra after 3 h of reaction. The most remarkable fact is the appearance of three doublets ($J_{PF} = 927.8$, 967.4 and 961.4 Hz) in the difluorophosphate region of the ^{19}F-NMR spectrum. The same coupling constant are found in three doublets of the corresponding ^{31}P-NMR spectrum. Consequently an evolution of HPO_2F_2 (or $PO_2F_2^-$) towards species containing a single fluorine atom bonded to phosphorus, has taken place.

3. Conclusions

The results reported above indicate that in palladium complexes the difluorophosphate group is easily replaced by P-donor ligands. In case of S-donor ligands, a competition between the two groups is observed and a dissociation of $SPPh_3$ evidenced. The difluorophosphate anion is easily transferred to early metals and this process has allowed the synthesis of the first metallocene–PO_2F_2 complexes. The formation of the highly insoluble salts $AgPO_2F_2$ or $Cu(PO_2F_2)_2$ seems to prevent the formation of heteronuclear Pd–Ag or Pd–Cu complexes. The formation of the stable dimers *trans*-[Pd(μ-Cl)Cl(PR_3)]$_2$, R = Ph, Cy leads to the mutual transfer of PR_3 and PhCN ligands between the 'PdCl$_2$' and 'Pd(η^3-C_4H_7)' fragments while the difluorophosphate group remains uncoordinated. It is possible to remove the PO_2F_2 fragment by protonation only with strong acids. When the process is carried out with HBF_4 in a non coordinating solvent, it is possible to see at low temperature species with the BF_4^- anion coordinated.

In summary, the results presented in this paper give an illustration of the potential of the difluorophosphate complexes, being that a group easily seen in ^{19}F- and ^{31}P-NMR that may constitute an alternative to other more common anions.

4. Experimental details

4.1. General

All reactions were performed using standard Schlenk techniques under an atmosphere of dry, oxygen-free, nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. Elemental analyses were performed with a Perkin-Elmer 2400 microanalyser. IR spectra were recorded as KBr pellets or Nujol mulls with a Perkin-Elmer PE 883 IR spectrometer. NMR spectra were recorded on a Varian Unity 300 MHz and a Gemini 200 MHz. Chemical shifts (ppm) are relative to $SiMe_4$ (^{1}H- and ^{13}C-NMR),$CClF_3$ (^{19}F-NMR) and 85% H_3PO_4 (^{31}P-NMR). Coupling constants (J) are in Hertz. Mass spectra were performed with a VG Autospec instrument using the FAB technique and nitrobenzyl alcohol as matrix. [Pd(η^3-C_4H_7)(μ-PO_2F_2)]$_3$ (**1**) and [Pd(η^3-C_4H_7)(PO_2F_2)(PR_3)] (R = Ph, **2**; Cy, **3**; *p*-tolyl, **4**) [1], [Ti(η^5-C_5H_5)$_2$Cl$_2$] [42], [Ti(η^5-C_5Me_5)$_2$Cl$_2$] [43], [Mo(η^5-C_5H_5)$_2$Cl$_2$] [44] and $PdCl_2(PhCN)_2$ [27] were prepared according to the published methods. Free energies of activation were calculated from the coalescence temperature (T_c), and the frequency difference between the coalescing signals with the formula $\Delta G^{\neq} = aT_c(10.319 + \log T_c/k)$; k values were calculated according to the Shanan-Atidi and Bar-Eli method [45].

4.2. Synthesis of [Pd(η^3-C_4H_7)(PO_2F_2)($PMePh_2$)] (5)

To a solution of **1** (0.200 g, 0.254 mmol) in 20 ml of CH_2Cl_2, $PMePh_2$ (143.39 μl, 0.762 mmol) was added. The reaction mixture was allowed to stir at r.t. and after 1 h the solvent was removed in vacuo and an oil was isolated. ^{19}F-NMR ($CDCl_3$): −81.5 (d, $J_{FP} = 962.9$ Hz). ^{31}P{^{1}H}-NMR ($CDCl_3$): −11.2 (t, PO_2F_2); 13.4 (s, $PMePh_2$).

4.3. Reaction of 1 with the phosphites P(OMe)$_3$, P(OEt)$_3$ and P(OPh)$_3$

The procedure is identical to that described for the isolation of complex **5**. Amounts used are as follows:

1 (0.150 g, 0.190 mmol) in 20 ml of CH_2Cl_2 and $P(OMe)_3$ (69.31 μl, 0.570 mmol). An oil is obtained corresponding to a mixture of complex **6** with minor amounts of complex **9**. **6**: ^{19}F-NMR ($(CD_3)_2CO$): −82.3 (d, $J_{FP} = 953.1$ Hz). ^{31}P{^{1}H}-NMR ($(CD_3)_2CO$): −9.5 (t, PO_2F_2); 134.7 (s, $P(OMe)_3$). **9**: ^{19}F-NMR ($(CD_3)_2CO$): −82.3 (d, $J_{FP} = 953.1$ Hz). ^{31}P{^{1}H}-NMR ($(CD_3)_2CO$): −9.5 (t, PO_2F_2); 136.7 (s, $P(OMe)_3$).

1 (0.150 g, 0.190 mmol) in 20 ml of CH_2Cl_2 and $P(OEt)_3$ (99.43 μl, 0.570 mmol). An oil is obtained corresponding to a mixture of complex **7** with minor

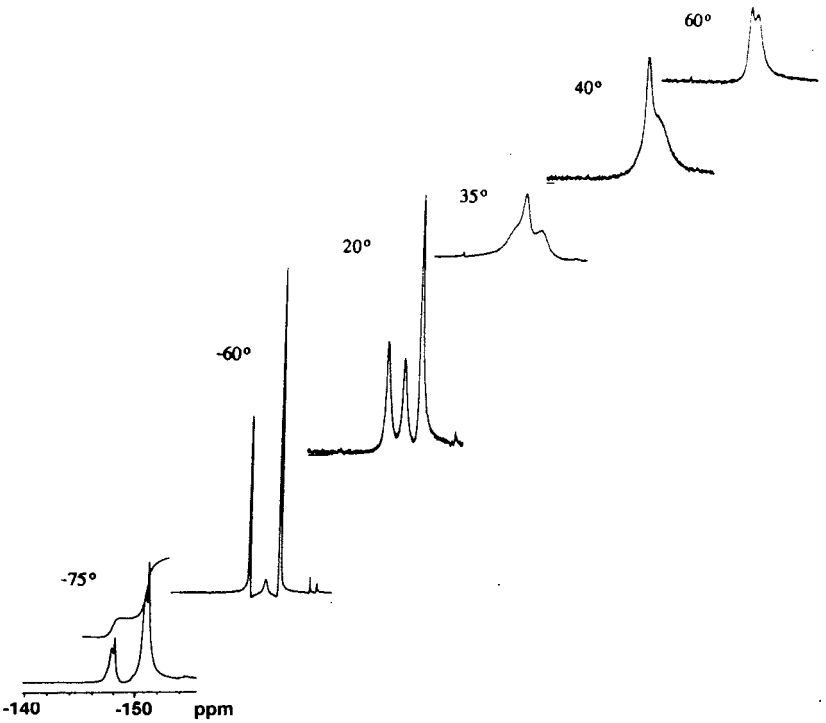


Fig. 1. Selected spectra from the variable-temperature ^{19}F-NMR study for the reaction between complex **1** and $HBF_4 \cdot Et_2O$ ($CDCl_3$) in the BF_4^- region.

amounts of complex **10**. **7**: ^{19}F-NMR ($CDCl_3$): -82.4 (d, $J_{FP} = 963.2$ Hz). $^{31}P\{^1H\}$-NMR ($CDCl_3$): -9.2 (t, PO_2F_2); 130.2 (s, $P(OEt)_3$). **10**: ^{19}F-NMR ($CDCl_3$): -82.4 (d, $J_{FP} = 963.2$ Hz). $^{31}P\{^1H\}$-NMR ($CDCl_3$): -9.2 (t, PO_2F_2); 128.0 (s, $P(OEt)_3$).

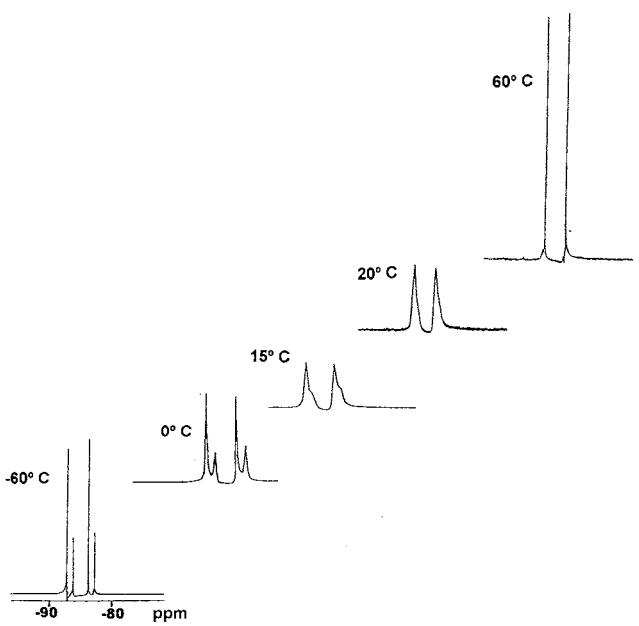


Fig. 2. Selected spectra from the variable-temperature ^{19}F-NMR study for the reaction between complex **1** and $HBF_4 \cdot Et_2O$ ($CDCl_3$) in the $PO_2F_2^-$ region.

1 (0.150 g, 0.190 mmol) in 20 ml of CH_2Cl_2 and $P(OPh)_3$ (0.150 μl, 0.570 mmol). An oil is obtained corresponding to a mixture of complex **8** with minor amounts of complex **11**. **8**: ^{19}F-NMR ($CDCl_3$): -84.0 (d, $J_{FP} = 961.0$ Hz). $^{31}P\{^1H\}$-NMR ($CDCl_3$): -9.1 (t, PO_2F_2); 125.5 (s, $P(OPh_3)$). **11**: ^{19}F-NMR ($CDCl_3$): -84.0 (d, $J_{FP} = 961.0$ Hz). $^{31}P\{^1H\}$-NMR ($CDCl_3$): -9.1 (t, PO_2F_2); 123.3 (s, $P(OPh_3)$).

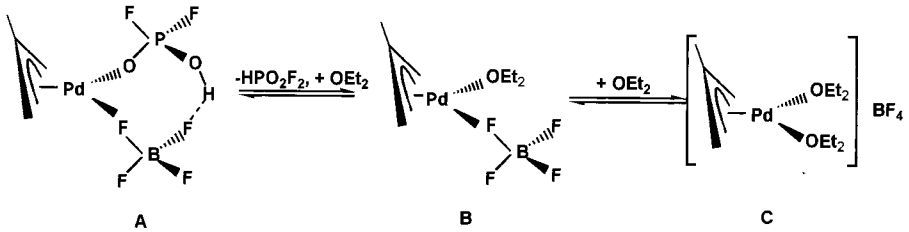
Several attempts were made to crystallize the oils obtained in Sections 4.2 and 4.3. The oils were treated with different solvent mixtures (CH_2Cl_2/Et_2O, CH_2Cl_2/pentane, thf/hexane, thf/Et_2O) or dried under vacuum for a long period of time at low temperature. Only in the case of $P(OPh)_3$ a solid was obtained at low temperature but it became an oil when it was warmed to r.t.

*4.4. Spectroscopic characterization of [Pd(η^3-C_4H_7)(PO_2F_2)(tht)] (**12**)*

To a yellow solution of **1** (0.030 g, 0.038 mmol) in 5 ml of $CDCl_3$ was added tht (10.15 μl, 0.114 mmol) in a NMR tube and the solution changed to a pale yellow color. After 5 min the solution was studied by ^1H-NMR.

*4.5. Spectroscopic characterization of [Pd(η^3-C_4H_7)(tht)$_2$](PO_2F_2) (**13**)*

To a yellow solution of **1** (0.030 g, 0.038 mmol) in 5 ml of $CDCl_3$ in a NMR tube, tht (20.30 μl, 0.228 mmol)



Scheme 6.

was added. The solution turned pale yellow. After 5 min the solution was studied by ^{1}H-NMR.

4.6. Synthesis of [Pd(η^3-C$_4$H$_7$)(PO$_2$F$_2$)(SPPh$_3$)] (**14**)

To a yellow solution of **1** (0.150 g. 0.190 mmol) in 20 ml of CH_2Cl_2, $SPPh_3$ (0.171 g, 0.570 mmol) was added. The solution was allowed to stir at r.t. and after 14 h the solvent was removed in vacuo. Dry hexane was added to triturate the beige oil. The resulting solid was isolated by filtration and crystallized from CH_2Cl_2 layered with Et_2O. Anal. Calc. for $C_{22}H_{22}F_2O_2P_2PdS$: C, 47.45; H, 3.98. Found: C, 47.21; H, 4.21%. ^{19}F-NMR ($CDCl_3$): −83.1 (d, $J_{FP} = 967.4$ Hz). ^{31}P{^{1}H}-NMR ($CDCl_3$): −14.4 (t, PO_2F_2); 45.7 (s, $SPPh_3$); (free $SPPh_3$ 45.2 (s) in $CDCl_3$). IR: ν_{assym} (PO_2) 1310; ν_{sym} (PO_2) 1152; ν_{assym} (PF_2) 849; ν_{sym} (PF_2) 836; δ(PO_2) 513; δ(POF) 497 cm^{-1}.

4.7. Synthesis of [Pd(η^3-C$_4$H$_7$)(SPPh$_3$)$_2$](PO$_2$F$_2$) (**15**)

To a yellow solution of **1** (0.100 g, 0.127 mmol) in 20 ml of CH_2Cl_2, $SPPh_3$ (0.229 g, 0.762 mmol) was added. The pale green solution thus formed was allowed to stir at r.t. and after 20 h the solvent was removed in vacuo. Dry hexane was added to triturate the beige oil. The resulting solid was isolate via filtration and crystallized from CH_2Cl_2 layered with Et_2O. Anal. Calc. for $C_{40}H_{37}F_2O_2P_3PdS_2$: C, 47.45; H, 3.98. Found: C, 47.21; H, 4.21%. ^{31}P{^{1}H}-NMR (acetone-d^6): −10.7 (t, PO_2F_2, $J_{PF} = 949.0$ Hz); 46.8 (s, $SPPh_3$). IR: ν_{assym} (PO_2) 1320; ν_{sym} (PO_2) 1152; ν_{assym} (PF_2) 850; ν_{sym} (PF_2) 807; δ(PO_2) 515 cm^{-1}.

4.8. Synthesis of [Ti(η^5-C$_5$H$_5$)$_2$(PO$_2$F$_2$)$_2$] (**16**)

To a yellow solution of **1** (0.150 g, 0.190 mmol) in 20 ml of THF, [Ti(η^5-C_5H_5)$_2$$Cl_2$] (0.071 g, 0.285 mmol) was added. The orange solution thus formed was stirred for 15 min and then evaporated under reduced pressure to a small volume. After that, toluene was added. After standing for 24 h, a mixture of yellow and red crystals were obtained by filtration. The two types of crystals were manually separated. The resulting red crystals were complex **16**. Anal. Calc. for $C_{10}H_{10}F_4O_4P_2Ti$: C, 31.61; H, 2.65. Found: C, 31.68; H, 2.73%. ^{19}F-NMR (acetone-d^6): −85.4 (d, $J_{FP} = 958.3$ Hz, PO_2F_2). ^{31}P{^{1}H}-NMR (acetone-d^6): −16.1 (t, PO_2F_2). IR: ν_{assym} (PO_2) 1311; ν_{sym} (PO_2) 1149; ν_{sym} (PF_2) 834; δ(PO_2) 550; δ(POF) 496 cm^{-1} and for Cp ligand ν(C–C) 1442, δ(C–H) 1018 cm^{-1}.

4.9. Synthesis of [Ti(η^5-C$_5$Me$_5$)$_2$(PO$_2$F$_2$)$_2$] (**17**)

To a yellow solution of **1** (0.150 g, 0.190 mmol) in 20 ml of THF, [Ti(η^5-C_5Me_5)$_2$$Cl_2$] (0.111 g, 0.285 mmol) was added. The deep brown solution thus formed was stirred for 16 h. at r.t. and then filtered, and evaporated under reduced pressure to a small volume. Diethyl ether was added to the concentrated solution. After standing for 24 h, a mixture of yellow and brown crystals were obtained by filtration. The two types of crystals were manually separated. The resulting brown crystals were complex **17**. Anal. Calc. for $C_{20}H_{30}F_4O_4P_2Ti$: C, 46.17; H, 5.81. Found: C, 46.32; H, 5.75%. IR: ν_{assym} (PO_2) 1323; ν_{sym} (PO_2) 1111; ν_{assym} (PF_2) 851; δ(PO_2) 537; δ(POF) 485 cm^{-1} and for Cp ligand, ν(C–C) 1490.

4.10. Synthesis of [Mo(η^5-C$_5$H$_5$)$_2$(PO$_2$F$_2$)$_2$] (**18**)

To a yellow solution of **1** (0.144 g, 0.182 mmol) in 20 ml of THF, [Mo(η^5-C_5H_5)$_2$$Cl_2$] (0.814 g, 0.274 mmol) was added. The green solution was stirred for 15 min at r.t. and then evaporated under reduced pressure to a small volume. Hexane was added to the concentrated solution. A mixture of yellow and green crystals were obtained by filtration. The two types of crystals were manually separated. The resulting green crystals were complex **18**. Anal. Calc. for $C_{10}H_{10}F_4O_4P_2Mo$: C, 28.06; H, 2.35. Found: C, 27.60; H, 2.70%. ^{19}F-NMR (acetone-d^6): −75.4 (d, PO_2F_2, $J_{FP} = 955.2$ Hz). ^{31}P{^{1}H}-NMR (acetone-d^6): −5.5 (t, PO_2F_2). IR: ν_{assym} (PO_2) 1311; ν_{sym} (PO_2) 1109; ν_{assym} (PF_2) 887; ν_{sym} (PF_2) 839; δ(PO_2) 542; δ(POF) 496 cm^{-1} and for Cp ligand ν(C–C) 1426, δ(C–H) 1019 cm^{-1}.

4.11. Reaction of [Pd(η^3-C$_4$H$_7$)(PO$_2$F$_2$)(PPh$_3$)] (**2**) or [Pd(η^3-C$_4$H$_7$)(PO$_2$F$_2$)(PCy$_3$)] (**3**) with PdCl$_2$(PhCN)$_2$

To a yellow solution of complex **2** (0.150 g, 0.286 mmol) in 20ml of CH_2Cl_2, $PdCl_2(PhCN)_2$ (0.110 g,

0.286 mmol) was added at r.t. The red solution was stirred for 3 h, filtered and concentrated. Then Et_2O was added. After 24 h at low temperature an orange solid and a yellow solution were obtained. The solid was filtered, dried and characterized as $[PdCl(\mu\text{-}Cl)(PPh_3)_2]_2 \cdot CH_2Cl_2$. Yield: 0.079 g (60%). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 31.32 (s, PPh_3).

The yellow solution was concentrated and hexane added to obtain a yellow solid. This solid was filtered and dried at vacuum and characterized as $[Pd(\eta^3\text{-}C_4H_7)(PhCN)_2]PO_2F_2$ (**19**). Anal. Calc. for $C_{18}H_{17}F_2N_2O_2PPd$: C, 46.15; H, 3.66. Found: C, 45.83; H, 3.49%. $^{31}P\{^1H\}$-NMR ($CDCl_3$): −11.61 (t, PO_2F_2, $J_{PF} = 950.9$). ^{19}F-NMR ($CDCl_3$): −83.80 (d, PO_2F_2).

A similar reaction of **3** (0.200 g, 0.368 mmol) in 20 ml of CH_2Cl_2 and $PdCl_2(PhCN)_2$ (0.141 g, 0.368 mmol) led to the isolation of $[PdCl(\mu\text{-}Cl)(PCy_3)_2]_2 \cdot 2CH_2Cl_2$ and $[Pd(\mu^3\text{-}C_4H_7)(PhCN)_2]PO_2F_2$ (**19**). Yield of $[PdCl(\mu\text{-}Cl)(PCy_3)_2]_2 \cdot 2CH_2Cl_2$: 0.129 g (77%). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 58.93 (s, PCy_3).

4.12. Reaction of $[Pd(\eta^3\text{-}C_4H_7)(\mu\text{-}PO_2F_2)]_3$ (**1**) with $HBF_4 \cdot Et_2O$ (54% Et_2O)

To a yellow solution of complex **1** (0.030 g, 0.038 mmol) in acetone-d^6 (0.75 ml), a solution of $HBF_4 \cdot Et_2O$ (16.40 μl, 0.114 mmol) was added in a NMR tube. The NMR spectra were immediately performed. The same reaction was made in $CDCl_3$ as solvent.

4.13. Reaction of **2** with an Et_2O solution of HCl

To a yellow solution of complex **2** (0.100 g, 0.190 mmol) in CH_2Cl_2 (50 ml), an Et_2O solution of HCl 0.26 M (0.910 ml, 0.190 mmol) was added. The solution was stirred for 24 h at r.t. Solvent was removed and Et_2O added to the yellow residue to obtain a yellow solid that was filtered and characterized as $[Pd(\eta^3\text{-}C_4H_7)Cl(PPh_3)]$. Yield: 0.06 g (81%).

4.14. Reaction of **2** with $HBF_4 \cdot Et_2O$ (54% Et_2O)

To a yellow solution of **2** (0.059 g, 0.114 mmol), $HBF_4 \cdot Et_2O$ (16.40 μl, 0.114 mmol) was added. The NMR spectra were performed immediately.

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