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Cationic hydroxyallylolefin rhodium complexes $[Rh(\eta^{2,3}\text{-}C_7H_6\text{-}3\text{-}R\text{-}2\text{-}CR^1\text{=}OH)(\eta^5\text{-}Cp)]^+PF_6^-$ (R, R^1 = H, Alk, Cp = C_5H_5, C_5H_4Me, C_5Me_5) with intramolecular O–H ··· Rh hydrogen bonds. Formation of $\{[CpRh(\eta^{2,3}\text{-}C_7H_6\text{-}3\text{-}R\text{-}2\text{-}CR^1\text{=}OH)]_2\text{-}F_2POO\}^+PF_6^-$ dimers as a result of partial hydrolysis of the PF_6^- anion

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Abstract

Protonation of the 2-acyl derivatives of Rh(η^4-norbornadiene)(η^5-Cp) (Cp = C_5H_5, C_5H_4Me, C_5Me_5) by HPF_6 in diethyl ether yields the stable cationic *O*-protonated complexes $[Rh(\eta^{2,3}\text{-}C_7H_6\text{-}3\text{-}R\text{-}2\text{-}CR^1\text{=}OH)(\eta^5\text{-}Cp)]^+PF_6^-$ (R, R^1 = H, Me), whose structure was established by IR, ^1H and ^{13}C NMR spectroscopy. The formation of the intramolecular hydrogen bond O–H ··· Rh was found on the basis of IR and ^1H NMR spectra of the cations. CH_2Cl_2 solutions of the cationic complexes that contained traces of moisture caused the partial hydrolysis of the PF_6^- anions, to give the novel "dimeric" complexes, $\{[CpRh(\eta^{2,3}\text{-}C_7H_6\text{-}3\text{-}R\text{-}2\text{-}CR^1\text{=}OH]_2F_2P(O)O\}^+PF_6^-$. The $F_2P(O)O$ group of this complex is involved in the strong intermolecular hydrogen bond, O–H ··· O-P(F_2)-O ··· H–O. An X-ray diffraction study has been carried out on one of the "dimeric" cations (R = Me, R^1 = H).

Introduction

We recently studied the protonation of 2-acyl derivatives of the Rh(η^4-C_7H_8)(η^5-Cp) complexes (Cp = C_5H_5 and C_5H_4Me) by HCl and $F_2P(O)OH$ in diethyl ether [1,2], reactions which proceed regioselectively at the carbonyl oxygen atom. Whereas most of the previously reported π-complexes with an *O*-protonated carbonyl group in the side chain of the ligand are usually only stable in the solutions of strong acids [3–6], our *O*-protonated products are remarkably stable. The cationic compounds

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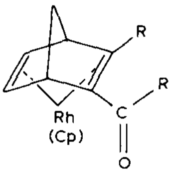
obtained proved to be complexes with allylolefinic metal–norbornadienyl ligand bonding, $[Rh(\eta^{2,3}\text{-}C_7H_7\text{-}2\text{-}CR\text{=}OH)(\eta^5\text{-}Cp)]^+$ An^-($An = Cl$, $F_2P(O)O$), in which both the O and Rh atoms take part in the stabilization of their α-carbocationic center [1,2]. IR and ^1H NMR spectroscopy indicated that the O–H ··· An interionic hydrogen bond exists in these complexes [2]. Such hydrogen bonding is not uncommon in the organoelement compounds, e.g. in enolized β-ketophosphonium salts [7,8]. As was pointed out previously [2], analogous hydrogen bonding occurs in some of π-enol iron complexes, and in acylferrocenes, which had been *O*-protonated by hydrogen chloride.

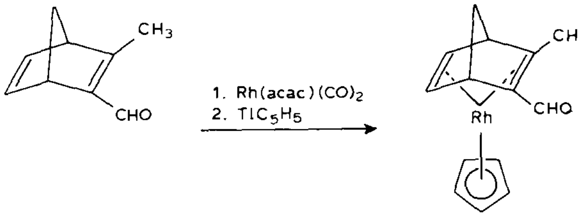
At present we have prepared a series of new allylolefinic cationic complexes with a weakly coordinating PF_6^- anion. It has been shown that a decrease in coordinating ability from Cl^-, $F_2P(O)O^-$ to PF_6^- results in a change in the type of hydrogen bond which involves the participation of the protonated carbonyl group. In cationic complexes with PF_6^- anion, an intramolecular hydrogen bond of the type O–H ··· Rh is formed. Traces of moisture in CH_2Cl_2 solutions of the complexes give rise to partial hydrolysis of the PF_6^- anion and lead to the formation of dimeric cationic products with bridging difluorophosphate group. In the present paper the results of the ^1H, ^{13}C, ^{19}F NMR and IR spectroscopic studies of these compounds and the X-ray structural study of one of them are reported *.

Results and discussion

The starting materials, 2-acylnorbornadienerhodium complexes (Ia–d) were prepared and characterized previously [2,10], (3-methyl-2-formylnorbornadiene)cyclopentadienylrhodium (Ie) was prepared in two steps from the corresponding diene according to the following scheme:



(Ia-Id)



(Ie)

a . $R = R^1 = H$, $Cp = \eta^5\text{-}C_5H_5$
b : $R = H$, $R^1 = Me$, $Cp = \eta^5\text{-}C_5H_5$
c . $R = R^1 = H$, $Cp = \eta^5\text{-}C_5H_4Me$
d : $R = R^1 = H$, $Cp = \eta^5\text{-}C_5Me_5$
e : $R = Me$, $R^1 = H$, $Cp = C_5H_5$

Protonation of the complexes Ia–Ie by 70% HPF_6 in absolute diethyl ether produced cationic complexes IIa–IIe, of which most were isolated as relatively stable crystalline salts.

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* See Ref. 9 for a preliminary report.

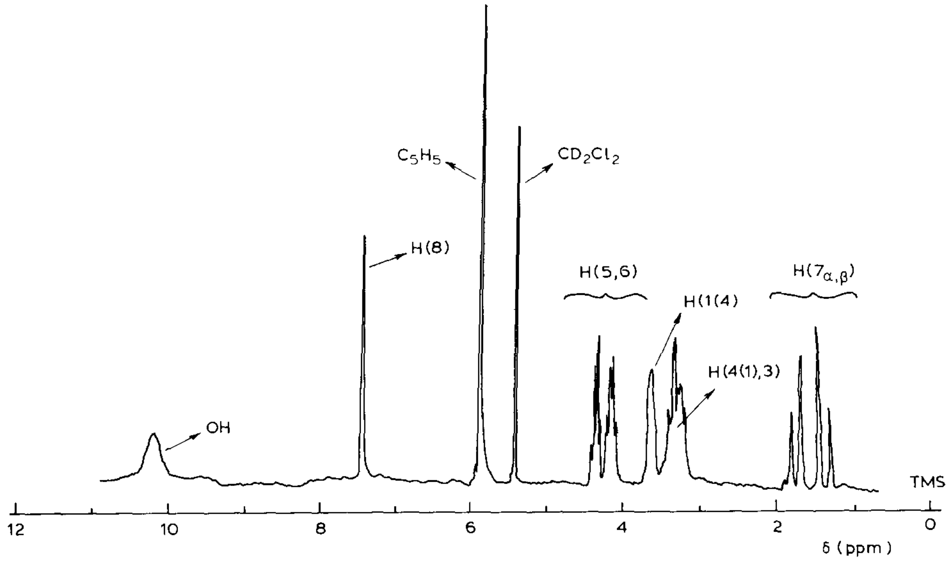


Fig. 1. The ^{1}H NMR spectrum of complex IIa in CD_2Cl_2 solution.

$$\text{Ia–Ie} \xrightarrow{70\%\ HPF_6/\text{diethyl ether}} [Rh(C_7H_6\text{-3-R-2-CR}^IOH)(\eta^5\text{-Cp})]^+ PF_6^-$$
$$(\text{IIa–IIe})$$

In the ^{1}H NMR spectra of the cations IIa–IIe in the low field region, signals of the OH-group protons as one-proton resonance were found, which, e.g. for IIa, IIc, disappeared on addition of D_2O. The ^{1}H NMR spectrum of complex IIa, typical of all the cationic complexes of the series IIa–IIe, is shown in Fig. 1. In accordance with the cationic nature of IIa–IIe almost all of the signals of the norbornadiene and Cp ligands in the NMR spectra are noticeably shifted downfield compared with those in the spectra of the initial 2-acyl derivatives Ia–Ie (Table 1). By contrast the signals of H(8) in the ^{1}H NMR spectra of the complexes IIa, IIc–IIe are shifted upfield owing to weakening of the anisotropic effect of the protonated carbonyl group [11]. It is noteworthy that the methyl group signal in the spectrum of IIe is also shifted upfield with respect to that of Ie ($\Delta\delta$ ∼ 0.3 ppm). This is rather unexpected as nothing of the kind was observed, for example, in the case of *O*-protonated (3-methyl-3,5-hexadienone)tricarbonyliron [3] or some of the *O*-protonated organic α,β-unsaturated aldehydes and ketones [12].

Two types of resonance structures (**A** and **B**) for the complexes IIa–IIe, corresponding to the two possible ways by which the exocyclic carbocationic center C(8) is stabilized in these complexes, can be considered:

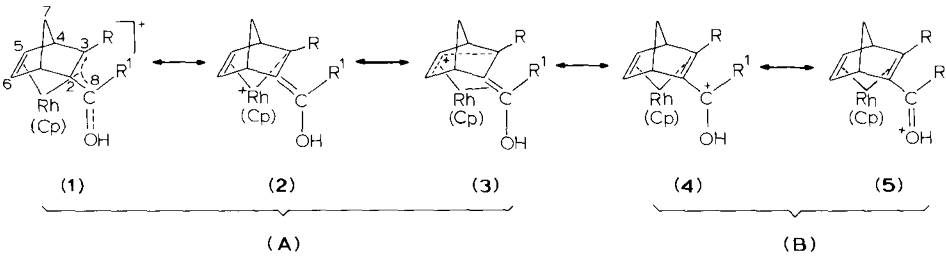


Table 1

^{1}H NMR spectral data (δ (ppm), J (Hz)) for the cations IIa–IIe and IIIe in CD_2Cl_2 ^{a,b}

Compound	
IIa	10.2 (s,1H,CH$\doteq$O*H*), 7.52 (s,1H,C*H*$\doteq$OH), 5.65 (d,5H,$J(^{103}$Rh–^{1}H) 0.8,C_5H_5), 4.34 ($\mathrm{m}^{\star}$,1H,H(5(6))), 4.27 ($\mathrm{m}^{\star}$,1H,H(6(5))), 3.86 (m,1H,H(1(4))), 3.70 (m,2H,H(4(1),3)), 1.63 (d,1H,J_{AB} 10.7,H($7_{\alpha(\beta)}$), 1.44 (d,1H,J_{BA} 10.7,H($7_{\beta(\alpha)}$)
IIb	11.6 (s,1H,CMe$\doteq$O*H*), 5.36 (d,5H,$J(^{103}$Rh–^{1}H), 0.6,C_5H_5), 4.26 ($\mathrm{m}^{\star}$,1H,H(5(6))), 4.04 ($\mathrm{m}^{\star}$,1H,H(6(5))), 4.11 (m,1H,H(1(4))), 3.70 (m,2H,H(4(1),3)), 2.33 (s.br.,3H, Me), 1.51 (d,1H,J_{AB} 9.9,H($7_{\alpha(\beta)}$)), 1.31 (d,1H,J_{BA} 9.9,H($7_{\beta(\alpha)}$))
IIc	7.3 (s.br.,1H,C*H*$\doteq$OH), 7.1 (s.br.,1H,CH$\doteq$O*H*), 5.69 (m,1H,C_5*H_4*Me), 5.57 (m,1H, C_5*H_4*Me), 5.47 (m,2H,C_5*H_4*Me), 4.11 ($\mathrm{m}^{\star}$,2H,H(5,6)), 3.86 (m,1H(H1(4))), 3.72 (m, 1H,H(4(1))), 3.58 (m,1H,H(3)), 1.90 (s,3H,Me), 1.70 (d.br., 1H,J_{AB} 10.3,H($7_{\alpha(\beta)}$)), 1.50 (d.t,1H,J_{BA} 10.3,J_t 1.8H,H($7_{\beta(\alpha)}$))
IId	6.44 (s.br.,1H,CH$\doteq$O*H*), 6.08 (s.br.,1H,C*H*$\doteq$OH), 3.80 (m,1H,H(1(4))), 3.74 (m,1H, H(4(1))), 3.59 ($\mathrm{m}^{\star}$,1H,H5(6)), 3.35 ($\mathrm{m}^{\star}$,1H,H(6(5))), 2.78 (t,1H,H(3)), 1.87 (s,15H, Me), 1.61 (d.br.,1H,J_{AB} 10,H($7_{\alpha(\beta)}$)), 1.46 (d.t.,1H,J_{BA} 10,J_t 1.8,H($7_{\beta(\alpha)}$))
IIe	7.66 (s.br.,1H,C*H*$\doteq$OH), 7.56 (s.br.,1H,CH$\doteq$O*H*), 5.58 (d,5H,$J(^{103}$Rh–^{1}H) 0.9, C_5H_5), 4.54 ($\mathrm{m}^{\star}$,1H,H(5(6))), 4.26 ($\mathrm{m}^{\star}$,1H,H(6(5))), 3.82 (m,1H,H(1(4))), 3.58 (m, 1H,H(4(1))), 1.70 (d,1H,J_{AB} 10.4,H($7_{\alpha(\beta)}$)), 1.58 (s,3H,Me), 1.47 (d.t.,1H,J_{AB} 10.4,J_t 1.6,H($7_{\beta(\alpha)}$))
IIIe	7.90 (s,1H,C*H*$\doteq$OH), 5.52 (d,5H,$J(^{103}$Rh–^{1}H) 1.0,C_5H_5), 4.36 ($\mathrm{m}^{\star}$,1H,H(5(6))), 4.2 ($\mathrm{m}^{\star}$,1H,H(6(5))), 3.83 (m,1H,H(1(4))), 3.62 (s.br.,1H,CH$\doteq$O*H*), 3.51 (m,1H,H(4(1))) 1.70 (s,3H,Me), 1.60 (d.br.,1H,J_{AB} 10.1,H($7_{\alpha(\beta)}$)), 1.38 (d.t.,1H,J_{AB} 10.1, J_t 1.6,H($7_{\beta(\alpha)}$)).

[a] ^{1}H NMR data for complexes of type I have been reported earlier [2]. [b] $\mathrm{m}^{\star}$ = signal is a quadruplet-like.

The structures **A** imply the existence of direct Rh ··· C(8) interaction in the cations, whereas in **B** the stabilization of α-C^{+}(8) is achieved by the release of electrons from the metal to the carbocationic center via the π-coordinated diene ligand, either with (structure **5**) or without (structure **4**) participation of the electrons of protonated carbonyl group.

The ^{13}C NMR study of the cationic complexes IIa–IIe has led us to conclude that (a) the contribution by the resonance structures **B** is far less than the contribution by structures of type **A** and (b) of the **A** type structures the most significant contribution is that by the structure with hydroxyallylolefinic metal–dienyl ligand bonding (structure **1**).

It is noteworthy that in ^{13}C NMR spectra of cations IIa–IIe the exocyclic C(8) carbon signals are more strongly shielded than those in spectra of corresponding acylsubstituted complexes Ia–Ie (Table 2). An analogous effect in the ^{13}C NMR spectra is observed in the cationic π-complexes where the metal atom takes part in the direct interaction with the α-carbocationic center [13,14]. Furthermore in the ^{13}C NMR spectra of the *O*-protonated acylferrocenes or ferrocenyliminium salts in which such a center is stabilized by a conjugation mechanism, the α-carbon signals are slightly less shielded with respect to those in the starting acyl- or iminoferrocenes [15]. Thus the observed changes in the chemical shifts of the C(8) carbon signals in IIa–IIe relative to Ia–Ie are evidence for the existence of the direct Rh ··· C(8) interaction in the cationic complexes. We had previously come to an

Table 2

^{13}C NMR spectral data (δ (ppm), J (Hz)) for the cations IIa–IId and IIIe in CH_2Cl_2 [d]

Compound	C1(4)	C(2)	C(3)	C4(1)	C5(6)	C6(5)	C(7)	C(8)	R	R^1	Cp
IIa	39.3	64.5	39.1	46.8	41.7	45.7	53.8	135.5	–	–	89.8
	s	5.1	10.3	s	7.4	8.0	3.1	s br			4.8
IIb [a]	40.9	56.3	30.7	46.2	40.0	45.2	[b]	172.9	–	23.7	89.7
	s br	4.4	10.3	s	7.4	7.4		s br		s br	4.4
IIc	39.3	66.6	31.9	46.6	44.7	47.8	53.7	132.6	–	–	C_{Me} 12.6/s; C_i 108.4/4.6 $C_{\alpha,\beta}C_{\alpha',\beta}$ 108.4/4.6, 90.5/4.6, 89.5/5.3, 88/5.3
	s	4.5	10.7	s	7.6	7.6	(?)	s br			
IId [c]	39.3	68.2	32.7	45.9	50.3	52.9	[b]	132.1	–	–	C_{Me} 9.4/s; G_i 101.3/5.4
	s	3.4	8.1	s	6.8	8.2		s br			
IIIe	40.9	66.9	(?)	52.7	43.2	47.6	52.2	130.8	18.8	–	90.5
	s	4.6		2.0	8.4	8.6	3.0	s br	s		4.9

[a] Recorded at −40 °C. [b] The signal is overlapped by the signal of the solvent. [c] Recorded at −30 °C. [d] The ^{13}C NMR data for the complexes of type I have been published earlier [2].

Table 3

IR spectral data for cationic complexes IIa–IIe and IIIe

Compound	Conditions	Absorption bands (cm^{-1})	
		ν(C(3)≃C(2)≃C(8)≃O)	ν(OH)
IIa-^{18}O	KBr	1570	3450
IIa-^{16}O	KBr	1570	3450
	CH_2Cl_2	1582	3435
IIb	CH_2Cl_2	1575	3390
	Nujol mull	1580	3455
IIc	Oil	1577	3400
IId	Nujol mull	1575	3490
IIe	Nujol mull	1572	3500
	HCBD [a]	–	3510
	CH_2Cl_2	1580	2200–3000, 3435
IIIe	Nujol mull	1580	2000–3000 (centered at 2600)
	CH_2Cl_2		2200–3000

[a] Hexachlorobutadiene.

analogous conclusion when studying similar hydroxyallyl cations in their Cl^- and $F_2P(O)O^-$ salts [1,2], and in the case of cation IIa [16] when its ^{13}C NMR spectrum was compared with that of the methoxyallylolefinic complex, $[Rh(\eta^5\text{-}C_7H_7\text{-}2\text{-}CH{\simeq}OMe)(\eta^5\text{-}C_5H_5)]^+PF_6^-$ the structure of which was established unambiguously by X-ray crystallography [17]. However, as has been mentioned in ref. 2, the metal–C(8) interaction in complexes of such a type is rather weak owing to the strong resonance-stabilizing effect of the α-hydroxyl group, which competes with the metal. Therefore the $J(^{103}Rh\text{–}^{13}C(8))$ values in the spectra of IIa–IIe are small and are in fact the same as for the spectra of the starting acylsubstituted complexes Ia–Ie. Moreover this fact means that the resonance forms **2** and **3** in structures of type **A** only contribute to the bonding in the present complexes to a small extent.

The IR spectra of cations IIa–IIe (Table 3) contain strong bands in the region 1500–1600 cm^{-1} shifted by 100 cm^{-1} towards the low frequency range relative to those in spectra of initial acyl-substituted complexes Ia–Ie. These bands by analogy to salts of this type with Cl^- and $F_2P(O)O^-$ anions previously studied [1,2] were assigned to a mixed stretching vibration of the oxoallylic fragment C(3)≃C(2)≃C(8)≃O. The validity of the assignment was confirmed by the absence of isotopic shift of the band at 1570 cm^{-1} in the IR spectrum of the ^{18}O-labelled cationic complex IIa (Table 3).

In IR spectra of complexes IIa–IIe strong bands are observed in the OH-group absorption region 3380–3500 cm^{-1} (Fig. 2a). Judging from the position and intensity of the bands the latter cannot be assigned to the stretching vibration of the free OH groups. It is noteworthy that the position of these bands in the IR spectra of these complexes in the solid state and in CH_2Cl_2 solution is in fact the same.

It is well known that the PF_6^- anion, despite its low basicity, can participate in the weak $O\text{–}H \cdots FPF_5^-$ hydrogen bond. In the corresponding IR spectra the relatively narrow band of medium intensity at 3570 cm^{-1} is observed, which is usually assigned to absorption by H-bonded OH group [18]. Taking into account the high proton-donating ability of the $CR^1{\simeq}OH$ group it may be assumed, that

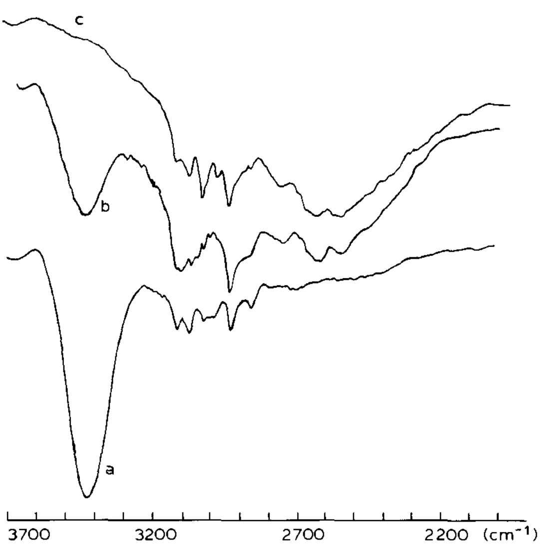


Fig. 2. IR spectra of complex IIa in CH_2Cl_2 solution (OH group absorption); a, recorded immediately after formation; b, after storage for 12 h; or c, for 24 h.

hydrogen bonds of the same type are formed in cations IIa–IIe. However, the study of concentration dependence of the IR spectra of cations IIa, IIb in the CH_2Cl_2 solution has shown that in these compounds the hydrogen bond is of intra- and not intermolecular character (the values of the ν(OH) absorption frequencies in the IR spectra of the complexes remain constant up to a concentration of 0.005 *M*).

In general, two types of intramolecular chelates can exist in the solutions of the cationic complexes formed owing to (a) a hydrogen bond of the type O–H ··· π, i.e. with participation of the π-electrons in the coordinated C(2)=C(3) bond of the diene ligand and (b) a hydrogen bond of the type O–H ··· Rh with participation of the metal atom electrons. Analysis of molecular models of the cations confirms that in the case of intramolecular O–H ··· π hydrogen bonding the oxygen atom should be significantly displaced from the C(3)C(2)C(8) plane, thus breaking the conjugation between the C(3)$\overset{...}{=}$C(2) and C(8)$\overset{...}{=}$O double bonds. The O–H ··· Rh hydrogen bond in such complexes however does not interfere with the conjugation, and is energetically more favourable than the interionic O–H ··· FPF_5^- hydrogen bond. We recently unambiguously confirmed the existence of the O–H ··· Rh hydrogen bond in the Rh(η^4-C_7H_7-2-CHOHR)(η^5-C_5H_5) (R = H, Me, Ph) series of carbinols by IR spectroscopy and by a structural study of one of the complexes [19].

IR spectroscopy of cations IIa–IIe revealed that these complexes are not inert in CH_2Cl_2 solutions; new products are formed after a certain period of time. Drastic changes were observed in the IR spectra of the solutions even within a few hours. New, strong, and very broad ν(OH) bands in the region of 2000–3000 cm^{-1} centered at 2600 cm^{-1} appeared in place of the initial ν(OH ··· Rh) bands at 3380–3500 cm^{-1} (Fig. 2b, c). Some new bands in the region of the P=O vibration at 1100–1300 cm^{-1} were also observed in the spectra of the solutions of IIa–IIe after storage, but the position of the ν(C(3)$\overset{...}{=}$C(2)$\overset{...}{=}$C(8)$\overset{...}{=}$O) bands in fact did not change significantly, which indicates that hydroxyallylolefinic structure is retained

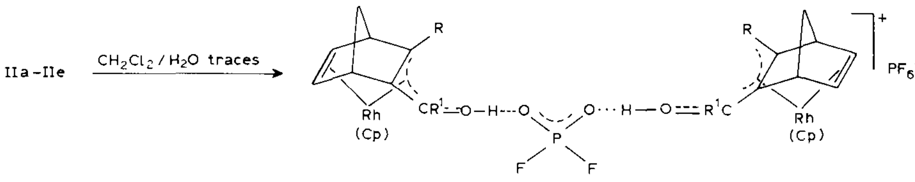
Table 4

^{19}F NMR spectral data for cations IIa–IIe in CD_2Cl_2

Compound	δ (ppm)/$J(^{19}F-^{31}P)$ (Hz) [a]		PF_6/F_2POO integral intensities ratio
	PF_6 [d]	F_2POO [d]	
IIa	5.12/712	−5.43/958	9/1
IIa [b]	5.10/712	−5.42/959	4/1
IIb	4.79/713	−6.04/969	–
IIc	5.31/712	−5.37/961	11/1
IId	4.82/711	−5.38/961	12/1
IIe [c]	5.2/712	−5.29/959	32/1

[a] CF_3COOH used as an external standard. [b] After 16 h at 22° C. [c] Spectrum was recorded in specially purified solvent (see Experimental). [d] ^{19}F NMR spectral data for PF_6 and $F_2P(O)O$ groups see [20].

in the products formed. The ^{19}F and ^{31}P NMR spectra of the CH_2Cl_2 solutions of cations IIa–IIe show that these products (IIIa–IIIe) are "dimeric" complexes with a bridging $F_2P(O)O$ group. Complex IIIe was isolated in the solid state by the addition of moist ether to a CH_2Cl_2 solution of cation IIe *, the structure of IIIe was confirmed by X-ray crystallography (vide infra).



(IIIa-IIIe)

In the ^{19}F NMR spectra of cations IIa–IIe in CD_2Cl_2 solution from the beginning two doublets are observed, their chemical shifts and $J(^{19}F-^{31}P)$ coupling constant are in a good agreement with the literature data for PF_6^- and $F_2P(O)O^-$ anions (Table 4). In the ^{19}F NMR spectrum of "dimer" IIIe integral intensity ratio of the doublets with δ_1 +4.75 ppm ($J(^{19}F-^{31}P)$ 711 Hz) and δ_2 −5.39 ppm ($J(^{19}F-^{31}P)$ 958 Hz) is 3/1. The fact that there are two signals in the ^{31}P NMR spectrum representing the complex septet (δ −144 ppm, $J(^{31}P-^{19}F)$ 712 Hz) and triplet (δ −16.6 ppm, $J(^{31}P-^{19}F)$ 962 Hz) confirms that their assignment to PF_6^- and $F_2P(O)O^-$ group, respectively is correct. In other cases, when "dimeric" cationic complexes IIIa–IIId are formed in CH_2Cl_2 solution from the cations IIa–IId, the intensity ratio of the PF_6^- and $F_2P(O)O^-$ signals in the ^{19}F NMR spectra strongly depends on the time that has elapsed from the moment of sample preparation till the moment of recording the spectrum. It has been shown that the rate of transformation of cation, e.g. IIa into "dimer" IIIa depends on the amount of hydroxyl-containing impurities in the solvent. Thus a solution of IIa in specially purified and dried solvent (see Experimental) immediately after its preparation shows a ratio of intensities of PF_6^- and $F_2P(O)O^-$ doublets of 42/1, however after 12 and 24 h the ratio becomes 30/1 and 18/1 respectively; the use of conventional

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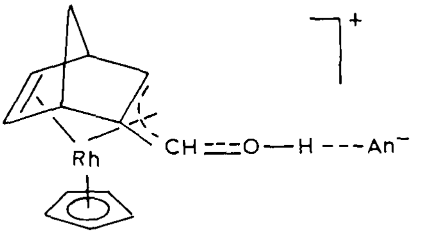
* Our attempts to isolate the other cationic complexes IIIa–IIId analytically pure in a similar way was unsuccessful.

solvent leads to a sharp decrease in the ratio of the signals, from 9/1 immediately after preparation to 4/1 after 16 h at 22°C.

The data obtained indicate that the formation of "dimers" IIIa–IIIe from the cationic complexes IIa–IIe is probably the result of the partial hydrolysis of the PF_6^- anion by traces of moisture or other hydroxyl-containing impurities in the solvent. The PF_6^- anion is known to be extremely stable in neutral and alkaline solutions [21], however, in acidic solutions it is slowly hydrolyzed to form phosphate ion [22]. Therefore the partial hydrolysis of PF_6^- anion in complexes IIa–IIe occurs under mild conditions, as mentioned above, is unusual, as the examples in the literature of such reactions are scarce [23–26]. The formation of $F_2P(O)O^-$ group is observed in situations, where it can compete as a mono- or bidentate ligand with weaker donors such as Cl, Me_2CO, etc., for a coordination site on a metal center. In the present case the $F_2P(O)O^-$ group, which forms as a result of the PF_6^- anion hydrolysis, stabilizes the *O*-protonated form of the acyl-substituted norbornadiene complexes by the formation of a $O\text{–}H \cdots OP(F_2)O \cdots H\text{–}O$ hydrogen bond in "dimers" IIIa–IIIe, more stable than the $O\text{–}H \cdots Rh$ type in the initial cations IIa–IIe.

It is noteworthy that the direct protonation of aldehyde Ia by $F_2P(O)OH$ in ether yields cation IV with a $O\text{–}H \cdots An$ ($An = F_2POO^-$) hydrogen bond [1]. From the IR spectrum of the cation it can be seen that the interionic hydrogen bond is even more stable ($\nu(OH \cdots An)$ 2100–2800 cm^{-1}, centered at 2500 cm^{-1}) than in "dimers" IIIa–IIIe. It is thus quite logical to assume that the latter are only the intermediates and not the final hydrolysis products of the hexafluorophosphate salts of cations IIa–IIe, which is probably what the cationic complexes IV are.



(IV)

An X-ray crystallographic study of cation IIIe has confirmed the tentative structure put forward on the basis of the NMR and IR spectral data. The cationic complex IIIe can be regarded as a "composite" as it consists of two positively charged groups $Rh(C_7H_6\text{-}3\text{-}Me\text{-}2\text{-}CHOH)(\eta^5\text{-}C_5H_5)^+$ attached to the difluorophosphate anion by the $O\text{–}H \cdots O$ hydrogen bond (Fig. 3).

Geometry of the Rh atom coordination in IIIe is in fact the same as in the cationic allylolefinic complexes $[Rh(\eta^{2,3}\text{-}C_7H_7\text{-}2\text{-}CH_2)(\eta^5\text{-}C_5H_5)]^+PF_6^-$ (V) [13] and $[Rh(\eta^{2,3}\text{-}C_7H_7\text{-}2\text{-}CH\text{=}OMe)(\eta^5\text{-}C_5H_5)]^+PF_6^-$ previously studied [17]. The distances between the Rh atom and the C(2), C(3) and C(8) atoms of the η^3-coordinated allyl fragment differ significantly, the Rh–C(2) (2.153(6) Å) and Rh–C(3) (2.127(6) Å) bonds being shorter, and the Rh–C(8) (2.374(6) Å) bond being considerably longer than the distance from the Rh atom to the carbon atoms of the η^2-coordinated double bond C(5)=C(6) (Rh–C(5) (2.189(7) Å) and Rh–C(6) (2.184(6) Å)).

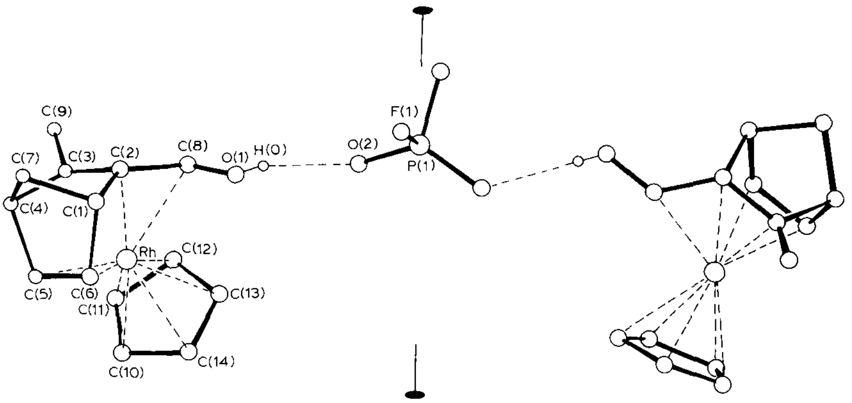


Fig. 3. Structure of "composite" cationic complex $\{[CpRh(\eta^{2,3}\text{-}C_7H_6\text{-}3\text{-}Me\text{-}2\text{-}CH\overset{..}{-}OH)]_2F_2POO\}^+\ PF_6^-$.

The non-symmetrical character of rhodium atom coordination by the norbornadiene ligand is reflected in its geometry; the C(5)=C(6) bond length of 1.383(9) Å is in good agreement with the values usually observed for η^2-coordinated olefins. At the same time the C(2)–C(3) bond of 1.434(8) Å is noticeably longer, the difference in the C(2)–C(3) and C(2)–C(8) bond lengths (1.388(8) Å) indicating non-symmetrical character of metal atom coordination by the π-allyl system. Quite naturally the most significant elongation on coordination is exhibited by that bond of the π-allyl system, which is involved in the strongest interactions with the metal atom (in our case C(2)–C(3)).

Comparison of geometrical parameters of the cationic complexes V and IIIe reveals significant differences in the Rh-exocyclic C(8) atom distances (2.27(1) and 2.374(6) Å in V and IIIe, respectively) and in the inclination angles of the C(2)–C(8) bond to the C(1)C(2)C(3)C(4) plane which are equal to 20.5° V and 17.7° IIIe. It is noteworthy that in both cases the C(8) atom is displaced from the C(1)C(2)C(3)C(4) plane towards the Rh atom, whereas in $Rh(\eta^4\text{-}C_7H_7\text{-}2\text{-}CHOHMe)(acac)$ complex with normal diolefin type metal atom coordination, the C(8) atom is displaced in the opposite direction (i.e. away from the metal center), with a C(2)–C(8) bond inclination angle of 16.0° [27]. An important feature of the geometry of molecule IIIe is the C(8)–O(1) bond length of 1.321(9) Å, which is intermediate between single and double carbon–oxygen bond distances, the oxygen atom, in fact lies in the plane of the π-allyl fragment (the C(3)C(2)C(8)O(1) torsion angle is ~ 168(1)°). These results are consistent with the assumption that the O-atom participates in the stabilization of the adjacent carbocationic center $C^+(8)$. At the same time the distance Rh ··· O(1) of 3.233(7) Å in complex IIIe precludes direct interaction between Rh and oxygen atoms. The unique coordination of the Rh atom by norbornadienyl ligand in complex IIIe gives rise to some distortion of ligand conformation. Although both five-membered cycles have the envelope conformation the folding angle along the C(1) ··· C(4) line in the C(1)C(2)C(3)C(4)C(7) cycle is 3.3° greater than in the C(1)C(6)C(5)C(4)C(7) cycle. The projection of complex IIIe along the C(1) ··· C(4) line is shown in Fig. 4, the inclination angles of the C(2)–C(8) and C(3)–C(9) bonds to the C(1)C(2)C(3)C(4) plane are indicated.

On the basis of the structural results on the cyclopentadienylrhodium complexes the authors of refs. 28–30 assumed that the π-electron density of the Cp ligand is

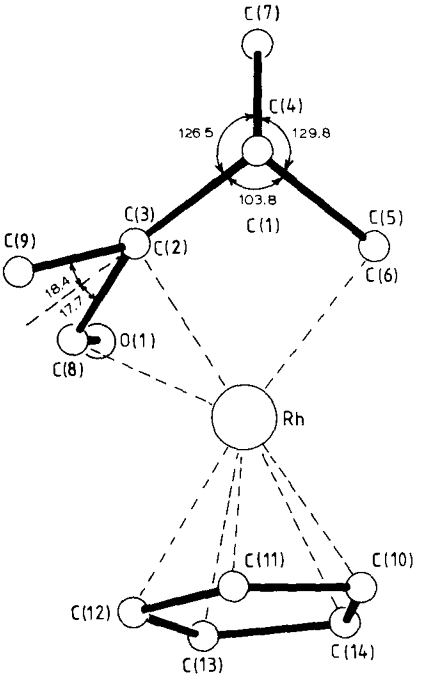


Fig. 4. Projection of complex $[CpRh(\eta^{2,3}\text{-}C_7H_6\text{-}3\text{-}Me\text{-}2\text{-}CH{\doteq}OH)]PF_6^-$ along the C(1)...C(4) line.

not fully delocalized. Partial π-bond localization is also noticeable in the geometry of the Cp ligand of the IIIe complex. Some geometrical features, viz. a certain shortening of the C(10)–C(11), C(11)–C(12) and C(13)–C(14) bonds compared with the C(10)–C(14) and C(12)–C(13) bonds and the differences in the Rh–C(Cp) bond distances (Table 6) are characteristic of the allylolefinic coordination of the Cp ligand.

Interestingly, in connection with this, the line joining the midpoint of the C(13)–C(14) bond with the C(10)C(11)C(12) triangle centroid is almost perpendicular (89.1°) to the line joining the midpoint of the C(5)=C(6) bond with the C(3)C(2)C(8) allyl system centroid. Thus the Rh atom coordination polyhedron in cation IIIe may be considered, perhaps with some exaggeration, as a distorted tetrahedron in accordance with the closed 18-electron shell of the metal.

Difluorophosphate anion geometry has been studied in the structure of its potassium [31], rubidium and cesium [32] salts and in crystals of the solvate $Ca[PO_2F_2]_2 \cdot 2MeCOOEt$ [33]. The P–O (1.445(6) Å) and P–F (1.524(5) Å) bond lengths in IIIe are similar to those found in the sufficiently accurate structural study of $K[PO_2F_2]$ (P–O 1.457; P–F 1.552 Å [31]). On the basis of the well-known bond length–bond order correlations [34] the authors came to the conclusion that the π-order of the P–O and P–F bonds in the $PO_2F_2^-$ anion are ~ 0.8 and ~ 0.2 respectively. Greater contributions by the π-component in the P–O bond compared with the P–F bond is also reflected in the bond angles in the PO_2F_2 tetrahedron; in accordance with the VSEPR theory [35] the OPO angle formed by the almost double P–O bonds is significantly larger (120.5(3)°) and the FPF angle is noticeably smaller (98.1(3)°) than the ideal tetrahedral value. The OPF angles have inter-

Table 5

Atomic coordinates ($\times 10^4$, for Rh$\times 10^5$, for H$\times 10^3$) and temperature factors (isotropic for H atoms, equivalent isotropic for non-hydrogen atoms)

Atom	*x*	*y*	*z*	*B* (Å^2)	Atom	*x*	*y*	*z*	*B* (Å^2)
Rh	21958(3)	49802(4)	45226(2)	3.15(1)	C(10)	2275(8)	3504(5)	4510(7)	6.2(3)
P(1)	0	6880(2)	3/4	4.05(7)	C(11)	3151(7)	3801(5)	4924(6)	5.3(2)
P(2)	0	1080(2)	3/4	4.01(6)	C(12)	2955(7)	4264(5)	5655(5)	5.5(2)
F(1)	−565(4)	7555(3)	6891(3)	7.5(2)	C(13)	1909(8)	4209(6)	5713(6)	6.4(3)
F(2)	1105(3)	1079(3)	7969(3)	7.8(2)	C(14)	1467(7)	3735(6)	5016(7)	6.3(3)
F(3A)	265(13)	1820(10)	6840(9)	8.1(6)	H(O)	105(5)	658(5)	584(4)	3(2)
F(3B)	509(16)	1021(16)	6658(10)	13.1(8)	H(1)	90(5)	694(4)	372(4)	5(2)
F(4A)	248(12)	374(10)	6836(10)	9.3(7)	H(4)	349(4)	592(3)	284(3)	3(1)
F(4B$_1$)	0	2087(11)	3/4	13(1)	H(5)	207(6)	463(5)	272(5)	7(2)
F(4B$_2$)	0	−5(12)	3/4	11(1)	H(6)	62(4)	534(4)	343(3)	3(1)
O(1)	1042(4)	6585(4)	5436(4)	5.2(2)	H(71)	184(4)	680(3)	236(3)	3(1)
O(2)	705(4)	6395(4)	7024(3)	6.7(2)	H(72)	249(4)	739(4)	310(3)	3(1)
C(1)	1456(5)	6557(4)	3630(4)	3.9(2)	H(8)	249(4)	627(3)	574(3)	2(1)
C(2)	2212(5)	6431(4)	4425(4)	3.2(2)	H(91)	418(5)	613(4)	517(4)	5(2)
C(3)	3104(4)	6055(4)	4130(4)	3.3(1)	H(92)	455(5)	560(5)	440(4)	5(2)
C(4)	2854(5)	5992(4)	3149(4)	3.9(2)	H(93)	445(6)	648(6)	439(5)	7(3)
C(5)	2112(6)	5214(4)	3125(4)	4.2(2)	H(10)	211(5)	319(4)	400(4)	5(2)
C(6)	1253(6)	5558(5)	3428(4)	4.1(2)	H(11)	379(5)	369(5)	475(4)	6(2)
C(7)	2173(6)	6809(4)	2952(4)	4.5(2)	H(12)	346(4)	457(4)	597(4)	4(1)
C(8)	1954(5)	6353(4)	5268(4)	3.5(2)	H(13)	150(5)	450(5)	607(5)	5(2)
C(9)	4138(5)	6101(6)	4558(5)	4.2(2)	H(14)	72(6)	362(5)	484(5)	8(2)

mediate values 108.7(3) and 109.3(3)°. The hydrogen bond O(1)–H(O) ··· O(2) in the cation IIIe is considered to be a strong one (according to the classification given in the review [36]), its geometrical characteristics being equal to 2.560(7), 0.62(6), 1.96(6) Å and 164(8)° for the O(1) ··· O(2), O(1)–H(O), H(O) ··· O(2) distances and the O(1)–H ··· O(2) angle respectively.

Experimental

^{1}H, ^{19}F, ^{31}P and ^{13}C NMR spectra were recorded with a Bruker WP-200-SY spectrometer with TMS as internal, and CF_3COOH and H_3PO_4 as external, standards. IR spectra were recorded with an UR-20 spectrometer, in CH_2Cl_2 and CD_2Cl_2 solutions. In the cases, specified in the tables by an appropriate footnote, IR and NMR spectra were recorded in specially purified solvent, which was dried over 4 Å molecular sieves for several days and distilled over a new portion of sieves under argon immediately before use.

Preparation of (3-methyl-2-formylnorbornadiene)cyclopentadienylrhodium (Ia)

A mixture of 0.5 g (1.9 mmol) of $Rh(acac)(CO)_2$ in 40 ml of dry benzene and 0.8 g (5.9 mmol) of 3-formyl-2-methylnorbornadiene (made by a standard procedure [37] and used without additional purification) is refluxed for 16 h until disappearance of $Rh(acac)(CO)_2$ (TLC control) is complete. The solvent is evaporated off, the residue is dissolved in 30 ml of dry CH_2Cl_2, and refluxed under argon with 0.8 g (3.0 mmol) of TlC_5H_5 for 4 h. After the reaction is complete solvent is evaporated and the crude product is purified by chromatography on silica gel column using an ether/hexane (1/1) mixture as eluent. The yellow-orange fraction is collected and purified once again by an analogous procedure, to give 0.25 g (1.16 mmol, 61%) of complex Ie as a dark-orange oil.

Mass-spectrum: M^+ (302), $M^+ - CH_3$ (287), $M^+ - CHO$ (273), $(C_5H_5)_2Rh^+$ (233), $C_5H_5Rh^+$ (168), Rh^+ (103). ^{1}H NMR (δ (ppm), $CDCl_3$): 9.05 (s, 1H, CHO), 5.25 (d, 5H, $J(^{103}Rh-^{1}H)$ 0.85 Hz, C_5H_5), 3.87 (m, 1H, H(1)), 3.75 (m, 2H, H(5,6)), 3.3 (m, 1H, H(4)), 1.89 (s, 3H, Me), 1.14 (d, br, 1H, $J(H(7_\alpha)-H(7_\beta))$ 9.6 Hz, $H(7_{\alpha(\beta)})$), 0.96 (dt, 1H, $J(H(7_\beta)-H(7_\alpha))$ 9.6, $J(H(7_\beta)-H(1.4))$ 1.6 Hz, $H(7_{\beta(\alpha)})$). IR spectra: $\nu(C{=}O)$ 1650, $\nu(CH_3)$ 1355 cm^{-1} in CCl_4.

General procedure for the preparation of O-protonated cationic complexes

An excess of 70% HPF_6 (0.5 ml) is added dropwise to a solution of aldehyde Ia (0.3 g, 0.104 mmol) in 30 ml of dry diethyl ether at 0°C. After precipitation is complete, the solvent is decanted and the yellow salt is washed twice with dry diethyl ether to give 0.32 g of complex IIa after thorough drying in vacuum. (Found: C, 36.05; H, 3.25; P, 7.32. $C_{13}H_{14}F_6OPRh$ calc.: C, 35.94; H, 3.22; P, 7.14%.) An analogous procedure was used for the synthesis from ketone Ib of the cationic complex IIb which is isolated in the form of a dark-red amorphous salt (yield 56%). (Found: C, 37.32; H, 3.61; F, 25.45. $C_{14}H_{16}F_6OPRh$ calc.: C, 37.50; H, 3.57; F, 25.42%). The cationic complex IId is obtained from the aldehyde Id in the form of orange crystals, by reprecipitation from dry CH_2Cl_2 solution into dry diethyl ether, yield 68%, M.p. 122–126°C (with dec.). (Found: C, 43.17; H, 4.89; Rh, 19.74. $C_{18}H_{24}F_6OPRh$ calc.: C, 42.86; H, 4.76; Rh, 20.44%); yellow-orange precipitate was obtained from aldehyde Ie in 72% yield, which, from elemental analysis, NMR and

Table 6

Bond lengths (Å) for complex IIIe

Rh–C(2)	2.153(6)	C(1)–C(6)	1.530(9)	C(12)–C(13)	1.42(1)
Rh–C(3)	2.127(6)	C(1)–C(7)	1.536(9)	C(13)–C(14)	1.37(1)
Rh–C(5)	2.184(6)	C(2)–C(3)	1.434(8)	P(1)–F(1) [a]	1.524(5)
Rh–C(6)	2.189(7)	C(2)–C(8)	1.388(8)	P(1)–O(2) [a]	1.445(6)
Rh–C(8)	2.374(6)	C(3)–C(4)	1.527(8)	P(2)–F(2) [b]	1.587(5)
Rh–C(10)	2.187(7)	C(3)–C(9)	1.480(9)	P(2)–F(3A) [b]	1.56(1)
Rh–C(11)	2.218(8)	C(4)–C(5)	1.520(9)	P(2)–F(3B) [b]	1.53(2)
Rh–C(12)	2.211(8)	C(4)–C(7)	1.529(9)	P(2)–F(4A) [b]	1.52(2)
Rh–C(13)	2.233(9)	C(5)–C(6)	1.383(9)	P(2)–F(4B$_1$) [b]	1.49(2)
Rh–C(14)	2.254(9)	C(10)–C(11)	1.36(1)	P(2)–F(4B$_2$) [b]	1.60(2)
O(1)–C(8)	1.321(9)	C(10)–C(14)	1.44(2)		
C(1)–C(2)	1.529(9)	C(11)–C(12)	1.37(1)		

[a] Bond in PO_2F_2 group. [b] Bond in the disordered PF_6^- anion.

IR spectra is deduced to be the cationic complex IIe without admixture of cation IIIe. (Found: C, 37.55; H, 3.61; F, 24.25; $C_{14}H_{16}F_6OPRh$ calc.: C, 37.50; H, 3.57; F, 25.45%).

Preparation of cationic "dimeric" complex (IIIe)

To a solution of 0.26 g (0.58 mmol) of cationic complex IIe in 1.5 ml of CH_2Cl_2 was added slowly 5–8 drops of ether without stirring; after the solution has been left for 20–25 min well-shaped cherry-coloured crystals are formed on the walls of the vessel, then more diethyl ether is added (0.5 ml) at intervals of 0.5–1 min, and the solution left to stand for 12 h at 0 °C to give 0.2 g (0.235 mmol, 81%) of crystalline complex IIIe M.p. 146–148 °C. (Found: C, 39.21; H, 3.78; F, 17.78. $C_{28}H_{32}F_8O_4P_2Rh_2$ calc.: C, 39.44; H, 3.76; F, 17.84%.)

X-Ray structural study of complex IIIe

Crystals of IIIe are monoclinic; at +20 °C *a* 13.420(8), *b* 14.793(8), *c* 15.49(1) Å, β 95.55(5)°, *V* 3060(3) Å^3, D_{calc} 1.789 g cm^{-3}, space group *C*2/*c*, *Z* = 4, cation and anion occupy special positions on the two-fold axis. Unit cell parameters and intensities of 1664 unique reflections with $F^2 > 4\sigma$ were measured with a four-circle

Table 7

Relevant bond angles (°) for complex IIIe

C(2)C(1)C(6)	98.0(5)	C(3)C(4)C(5)	98.7(5)	C(11)C(12)C(13)	107.2(8)
C(2)C(1)C(7)	99.8(5)	C(3)C(4)C(7)	102.7(5)	C(12)C(13)C(14)	109.5(8)
C(6)C(1)C(7)	101.8(5)	C(5)C(4)C(7)	102.4(5)	C(10)C(14)C(13)	105.0(8)
C(1)C(2)C(3)	107.4(5)	C(4)C(5)C(6)	106.2(5)	C(8)O(1)H(O)	106(6)
C(1)C(2)C(8)	124.2(5)	C(1)C(6)C(5)	106.6(6)	F(1)P(1)F(1′) [a]	98.1(3)
C(3)C(2)C(8)	124.0(5)	C(1)C(7)C(4)	94.2(5)	F(1)P(1)O(2) [a]	108.7(3)
C(2)C(3)C(4)	103.4(5)	O(1)C(8)C(2)	118.9(6)	F(1)P(1)O(2′) [a]	109.2(3)
C(2)C(3)C(9)	128.0(5)	C(11)C(10)C(14)	109.3(8)	O(2)P(1)O(2′) [a]	120.5(3)
C(4)C(3)C(9)	123.6(5)	C(10)C(11)C(12)	108.9(8)		

[a] Bond angles in PO_2F_2 groups.

automatic diffractometer Syntex $P2_1$ (20 °C, Mo-K_α radiation, graphite monochromator, $\theta/2\theta$ scan, $\theta \leqslant 26°$).

The structure was solved by the heavy-atom technique. The Rh atom coordinates were determined from Patterson synthesis, and other non-hydrogen atoms were located in the subsequent electron density synthesis. The PF_6^- anion is disordered over two positions which are rotated by 45° to each other around the axis perpendicular to the crystallographic two-fold axis. One of the independent fluorine atoms of the anion (F(2)) is in general position (this atom is not disordered) and each of the two other fluorine atoms F(3) and F(4) is disordered over two positions in the plane passing through the two-fold axis. Thus the observed disorder of the PF_6^- anion corresponds to the superposition of two possible variants of disposition of the octahedron on the two-fold axis. In the first variant two fluorine atoms are situated on the same two-fold axis as the P atom, in the second variant all three fluorine atoms are in general positions.

The structure was refined by the full-matrix least-squares technique at first to an isotropic and then to an anisotropic approximation. All of the hydrogen atoms including the H(O) atom, which participates in the H bond, were directly located in the difference Fourier synthesis and included in the final refinement to isotropic approximation. The final R factor is 0.031; the weighted R_w factor is 0.037. Atomic coordinates and temperature factors are listed in Table 5, bond lengths and bond angles are given in Tables 6 and 7, respectively. All calculations were carried out by an Eclipse S/200 computer using INEXTL programmes [38].

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