A New Synthesis of Organodifluorophosphites and their Reactions with Platinum(II) Complexes

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Dedicated to Professor H. J. Emeléus, F.R.S. on the occasion of his 80th birthday

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Organodifluorophosphites, Difuorophosphonate Complexes, Platinum, NMR Spectra

Alkyldifluorophosphites, ROPF₂ (R = p-substituted benzyl group, neopentyl, 1-adamantyl) have been obtained by a new method, involving reaction of the appropriate alkyltrimethylsilylether, ROSiMe₃ with chlorodifluorophosphine, PF₃Cl. Reactions of these difluorophosphites with platinum(II) complexes of the type [L₂PtCl₂] (L = PEt₃, PPh₃) led to products such as trans-[L₂PtCl₂(PF₃)] and ([p-XC₆H₄CH₂OPF₂]Cl₂)[Pt₂(PF₃)₄], (X = H, Me, Cl, NO₂). The ease of carbon-oxygen cleavage in ROPF₂ is characteristically related to the nature of the leaving group, R.

Introduction

Krück and his co-workers [1–3] have demonstrated in 1968, for the first time, that the formation of complexes of the anionic ligand, [P( :O)F₂]⁻, is possible via hydrolysis of PF₃ coordinated to zero-valent metals such as nickel or cobalt. A novel mode of formation of [P( :O)F₂]⁻ (isoelectronic to PF₃) has been found in the dealkylation of difluorophosphites, ROPF₂ (R = alkyl), and led to the synthesis of numerous difluorophosphonate complexes, especially of palladium and platinum [4, 5]. Typical species obtained upon reaction of complexes of the types [MCl₂L₂] (M = Pd, Pt; L = tert. phosphine, trimethylamine, pyridine) with ROPF₂ have the composition [ML₆(Cl(OPF₂))₂][L₂(POF₂)₂]²⁻, and [M(POF₂)₄]²⁻. The counterions in the case of the two ionic species are the cations resulting from the quaternisation of L. Complexes involving ligands which cannot be quaternized, such as the benzonitrile ligand in [MC₆H₄(C₆H₅)₃] (M = Pd, Pt), also react with dealkylation of ROPF₂ and displacement of chlorine by the difluorophosphonate group. The ultimate products are obtained by displacement of benzonitrile with phosphine ligands [6]. Furthermore, the formation of platinum complexes with the ligands, [P( :Y)F₂]⁻ (Y = S, Se), by reaction of the hydride complexes, [P( :Y)Pt₂] (X = Cl, Br or I), with P( :Y)F₂H has been reported, with hydrogen as the other product [7].

The aim of the present work was to obtain information on the dependence of the formation of difluorophosphonate complexes of platinum on the nature of the group R in the difluorophosphite, ROPF₂. In this connection, the para-substituted benzyl difluorophosphites, p-XC₆H₄CH₂OPF₂ (X = H, Me, Cl, NO₂, OMe) appeared particularly suitable, since variation of the substituent X is well known to control the inductive and mesomeric properties of the organic group R. Two further compounds, neopentyl and 1-adamantyl difluorophosphite, were also included in this study. As platinum(II) complexes, compounds of type [MCl₂L₂] (L = PEt₃, PPh₃) were employed.

Results and Discussion

The cleavage of the Si-O bond in trimethylsilyl ethers, ROSiMe₃ with PF₃Cl provides a convenient method of synthesis for alkyldifluorophosphites [8],

\[
\text{ROSiMe₃} + \text{PF₃Cl} \rightarrow \text{ROPF₂} + \text{CSI₃Me₃} \quad (1)
\]

and has been employed for the synthesis of the compounds ROPF₂ (R = p-XC₆H₄CH₂, neopentyl, 1-adamantyl) used in the present study. This reaction, occurring under mild conditions and with high yields, is frequently superior to the direct chlorine-fluorine exchange in dichlorophosphites with, e.g. NaF or SbF₃ [9]; besides, there are some instances in which no fluorophosphites are obtained upon attempted fluorination of chlorophosphites.

The trimethylsilyl ethers are formed by the reaction of the appropriate hydroxy compound with...
hexamethyldisilazane [10]; the silylation is complete within a few hours.

Chlorodifluorophosphine, PFCl₂, has first been reported as a product of incomplete fluorination of PCl₃ in 1939 [11]. The synthesis used in the present work, however, is based on a reaction first mentioned by Ivanova [12],

\[ \text{Et}_2\text{NPF}_2 + \text{PCl}_3 \xrightarrow{50^\circ \text{C}} 3 \text{h} \text{PF}_2\text{Cl} + \text{Et}_2\text{NPCl}_2 (2) \]

involving equilibration of the readily available diethylaminodifluorophosphine [13] with PCl₃ [8, 14]. The volatile PFCl₂ (b.p. —47.3 °C) is removed from the system by a stream of nitrogen and may be condensed at liquid nitrogen temperature. Diethylchlorodifluorophosphine recovered in the reaction may be converted back into Et₂NPF₂ by fluorination with NaF or SbF₅ [13].

Characterisation of the new difluorophosphites, 1b–7b, prepared in the course of the present work, was by ¹H, ³¹P NMR spectroscopy. Chemical shifts and J(P-F) values are typical of this class of compounds [15]. Relevant data, including yields and boiling points, are listed in Table I.

Reactions of the benzyldifluorophosphites, 1b–5b, with the platinum(II) complexes, [PtCl₂L₂], 8 and 9

The reaction of 1b–5b with [PtCl₂(PEt₃)₂], with formation of the monofluorophosphonate complex, 10, is thought to occur in an Arbuzov-Michaelis type fashion [5], c.f. eqn. (3).

NMR studies have shown that reactions of the above type (involving excess difluorophosphite; molar ratio ROPF₂:[PtCl₃(PEt₃)₂] ca. 6:1) in benzene as a solvent are complete within a few seconds. No variation in the reactivity of the benzyldifluorophosphites on changing X was evident under these conditions. The benzylic chlorides, p-XC₆H₄CH₂Cl, formed in the reactions, were identified in the volatile product by ¹H NMR spectroscopy.

No further reaction of 10 with benzyldifluorophosphites was observed over a period of 3 weeks under the same conditions as above, apparently due to the stabilizing effect of the [POF₂⁻] group.

In contrast, a characteristic variation in reactivity was observed for the analogous reactions of 1b–5b with the triphenylphosphine complex, [PtCl₂(PPh₃)₂], 9. While p-MeOCH₂CH₂OPF₂, 5b,

\[
\text{p-XC}_6\text{H}_4\text{CH}_2\text{OPF}_2 + [\text{PtCl}_2(\text{PEt}_3)_2] \quad \rightarrow \quad \text{p-XC}_6\text{H}_4\text{CH}_2\text{OP}^\text{F}^\text{PEt}_3 \quad \text{Cl}^- \quad \text{Cl}^- \quad \text{F}^- \text{Cl}^- \text{F}^- \text{Cl}^- \\
1b: \text{X} = \text{H} \\
2b: \text{X} = \text{Me} \\
3b: \text{X} = \text{Cl} \\
4b: \text{X} = \text{NO}_2 \\
5b: \text{X} = \text{MeO}
\]

was observed for the analogous reactions of 1b–5b with the triphenylphosphine complex, [PtCl₂(PPh₃)₂], 9. While p-MeOCH₂CH₂OPF₂, 5b,

\[
\begin{align*}
\text{p-XC}_6\text{H}_4\text{CH}_2\text{OPF}_2 + [\text{PtCl}_2(\text{PEt}_3)_2] & \quad \rightarrow \quad \text{p-XC}_6\text{H}_4\text{CH}_2\text{OP}^\text{F}^\text{PEt}_3 \quad \text{Cl}^- \quad \text{Cl}^- \quad \text{F}^- \text{Cl}^- \text{F}^- \text{Cl}^- \\
1b: \text{X} = \text{H} & \quad 8 \\
2b: \text{X} = \text{Me} & \\
3b: \text{X} = \text{Cl} & \\
4b: \text{X} = \text{NO}_2 & \\
5b: \text{X} = \text{MeO}
\end{align*}
\]

Table I. Yields and physical data of the difluorophosphites, 1b–7b.

<table>
<thead>
<tr>
<th>Compound</th>
<th>No.</th>
<th>Yield [°C/mm Hg]</th>
<th>b.p. [°C/mm Hg]</th>
<th>δ¹PF [ppm]a</th>
<th>δ³¹P [ppm]b</th>
<th>δ(P-F) [Hz]c</th>
<th>δ(H) [ppm]d,e</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-HC₆H₄CH₂OPF₂</td>
<td>1b</td>
<td>82</td>
<td>58–59/16</td>
<td>—48.7</td>
<td>111.3</td>
<td>1288</td>
<td>6.60 (ar); 4.22 (CH₂)</td>
</tr>
<tr>
<td>p-MeC₆H₄CH₂OPF₂</td>
<td>2b</td>
<td>80</td>
<td>49–50/3.5</td>
<td>—47.9</td>
<td>112.1</td>
<td>1282</td>
<td>6.45 (ar); 4.20 (CH₂)</td>
</tr>
<tr>
<td>p-ClC₆H₄CH₂OPF₂</td>
<td>3b</td>
<td>81</td>
<td>60/0.3</td>
<td>—47.5</td>
<td>111.8</td>
<td>1290</td>
<td>6.75 (ar); 4.55 (CH₂)</td>
</tr>
<tr>
<td>p-NO₂C₆H₄CH₂OPF₂</td>
<td>4b</td>
<td>76</td>
<td>88–90/0.5</td>
<td>—48.9</td>
<td>111.5</td>
<td>1293</td>
<td>6.93 (ar); 4.50 (CH₂)</td>
</tr>
<tr>
<td>p-MEOCH₂CH₂OPF₂</td>
<td>5b</td>
<td>85</td>
<td>58/0.2</td>
<td>—47.8</td>
<td>111.7</td>
<td>1281</td>
<td>6.40 (ar); 4.36 (CH₂)</td>
</tr>
<tr>
<td>(Me)₂C₆H₄OPF₂</td>
<td>7b</td>
<td>60</td>
<td>58/0.6</td>
<td>—49.0</td>
<td>111.5</td>
<td>1280</td>
<td>3.05 (CH₂); 6.65 (Me)</td>
</tr>
<tr>
<td>C₂H₅OPF₂</td>
<td>8b</td>
<td>75</td>
<td>97/16</td>
<td>—93.5</td>
<td>122.7</td>
<td>1296</td>
<td>2.05 (y-CH); 1.52 (β-CH₂)</td>
</tr>
</tbody>
</table>

a Ext. CFCI₃; b Ext. P(OMe)₃; c from ¹PF NMR spectra; d Ext. CHCl₃, TMS; e In all cases 3J(P-F) = 6.8 Hz; f average proton shift for aryl group.
was found to react predominantly in an Arbuzov-
Michaelis fashion (c.f. eq. (3)) with formation of
trans-[PtCl₂(POF₂)₂(PPh₃)₂], 11, reactions of the other
benzyl difluorophosphites, 1b–4b, were found to
give rise to the tetrakis-difluorophosphonate com-
plexes, 12a–12d.

\[
[PtCl₂(PPh₃)₂] + 4 p-XC₆H₄CH₂OPF₂ \rightarrow [(p-XC₆H₄CH₂PPh₃)₂]²⁺[Pt(POF₂)₂]²⁻ + 2 p-XC₆H₄CH₂Cl
\]

Reactions of the alkyl difluorophosphites, 5b–7b,
with the platinum complexes 8 and 9

In all cases the mono-substituted difluorophos-
phonate complexes, 10 and 11, were obtained in
small yield. The adamantyl compound, 7b, was
found to react very slowly, even at elevated tem-
perature (60 °C) and in acetonitrile as a polar
solvent. Steric hindrance, by the bulky adamantyl

group, therefore is indicated. The compounds
5b, 6b, and 7b, in the absence and, especially, in the
presence of the platinum(II) complexes, preferably
undergo reactions of the Michaelis-Arbuzov type, as
well as scrambling processes,

\[
ROPF₂ \rightarrow (RO)₂PF, (RO)₂P, PF₃
\]

\[
\downarrow \quad \downarrow \quad \downarrow
\]

\[
RP(=O)F₂ \quad RP(=O)(OR)F \quad RP(=O)(OR)₂
\]

\[
(R = p-MeOC₆H₄CH₂, neopentyl, 1-adamantyl).
\]

Such Arbuzov-Michaelis reactions have not pre-
viously been observed for other pure alkyl difluoro-
phosphites.

In all our experiments involving reactions of
5b–7b with the platinum complexes, 8 and 9,
complex mixtures of products were obtained,
often as oils, from which the crystalline products,
10 and 11, could be obtained only very slowly or not
at all. The formation of some of these products
suggests that the reaction follows eq. (3), to a minor
extent, while excess ROPF₂ is consumed in
Arbuzov-Michaelis and scrambling reactions. Thus,
only small quantities of ROPF₂ are effectively
available for reaction with the platinum complexes,
8 and 9, in which only one chlorine is displaced,
while quaternisation of the phosphine ligands and
formation of the ionic products, 12, does not occur.

In conclusion, our work has served to illustrate
that there are certain limitations to the use of
difluorophosphites in the preparation of fluorophos-
phonate complexes: while aryl difluorophosphites
undergo neither a carbon-oxygen cleavage reaction,
with release of the [P(=O)F₂]⁻ group, nor an
Arbuzov-Michaelis type reaction [5], alkyl difluorophosphites
with certain stabilized and/or sterically demanding
substituents (e.g. p-methoxybenzyl, neopentyl, and
1-adamantyl), upon reaction with phosphine complexes of platinum(II) chloride undergo other transformations, such as scrambling or Michaelis-Arbuzov processes. The reactions of a limited number of alkyl difluorophosphites, e.g. compounds 1b–4b, as well as allyl, α-propyl and α-butyl difluorophosphites [5], with phosphine complexes of platinum(II) chloride, however, do indeed occur cleanly and unambiguously, with cleavage of the carbon-oxygen bond.

**Characterization of the fluorophosphonate complexes, 10, 11 and 12a–12d**

Characterization of the fluorophosphonate complexes described above was by IR, $^1$H, $^{19}$F and $^{31}$P NMR, by mass spectroscopy and, in certain cases, by elemental analysis.

The IR spectra of all the complexes were found to exhibit bands characteristic of the difluorophosphonate group [3, 5a, b, 6]. The stretching vibration, $\nu$(P=O) gives rise to a strong band at ca. 1235 cm$^{-1}$, suggesting that the [POF$_2$]$^-$ group is bonded to the metal, as has been established in several cases by X-ray crystal structure determinations [16]. Further, P–F stretching vibrations are found in the region around 800 cm$^{-1}$.

The fragmentation in the mass spectra of compounds 10 and 11 can be unambiguously interpreted. The most intense signals correspond, besides a molecular peak, [M]$^+$, to the following fragments: [PtL$_2$(POF$_2$)]$^+$, [PtL$_3$]$,^+$, [PtL$_2$]$^+$, [L : (POF)$_2$]$,^+$, [L]$^+$, as well as degradation products of L (L = PEt$_3$, PPh$_3$).

As would be expected, in the mass spectra of the ionic complexes, 12a–12d, only fragments of the cationic part are observed. Thus, the peak of highest mass corresponds to [XC$_6$H$_4$CH$_2$PPh$_3$]$^+$ (X = H, Me, Cl, NO$_2$). Further signals are due to [Ph$_3$PCH$_2$]$^+$, [PPh$_3$]$^+$, [PPh$_2$]$^+$, [PPh]$^+$, and [Ph]$^+$.

### Table II. NMR data for the fluorophosphonate complexes, 10, 11 and 12a–12d.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta^{19}$F [ppm]</th>
<th>$\delta^{31}$P* [ppm]</th>
<th>$\delta^{31}$P** [ppm]</th>
<th>$^1$J(P–F) [Hz]</th>
<th>$^2$J(P–F) [Hz]</th>
<th>$^3$J(P–F) [Hz]</th>
<th>$^3$J(P=P***) [Hz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(PEt$_3$)$_2$PtCl(POF$_2$)]</td>
<td>10</td>
<td>-13.0</td>
<td>38.0</td>
<td>21.8</td>
<td>1169</td>
<td>892</td>
<td>2289</td>
</tr>
<tr>
<td>[(PPh$_3$)$_2$PtCl(POF$_2$)]</td>
<td>11</td>
<td>-15.8</td>
<td>a</td>
<td>24.0</td>
<td>1277</td>
<td>1023</td>
<td>a</td>
</tr>
<tr>
<td>[(p-XC$_6$H$_4$CH$_2$PPh$_3$)$_2$Pt(POF$_2$)$_4$]$^-$</td>
<td>12a–d</td>
<td>-12.4</td>
<td>70.0</td>
<td>22.6$^b$</td>
<td>1076</td>
<td>696</td>
<td>a</td>
</tr>
</tbody>
</table>

$^a$ Not observed, due to poor solubility; $^b$ P atom of the cation.
Experimental

All the experiments were carried out with exclusion of air and moisture in r. b. flasks or Schlenk tubes. Solvents were dried by standard procedures and saturated with nitrogen. The compounds, [PtCl₂(P₂Et₃)₂] [18], [PtCl₂(P₂Ph₂)₂] [18], HN(SiMe₃)₂ [19], and Et₂NPF₃ [13] were prepared by published methods.

NMR spectra (1H, 19F and 31P) were recorded on the JEOL-JNMC 60 HL, and Varian XL 100–12 instruments at 60, 56.4 and 24.3 MHz (JEOL), and 100, 94.13 and 40.5 MHz (Varian), respectively. References: 1H: ext. CHCl₃, TMS; 19F: ext. CFCl₃; 31P: ext. 95% H₃PO₄. Down-field shifts are listed with a positive, and high-field shifts with a negative sign. IR spectra were recorded on a Beckman IR 4260 instrument.

Preparation of the alkyltrimethylsilyl ethers, ROSiMe₃, 1a–7a

(General method)

In a r. b. flask equipped with a reflux condenser, protected by a drying tube, 0.2 mol of the alcohol and 0.1 mol of hexamethyldisilazane were combined with magnetic stirring in a nitrogen atmosphere. Solid alcohols were dissolved in acetone or toluene as a solvent (40 ml). After the addition of a few drops of trimethylchlorosilane (catalytic quantities) the reaction mixture was heated to between 90 to 100° for ca. 2 h until ammonium chloride started to sublime into the reflux condenser. The products were recovered by vacuum distillation. Yields, boiling points and analyses are listed in Table III.

Preparation of chlorodifluorophosphine, PF₂Cl [8, 14]

In an atmosphere of dry nitrogen, diethylaminodifluorophosphine [13] (70 g; 0.5 mol) and phosphorus trichloride (69 g; 0.5 mol) were combined in a two-necked flask, fitted with a nitrogen inlet and a reflux condenser, held at —40 °C, which was connected to a trap cooled with liquid nitrogen. The mixture was heated in an oil bath, with magnetic stirring, to a maximum temperature of 55 °C while the PF₂Cl formed was swept out of the reaction mixture in a slow stream of nitrogen, and condensed in the trap. The crude product formed in the course of 5 h was fractionated through a system of traps, held at —78°, —160°, and —196°, respectively. The —160° trap contained PF₂Cl, formed in a yield of ca. 47 g (90%). From the higher-boiling residue Et₂NPF₃ (74 g; 85%) was recovered by distillation (b.p. 78°/14 mm), and was again employed in the synthesis of Et₂NPF₃ [13].

Reaction of the alkyltrimethylsilyl ethers, 1a–7a with PF₂Cl: Preparation of the difluorophosphites, ROPF₂, 1b–7b

(General procedure)

The reactions were conducted in Schlenk tubes which were baked out in vacuo, and filled with dry nitrogen. In a counter-current of nitrogen the appropriate trimethylsilyl ether (45 mmol) was placed into the tube which was subsequently cooled to liquid nitrogen temperature under vacuum. Chlorodifluorophosphine (5.2 g; 50 mmol) was then condensed onto the trimethylsilyl ether. After the reaction mixture had been held at —30° (using a cryostat) for 12 h the temperature was reduced to —63° (CHCl₃/N₂) and volatile products were pumped off. Fractionation of the remaining liquid furnished the difluorophosphites, 1b–7b. For experimental details, c.f. Table II.

Reactions of the benzyl difluorophosphites, 1b–5b, with [PtCl₂(P₂Et₃)₂], 8: Formation of trans-(difluorophosphonato)(chloro)bis(triethylphosphine)-platinum(II). 10

To a suspension of complex 8 (0.51 g; 1.0 mmol) in 10 ml of benzene was added a six-fold molar

Table III. Experimental data of trimethylsilyl ethers 1a–7a.

<table>
<thead>
<tr>
<th>Compound</th>
<th>No.</th>
<th>Yield [%]</th>
<th>b.p. [°C/mm Hg]</th>
<th>Analyses, found (ealed.) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-HC₆H₄CH₂OSiMe₃</td>
<td>1a</td>
<td>74</td>
<td>42/0.3</td>
<td>66.7 (66.6)</td>
</tr>
<tr>
<td>p-MeC₆H₄CH₂OSiMe₃</td>
<td>2a</td>
<td>88</td>
<td>56/0.3</td>
<td>68.3 (68.0)</td>
</tr>
<tr>
<td>p-CIC₆H₄CH₂OSiMe₃</td>
<td>3a</td>
<td>87</td>
<td>76/0.3</td>
<td>63.2 (62.8)</td>
</tr>
<tr>
<td>p-NO₂C₆H₄CH₂OSiMe₃</td>
<td>4a</td>
<td>83</td>
<td>71/0.5</td>
<td>54.0 (53.4)</td>
</tr>
<tr>
<td>p-MeOC₆H₄CH₂OSiMe₃</td>
<td>5a</td>
<td>72</td>
<td>111/0.7</td>
<td>63.2 (62.8)</td>
</tr>
<tr>
<td>Me₂CCH₂OSiMe₃</td>
<td>6a</td>
<td>77</td>
<td>63/85</td>
<td>60.7 (60.0)</td>
</tr>
<tr>
<td>C₁₉H₃₉OSiMe₃ (1-adamantyl)</td>
<td>7a</td>
<td>80</td>
<td>100/0.1</td>
<td>69.6 (69.6)</td>
</tr>
</tbody>
</table>
excess of difluorophosphite 1b-5b (i.e. 6.0 mmol) at room temperature. The complex 8 was immediately dissolved. After stirring for 5 min solvent and excess difluorophosphite were pumped off. The remaining solid was recrystallized from toluene/dichloromethane (1:1) to furnish 10 in yields, ranging between 0.44 to 0.5 g (80-90%); m.p. 107 °C (lit. [5a]: 107-108°). Compound 10 was also identified from its NMR and IR data [5a].

Reactions of 6b and 7b with 8

Using benzene as a solvent no reaction was observed after 6 d at room temperature. A slow reaction (10 h) took place in acetonitrile. An oil remaining after volatile products had been pumped off was dissolved in the minimum amount of toluene. Sluggish crystallization occurred after addition of dichloromethane. No attempt at the accurate determination of the yield of 10 was made.

Reaction of the difluorophosphites, 5b, 6b, and 7b, with [PtCl2(PPh3)2], 9: Formation of trans-(difluorophosphonato)(chloro)bis(triphenylphosphine)platinum(II), 11

To a solution of 9 (0.8 g; 1.0 mmol) in 10 ml of acetonitrile a six-fold molar excess of difluorophosphite, 5b, 6b, and 7b, respectively, was added at room temperature. After 30 min stirring volatile products were pumped off. The remaining oil was dissolved in dichloromethane, crystallization commenced upon addition of a mixture of acetone/pentane (1:1). The product, 11, was obtained in yields up to 35%. Characterization was by IR and NMR spectroscopy; m.p. 198 °C (lit. [20]: 195 °C).

Reaction of the benzyldifluorophosphites, 1b-4b, with [PtCl2(PPh-i)2] to form the tetrakis(difluorophosphonato)platinum(II) complexes, 12a-12d

To a suspension of 9 (0.8 g; 1.0 mmol) in 10 ml of benzene was added 4 mmol of 1b-4b. At room temperature, during a period of 1 h 9 was gradually dissolved; subsequently, precipitation of the product commenced. The product remaining after pumping off volatiles was dissolved in dichloromethane, and crystallized upon addition of a mixture of acetone/pentane (1:1). For experimental data, c.f. Table IV.

One of us (M. S.) is indebted to Stiftung Stipendienfonds of Verband der Chemischen Industrie, Frankfurt am Main, for a maintenance grant. We are grateful to BASF AG, Bayer AG, and Hoechst AG for various chemicals and solvents and, especially, to Dr. R. Schwarz of DEGUSSA for generous supplies of K2PtCl4. NMR spectra have been recorded by Frau I. Mack of this Laboratory and by Dr. V. Wray, Gesellschaft für Biotechnologische Forschung mbH, Stöckheim/Braunschweig. Support by Fonds der Chemischen Industrie and by Land Niedersachsen is gratefully acknowledged.

Table IV. Experimental data of the tetrakis(difluorophosphonato)platinum(II) complexes, {[p-XC6H4CH2PPh3]2}[Pt(POF2)4]2-, 12a-12d.

<table>
<thead>
<tr>
<th>Compound</th>
<th>No.</th>
<th>m.p. [°C]</th>
<th>Yield [%]</th>
<th>Analyses, found (caled.) [%]</th>
<th>C</th>
<th>H</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = H</td>
<td>12a</td>
<td>215</td>
<td>94</td>
<td></td>
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