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## PENTAMETHYLCYCLOPENTADIENYL-RHODIUM AND -IRIDIUM COMPLEXES

### XV \*. CATIONIC COMPLEXES WITH TERTIARY PHOSPHINES AND PHOSPHITES AND THEIR REARRANGEMENT REACTIONS

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#### Summary

The acetone solvent complexes  $[M(C_5Me_5)(Me_2CO)_3](PF_6)_2$  (IIa, M = Rh; IIb, M = Ir) reacted with L to give  $[M(C_5Me_5)L_3](PF_6)_2$ , where L =  $(MeO)_3P$ ,  $(EtO)_3P$ , or  $Me_2PhP$  but  $(MeO)_3P$  reacted further with IIb to give  $[HIr(C_5Me_5)\{P(OMe)_3\}_2]PF_6$ .  $(PhO)_3P$  reacted with II to give the *ortho*-metallated products  $[M\{C_6H_4OP(OPh)_2\}\{P(OPh)_3\}(C_5Me_5)]PF_6$ , while  $[Rh(C_5Me_5)(MeCN)_3](PF_6)_2$  gave  $[Rh(C_5Me_5)(MeCN)_2(PPh_3)](PF_6)_2$  with  $Ph_3P$ . The coordination of ligands to  $[M(C_5Me_5)]^{2+}$  is subject to strong steric restraints and only one or two molecules of the bulkier phosphines and phosphites can coordinate.

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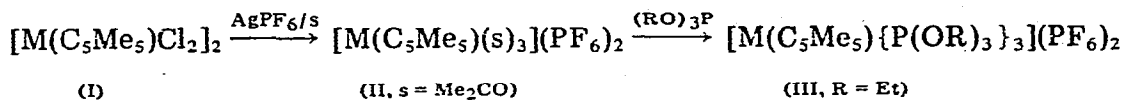
We have previously described the cationic solvent complexes  $[M(C_5Me_5)(s)_3]^{2+}$  which are obtained from  $[M(C_5Me_5)Cl_2]_2$  (I) [2] on reaction with  $AgPF_6$  in the presence of a solvent, s, (acetonitrile, dimethyl sulphoxide, pyridine, acetone, methanol, etc.) [3]. The more weakly bound solvent complexes, especially (II, s = acetone) cannot be isolated as solids [1] but, when they are generated in situ, the solvent molecules are easily replaced by other ligands. This allows the study of the properties of such ligands in highly charged complexes, and novel deprotonation or nucleophilic attack reactions are often observed [3,4]. We report here the formation and properties of such complexes containing triethyl, trimethyl or triphenyl phosphite, dimethylphenylphosphine or triphenylphosphine.

\* For part XIV see ref. 1.

## Results and discussion

### (i) Triethyl phosphite complexes

Addition of three equivalents of triethyl phosphite to solutions of the acetone-solvent complexes (IIa, IIb) gave the tris(triethyl phosphite)pentamethylcyclopentadienyl-rhodium or -iridium hexafluorophosphates (IIIa, IIIb) as precipitates on the addition of ether.



(a, M = Rh; b, M = Ir)

(IV, R = Me)

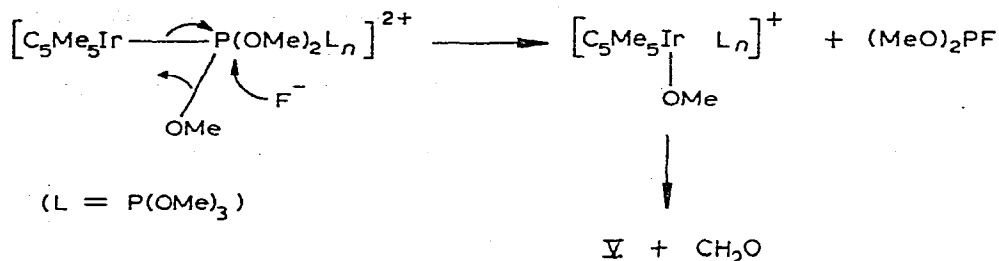
The complexes were characterised by their  $^1H$ ,  $^{13}C\{H\}$  and particularly by their  $^{31}P\{H\}$  NMR spectra which showed a singlet for the iridium complex IIIb (at  $\delta$  56.7 ppm) and a doublet for the rhodium complex IIIa ( $\delta$  107.9 ppm,  $J(P-Rh)$  200 Hz). As expected, all three phosphite ligands were equivalent.

### (ii) Trimethyl phosphite complexes

Addition of three equivalents of trimethyl phosphite to IIa gave an immediate precipitate of the tris(trimethyl phosphite)rhodium complex (IVa) ( $^{31}P$  NMR,  $d$  at  $\delta$  113.1 ppm,  $J(P-Rh)$  200 Hz). When the same reaction was carried out with IIb, no precipitation occurred but if ether was immediately added to the reaction mixture it was possible to isolate the expected tris(trimethyl phosphite)iridium complex IVb. However, if the reaction mixture was allowed to stand (96 h/20°C) a new product, identified as hydridobis(trimethylphosphite)(pentamethylcyclopentadienyl)iridium hexafluorophosphate (V), was obtained.

The formulation of V rests on the  $^1H$  NMR spectrum which showed a triplet at  $\delta$  -16.6 (ppm ( $J(H-P)$  65 Hz), due to the hydride split by two equivalent  $^{31}P$  atoms, a double triplet at 2.13 ppm ( $J(H-P)$  2,  $J(H-H)$  0.8 Hz due to the  $C_5Me_5$  group, as well as a multiplet at 3.72 due to the six methoxy groups of the  $P(OMe)_3$  ligands. The presence of an iridium hydride was confirmed by the observation of  $\nu(Ir-H)$  at  $2140\text{ cm}^{-1}$  in the IR spectrum.

When the reaction of I with trimethyl phosphite and  $AgPF_6$  was carried out in dry acetone- $d_6$  the same hydride product was again obtained indicating that there was no solvent participation in the reaction to form V, and therefore the hydride must have come from a methyl of one trimethyl phosphite. The  $^{31}P$  NMR spectrum of this crude reaction mixture showed the presence of V and some broad resonances which were sharpened at  $-60^\circ C$ . Apart from resonances due to V the main peaks were a singlet at  $\delta$  -1.6 and a doublet at  $-10.0$  ppm, which was shown to arise from coupling to fluorine ( $J(P-F)$  920 Hz). These resonances are consistent with the presence of  $X_3P=O$  species in solution such as  $(RO)_3P=O$  and  $F(RO)_2P=O$  (where  $R = Me$  and/or  $H$ ) [5]. While a discussion of the precise course of the reaction must await further data, it is plausible that the mechanism involves an attack by fluoride (arising from the catalysed decomposition of  $PF_6^-$  [3,1] at a coordinated phosphite.



The methoxyiridium intermediate could then undergo a conventional  $\beta$ -elimination to give V and formaldehyde. The phosphoryl species observed could be derived from “(MeO)<sub>2</sub>PF” by exchange, hydrolysis, or even oxidation reactions with other species in solution.

An analogy for part of this reaction sequence is the well-known reverse process wherein alkoxide attacks PF<sub>3</sub> coordinated to a metal, giving the trialkyl phosphite complex, for example [6]:

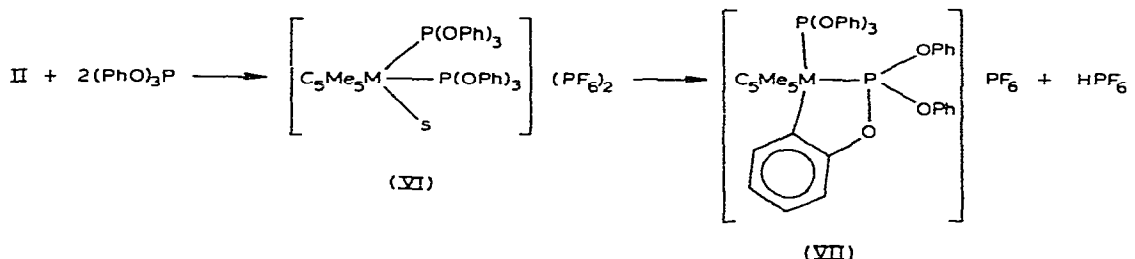


An alternative possibility involves the intermediate formation of an iridium(I) species, (e.g. Ir(C<sub>5</sub>Me<sub>5</sub>){P(OMe)<sub>3</sub>}<sub>2</sub>), which is then protonated [7], but the origin of the H<sup>+</sup> needed is obscure, especially for the reaction carried out in acetone-d<sub>6</sub>. Another possible pathway would be via an “*ortho*-metallation” type of reaction, of which many examples are known [8]. However, there have been no reports of such reactions involving alkyl phosphites or of reactions in which H-transfer from the ligand to the metal is not accompanied by M—C bond formation [9].

All the tris(trimethyl phosphite) and the tris(triethyl phosphite) complexes were stable in the solid and in solution, even on warming to +50°C for extended periods.

### (iii) Triphenyl phosphite complexes

When three equivalents of triphenyl phosphite were added to an acetone solution of IIa and the reaction monitored by <sup>1</sup>H NMR spectroscopy, two species were initially detected which both showed triplets in the C<sub>5</sub>Me<sub>5</sub> region at  $\delta$  1.91 ( $J(\text{H}-\text{P})$  6) and 1.68 ppm ( $J(\text{H}-\text{P})$  7 Hz). The observation of triplets indicated that each species was associated with only two phosphite ligands presumably for steric reasons; by contrast, the C<sub>5</sub>Me<sub>5</sub> <sup>1</sup>H resonances of the tris-complexes IIIa, b and IVa, b were of course quartets. After 12 h/20°C the lower field signal had disappeared and only the signal at  $\delta$  1.91 ppm remained; on working up the solution the *ortho*-metallated complex VIIa was isolated. Exactly analogous behaviour was shown by the iridium complex on reaction with triphenyl phosphite and



the corresponding complex VIIb was isolated. It was not possible to isolate the intermediates, but they are presumably the bis(triphenyl phosphite) complexes VIa, b containing a loosely held molecule of solvent in the sixth coordination site.

The complexes VIIa, b were formulated as shown on the basis of analytical data and NMR spectroscopy. The  $^{31}\text{P}\{\text{H}\}$  spectra complemented the  $^1\text{H}$  spectra, which showed triplets for the  $\text{C}_5\text{Me}_5$  groups, and showed two doublets for the iridium complex VIIb (at  $\delta$  51.5 and 93.2 ppm,  $J(\text{P}-\text{P}')$  64 Hz) indicating that the two phosphorus atoms were inequivalent. A similar situation was observed for the rhodium complex VIIa except that each doublet was again split into a further doublet due to coupling to rhodium (at  $\delta$  + 104,  $J(\text{P}-\text{Rh})$  238,  $J(\text{P}-\text{P}')$  112, and 140.3 ppm,  $J(\text{P}-\text{Rh})$  231 Hz).

The IR spectra of the complexes showed bands at 799 and 1104  $\text{cm}^{-1}$  (VIIa), and 802 and 1109  $\text{cm}^{-1}$  (VIIb), which have been recognised as characteristic of *ortho*-metallated triphenyl phosphite ligands [8,10].

#### (iv) *t*-Phosphine complexes

The rhodium—acetone complex IIa underwent ready reaction with three equivalents of dimethylphenylphosphine to give the tris(dimethylphenylphosphine) complex VIII. This was characterised by the  $^1\text{H}$  NMR spectrum, which showed the  $\text{C}_5\text{Me}_5$  signal as a quartet ( $\delta$  1.68 ppm,  $J(\text{H}-\text{P})$  4 Hz), and the  $^{31}\text{P}\{\text{H}\}$  spectrum which showed a doublet ( $\delta$  - 1.7 ppm,  $J(\text{P}-\text{Rh})$  127 Hz) and indicated that the three phosphines were equivalent and coupled to rhodium.



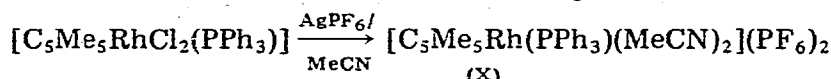
(VIII)

In contrast, all attempts to obtain complexes from either IIa or IIb with triphenylphosphine failed; reaction did occur to give a complex mixture from which no product could be obtained. Neither tricyclohexylphosphine nor tri-*o*-tolylphosphine reacted at all under these conditions.

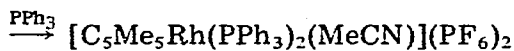
However, tris(acetonitrile)pentamethylcyclopentadienylrhodium hexafluorophosphate (IX) (obtained from Ia and  $\text{AgPF}_6$  in acetonitrile) gave a clean reaction with one equivalent of triphenylphosphine to give the monotriphenylphosphine complex X. This was also prepared by reaction of  $[\text{Rh}(\text{C}_5\text{Me}_5)\text{Cl}_2(\text{PPh}_3)]$  [2] with  $\text{AgPF}_6$  in acetonitrile.



(IX)  $\downarrow$   $\text{PPh}_3$



(X)



(XI)

The complex X showed a doublet in the  $^1\text{H}$  NMR spectrum of the  $\text{C}_5\text{Me}_5$  region ( $\delta$  1.60 ppm,  $J(\text{H}-\text{P})$  4 Hz), as well as coordinated acetonitrile ( $\delta$  2.40 ppm, s) and phenyl resonances ( $\delta$  7.7 ppm, m). The presence of acetonitrile was also

observed in the IR spectrum by  $\nu(\text{CN})$  at 2290 and 2318  $\text{cm}^{-1}$ .

Addition of one further equivalent of triphenylphosphine to a solution of X generated a new species, the  $^1\text{H}$  NMR spectrum of which showed the presence of a triplet in the  $\text{C}_5\text{Me}_5$  region ( $\delta$  1.37 ppm) and a singlet at  $\delta$  2.79 ppm due to free acetonitrile. This spectrum was consistent with the formation of a bis(triphenylphosphine) complex XI but attempts to isolate this compound gave a complex mixture which contained no acetonitrile, and the major component of which now showed the  $\text{C}_5\text{Me}_5$  resonance as a triplet at  $\delta$  1.18 ppm. Clearly further reaction had occurred, possibly involving an *ortho*-metallation reaction.

Attempts were made to prepare the tri-*o*-tolylphosphine analogue of X by reaction of the ligand with IX in acetone. A very slow reaction was observed which generated a species showing a doublet ( $\delta$  1.62 ppm,  $J(\text{H}-\text{P})$  3 Hz) in the  $^1\text{H}$  NMR spectrum but only after 5 days at 50°C.

## Conclusion

Dicationic pentamethylcyclopentadienyl-rhodium and -iridium solvent complexes reacted with *t*-phosphines and phosphites to give tris-complexes for the smaller ligands  $\text{P}(\text{OMe})_3$ ,  $\text{P}(\text{OEt})_3$ ,  $\text{PMe}_2\text{Ph}$ .

Triphenyl phosphite gave a bis-complex which then underwent *ortho*-metallation, and triphenylphosphine gave only an isolable mono-adduct though a bis-complex appeared to be found in solution; the larger *t*-phosphines reacted very slowly with the solvent complexes and no products could be isolated.

These results show that the pentamethylcyclopentadienyl ligand causes severe constraint on the number and sizes of other ligands on the metal the magnitude of which is qualitatively consistent with steric effects of  $\text{PX}_3$  ligands discussed by Toiman [11].

## Experimental

All reactions were carried out under nitrogen. Yields and analytical data are given in Table 1: All the complexes showed a strong band near 840  $\text{cm}^{-1}$  in the IR spectrum and a septet at ca.  $\delta$  - 144 ppm in the  $^{31}\text{P}$  NMR spectrum due to the  $\text{PF}_6^-$  ion.

### *Tris(triethyl phosphite)(pentamethylcyclopentadienyl)rhodium hexafluorophosphate (IIIa)*

A solution of complex IIa was made up by adding  $\text{AgPF}_6$  (0.37 g, 1.34 mmol) to complex Ia (0.2 g, 0.32 mmol) in acetone (10 ml). The silver chloride was removed by filtering the solution through a short cellulose column. Triethyl phosphite (0.32 g, 1.9 mmol) was added to this solution with stirring. After 5 min diethyl ether was slowly added to the solution until a white precipitate appeared. When the precipitation was complete, the solid was filtered off, washed with ether and air-dried to give the pure IIIa (0.43 g, 65%).  $^1\text{H}$  NMR ( $\delta$ , ppm): 1.45 (t, Me(phosphite),  $J(\text{H}-\text{H})$  7 Hz), 1.99 (q,  $\text{C}_5\text{Me}_5$ ,  $J(\text{H}-\text{P})$  7 Hz), 4.43 (m,  $\text{CH}_2(\text{phosphite})$ );  $^{13}\text{C}$  NMR ( $\delta$  ppm): 10.2 (s,  $\text{C}_5\text{Me}_5$ ), 16.0 (s,  $\text{OCH}_2\text{CH}_3$ ), 67.5 (m,  $\text{OCH}_2\text{CH}_3$ ), 111.1 (m,  $\text{C}_5\text{Me}_5$ ).

The following complexes were prepared in the same way:

TABLE I  
ANALYTICAL DATA AND YIELDS

Compound	Found (calcd.) (%)		Yield (%)
	C	H	
IIIa	32.9(32.8)	5.9(5.9)	65
IIIb	30.0(30.1)	5.4(5.4)	49
IVa	25.3(25.3)	4.7(4.7)	33
IVb	23.0(23.1)	4.1(4.3)	16
V	26.6(26.6)	4.7(4.7)	28
VIIa	52.6(55.0)	4.7(4.5)	49
VIIb	50.7(50.6)	4.4(4.1)	36
VIII	43.7(43.3)	5.5(5.1)	98
X	43.9(44.0)	4.4(4.2) <sup>a</sup>	88 <sup>b</sup> , 82 <sup>c</sup>

<sup>a</sup> N 3.1(3.2)%. <sup>b</sup> From IX. <sup>c</sup> From [Rh(C<sub>5</sub>Me<sub>5</sub>)Cl<sub>2</sub>(PPh<sub>3</sub>)].

IIIb: <sup>1</sup>H NMR (δ, ppm): 1.46 (t, Me(phosphite), *J*(H—H) 7 Hz), 2.07 (q, C<sub>5</sub>Me<sub>5</sub>, *J*(H—P) 4 Hz), 4.50 (m, CH<sub>2</sub>(phosphite)); <sup>13</sup>C NMR (δ, ppm): 9.7 (s, C<sub>5</sub>Me<sub>5</sub>), 16.0 (s, br, OCH<sub>2</sub>CH<sub>3</sub>), 67.3 (q, OCH<sub>2</sub>CH<sub>3</sub>, *J*(C—P) 3 Hz), 106.7 (d, C<sub>5</sub>Me<sub>5</sub>, *J*(C—P) 3 Hz).

IVa: <sup>1</sup>H NMR (δ, ppm): 1.83 (q, C<sub>5</sub>Me<sub>5</sub>, *J*(H—P) 5 Hz), 3.92 (m, OMe); <sup>13</sup>C NMR (δ, ppm): 10.1 (s, C<sub>5</sub>Me<sub>5</sub>), 57.7 (m, OMe), 111.4 (d, C<sub>5</sub>Me<sub>5</sub>, *J*(C—Rh) 3 Hz).

IVb; <sup>1</sup>H NMR (δ, ppm): 1.88 (q, C<sub>5</sub>Me<sub>5</sub>, *J*(H—P) 3 Hz), 6.2 (m, br, OMe).

*Hydridobis(trimethyl phosphite)(pentamethylcyclopentadienyl)iridium hexafluorophosphate (V)*

Trimethyl phosphite (0.24 g, 1.9 mmol) was added to a filtered solution of IIIb (from Ib (0.4 g), AgPF<sub>6</sub> (0.5 g), in acetone (10 ml)) and the resulting solution was stirred for 96 h/20°C. The solvent was removed in vacuo, and the solid was crystallised from chloroform/ether to give V as a white solid (0.21 g). <sup>1</sup>H NMR (δ, ppm) — 16.60 (t, hydride(H'), *J*(H'—P) 65 Hz), 2.13 (dt, C<sub>5</sub>Me<sub>5</sub>, *J*(H—P) 2, *J*(H—H') 0.8 Hz) 3.72 (m, OMe); <sup>13</sup>C NMR (δ, ppm) 9.7 (s, C<sub>5</sub>Me<sub>5</sub>), 53.8 (m, OMe), 99.7 (m, C<sub>5</sub>Me<sub>5</sub>); <sup>31</sup>P NMR (δ, ppm): 85.2 (s, {P(OMe)<sub>3</sub>}<sub>2</sub>), —144.4 (septet, PF<sub>6</sub><sup>-</sup>).

*Triphenyl phosphite{2-(diphenyl phosphito)phenyl}(pentamethylcyclopentadienyl)iridium hexafluorophosphate (VIIb)*

Triphenyl phosphite (0.35 g, 1.12 mmol) was added to a filtered solution of IIIb (from Ib (0.2 g) and AgPF<sub>6</sub> (0.25 g), in acetone (10 ml)). The solution was stirred for 2 h/20°C and the solvent was then removed in vacuo to leave an oily residue. This was triturated first with a little diethyl ether and then with a little water, after which it was crystallised from chloroform/diethyl ether to give VIIb as a colourless solid (0.27 g). <sup>1</sup>H NMR; (δ, ppm); 2.01 (t, C<sub>5</sub>Me<sub>5</sub>, *J*(H—P) 4 Hz), 3.0 (m, Ph); <sup>13</sup>C NMR (δ, ppm): 9.6 (s, C<sub>5</sub>Me<sub>5</sub>), 103.6 (s, C<sub>5</sub>Me<sub>5</sub>), 120.9(d), 126.4(d), 130.7(s), 152.2 (d, *J*(C—P) 14 Hz) (all PhOP), 112.4 (d, *J*(C—P) 15 Hz), 125.6(s), 127.9(s), 140.4(s), (all C—H), 152.6(m), 160.5 (d, *J*(C—P) 18 Hz)

(C without H). VIIa was prepared similarly \*:  $^1\text{H}$  NMR ( $\delta$ , ppm): 1.96 (t,  $\text{C}_5\text{Me}_5$ ,  $J(\text{H}-\text{P})$  5 Hz), 3.0 (m, Ph).  $^{13}\text{C}$  NMR ( $\delta$ , ppm): 9.8 (s,  $\text{C}_5\text{Me}_5$ ), 107.0 (d,  $\text{C}_5\text{Me}_5$ ,  $J(\text{C}-\text{Rh})$  3 Hz), 119.9(d), 125.7(d), 129.8(s), 152.0 (d,  $J(\text{C}-\text{P})$  15 Hz) (all PhOP), 112.7 (d,  $J(\text{C}-\text{P})$  15 Hz), 125.2(s), 127.4(s), 139.4 (d,  $J$  4.5 Hz) (all C-H), 150.9(m), 157.4 (d,  $J(\text{C}-\text{P})$  21 Hz) (C without H).

*Tris(dimethylphenylphosphine)(pentamethylcyclopentadienyl)rhodium hexafluorophosphate (VIII)*

This complex was prepared from IIa and dimethylphenylphosphine in acetone. After 10 min the solution was evaporated to dryness, the residue was washed with diethyl ether and crystallised from acetone/diethyl ether to give yellow crystals of VIII (yield 98%).  $^1\text{H}$  NMR ( $\delta$ , ppm): 1.68 (q,  $\text{C}_5\text{Me}_5$ ,  $J(\text{H}-\text{P})$  4 Hz), 2.12 (m, Me-P), 2.4 (m, Ph).

*Bis(acetonitrile)(triphenylphosphine)(pentamethylcyclopentadienyl)rhodium hexafluorophosphate (X)*

A solution of the tris-acetonitrile complex IX (0.4 g) and triphenylphosphine (0.18 g) in acetone (10 ml) was stirred (10 min). The solvent was removed in vacuo to leave a yellow solid which was washed with ether and a little acetone to give pure X (0.5 g).

The complex (0.3 g) was also obtained from reaction of  $[\text{Rh}(\text{C}_5\text{Me}_5)\text{Cl}_2(\text{PPh}_3)]$  (0.25 g) and  $\text{AgPF}_6$  (0.23 g) in acetonitrile (10 ml).  $^1\text{H}$  NMR ( $\delta$ , ppm): 1.60 (q,  $\text{C}_5\text{Me}_5$ ,  $J(\text{H}-\text{P})$  4 Hz), 2.40 (s, MeCN), 2.4 (m, Ph).

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\* All samples of VIIa showed a small doublet at  $\delta -5.8$  ppm ( $J$  910 Hz) in the  $^{31}\text{P}$  NMR spectrum. This is probably an impurity arising from decomposition of the  $\text{PF}_6^-$  anion and explains why the microanalytical results are not wholly satisfactory for this complex.