DIENE AND DIENYL COMPLEXES OF TRANSITION ELEMENTS

X*. η^5-CYCLOPENTADIENYL-η^5-1-ARYLPENTADIENYLRHODIUM HEXAFLUOROPHOSPHATES. REACTIONS WITH HALIDE IONS. CRYSTAL AND MOLECULAR STRUCTURE OF η^5-CYCLOPENTADIENYL-η^5-1-PHENYLPENTADIENYLRHODIUM HEXAFLUOROPHOSPHATE

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Summary

The structure of η^5-cyclopentadienyl-η^5-1-phenylpentadienylrhodium hexafluorophosphate has been determined by X-ray methods. Crystals are monoclinic, spacegroup $P2_1/a$, $Z = 4$, with a 11.056(8), b 19.741(13), c 8.033(9) Å, β 94.5(1)°. 1204 above background reflections have been collected on a diffractometer and the structure refined to R 0.070. The structure contains discrete cations and anions. In the cation the rhodium atom is bonded to the cyclopentadienyl ring (Rh–C 2.136(20), 2.152(23), 2.146(21), 2.164(22), 2.194(22) Å) and to the pentadienyl moiety of the 1-phenylpentadienyl ligand (Rh–C 2.236(17), 2.105(22), 2.217(24), 2.081(21), 2.138(25) Å).

Kinetics of reactions of η^5-cyclopentadienyl-η^5-pentadienyl salts with LiCl, LiBr and NaI in acetone have been measured. Reaction rates are essentially independent of the nature and concentration of halide.

Introduction

The protonation of η^5-cyclopentadienyl-η^4-dienol complexes of rhodium and iridium affords η^5-cyclopentadienyl-η^5-pentadienyl-rhodium and -iridium cations [2]. ^{1}H NMR studies have shown that protonation occurs at the terminal carbon atom of the diene ligand adjacent to the alcohol function, followed by elimination

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* For part IX, see ref. 1.

of water. Another possible method for preparing the η^5-pentadienyl cations involved protonation of η^4-triene complexes. In the case of [Rh{4–7-η-PhCOCH= CH(CH=CH)$_2$Ph}(η^5-C$_5$H$_5$)] the η^5-pentadienyl salt was obtained, [3] but [Rh(η^4-Ph(CH=CH)$_2$CH=CHR}(η^5-C$_5$H$_5$)] (R = H, Ph) yielded the allyl-olefin cations [Rh{1–3 : 5–6-η-Ph(CH)$_3$CH$_2$CH=CHR}(η^5-C$_5$H$_5$) [4].

We have now applied our general method of preparation via the dienol complexes to a series of η^5-1-arylpentadienylrhodium salts containing a variety of substituents in the aryl group. The reactions of these salts with halide ions have been studied in acetone solution by ^{1}H NMR spectroscopy and also kinetically using stopped-flow spectrophotometry. The crystal and molecular structure of η^5-cyclopentadienyl-η^5-1-phenylpentadienylrhodium hexafluorophosphate has also been determined.

Results and discussion

The preparation of the η^5-cyclopentadienyl-η^5-1-arylpentadienylrhodium salts follows previously described procedures [2,4] and is outlined in Scheme 1. 5-Aryl-2,4-pentadien-1-als are readily obtained from aryl aldehydes by the method of Marshall and Whiting [5]. These dienals react with [Rh(cyclooctene)$_2$Cl]$_2$ to give 1 : 1 complexes [RhCl{Ar(CH=CH)$_2$CHO}]$_2$, although chemical analysis indicate

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES

Complex	Substituent X	Yield (%)	M.p. (°C)	Analysis (Found (calcd.)) (%)	
				C	H
Ia	H	Previously reported, ref. 3.			
Ib	3-OMe	83	109–110	56.8	4.7
				(57.3)	(4.8)
Id	4-F	86	160–162	55.6	4.0
				(55.8)	(4.1)
Ie	3-Me	37	115	59.7	5.0
				(60.0)	(5.0)
IIa	H	95	128–129	58.2	5.4
				(58.6)	(5.2)
IIb	3-OMe	87	106–108	57.1	5.3
				(57.0)	(5.3)
IId	4-F	67	151–153	55.7	4.6
				(55.5)	(4.7)
IIIa	H	89	168–170	42.1	3.6
				(42.1)	(3.5)
IIIb	3-OMe	85	175–177	42.0	3.7
				(42.0)	(3.7)
IIIc	4-OMe	53	142–144	42.8	3.7
				(42.0)	(3.7)
IIId	4-F	72	142–144	40.8	3.1
				(40.5)	(3.2)
VIII	H	50	169	65.6	5.2
				(65.8)	(5.0)
IX	4-OMe	65	143–145	63.4	4.9
				(64.0)	(5.1)
X	4-Me	72	160–161	67.0	5.0
				(66.5)	(5.3)

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$Ar(CH=CH)_2CHO \xrightarrow{[Rh(cyclo\ octene)_2Cl]_2} [RhCl\{Ar(CH=CH)_2CHO\}]_2 \xrightarrow{TlCp}$

$Ar-\overset{H^2\ H^3}{C=C}-CH^5O$ (Rh Cp) $\xrightarrow[\text{aq. MeOH}]{NaBH_4}$ (IIa–IIe) $\xrightarrow{HPF_6 \cdot Et_2O}$ (IIIa–IIIe)

(Ia - Ie) (IIa-IIe) (IIIa -IIIe)

$\xrightarrow[\substack{(X=Cl,Br,I)\\ \text{acetone}}]{X^-}$

(IV , X = Cl ;
V , X = Br ;
VI, X = I)

(VII)

Ia $\xrightarrow{Ar'NH_2}$ Ph—CH=NAr' (Rh Cp)

(VIII , Ar = Ph ;
IX , Ar = 4-MeOC$_6$H$_4$;
X , Ar = 4-MeC$_6$H$_4$)

SCHEME 1

that some 2:1 complex [RhCl{Ar(CH=CH)$_2$CHO}$_2$] is often formed as well. The aldehyde complexes (Ia–Ie) are orange crystalline materials, stable for long periods in air, unlike the parent aldehydes which gradually polymerise on standing. They undergo reactions typical of aldehydes, for example crossed aldol condensations [3], the Wittig reaction [1], reduction to the dienol complex [2] and Schiff's base formation. Characterising data and ^{1}H NMR spectra of three Schiff's bases (VIII, IX, X) derived from Ia and aryl aldehydes are included in Tables 1 and 2.

Protonation of the dienol complexes (IIa–IIe) with hexafluorophosphoric acid diethyl etherate in diethyl ether affords pentadienyl salts IIIa–IIIe. The ^{1}H NMR spectra of these complexes show that they contain the cis-η^5-pentadienyl ligand. This was confirmed by a single crystal X-ray diffraction determination of the crystal

TABLE 2

^{1}H NMR SPECTRA OF SELECTED COMPLEXES ^{a}

Complex	H^1	H^2	H^3	H^4	H^5 or H^{5s}	H$^{5'}$ or H^{5s}	C$_5$H$_5$	Ph	Other
Ib (CDCl$_3$)	2.77(dd) $J(H^2)$ 8.1 $J(Rh)$ 1.7	5.54(m) $J(H^1)$ 8.1 $J(H^3)$ 4.5 $J(Rh)$ 1.7	5.45(m) $J(H^4)$ 7.0 $J(H^2)$ 4.5 $J(Rh)$ 1.4	1.90(td)	9.05(d) $J(H^4)$ 6.9		4.99(d) $J(Rh)$ 0.8	7.14(t), 6.83(dd) 6.78(m), 6.69(m)	3.80(s) MeO
IIb (CDCl$_3$)	2.19(dd) $J(H^2)$ 8.0 $J(Rh)$ 1.8	5.29(m)	4.97(m)	1.56(q)	3.58(m)	3.66(m)	5.00(d) $J(Rh)$ 0.8	7.09(t), 6.83(dd) 6.78(t), 6.64(m)	3.79(s) MeO 1.34(t) $J(H^5)$ 5.4 OH
IIIb	4.37(d) $J(H^2)$ 11.0	6.66(dd) $J(H^1)$ 11.0 $J(H^3)$ 6.8	6.95 (overlapped by Ph)	5.90(m)	4.47(dd) $J(H^4)$ 9.0 $J(H^5)$ 2.8	2.94(m) $J(H^4)$ 12.4	5.82(d) $J(Rh)$ 0.7	7.33(t), 7.23(t) 7.20(d), 6.96(m)	3.84(s) MeO
IIId	4.43(d)	6.62(dd)	6.98(t)	5.91(m)	4.47(dd)	2.95(m)	5.84(d)	7.72(m), 7.18(t)	
Vb (IIIb + LiBr)	6.61(d) $J(H^2)$ 14.3	5.95(m) Overlapping	5.95(m)	5.00(m)	4.67(d) $J(H^4)$ 7.3	3.37(d) $J(H^4)$ 12.6	5.51(d) $J(Rh)$ 0.7	7.10(t), 6.92(m) 6.73(m)	3.71(s) MeO
Va (IIIa + LiBr)	6.68(d) $J(H^2)$ 14.3	6.0(m) Overlapping	6.0(m)	5.08(m) $J(H^{5a})$ 12.3 $J(H^4)$ 7.3 $J(H^{5s})$ 7.3 $J(Rh)$ 1.8	4.72(d) $J(H^4)$ 7.3	3.36(d) $J(H^4)$ 12.4	5.57(a) $J(Rh)$ 1.1	7.11–7.4(m)	
VIa (IIIa + NaI)	6.53(d) $J(H^2)$ 15.0	6.13(dd) $J(H^2)$ 15.0 $J(H^3)$ 11.0	5.96(dd) $J(H^2)$ 11.0 $J(H^4)$ 7.3	4.93(m) $J(H^{5a})$ 12.1 $J(H^4)$ 7.3 $J(H^{5s})$ 7.3 $J(Rh)$ 1.8	4.50(d) $J(H^4)$ 7.3	3.60(d) $J(H^4)$ 12.1	5.64(d) $J(Rh)$ 1.1	7.07–7.4(m)	
VIa (CDCl$_3$)	6.67(d)	6.12(dd)	5.81(dd)	4.55(m)	4.44(d)	3.73(d)	5.50(d)	7.1–7.4(m)	
Ve	6.67(d)	5.94(dd)	6.10(dd)	5.15(m)	4.70(d)	3.33(d)	5.60(d)	7.1–7.2(m)	2.17(s)

Compound									
(IIIe + LiBr)	$J(H^2)$ 15.1	$J(H^3)$ 11.2		$J(H^{5a})$ 12.3 $J(H^4)$ 7.4 $J(Rh)$ 1.7		$J(H^4)$ 12.3	5.60(d)	6.97(d)	Me
VIe (IIIe + NaI)	6.55(d) $J(H^2)$ 14.7	6.1(m) Overlapping		5.07(m) $J(H^{5a})$ 12.2 $J(H^4)$ 7.3 $J(H^{5'})$ 7.3 $J(Rh)$ 1.7	4.57(d) $J(H^4)$ 7.3	3.54(d) $J(H^4)$ 12.2	5.70(d)	7.1–7.2(m) 6.97(d)	2.26(s) Me
RhCp(1-MeC_5H_6) PF_6^- + LiCl	5.26(dq)	4.94(ddd)	5.43(dd)	4.80(m) $J(H^{5a})$ 12.4 $J(H^4)$ 7.3 $J(H^{5'})$ 7.3 $J(Rh)$ 1.8	4.63(m)	2.95(d) $J(H^4)$ 12.1	5.43(d) $J(Rh)$ 1.1		1.49(dd) Me $J(H^1)$ 6.9 J 1.4
+ LiBr	5.65(dq) $J(H^2)$ 15.0 $J(Me)$ 6.7	5.04(ddd) $J(H^1)$ 15.0 $J(H^3)$ 10.8 J 1.6	5.77(dd) $J(H^2)$ 10.8 J 1.6	4.77(m) $J(H^{5a})$ 12.1 $J(H^4)$ 7.2 $J(H^{5b})$ 7.3 J 2	4.50(d) $J(H^4)$ 7.2	3.03(d) $J(H^4)$ 12.1	5.44(d) $J(Rh)$ 1.1		1.47(dd) Me $J(H^1)$ 6.7 J 1.8
+ NaI (Major product)	5.5(dq) $J(H^2)$ 15.0 $J(Me)$ 6.6	5.17(ddd) $J(H^1)$ 15.0 $J(H^3)$ 11.0 J 1.8	5.73(dd) $J(H^2)$ 10.3 J 1.8	4.72(m) $J(H^{5a})$ 12.4 $J(H^4)$ 7.3 $J(H^{5'})$ 7.3 J 1.8	4.30(d) $J(H^4)$ 7.3	3.22(d) $J(H^4)$ 12.1	$J(Rh)$ 1.1		1.51(dd) Me
+ NaI (Minor product)	4.23(m)	4.90(ddd) $J(H^1)$ 11.5 $J(H^3)$ 7.0 $J(Rh)$ 2.0	not assigned		4.61(dd) $J(H^4)$ 16.5 $J(H^{5'})$ 2.0	4.99(dd) $J(H^4)$ 9.5 $J(H^5)$ 2.0	5.51(d)		1.82(d)Me $J(H^1)$ 6.2
XII XI + LiCl	6.50(d) $J(H^2)$ 10.7	5.20(t) $J(H^1,H^3)$ 12	6.23(dd) $J(H^2)$ ~11 $J(H^4)$ 7.2	6.04(ddd) $J(H^3)$ 11.9 $J(H^4)$ 11.9 $J(Rh)$ 2.0	4.98(a)		5.32(d) $J(Rh)$ 0.6	7.1–7.7(m)	

TABLE 2 (continued)

Complex	H^1	H^2	H^3	H^4	H^5 or H^{5s}	H$^{5'}$ or H^{5s}	C$_5$H$_5$	Ph	Other
XII XI + LiBr	6.39(d) J(H^2) 11.3	5.21(t) J(H^1,H^3)	6.18(m) Overlapping	6.18(m)	5.13(d) J(H^4) 11.1		5.40(d) J(Rh) 0.7	7.2–7.8(m)	
XII XI + NaI	6.22(d) J(H^2) 11.3	5.24(t) J(H^1,H^3) 11.3	6.10(dd) J(H^2) 11.7 J(H^4) 7.1	6.31(ddd) J(H^5) 11.8 J(H^3) 7.1 J(Rh) 1.7	5.33(d) J(H^4) 11.8		5.53(d) J(Rh) 0.6	7.2–7.8 (m)	
VIII (CDCl$_3$)	2.70(dd) J(H^2) 7.9 J(Rh) 1.9	2.34(t) J(H^1,H^3) J(Rh) ~ 2	5.45(m) Overlapping	5.45(m)	5.45(m) J(H^4) 8.4	7.59(d)	4.97(d) J(Rh) 1.1	7.05–7.37(m)	
IX (CDCl$_3$)	2.68(dd) J(H^2) 7.9 J(Rh) 1.6	2.34(t) J(H^1,H^3) ~ 8 J(Rh) ~ 2	5.44(m) Overlapping	5.35(m)	7.59(d) J(H^4) 8.4		4.96(d) J(Rh) 1.4	6.85–7.25(m)	3.81(s)
X (CDCl$_3$)	2.69(dd) J(H^2) 7.9 J(Rh) ~ 2	2.34(td) J(H^1,H^3) J(Rh) ~ 2	5.44(m) Overlapping	5.35(m)	7.59(d) J(H^4) 8.4		4.96(d) J(Rh) 1.5	6.95–7.25(m)	2.36(s) Me

^{a} δ in ppm, relative to tetramethylsilane, δ = 0. J in Hz. Solvent (CD$_3$)$_2$CO, except where otherwise indicated.
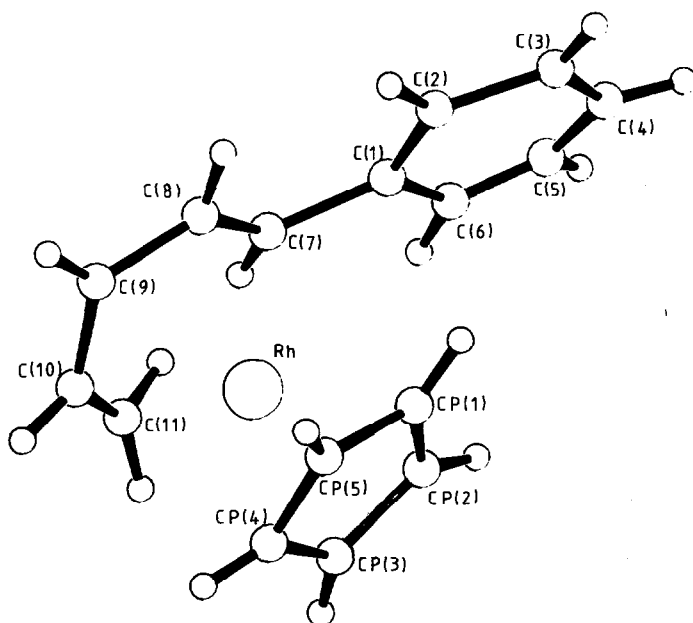
Fig. 1. The structure of η^5-cyclopentadienyl-η^5-1-phenylpentadienylrhodium hexafluorophosphate (IIIa).

and molecular structure of the 1-phenylpentadienyl compound IIIa.

The structure contains discrete cations and PF_6^- anions. The cation is shown in Fig. 1 together with the atomic numbering scheme. The rhodium atom is η^5-bonded to a cyclopentadienyl ring with bond lengths 2.136(20), 2.152(23), 2.146(21), 2.164(22), 2.194(22) Å and η^5-bonded to a 1-phenylpentadienyl ligand with distances 2.236(17), 2.105(22), 2.217(24), 2.081(21), 2.138(25) Å. Figure 2 shows a view of the cation projected on to the plane of the cyclopentadienyl ring. The cyclopentadienyl ring and the pentadienyl group intersect at an angle of 9.6°. The phenyl ring, which is not bonded to the metal is twisted out of the plane of the pentadienyl group by an angle of 25.9°.

Three structures containing the pentadienyl ligand η^5-bonded to a transition metal, namely tetrakis(3-methylpentadienyl)-tri-manganese [6] bis(η^5-2,3,4-trimethylpentadienyl)ruthenium [7] and bis(η^5-2,4-dimethylpentadienyl)iron [8] have recently been determined. The bonding of the pentadienyl ligand and the disposition of the ligand relative to the metal is similar in all four structures.

In the present structure the atoms in the cation are undergoing high thermal motion and the positions of the carbon atoms are not very accurately determined. This gives rise to relatively high standard deviations for the bond lengths and angles. It is therefore not possible to determine with any accuracy the distribution of any residual double bond character in the pentadienyl group. The other three structures, listed above, give a more accurate picture of the bonding pattern between the metal and the pentadienyl ligand.

However, the present structure is the only one to contain both an 'open' pentadienyl ligand as well as a closed cyclopentadienyl ring. This permits a direct comparison of bond lengths. In I the mean Rh–C distances are rather similar being 2.154 Å to the pentadienyl ligand and 2.158 Å to the cyclopentadienyl ligand. The
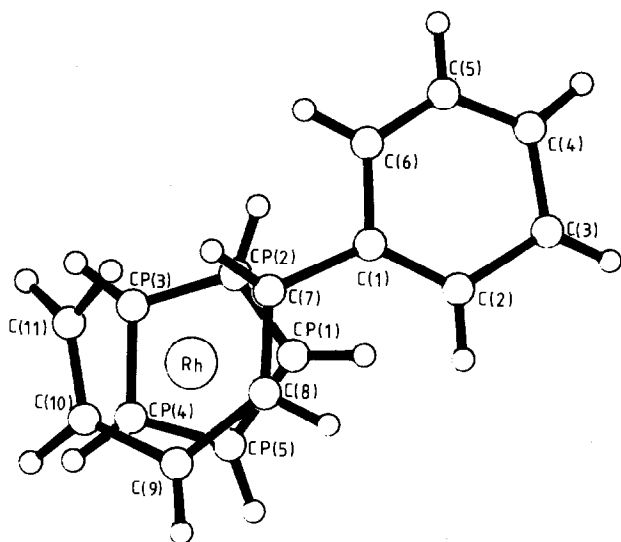
Fig. 2. A view of IIIa on to the plane of the cyclopentadienyl ring.

distance to the centre of gravity is rather different however being 1.67, 1.84 Å respectively. A similar difference is found when bis(2,4-dimethylpentadienyl)iron is compared with ferrocene (1.50 vs. 1.66 Å) but here the individual Fe–C bond lengths are slightly longer (by ca. 0.02 to 0.05 Å) in the open chain compound.

The positions of the two hydrogen atoms on C(11) are governed by two considerations, attempts by the ligand to improve overlap with the metal atom and repulsion between H atoms, particularly between H(111) and H(7). If the ligand were planar, these two atoms would be positioned within 1 Å of each other. In the manganese compound [6] the exo-H atom is 0.28 Å out of the ligand plane towards the metal and the endo-H atom is 0.72 Å away from the metal. This also happens in the Ru compound (exo 0.05, 0.30, 0.31, 0.39 Å towards and endo 0.50, 0.73, 0.71, 0.67 Å away from the metal) and in the Fe compound [6] (exo 0.20, 0.87, 0.57, 0.5 Å, towards and endo 0.31, 0.79, 0.47, 0.73 Å away from the metal). Values in the present compound are exo-H(112) 0.31 towards and endo-H(111) 0.450 Å away from the rhodium atom. So despite the limited accuracy of the location of hydrogen atoms in these structures, it is clear that the displacement of the hydrogen atoms from the C_5 plane is very similar.

There are no close contacts between ions less than the sum of Van der Waals' radii.

^{13}C NMR spectra of the parent complex [Rh(η^5-C_5H_5)(η^5-C_5H_7)]$^+$ PF$_6^-$ and of four arylpentadienyl salts IV–IVe are listed in Table 3. The central carbon nucleus of the pentadienyl system C(3) resonates to the lowest field as in the spectrum of the parent open chain ferrocene Fe(η^5-C_5H_7)$_2$ but in contrast with observations on tricarbonylpentadienyliron salts [9,10] and on tricarbonylpentadienylmanganese [11]. It is also apparent that substituents on the aryl ring have little effect on the carbon shifts and hence on the electron density at the carbon atoms of the pentadienyl system. It is likely that the twist of the aryl substituent out of conjugation with the pentadienyl group which is observed in the solid state is maintained also in solution. Such twisting of the terminal CH$_2$ or CHAr groups is a feature of acyclic pentadi-

TABLE 3

^{13}C NMR SPECTRA FOR PENTADIENYL SALTS [Rh(η^5-C$_5$H$_5$)(η^5-1-RC$_5$H$_6$)]$^+$ PF$_6^-$ ^{a}

R	Chemical shifts, δ (rel. TMS $\delta = 0$); J (^{103}Rh–^{13}C) in parentheses							
	C^1	C^2	C^3	C^4	C^5	C$_5$H$_5$	Ph	Other
H	59.1	96.4	102.8	96.4	59.1	90.2		
	(11.2)	(5.7)	(4.4)	(5.7)	(11.2)	(5.8)		
m-MeOC$_6$H$_4$	82.2	93.0	99.3	95.8	59.5	92.3	112.7, 115.8,	55.7 (Me)
	(9.3)	(5.4)	(5.5)	(5.9)	(11.3)	(6.2)	119.9, 131.1,	
							141.3, 161.2	
p-MeOC$_6$H$_4$	84.6	91.5	98.8	95.2	58.7	92.2	115.7, 129.6,	55.8 (Me)
	(8.6)	(5.5)	(5.4)	(5.9)	(11.4)	(6.1)	132.0, 161.5	
p-FC$_6$H$_4$	81.5	93.0	99.4	95.9	59.6	92.4	117.2(22.1) ^{b},	
							130.1(8.5)	
	(9.2)	(5.4)	(5.4)	(5.9)	(11.2)	(6.1)	136.4(3.0),	
							163.7(248)	
m-MeC$_6$H$_4$	82.8	92.9	99.3	95.7	59.4	92.3	124.9, 128.5,	21.3(Me)
	(9.1)	(5.6)	(5.3)	(5.8)	(11.3)	(6.1)	130.1, 130.6,	
							139.7$_7$, 139.8$_3$	

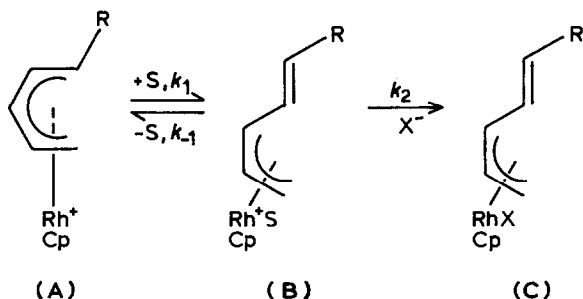^{a} In (CD$_3$)$_2$CO. ^{b} J(^{13}C–^{19}F) in parentheses.

enyl structures and is caused by the need to reduce the considerable non-bonded interactions which would arise between the *anti*-substituents in a completely planar pentadienyl ligand [7,8].

Reactions of IIIa–e with alkali metal halides in acetone have been investigated. The products are η^3-pentadienyl complexes IV, V, VI in which the halogen is directly bonded to the metal. Two structures (IV, V, VI) or VII should be considered in the case of the unsymmetrically substituted pentadienyl salts. The proton NMR spectra of the η^5-1-aryl pentadienyl salts after treatment with excess halide (LiCl, LiBr or LiI) in (CD$_3$)$_2$CO showed that clean reaction occurred, leading to only one detectable product which has structure (IV, V or VI) (Table 2). Assignment of the spectra, in selected cases, has been aided by double resonance experiments. The *trans* stereochemistry of the aryl substituent and the coordinated allyl across the olefinic bond in the η^3-pentadienyl products is indicated by the coupling constants, J(H^{1}H^2) ~ 15 Hz. An *anti* rather than a *syn* stereochemistry for the vinyl substituent on the allyl system is strongly suggested both by the low field chemical shifts of H^3 in relation to H^4, H^{5s} and H^{5a} and also by the coupling constants J(H^{3}H^4) ~ 7 Hz, which are typical of *cis* vicinal rather than *trans* vicinal protons.

The reactions of [Rh(η-C$_5$H$_5$)(η^5-1-MeC$_5$H$_6$)]$^+$ PF$_6^-$ with alkali metal halides give analogous products with very similar NMR spectra to those obtained from the aryl complexes. There was evidence, however, for the formation of VII (R = Me) to an extent less than 10% of the total product (see Table 2 for ^{1}H NMR).

The diphenylpentadienyl complex [Rh(η^5-C$_5$H$_5$)(1,5-Ph$_2$C$_5$H$_5$)]$^+$ PF$_6^-$ (XI) [2] reacts with halide ions to give single products. The starting compound possesses one *syn*- and one *anti*-phenyl substituent, and this stereochemistry about the displaced 1,2-bond is retained after conversion into the η^3-derivative.

(X = Cl, Br, I)

(XI)   (XII)

On the basis of the ^{1}H NMR spectra of the products, it is suggested that they have structure XII, in which the phenyl and η^3-allyl substituents are arranged *cis* about the double bond of the vinyl group. This conclusion is drawn from the magnitude of the coupling constant $J(H^1H^2) \sim 11$ Hz, which is more typical of *cis* vicinal protons than *trans*, for which a coupling constant of about 15 Hz would be expected.

The kinetics of the reactions of several of the pentadienyl salts sodium iodide in acetone at 25°C have been measured using visible spectrophotometry. For all the complexes except the unsubstituted compound $[Rh(C_5H_5)(C_5H_7)]$ PF_6^- the stopped flow method was used. The reactions were performed using excess of alkali metal halide. Under these conditions pseudo first order kinetics were obtained and the rates, apart from exceptions discussed below, were essentially independent of the concentration of iodide over the range 5×10^{-3} to 0.5 mol dm^{-3}. The results of the kinetic work are summarised in Table 4. The rates of reaction of compound IIIa with lithium chloride and with lithium bromide were also independent of the concentration of halide. They were also very close to that of the attack of iodide on IIIa.

These results could suggest that the reactions take place by a mechanism in which the rate-determining step does not involve halide. A possible mechanism is given below. The first slow step involves dissociation of the η^5-pentadienyl ligand to give an η^3-pentadienyl intermediate. This intermediate could have a 16-electron con-

TABLE 4

PSEUDO-FIRST ORDER RATE CONSTANTS (limiting rate), k_{obs}, FOR REACTIONS OF η^5-CYCLOPENTADIENYL-η^5-PENTADIENYLRHODIUM HEXAFLUOROPHOSPHATES WITH SODIUM IODIDE IN ACETONE AT 25.0±0.1°C

Complex	X	$10^3 k_{obs}$ (s^{-1})
$[Rh(C_5H_5)(C_5H_7)]^+$ PF_6^-	–	1.8 (LiBr, 1.5)
$[Rh(C_5H_5)(1\text{-}MeC_5H_6)]^+$ PF_6^-	–	17 (LiBr, 15)
IIIa	H	80 (LiCl, 72; LiBr, 69)
IIIb	3-OMe	52
IIIc	4-OMe	95
IIId	4-F	80
IIIe	3-Me	70

$$
\begin{array}{ccc}
\text{(A)} & \text{(B)} & \text{(C)}
\end{array}
$$

figuration or, more likely, could coordinate one molecule of solvent, acetone, which is then displaced by halide in a fast subsequent step. The postulated η^3-pentadienyl intermediate must be present in low concentration as it could not be detected by ^{1}H NMR spectroscopy in solutions of the η^5-pentadienyl salts in $(CD_3)_2CO$.

If the intermediate **B** reaches a steady state

$$
\text{Rate} = k_2[\mathbf{B}][X] = \frac{k_1 k_2 [\mathbf{A}][X]}{k_{-1} + k_2[X]}
$$

When $k_2[X] \gg k_{-1}$, Rate $\rightarrow k_1[A]$, so that the limiting k_{obs} corresponds to k_1. The observed rate constant, however, might be expected to show a decrease from this limiting value at low concentrations of halide, if $k_2[X]$ should become comparable in magnitude with k_{-1}. Such behaviour has been observed only for two complexes, the unsubstituted salt $[Rh(C_5H_5)(C_5H_7)]^+$ PF_6^- with LiBr and NaI and the diphenylpentadienyl complex $[Rh(C_5H_5)(1,5-Ph_2C_5H_5)]^+$ PF_6^- (XI) with LiCl and LiBr. Details of the kinetics of the reactions of XI with LiCl, LiBr and NaI are not presented here as the results do not conform to the pattern shown by the other complexes *.

Experimental

Most of the complexes described here are stable to air. The dienol complexes II, however, are somewhat air-sensitive in solution, and their preparations and reactions were carried out under dry nitrogen. Microanalyses were by Butterworth Laboratories Ltd. and by Mrs E. Whitaker of this Department. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker 250 MHz instrument at King's College, London.

General procedures described earlier for the preparation of η-cyclopentadienyl-η-pentadienylrhodium hexafluorophosphates were followed [2,4]. 5-Aryl-2,4-pentadien-1-als were obtained by the method of Marshall and Whiting [5]. The crude aldehyde complexes Ia–Ie obtained from the reaction of TlC_5H_5 were conveniently purified by Soxhlet extraction with boiling petroleum ether (b.p. 60–80°C).

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* For XI the reactions are faster than for the other complexes and the limiting rates depend markedly on the nature of the halide NaI > LiBr > LiCl. The observed rate constants also show a dependence on concentration of halide below ca. 0.06 mol dm^{-3} for LiCl and LiBr and below ca. 0.2 mol dm^{-3} for NaI. These results cannot be explained by the simple mechanism presented above.

Schiff's base complexes (VIII, IX, X) derived from Ia

The aldehyde complex Ia (0.250 g) in ethanol (6 cm^3) was heated under reflux with *p*-anisidine (0.30 g) for 6 h. A deep red-brown solution was formed, which was evaporated in vacuo until crystals separated. The product was filtered, washed with ice-cold methanol and dried in air. Yield (0.201 g, 65%). Recrystallised from methanol, m.p. 145°C.

η-Cyclopentadienyl-η(1–3)-5-phenylpentadienyliodorhodium

$η^5$-Cyclopentadienyl-$η^5$-1-phenylpentadienylrhodium hexafluorophosphate (IIIa) (200 mg) in acetone (10 cm^3) was treated with sodium iodide (0.5 g) in acetone (5 cm^3). After 5 min the solvent was removed in vacuo and the residue extracted with dichloromethane (5 cm^3) filtered and petroleum ether (50 cm^3) added to the filtrate. The extracts were cooled to 0°C overnight, when the product separated as deep purple needles, 156 mg (81%) m.p. 120°C. Found: C, 43.5; H, 3.6. $C_{16}H_{16}IRh$ calcd.: C, 43.9; H, 3.7%.

Similar reactions with lithium chloride and lithium bromide yielded solutions of the desired products in acetone, as evidenced by ^{1}H NMR and visible spectroscopy (see text). Attempts to isolate the pure products, however, were unsuccessful, as they partly reverted to starting material on work up.

η-Cyclopentadienyl-η-pentadienylrhodium hexafluorophosphate

2,4-Pentadien-1-ol was prepared in 36% yield by reduction of 2,4-pentadienoic

TABLE 5

ATOMIC COORDINATES FOR COMPLEX IIIa ($\times 10^4$) (with estimated standard deviations in parentheses)

Atom	x	y	z
Rh	2686(1)	6131(1)	−2078(2)
P(1)	2668(5)	4139(3)	3831(9)
F(1)	2889(23)	3994(9)	2023(25)
F(2)	3373(14)	4802(7)	3633(22)
F(3)	1506(15)	4499(10)	3052(28)
F(4)	1898(14)	3485(8)	3978(23)
F(5)	3791(17)	3700(10)	4226(29)
F(6)	2466(26)	4286(13)	5580(22)
C(1)	860(17)	7070(10)	−317(25)
C(2)	−41(21)	6722(14)	276(33)
C(3)	−399(19)	6847(18)	1971(27)
C(4)	216(35)	7389(18)	2750(31)
C(5)	979(39)	7730(18)	1974(59)
C(6)	1366(27)	7576(13)	634(28)
C(7)	1391(20)	6998(10)	−1987(24)
C(8)	965(22)	6487(18)	−2989(37)
C(9)	1501(31)	6148(17)	−4435(30)
C(10)	2732(37)	6317(14)	−4622(27)
C(11)	3300(29)	6818(17)	−3887(40)
CP(1)	2634(22)	5596(14)	226(30)
CP(2)	3532(23)	6045(14)	418(31)
CP(3)	4398(18)	5902(15)	−752(39)
CP(4)	3962(20)	5302(13)	−1734(30)
CP(5)	2931(29)	5106(14)	−1047(31)

acid [11] with lithium aluminium hydride. It had b.p. 81–83°C/55 mmHg.

2,4-Pentadien-1-ol (3.0 g) was stirred with the bis(cyclooctene)chlororhodium dimer (2.00 g) in light petroleum (b.p. 40–60°C) (50 cm³) for 2 h. The pale yellow precipitate (1.58 g, 92%) was filtered, washed with light petroleum and dried in air. M.p. 104–105°C (decomp.). Found: C, 39.2; H, 5.3. $C_{10}H_{16}ClO_2Rh$ calcd.: C, 39.2; H, 5.3%.

The above product (1.55 g) was stirred in the dark with cyclopentadienylthallium (1.4 g) in dichloromethane (50 cm³) for 36 h. Thallium chloride was filtered off and the filtrate evaporated to dryness leaving a brownish orange solid. The solid was extracted with diethyl ether, filtered and cooled to −78°C. Hexafluorophosphoric acid diethyl-etherate (1 cm³) was added and the mixture allowed to warm up gradually to room temperature. The cream precipitate was filtered and recrystallised from nitromethane/ether. Yield 1.11 g (58%) decomp. 180°C. Found: C, 31.6; H, 3.1; $C_{10}H_{12}F_6PRh$ calcd.: C, 31.6; H, 3.2%.

The method described earlier for the preparation of η-cyclopentadienyl-η-1-methylpentadienylrhodium tetrafluoroborate which involved an aqueous extraction [12] was unsuccessful in the case of the parent compound.

Kinetic measurements

Stopped flow kinetics were measured in AnalaR acetone at 25.0 ± 0.1°C using a Nortech Canterbury SF3 spectrophotometer at 390 nm. The output from the photomultiplier was passed to a Datalab DL 901 transient recorder and rate constants calculated using a Commodore PET Minicomputer. About ten reactions were carried out at each concentration of halide.

Kinetic measurements of the reactions of η-cyclopentadienyl-η-pentadienyl-

TABLE 6

DIMENSIONS IN THE CATION OF IIIa: DISTANCES (Å) AND ANGLES (°)

Rh(1)–C(7)	2.236(17)	C(2)–C(3)	1.469(29)
Rh(1)–C(8)	2.105(22)	C(3)–C(4)	1.390(42)
Rh(1)–C(9)	2.217(24)	C(4)–C(5)	1.28 (5)
Rh(1)–C(10)	2.081(21)	C(5)–C(6)	1.226(45)
Rh(1)–C(11)	2.138(25)	C(7)–C(8)	1.351(33)
Rh(1)–CP(1)	2.136(20)	C(8)–C(9)	1.503(36)
Rh(1)–CP(2)	2.152(23)	C(9)–C(10)	1.420(44)
Rh(1)–CP(3)	2.146(21)	C(10)–C(11)	1.291(39)
Rh(1)–CP(4)	2.164(21)	CP(1)–CP(2)	1.331(30)
Rh(1)–CP(5)	2.194(22)	CP(1)–CP(5)	1.462(33)
C(1)–C(2)	1.329(28)	CP(2)–CP(3)	1.422(35)
C(1)–C(6)	1.351(29)	CP(3)–CP(4)	1.481(31)
C(1)–C(7)	1.513(26)	CP(4)–CP(5)	1.361(32)
C(2)–C(1)–C(6)	117.9(23)	C(7)–C(8)–C(9)	130.7(29)
C(2)–C(1)–C(7)	128.5(21)	C(8)–C(9)–C(10)	114.6(28)
C(6)–C(1)–C(7)	113.6(21)	C(9)–C(10)–C(11)	124.5(29)
C(1)–C(2)–C(3)	120.6(24)	CP(2)–CP(1)–CP(5)	108.4(23)
C(2)–C(3)–C(4)	112.9(25)	CP(1)–CP(2)–CP(3)	109.0(23)
C(3)–C(4)–C(5)	120.2(29)	CP(2)–CP(3)–CP(4)	107.7(22)
C(4)–C(5)–C(6)	125.9(42)	CP(3)–CP(4)–CP(5)	105.0(22)
C(1)–C(6)–C(5)	121.5(35)	CP(1)–CP(5)–CP(4)	109.7(26)
C(1)–C(7)–C(8)	117.2(23)		

rhodium hexafluorophosphate with LiBr and NaI were made at $25.0 \pm 0.1°C$ and 400 nm using a Cecil Instruments CE393 spectrophotometer fitted with a thermostated cell block. In all the measurements the concentrations after mixing of the rhodium salts and the alkali metal halide were 5×10^{-4} mol dm^{-3} and 5×10^{-3} to 0.5 mol dm^{-3} respectively.

Crystal and molecular structure of η^5-cyclopentadienyl-η^5-1-phenylpentadienylrhodium hexafluorophosphate (IIIa)

Crystals of IIIa were prepared by recrystallisation from dibromomethane. Crystal data: RhPF$_6$C$_{16}$H$_{16}$, $M = 456.0$, monoclinic, space group $P2_1/a$, $Z = 4$, with a 11.056(8), b 19.741(13), c 8.033(9) Å, β 94.5(1)°, U 1747.8 Å^3, D_m 1.73, D_c 1.73 g cm^{-3}, $F(000) = 904$, Mo-K_α radiation λ 0.7107 Å, μ (cm^{-1}) 10.97.

A crystal of approximate size $0.25 \times 0.15 \times 0.25$ mm was mounted on a Stoe Stadi-2 Diffractometer and data collected via variable width ω scan. Background counts were 20 s and the scan rate of 0.033° s^{-1} was applied to a width of (2.0 + sin μ/tan θ). 2368 independent reflections were measured with $2\theta < 50°$ of which 1204 with $I > 3\sigma(I)$ were used in subsequent refinement. The structure was determined by the usual heavy-atom method and all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed in trigonal positions except for the two on C(11) which were located from a difference Fourier map and refined using constraints on C(11)–H and C(10)$\cdots$H distances. All these hydrogen atoms were given isotropic thermal parameters. The structure was refined by full-matrix least-squares to R 0.070 (R_w 0.078). Calculations were done using Shelx76 [13] on the Amdahl V7 at the University of Reading. Positional parameters are given in Table 5 and bond lengths and angles in Table 6. Thermal parameters and hydrogen positions are available in a Supplementary Publication.

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