Reactivity of Co-ordinated Ligands. Part VIII.[1] The Preparation and Reactivity of Some Rhodium(I) Derivatives of Tricyclo[5,2,1,$0^{2,6}$]deca-4,8-dien-3-one and Tricyclo[6,2,1,$0^{2,7}$]undeca-4,9-diene-3,6-dione

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The preparation and reactions of cyclopentadienyl(tricyclo[5,2,1,$0^{2,6}$]deca-4,8-dien-3-one)rhodium(I), (dp)Rh(π-C_5H_5), and cyclopentadienyl(tricyclo[6,2,1,$0^{2,7}$]undeca-4,9-diene-3,6-dione)rhodium(I), (cq)Rh(π-C_5H_5) are described. Both complexes undergo several characteristic reactions of ketones. The ketone group of (dp)Rh(π-C_5H_5) undergoes nucleophilic attack by R^- to give the corresponding alcohol, (π-C_5H_5)Rh{$C_{10}H_{10}$(OH)R} (R = H, Me, Pr^i, or $CH_2{\cdot}CO_2Me$). These alcohols react with hexafluorophosphoric acid or triphenylmethyltetrafluoroborate to give the corresponding cations, [(π-C_5H_5)Rh($C_{10}H_{10}$R)]$^+$. The complex (cq)Rh(π-C_5H_5) reacts with sodium borohydride to give a diol, (π-C_5H_5)Rh($C_{11}H_{14}O_2$) and with methylmagnesium iodide to give the alcohol, (π-C_5H_5)Rh($C_{12}H_{14}O_2$). Reaction of these alcohols with hexafluorophosphoric acid or triphenylmethyl tetrafluoroborate gives cationic(dienyl) complexes of the type [($R^2C_5H_5$)Rh{$C_{11}H_{10}R^1$(OH)}]-BF_4 and [($R^2C_5H_4$)Rh{$C_{11}H_{10}R^1$(O)}]BF_4 (R^1 = R^2 = H; R^1 = H, R^2 = CPh_3; R^1 = Me, R^2 = H).

To date, studies of the reactions of co-ordinated dienes containing functional groups, *e.g.* =CO, have been limited and directed mainly towards complexes containing a *conjugated* diene and a tricarbonylmetal unit. Amongst these complexes a number of interesting differences in reactivity have been noted.[2] In this paper we report the preparation, characterisation, and study of several complexes of rhodium(I) containing the dienones tricyclo[5,2,1,$0^{2,6}$]deca-4,8-dien-3-one (dp) and tricyclo-[6,2,1,$0^{2,7}$]undeca-4,9-diene-3,6-dione(cq). We have studied in particular the chemistry of two cyclopentadienyl complexes (π-C_5H_5)Rh(dp) and (π-C_5H_5)Rh(cq) since these provide good models for the examination of the reactivity of the carbonyl group in a co-ordinated *non-conjugated* dienone. The reactions to be discussed are outlined in Schemes 1 and 2.

Preparation of $(dp)_2Rh_2Cl_2$, (π-C_5H_5)Rh(dp), $(cq)_2Rh_2Cl_2$, (π-C_5H_5)Rh(cq), and (cq)Rh(RCO·CH·COR) (R = Me or Ph).—Tricyclo[5,2,1,$0^{2,6}$]deca-4,8-dien-3-one reacts with hydrated rhodium chloride in aqueous ethanol to give the orange-brown complex [($C_{10}H_{10}O$)-$RhCl]_2$ (1). Conversion of (1) into the corresponding cyclopentadienyl complex (2) was accomplished by treating (1) with cyclopentadienylthallium(I). The physical and spectral data support structure (2) for this complex. The essential features of the ^1H n.m.r. spectrum are a singlet at τ 4·86 (5H) assigned to the five equivalent protons of the C_5H_5 group, two AB doublets (1H per doublet) at τ 7·87 and 8·20 attributed to the protons of the methylene bridge, a multiplet at τ 4·55 (2H) arising from the olefinic protons (H^8 + H^9) (see Figure 1) and finally two multiplets (1H each) at τ 5·50 and 6·02 which may be assigned to the remaining olefinic protons (5- and 4-H respectively). From this information it appears that both double-bonds are co-ordinated to the metal and this is confirmed from the i.r. spectrum which shows no bands due to the C=C stretching vibration of a non-co-ordinated double-bond (in the free ligand such vibrations appear at 1585 and 1575 cm^{-1}). The corresponding complexes of tricyclo-[6,2,1,$0^{2,7}$]undeca-4,9-diene-3,6-dione (12) and (13) (Scheme 2) were prepared similarly. In addition two β-diketonato-complexes (13a) and (13b) have been prepared from the reaction of complex (12) with the appropriate thallium(I) β-diketonate. ^1H N.m.r. data for these complexes are presented in Table 1.

TABLE 1

N.m.r. spectra of cq complexes in deuteriochloroform (chemical shifts are in τ units) *

Compound Assignment	(cq)	(π-C_5H_5)Rh(cq)	(cq)Rh(acac)	(cq)Rh(dbm)
H^9 + H^{10}	3·82 (3t)	4·62 (4t)	3·74 (4t)	3·66 (4t)
H^4 + H^5	3·31 (1t)	6·00 (1t)	5·77 (1t)	5·62 (1t)
Bridgehead	6·42 (mt,2H)	6·26 (mt,2H)	6·22 (mt,2H)	6·23 (mt,2H)
Protons	6·72 (mt,2H)	7·52 (mt,2H)	7·18 (mt,2H)	7·19 (mt,2H)
H^{11}	8·45 (AB2t)	7·72 (AB2t)	7·65 (AB2t)	7·63 (AB2t)
H^{12}	8·52 (AB2t)	8·28 (AB2t)	8·19 (AB2t)	8·24 (AB2t)
Other Ligands		4·68 (1t,5H)Cp	8·02 (1t,3H)Me	3·37 (1t,1H)H
			7·98 (1t,3H)Me	2·1—2·6 (mt,10H) Phenyls
			5·49 (1t,1H)H	

* 1t = Singlet, 2t = doublet, *etc.*, dbm = conjugate base of dibenzoylmethane.

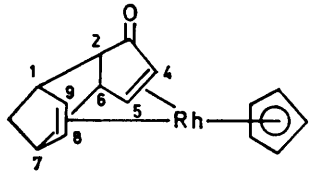


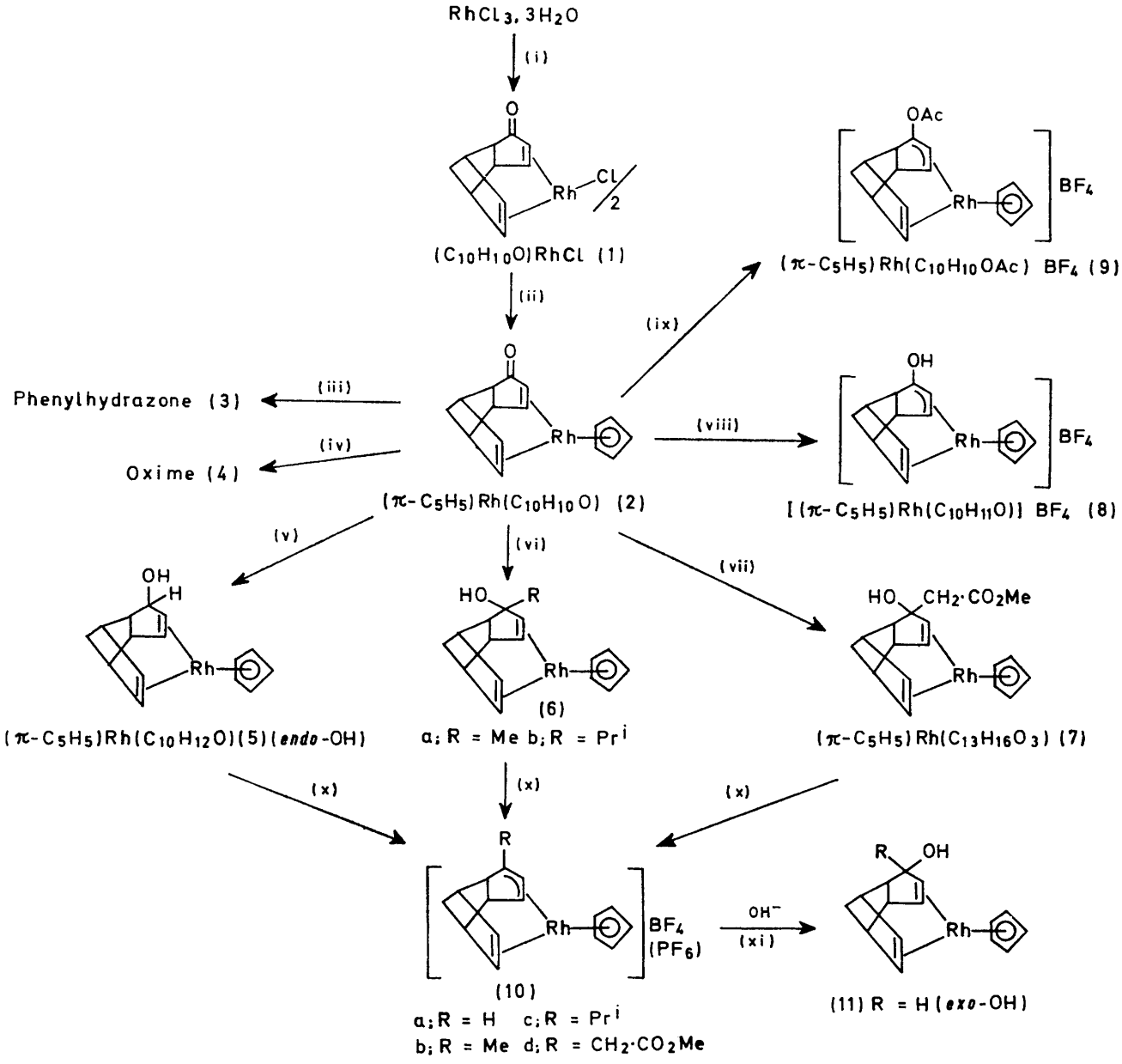
FIGURE 1 Structure of (dp)RhCp

[1] Part VII, B. F. G. Johnson, J. Lewis, P. McArdle, and G. L. P. Randle, preceding paper.

[2] See, *e.g.*, (*a*) E. Weiss, R. G. Merenyi, and W. Hubel, *Chem. Ber.*, 1962, **95**, 1170; *Chem. and Ind.*, 1960, 407; (*b*) A. W. Parkins, Ph.D. Thesis, University of Manchester, 1968.

Reactivity of the Ketone Group in Complexes (2) *and* (13).—(i) *General.* The reactions of the carbonyl groups in both dp and cq are not appreciably modified on co-ordination to the $(\pi\text{-}C_5H_5)Rh^I$ unit and both complexes (2) and (13) undergo some of the reactions typical of chloric acid. Significantly no decomposition of the parent compounds occurs under the conditions employed in the reactions.

(ii) *Reduction.* Reduction of (2) with sodium boro-hydride in methanol gave the pale yellow alcohol



SCHEME 1 (i) $C_{10}H_{10}O$ in refluxing EtOH–H_2O. (ii) $(\pi\text{-}C_5H_5)Tl^I$. (iii) Brady's reagent. (iv) Hydroxylamine hydrochloride. (v) $NaBH_4$. (vi) RMgI. (vii) Reformatski reaction. (viii) HBF_4. (ix) HBF_4 in Ac_2O. (x) Ph_3CBF_4 or HBF_4. (xi) Reaction with OH^-.

ketones. Thus with Brady's reagent in methanol they gave the expected dinitrophenylhydrazones (3) and (16) and with hydroxylamine hydrochloride the appropriate oximes (4) and (17). Neither oxime underwent the Beckmann rearrangement on treatment with hydro-

$(\pi\text{-}C_5H_5)Rh(C_{10}H_{12}O)$ (5). The simplicity of the ^1H n.m.r. spectrum and the single strong absorption at 3470 cm^{-1} (ν_{OH}) clearly indicated that only one isomeric form (*endo* see below) had been obtained. The corresponding reduction of $(\pi\text{-}C_5H_5)Rh(cq)$ gave high yields

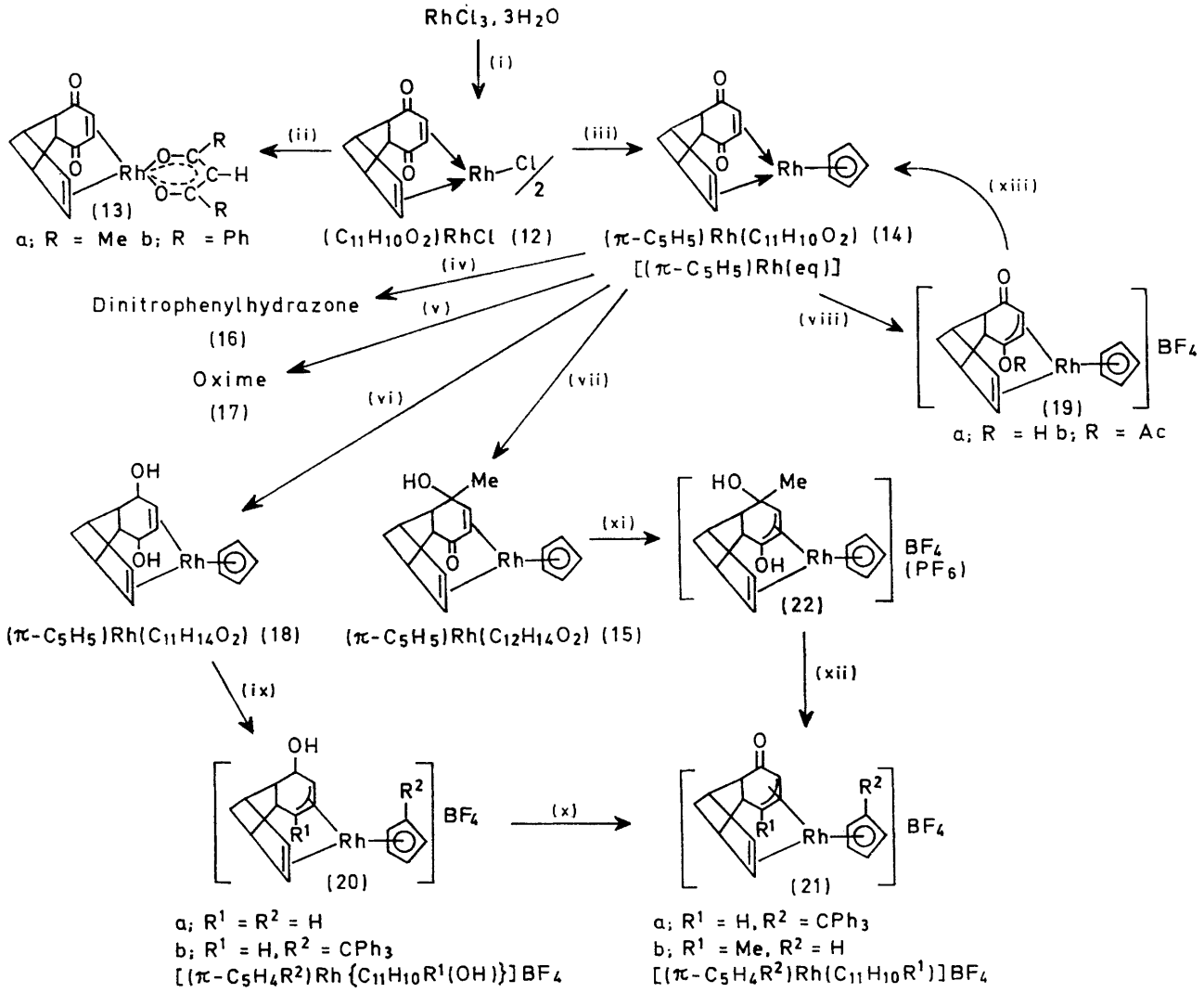
of the expected diol $(\pi\text{-}C_5H_5)Rh(C_{11}H_{14}O_2)$ (18) as pale yellow crystals. The proposed structure was supported by ^1H n.m.r. and i.r. data (see Table 2).

(iii) *Reactions with Grignard reagents.* Complexes (2) and (14) undergo the usual reactions with Grignard reagents. Addition of methylmagnesium iodide to (2) in ether afforded a pale yellow solid. Hydrolysis, followed by separation on silica gel gave the alcohol (6a) in moderate yield (75%). The corresponding isopropyl alcohol (6b) was obtained similarly. In the ^1H n.m.r. spectrum of (6a) (Table 3) the presence of only one methyl resonance (1H, s) at τ 7·20 and one cyclopentadienyl resonance (5H, s) at τ 4·87 confirms that only one isomer was produced.

In order to ascertain which isomer had been produced (*i.e.* OH group *exo* or *endo*) we prepared the alcohol (11) directly from the reaction of OH^- with the salt (10a) (see Scheme 1). Since nucleophilic addition to π-coordinated dienes has been shown [3] to occur *exo*, that is the attacking nucleophile becomes the *exo*-substituent in the product, alcohol (11) will have the *exo*-structure shown. On the other hand the epimeric alcohol (5) produced by sodium borohydride reduction of (2) will have the structure with OH *endo*. These conclusions are substantiated by the following observations. (*a*) The i.r. spectrum of (11) shows a broad band (ν_{OH}) at 3240 cm^{-1} whereas its epimer (5) shows a much sharper band (ν_{OH}) at 3470 cm^{-1}.

(*b*) The epimer (5) is eluted from silica gel by 5% ethyl acetate in benzene, whereas glacial acetic acid fails to elute isomer (11).

(*c*) The melting point of the so-called *exo*-alcohol is 122—123° whereas that of the *endo*-alcohol is 62—63°.

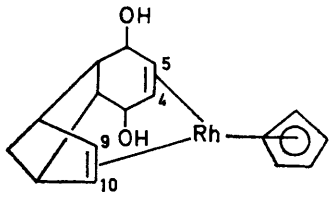


SCHEME 2 (i) $C_{11}H_{10}O_2$ in refluxing EtOH–H_2O. (ii) Tl(RCO·CH·COR). (iii) $(\pi\text{-}C_5H_5)Tl^I$. (iv) Brady's reagent. (v) Hydroxylamine hydrochloride. (vi) $NaBH_4$. (vii) MeMgI. (viii) HBF_4, Ph_3CBF_4, or HBF_4–Ac_2O. (ix) 1 mol Ph_3CBF_4. (x) 1 mol Ph_3CBF_4., (xi) HPF_6. (xii) Me_2CO/20°/48 h. (xiii) H_2O.

[3] See, *e.g.*, W. E. Oberhansli and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 629; C. B. Anderson and B. J. Buneson, *J. Organometallic Chem.*, 1967, **7**, 181; J. K. Stile and R. A. Morgan, *J. Amer. Chem. Soc.*, 1966, **88**, 5135.

TABLE 2

Important features of the i.r. and ^{1}H n.m.r. spectra of complex (18)



^{1}H N.m.r. spectrum		I.r. spectrum (cm^{-1})
Signal (τ)	Assignment	ν_{OH}
5·44 (2H,m)	$H^9 + H^{10}$	3320, 3450
6·16 (2H,m)	$H^4 + H^5$	

Woodward and Katz have shown that reduction of tricyclo[5,2,1,$0^{2,6}$]deca-4,8-dien-3-one by lithium aluminium hydride gives the *endo*-alcohol whereas selenium dioxide oxidation of dicyclopentadiene gives the *exo*-alcohol.[4] These assignments have recently been confirmed by the *X*-ray structure [5] of the *p*-bromobenzoate of the former. Hence it appears that reduction of both co-ordinated and unco-ordinated dp gives the product with the hydroxy-group *endo*.

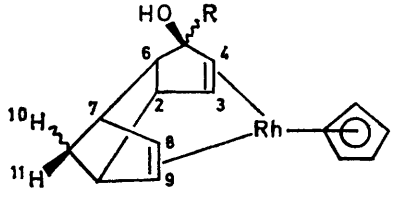
Treatment of $(\pi\text{-}C_5H_5)Rh(cq)$ with methylmagnesium iodide in anhydrous tetrahydrofuran gave an immediate precipitate which, after hydrolysis and separation on silica gel, yielded yellow crystals of the keto-alcohol (15). Relevant spectral data for this molecule are collected in Table 4 and it is assigned a structure with the OH group *endo*.

(iv) *Reformatski reaction.* The tricarbonyliron complexes of cyclohexa-2,4-dienone and cyclohepta-2,4-dienone react with zinc and methyl bromoacetate to give hydroxy-esters.[6] Complex (2) behaves similarly. Reaction of (2) with the same reagents in benzene gave, after chromatography on silica, the alcohol (7) as a pale yellow oil. The ^{1}H n.m.r. spectrum (Table 3) was similar in general appearance to the spectra observed for alcohols (6a) and (6b) and we therefore assign structure (7) to the complex with the OH group *endo*.

(v) *Reaction with electrophilic reagents.* Treatment of (2) with aqueous fluoroboric acid (42%) in ether gave orange needles of the salt $[(\pi\text{-}C_5H_5)Rh(C_{10}H_{10}OH)]BF_4$ (8). In acetic anhydride this reaction produces the corresponding acetyl derivative, $[(\pi\text{-}C_5H_5)Rh(C_{10}H_{10}OAc)][BF_4]$ (9). Salts (8) and (9) dissolve in acetone with decomposition but in water they are hydrolysed and complex (2) is regenerated. As with protonation attack by Ph_3C^+ occurs at the ketonic group to give as the initial product the salt $[(\pi\text{-}C_5H_5)Rh(C_{10}H_{10}OCPh_3)]BF_4$ which readily hydrolyses to give the alcohol (8). There is no

TABLE 3

N.m.r. spectra of the alcohols $(\pi\text{-}C_5H_5)Rh\{C_{10}H_{10}(OH)R\}$ (R = H, Me, Pr^i, or $CH_2{\cdot}CO_2Me$) in deuteriochloroform (chemical shifts are in τ units) *

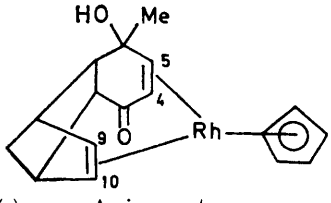


R	H	Me	Pr^i	CH_2CO_2Me
Assignment				
$H^8 + H^9$	4·80 (mt)	4·75 (mt)	4·78 (mt)	4·79 (mt)
C_5H_5	4·90 (1t)	4·87 (1t)	4·89 (1t)	4·87 (1t)
H^4 and H^5	5·30 (4t,1H)	5·36 (4t,1H)	5·21 (4t,1H)	5·31 (4t,1H)
	5·70 (mt,1H)	5·80 (mt,1H)	5·85 (mt,1H)	5·67 (mt,1H)
Bridgehead	6·19 (mt,1H)	6·13 (mt,1H)	6·11 (mt,1H)	6·13 (mt,1H)
Protons	6·9—7·6 (mt,3H)	6·8—7·6 (mt,3H)	6·9—7·6 (mt,3H)	6·9—7·6 (mt,3H)
H^{10}	7·96 (AB2t)	7·95 (AB2t)	7·95 (AB2t)	7·95 (AB2t)
H^{11}	8·30 (AB2t)	8·32 (AB2t)	8·30 (AB2t)	8·30 (AB2t)
OH	7·68 (1t)	7·20 (1t)	6·95 (1t)	7·01 (1t)
R	6·18 (mt)H	8·65 (1t)Me	9·08 (2t)Me	7·37 (1t)CH_2
			9·12 (2t)Me	6·33 (1t)Me

* 1t = Singlet, 2t = doublet, *etc.*

TABLE 4

Important features of the i.r. and ^{1}H n.m.r. spectra of complex (15)



Signal (τ)	Assignment	ν_{CO}	ν_{OH}/cm^{-1}
4·80 (5H,s)	C_5H_5 group	1645	3450
5·00 (2H,m)	H^9+H^{10}		
5·74 (1H,m)	H^4 or H^5		
6·48 (1H,m)	H^4 or H^5		
8·60 (3H,s)	CH_3 group		
7·73 (1H,s)	OH		

[4] R. B. Woodward and T. J. Katz, *Tetrahedron*, 1959, **5**, 70.
[5] R. Destro, M. Gramaccioli, and M. Simonetta, *Chem. Comm.*, 1968, 568.
[6] J. Lewis and A. W. Parkins, *Chem. Comm.*, 19 (see also ref. 3).

evidence that Ph_3C^+ also attacks the cyclopentadienyl ring as found with $(\pi\text{-}C_5H_5)Rh(C_8H_{12})$.

On treatment with HBF_4, $(\pi\text{-}C_5H_5)Rh(cq)$ undergoes single proton addition to give the salt $[(\pi\text{-}C_5H_5)Rh(C_{11}H_{11}O_2)]BF_4$ (19a) and with HBF_4–Ac_2O the salt

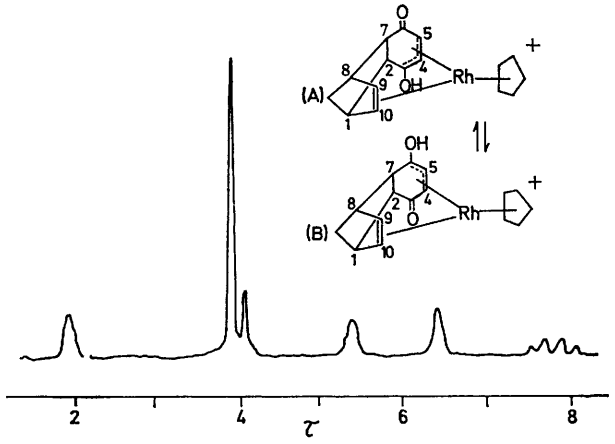


FIGURE 2 ^1H N.m.r. spectrum of $(\pi\text{-}C_5H_5)Rh(C_{11}H_{11}O_2)$ at 60 MHz in H_2SO_4

$[(\pi\text{-}C_5H_5)Rh(C_{13}H_{13}O_3)]BF_4$ (19b). Both are rapidly hydrolysed by water and are insoluble in most organic solvents. For this reason the ^1H n.m.r. spectra have not been measured. However, both $(\pi\text{-}C_5H_5)Rh(cq)$ and $[(\pi\text{-}C_5H_5)Rh(C_{11}H_{11}O_2)]BF_4$ dissolve in concentrated sulphuric acid to give red solutions which give rise to the same ^1H n.m.r. spectrum and must contain, therefore, the same cationic species, *viz.* $[(\pi\text{-}C_5H_5)Rh(C_{11}H_{11}O_2)]^+$. The spectrum is simple (see Figure 2) and indicates a higher degree of symmetry than expected for the proposed structure (19a). It may, however, be explained on the basis of rapid exchange between the two equivalent tautomers (A) and (B). In the limiting case, when exchange between these two tautomers is rapid (as Figure 2), the pairs of protons H^1 and H^8, H^2 and H^7, H^4 and H^5, and H^9 and H^{10} are equivalent. The spectrum may then be assigned as shown. Because of the unusually low-field value (τ 1·85) observed for the olefinic protons $[H^9 + H^{10}]$ we also considered the possibility that the olefinic group is not co-ordinated to the metal (Figure 3). For such a structure a C=C

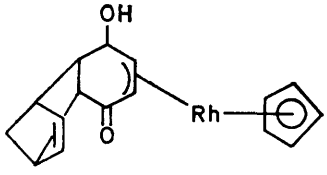


FIGURE 3 Alternative structure of $[(\pi\text{-}C_5H_5)Rh(C_{11}H_{12}O)]BF_4$ (20a)

stretching vibration is expected in the i.r. spectrum in the region 1500—1650 cm^{-1} but no such vibration is observed. The possibility that this vibration is obscured by the CO vibration cannot be ignored and we are unable, therefore, to completely exclude this second structural possibility on this basis. However a single-crystal *X*-ray study of molecule (19a) is in progress and the preliminary data at present available does indicate that carbon atoms 9 and 10 are within bonding distance of the metal.

Reactions of the Alcohols (5), (6a), (6b), *and* (7) *with Electrophilic Reagents.*—Mahler and Pettit [7] have shown that tricarbonyl(*trans*-penta-2,4-dien-1-ol)iron reacts with strong acids to give the tricarbonyl(*cis*-pentadienyl)-iron cation. It occurred to us that similar reactions of the alcohols (6a), (6b), and (7) should lead to cationic species of the type $[(\pi\text{-}C_5H_5)Rh(C_{10}H_{10}R)]^+$ containing a substituted pentadienyl unit. This is so. Treatment of the appropriate alcohol in ether with hexafluorophosphoric acid gave the salts $[(\pi\text{-}C_5H_5)Rh(C_{10}H_{10}R)]PF_6$ (10) in good yields (*ca.* 90%). These salts are stable, yellow solids soluble in acetone or liquid sulphur dioxide

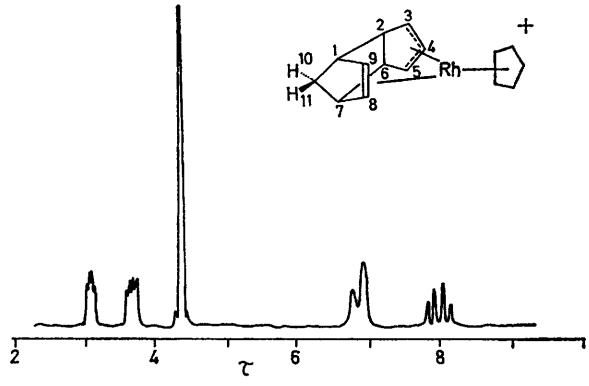


FIGURE 4 ^1H N.m.r. spectrum of $[(\pi\text{-}C_5H_5)Rh(C_{10}H_{11})]^+$ at 100 MHz in liquid SO_2

without decomposition but are insoluble in water. In all cases the presence of the new cyclopentadienyl unit was confirmed from the ^1H n.m.r. spectra (Table 4). The complete assignment of the spectrum obtained for the unsubstituted cation (10a) (Figure 4) was made with the aid of spin-decoupling measurements and agrees with that made by Parkins for $[(\pi\text{-}C_5H_5)Co(C_{10}H_{11})]^+$. A feature of this spectrum and that of Parkins [2b] is the appearance of the central allylic proton at higher field (τ 4·40) than that of the outer allylic protons (τ 3·58). In the majority of π-allyl complexes the reverse is true [8] although in the spectrum of $(\pi\text{-}C_5H_5)Co(C_3H_5)X$ [9] (X = Cl or Br) the central proton occurs in the region intermediate to those of the *syn*- and *anti*-protons. We are unable to account for this anomaly.

On reaction of the diol (18) with Ph_3CBF_4 hydroxide ion abstraction occurred together with electrophilic substitution of the cyclopentadienyl ring and two salts, *viz* $[(\pi\text{-}C_5H_5)Rh(C_{11}H_{13}O)]BF_4$ (20a) and $[(Ph_3C\text{-}C_5H_4)Rh(C_{11}H_{13}O)]BF_4$ (20b) were produced. Further treatment of (20a) with the same reagent gave an orange precipitate. Extraction with water gave an orange

[7] J. E. Mahler and R. Pettit, *J. Amer. Chem. Soc.*, 1963, **85**, 3955, 3959.

[8] M. L. H. Green and P. L. T. Nagy, *Adv. Organometallic Chem.*, 1964, **2**, 325; M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Adv. Organometallic Chem.*, 1965, **3**, 1.

[9] R. F. Heck, *J. Org. Chem.*, 1963, **28**, 604.

TABLE 5

N.m.r. spectra of the salts $[(\pi\text{-}C_5H_5)Rh(C_{10}H_{10}R)]PF_6$ (10; R = H, Me, Pr^i, or $CH_2{\cdot}CO_2Me$) (chemical shifts are in τ) *

R	H	Me	Pr^i	$CH_2{\cdot}CO_2Me$
Assignment				
$H^8 + H^9$	3·03 (4t)	2·95 (mt)	2·91 (mt)	2·87 (mt)
H^3, H^5	3·58 (mt)	3·72 (mt)	3·64 (mt)	3·62 (mt)
H^4	4·40 (mt)	4·21 (mt)	4·23 (mt)	4·04 (mt)
C_5H_5	4·40 (1t)	4·21 (1t)	4·18 (mt)	4·18 (mt)
$H^1 + H^7$	6·76 (mt)	6·7—7·1 (mt)	6·7—7·1 (mt)	6·6—7·0 (mt)
$H^2 + H^6$	6·92 (mt)			
H^{10}	7·87 (AB2t)	Obscured by solvents		
H^{11}	8·09 (AB2t)			
			8·40 (2t)Me	6·18 (1t)CH_2
R	3·58 (mt)	7·56 (1t)Me	8·65 (2t)Me	6·21 (1t)Me

* (*a*) In liquid sulphur dioxide at 100 MHz; (*b*) in [$^2H_6$]acetone at 60 or 100 MHz. 1t = Singlet, 2t = doublet, *etc.*

solution, which on addition of aqueous NH_4PF_6, gave the salt (21a). The assignment of structure (21a) to this salt rests upon its ^1H n.m.r. spectrum which is presented in Figure 5(a). Additional support comes from the i.r.

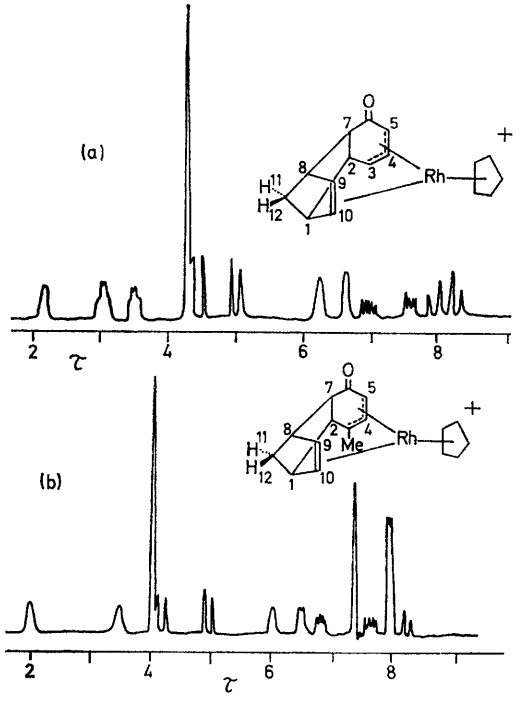


FIGURE 5 (a) ^1H N.m.r. spectrum of $[(\pi\text{-}C_5H_5)Rh(C_{11}H_{11}O)]^+$ at 100 MHz in liquid SO_2; (b) ^1H n.m.r. spectrum of $[(\pi\text{-}C_5H_5)Rh(C_{12}H_{14}O)]^+$ at 100 MHz in liquid SO_2

spectrum which exhibits a sharp, characteristic ketone band at 1670 cm^{-1} (compare with parent compounds, Table 6). The reaction of (20a) with Ph_3CBF_4 to give (21a) involves the loss of hydrogen. Since the organic product from this reaction is triphenylmethane both hydride-ion abstraction and deprotonation must occur although the precise mechanism of the reaction is unknown. The other related product (21b; R^1 = Me, R^2 = H) was obtained indirectly from the alcohol (15) by the means outlined in Scheme 2. The intermediate product is considered to be the salt (22). The i.r. spectrum showed two sharp μ_{OH} bands at 3540 and 3200 cm^{-1} but the ^1H n.m.r. spectrum is complicated and time variant. However, if this intermediate compound is left in acetone at 20 °C for 48 h then salt (21b) is produced. The ^1H n.m.r. spectrum of this salt is shown in Figure 5(b) where it may be compared directly with that of (21a).

TABLE 6

C–O Stretching vibrations observed (Nujol mulls)

Complex	ν_{CO}/cm^{-1}	Other bands
(1) $[(dp)RhCl]_2$	1701	
(2) $(dp)Rh(\pi\text{-}C_5H_5)$	1661	
(12) $[(cq)RhCl]_2$	1673	
(13) (cq)Rh(acac)	1670	1531 1562 (ν_{CO} acac)
(14) $(cq)Rh(\pi\text{-}C_5H_5)$	1651	

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage microscope. I.r. spectra were recorded with a Perkin-Elmer 257 instrument and, unless otherwise stated, refer to Nujol mulls. High-resolution ^1H n.m.r. spectra were measured on Varian A60, Varian HA 100 and Perkin-Elmer R10 spectrometers, with tetramethylsilane as internal standard Mass spectra were obtained from AEI MS9 or 12 instruments.

Tricyclo[5,2,1,$0^{2,6}$]*deca*-4,8-*dien*-3-*one* (*dp*).—The dienone dp was prepared by the oxidation of tricyclo[5,2,1,$0^{2,6}$]deca-4,8-dien-3-ol (α-dicyclopentadien-1-ol) by chromium trioxide in acetic acid, using the method of Alder and Flock.[10]

Reaction of dp with Rhodium Trichloride.—A solution of dp (2·92 g, 20 mmol) and rhodium trichloride trihydrate (2·64 g, 10 mmol) in ethanol (40 ml) and water (20 ml) was refluxed for 4 h. The solution was allowed to cool and was then partitioned between dichloromethane (150 ml) and water (100 ml). The dichloromethane layer was washed with water (3 × 30 ml), dried ($MgSO_4$), and concentrated to 75 ml. Hexane (25 ml) was added and further concentration of the solution to *ca.* 45 ml gave an orange-brown precipitate of *di-μ-chloro-bis*(*tricyclo*[5,2,1,$0^{2,6}$]*deca*-4,8-*dien*-3-*one*)*dirhodium* (1) (2·17 g, 76%). A portion of this was purified for analysis by differential solvent crystallisation from dichloromethane–hexane to give orange-brown needles which decomposed at 230° without melting (Found: C, 41·8; H, 3·6; Cl, 12·0. $C_{10}H_{10}ClORh$ requires C, 42·2; H, 3·5; Cl, 12·5%).

Cyclopentadienyl(*tricyclo*[5,2,1,$0^{2,6}$]*deca*-4,8-*dien*-3-*one*)-*rhodium* (2) $(\pi\text{-}C_5H_5)Rh(dp)$.—A suspension of the chloro-bridged dimer (1) (0·59 g, 1 mmol) and cyclopentadienylthallium (0·592 g, 2·2 mmol) in dichloromethane (80 ml) was stirred at 20° for 2 h. The resulting mixture was centrifuged and the dichloromethane solution was filtered through cellulose to remove thallous chloride. The filtrate was evaporated to dryness and the residue was extracted with

[10] K. Alder and F. H. Flock, *Chem. Ber.*, 1964, **87**, 1916.

boiling ether (3 × 50 ml). The ethereal solution was evaporated to dryness and the residue was crystallised from ether–pentane (−78°) to give orange needles of the pure *product* (0·563 g, 90%), m.p. 140—141° [Found: C, 57·7; H, 4·9%; *M* (mass spectrometry), 314. $C_{15}H_{15}ORh$ requires C, 57·4; H, 4·8%; *M*, 314].

Cyclopentadienyl(tricyclo[5,2,1,$0^{2,6}$]*deca-4,8-dien-3-one)-rhodium Oxime* (4).—The ketone (2) (0·157 g, 0·5 mmol) was dissolved in 30 ml of 0·5M-hydroxylamine hydrochloride in 50% aqueous ethanol, containing 0·4% pyridine. The solution was refluxed for 30 min and set aside. After 48 h orange plates of the pure *oxime* (4) (0·113 g, 67%), m.p. 210—212°, were filtered off (Found: C, 55·1; H, 5·3; N, 4·2. $C_{15}H_{16}NORh$ requires C, 54·8; H, 4·9; N, 4·2%).

Cyclopentadienyl(tricyclo[5,2,1,$0^{2,6}$]*deca-4,8-dien-3-endo-ol)rhodium* (5).—An excess of sodium borohydride (0·75 g) was added to a solution of (π-C_5H_5)Rh(dp) (2) (0·314 g, 1 mmol) in methanol (50 ml) at 0°; the mixture was stirred for 6 h and was then filtered and partitioned between dichloromethane (100 ml) and water (75 ml). The dichloromethane layer was separated, washed with water, dried ($MgSO_4$), and evaporated to dryness. The residue, a yellow gum, was dissolved in benzene (4 ml) and transferred to a column of silica gel (40 × 2·5 cm) made up in benzene. 5% Ethyl acetate in benzene eluted a pale yellow fraction which crystallised from pentane to give pale yellow needles of the pure *alcohol* (5) (0·210 g, 67%), m.p. 62—63° [Found: C, 57·4; H, 5·4%; *M* (mass spectrometry), 316. $C_{15}H_{17}ORh$ requires C, 57·0; H, 5·4%; *M*, 316].

Elution with 5% methanol in ethyl acetate gave an orange-yellow fraction, which was shown by its i.r. spectrum to be unchanged (π-C_5H_5)Rh(dp) (0·076 g, 24%).

Cyclopentadienyl(3-methyltricyclo[5,2,1,$0^{2,6}$]*deca-4,8-dien-3-endo-ol)rhodium* (6a).—A solution of methylmagnesium iodide in ether (5 ml; 1M) was added to a solution of (π-C_5H_5)Rh(dp) (2) (0·314 g, 1 mmol) in ether (60 ml) at 0°, under a nitrogen atmosphere. A pale yellow precipitate formed immediately and the mixture was stirred for 1 h. Water (10 ml) followed by 2N-sulphuric acid (10 ml) was then added. The ether layer was separated, washed with water, dried ($MgSO_4$), and evaporated to dryness to give a yellow gum. This was dissolved in benzene (5 ml) and transferred to a silica gel column (40 × 2·5 cm), made up in benzene. 5% Ethyl acetate in benzene eluted a pale yellow fraction which crystallised from pentane (−78°) to give pale yellow needles of the pure *product* (6a) (0·230 g, 70%), m.p. 94—96° [Found: C, 58·3; H, 5·6; O, 4·9%; *M* (mass spectrometry), 3·30. $C_{16}H_{19}ORh$ requires C, 58·2; H, 5·7; O, 4·9%; *M*, 330].

Elution with 5% methanol in ethyl acetate gave an orange fraction (0·053 g, 16%) which was shown by its i.r. spectrum to be unchanged (π-C_5H_5)Rh(dp).

Reaction of (π-C_5H_5)Rh(dp) (2) *with Isopropylmagnesium Bromide*.—The reaction of (π-C_5H_5)Rh(dp) (2) (0·314 g, 1 mmol) with isopropylmagnesium bromide similarly gave pale yellow needles of *cyclopentadienyl(3-isopropyltricyclo*[5,2,1,$0^{2,6}$]*deca-4,8-dien-3-endo-ol)rhodium* (6b) (0·276 g, 77%), m.p. 94—95° [Found: C, 60·5; H, 6·6%; *M* (mass spectrometry), 358. $C_{18}H_{23}ORh$ requires C, 60·4; H, 6·4%; *M*, 358]. The ketone (π-C_5H_5)Rh(dp) (0·034 g, 10%) was also recovered from the reaction.

Cyclopentadienyl(5-endo-hydroxy-5-methoxycarbonylmethyltricyclo[5,2,1,$0^{2,6}$]*deca-3,8-diene)rhodium* (6; R = CH_2CO_2Me).—Activated zinc (0·262 g, 4 mmol) was added to a solution of (π-C_5H_5)Rh(dp) (2) (0·314 g, 1 mmol) and methyl bromoacetate (0·5 ml) in dry benzene (80 ml). The mixture was refluxed under nitrogen for 3 h. The solution was cooled to 0° and water (10 ml), followed by 2N-sulphuric acid (20 ml), was added; the mixture was shaken for 15 min. The benzene layer was separated, washed with water, dried ($MgSO_4$), and evaporated to dryness to give an orange gum. This was dissolved in benzene (5 ml) and transferred to a column (40 × 2·5 cm) of silica gel made up in benzene. 5% Ethyl acetate in benzene eluted a pale yellow fraction. This was evaporated to dryness to give the *product* (6; R = CH_2CO_2Me) as a pale yellow oil which failed to crystallise [Found: *M* (mass spectrometry), 388. $C_{18}H_{21}O_3Rh$ requires *M*, 388].

5% Methanol in ethyl acetate eluted an orange fraction which was shown by its i.r. spectrum and m.p. to be unchanged ketone (0·063 g, 28%).

Reactions of the Alcohols (π-C_5H_5)Rh[$C_{10}H_{10}$(OH)(R)] (6; R = Me, Pr^i, *or* CH_2·CO_2Me) *with Hexafluorophosphoric Acid*.—Addition of 68% aqueous hexafluorophosphoric acid solution to a solution of (π-C_5H_5)Rh($C_{10}H_{11}OH$) (6; R = H) (0·316 g, 1 mmol) in ether (60 ml) gave a yellow precipitate. This precipitate was filtered off, washed with ether, and dissolved in an excess of acetone. The acetone solution was filtered and concentrated to 7 ml. Slow addition of ether to this solution precipitated yellow needles of pure *cyclopentadienyl(tricyclo*[5,2,1,$0^{2,6}$]*deca-4,8-dien-3-yl)-rhodium hexafluorophosphate* (0·412 g, 93%), m.p. 281—283° (Found: C, 40·5; H, 3·7; P, 7·3. $C_{15}H_{16}F_6PRh$ requires C, 40·6; H, 3·6; P, 6·9%).

The alcohol (π-C_5H_5)Rh[$C_{10}H_{10}$(OH)Me] (6; R = Me) (0·165 g, 0·5 mmol) similarly gave yellow needles of *cyclopentadienyl(3-methyltricyclo*[5,2,1,$0^{2,6}$]*deca-4,8-dien-3-yl)-rhodium hexafluorophosphate* (0·180 g, 80%) which decomposed at 260° without melting (Found: C, 43·0; H, 4·0. $C_{16}H_{17}F_6PRh$ requires C, 42·0; H, 3·9%).

The alcohol (π-C_5H_5)Rh[$C_{10}H_{10}$(OH)Pr^i] (0·179 g, 0·5 mmol) similarly gave yellow needles of *cyclopentadienyl(3-isopropyltricyclo*[5,2,1,$0^{2,6}$]*deca-4,8-dien-3-yl)rhodium hexafluorophosphate* (0·224 g, 92%), m.p. 221—222° (Found: C, 44·2; H, 4·6; P, 7·3. $C_{18}H_{22}F_6PRh$ requires C, 44·4; H, 4·5; P, 6·6%).

The alcohol (π-C_5H_5)Rh[$C_{10}H_{10}$(OH)CH_2·CO_2Me] (6; R = CH_2·CO_2Me) (0·195 g, 0·5 mmol) similarly gave yellow plates of *cyclopentadienyl(3-methoxycarbonylmethyltricyclo*[5,2,1,$0^{2,6}$]*deca-4,8-dien-3-yl)rhodium hexafluorophosphate* (0·243 g, 90%), m.p. 172—174° (Found: C, 42·0; H, 3·9; P, 6·0. $C_{18}H_{20}F_6O_2PRh$ requires C, 41·9; H, 3·9; P, 6·0%).

Reactions of the Alcohols (π-C_5H_5)Rh[$C_{10}H_{10}$(OH)R] (R = H, Me, Pr^i, *or* CH_2·CO_2Me) *with Trityl Fluoroborate*.—A solution of trityl fluoroborate (0·330 g, 1 mmol) in dichloromethane (5 ml) was added to a solution of (π-C_5H_5)-Rh[$C_{10}H_{11}$(OH)] (6; R = H) (0·316 g, 1 mmol) in dichloromethane (8 ml). After 10 min 'wet' ether (50 ml) was added to give a yellow precipitate. This was filtered off and washed with ether. Evaporation of the filtrate to dryness and recrystallisation of the residue from pentane gave triphenylmethanol (0·108 g), m.p. 163—164° (lit.,[11] 164—165°). The yellow precipitate was dissolved in excess of acetone and the solution was filtered and concentrated to 10 ml. Slow addition of ether to this solution precipitated yellow needles of *cyclopentadienyl(tricyclo*[5,2,1,$0^{2,6}$]*deca-4,8-dien-3-yl)rhodium fluoroborate* (10a)

[11] W. E. Bachmann and H. P. Hetzner, *Org. Synth.*, 1955, **3**, 839.

(0·329 g, 85%), m.p. 222—224° (Found: C, 46·8; H, 4·1. $C_{15}H_{16}BF_4Rh$ requires C, 46·6; H, 4·1%).

The alcohol $(\pi\text{-}C_5H_5)Rh[C_{10}H_{10}(OH)Me]$ (6; R = Me) (0·165 g, 0·5 mmol) similarly gave yellow needles of *cyclopentadienyl(3-methyltricyclo[5,2,1,0^{2,6}]deca-4,8-dien-3-yl)rhodium fluoroborate* (10b) (0·178 g, 89%) which decomposed at *ca.* 245° without melting (Found: C, 48·4; H, 4·5. $C_{16}H_{18}BF_4Rh$ requires C, 48·1; H, 4·5%).

The alcohol $(\pi\text{-}C_5H_5)Rh[C_{10}H_{10}(OH)Pr^i]$ (6b) (0·179 g, 0·5 mmol) similarly gave yellow needles of *cyclopentadienyl(3-isopropyltricyclo[5,2,1,0^{2,6}]deca-4,8-dien-3-yl)rhodium fluoroborate* (10c) (0·193 g, 90%), m.p. 225—227° (Found: C, 50·2; H, 5·3. $C_{18}H_{22}BF_4Rh$ requires C, 50·5; H, 5·1%).

The alcohol $(\pi\text{-}C_5H_5)Rh[C_{10}H_{10}(OH)CH_2CO_2Me]$ (6; R = $CH_2{\cdot}CO_2Me$) (0·194 g, 0·5 mmol) similarly gave yellow needles of *cyclopentadienyl(3-methoxycarbonylmethyltricyclo[5,2,1,0^{2,6}]deca-4,8-dien-3-yl)rhodium fluoroborate* (10d) (0·154 g, 67%), m.p. 132—135° (Found: C, 46·7; H, 5·3. $C_{18}H_{18}BF_4O_2Rh$ requires C, 47·2; H, 4·9%).

Reaction of $(\pi\text{-}C_5H_5)Rh(dp)$ *with Fluoroboric Acid.*—Addition of 42% fluoroboric acid solution (0·4 ml) to a solution of $(\pi\text{-}C_5H_5)Rh(dp)$ (0·157 g, 0·5 mmol) in acetone (5 ml) and ether (60 ml) gave an orange precipitate. This was filtered off and dissolved in acetone. Slow addition of ether to the acetone solution precipitated orange needles of *cyclopentadienyl(3-hydroxytricyclo[5,2,1,0^{2,6}]deca-4,8-dien-3-yl)rhodium fluoroborate* (8) (0·143 g, 71%) which did not melt sharply (Found: C, 44·9; H, 4·1. $C_{15}H_{16}BF_4ORh$ requires C, 44·8; H, 4·0%).

Reaction of $(\pi\text{-}C_5H_5)Rh(dp)$ (2) *with Fluoroboric Acid in Acetic Anhydride.*—A solution of 42% aqueous fluoroboric acid (0·5 ml) in acetic anhydride (5 ml) was added to a solution of $(\pi\text{-}C_5H_5)Rh(dp)$ (2) (0·157 g, 0·5 mmol) in acetic anhydride (10 ml). After 10 min ether (60 ml) was added, to give a yellow precipitate. This was filtered off, washed with ether, and dissolved in acetone. Slow additions of ether to the acetone solution precipitated yellow needles of *cyclopentadienyl(3-acetoxytricyclo[5,2,1,0^{2,6}]deca-4,8-dien-3-yl)rhodium fluoroborate* (9) (0·166 g, 75%), m.p. 172—174° (Found: C, 45·7; H, 4·1. $C_{17}H_{18}BF_4O_2Rh$ requires C, 46·0; H, 4·1%).

Reaction of $(\pi\text{-}C_5H_5)Rh(dp)$ (2) *with Trityl Fluoroborate.*—A solution of trityl fluoroborate (0·165 g, 0·5 mmol) in dichloromethane (5 ml) was added to a solution of $(\pi\text{-}C_5H_5)Rh(dp)$ (2) (0·157 g, 0·5 mmol). Addition of 'wet' ether to this solution gave an orange precipitate, which was filtered off. The filtrate was evaporated to dryness and the residue was crystallised from pentane to give triphenylmethanol (0·085 g). The orange precipitate was dissolved in acetone. Slow addition of ether to the acetone solution precipitated orange needles of *cyclopentadienyl(3-hydroxytricyclo[5,2,1,0^{2,6}]deca-4,8-dien-3-yl)rhodium fluoroborate* (0·147 g, 73%) which did not melt sharply (Found: C, 44·9; H, 4·0. $C_{15}H_{16}BF_4ORh$ requires C, 44·8; H, 4·1%).

Reaction of the $[(\pi\text{-}C_5H_5)Rh(C_{10}H_{11})]^+$ *Cation* (10) *with Hydroxide Ion.*—An aqueous solution of sodium hydroxide (5N; 5 ml) was added to a solution $[(\pi\text{-}C_5H_5)Rh(C_{10}H_{11})]BF_4$ (10a) (0·193 g, 0·5 mmol) in water (20 ml). A pale yellow precipitate formed, and after 1 h the precipitate and solution were extracted with ether (3 × 40 ml). The ethereal solution was washed with water, dried ($MgSO_4$), and evaporated to dryness. The pale yellow residue was crystallised from pentane to give pale yellow needles of *cyclopentadienyl-(tricyclo[5,2,1,0^{2,6}]deca-4,8-dien-3-exo-ol)-rhodium* (11) (0·118 g, 74%), m.p. 122—123° [Found: C, 57·0; H, 5·7; *M* (mass spectrometry), 316. $C_{15}H_{17}ORh$ requires C, 57·0; H, 5·4%; *M*, 316].

Reaction of the $[(\pi\text{-}C_5H_5)Rh(C_{10}H_{10}Pr^i)]^+$ *Cation* (10c) *with Hydroxide Ion.*—Aqueous sodium hydroxide solution (5N; 5 ml) was added to a solution of $[(\pi\text{-}C_5H_5)Rh(C_{10}H_{10}Pr^i)]BF_4$ (10c) (0·214 g, 0·5 mmol) in water (20 ml). A yellow precipitate formed slowly. After 1 h the precipitate and solution were extracted with ether (3 × 40 ml). The ethereal solution was washed with water, dried ($MgSO_4$), and evaporated to dryness to give a yellow-orange oil. This oil was dissolved in ether (5 ml) and pentane (15 ml) and the solution was cooled to −78° to give a pale yellow precipitate. This was filtered off and the orange filtrate (A) was reserved. Recrystallisation of the precipitate from pentane gave yellow needles of *cyclopentadienyl(3-isopropyltricyclo[5,2,1,0^{2,6}]deca-4,8-dien-3-exo-ol)rhodium* (11; R = Pr^i) (0·046 g, 26%) which did not melt sharply [Found: C, 60·8; H, 6·5%; *M* (mass spectrometry), 358. $C_{18}H_{23}ORh$ requires C, 60·4; H, 6·4%; *M*, 358].

Evaporation of the orange filtrate (A) gave *cyclopentadienyl(5-isopropylidenetricyclo[5,2,1,0^{2,6}]deca-3,8-diene)-rhodium* (0·093 g, 52%) as an orange oil which failed to crystallise [Found: *M* (mass spectrometry), 340. $C_{18}H_{21}Rh$ requires *M*, 340]. This compound was assigned the structure on the basis of the spectral data which have been discussed earlier.

Reaction of the $[(\pi\text{-}C_5H_5)Rh(C_{10}H_{10}CH_2{\cdot}CO_2Me)]^+$ *Cation* (10d) *with Hydroxide Ion.*—A solution of $[(\pi\text{-}C_5H_5)Rh(C_{10}H_{10}CH_2{\cdot}CO_2Me)]BF_4$ (10d) (0·229 g, 0·5 mmol) in water (40 ml) was warmed to give an orange precipitate. Extraction of the precipitate and solution with ether (3 × 40 ml) gave an orange ethereal solution, which was washed with water, dried ($MgSO_4$), and evaporated to dryness to give an oil (0·141 g, 76%) which could not be crystallised. The spectral data for this oil showed it to be a 50 : 50 mixture of the two geometrical isomers of *cyclopentadienyl(5-methoxycarbonylmethylenetricyclo[5,2,1,0^{2,6}]deca-3,8-diene)-rhodium* [Found: *M* (mass spectrometry), 370. $C_{18}H_{19}O_2Rh$ requires *M*, 370].

Reaction of the $[(\pi\text{-}C_5H_5)Rh(C_{10}H_{10}OH)]^+$ *Cation with Sodium Hydroxide.*—Addition of an aqueous sodium hydroxide solution (5N; 2 ml) to a solution of $[(\pi\text{-}C_5H_5)Rh(C_{10}H_{10}OH)]BF_4$ (0·100 g, 0·25 mmol) in water (15 ml) gave an orange precipitate. The precipitate and solution were extracted with dichloromethane (3 × 20 ml). The dichloromethane solution was washed with water, dried ($MgSO_4$), and evaporated to dryness. The residue was recrystallised from ether–pentane (−78°) to give yellow-orange needles of cyclopentadienyl(tricyclo-[5,2,1,0^{2,6}]deca-4,8-dien-3-one)rhodium which was identified by its m.p. and i.r. spectrum.

The reaction of the $[(\pi\text{-}C_5H_5)Rh(C_{10}H_{10}OAc)]^+$ cation with water similarly gave cyclopentadienyl(tricyclo[5,2,1,0^{2,6}]-deca-4,8-dien-3-one)rhodium.

Tricyclo[6,2,1,0^{2,7}]undeca-4,9-diene-3,6-dione (*cq*).—This dione was prepared by the method of Albrecht. A solution of freshly sublimed *p*-benzoquinone (27 g, 0·25 mol) and freshly cracked cyclopentadiene monomer (16·5 g, 0·25 mol) in benzene (500 ml) was stirred at 40° for 3 h. The solution was evaporated to dryness and the residue was recrystallised twice from hexane to give pale yellow needles of the pure product (38 g, 87%), m.p. 77—78° (lit., 77—78°).

Di-μ-chloro-bis(tricyclo[6,2,1,0^{2,7}]undeca-4,9-diene-3,6-dione)dirhodium (12).—A solution of cq (3·48 g, 20 mmol) and rhodium trichloride trihydrate (2·64 g, 10 mmol) in

ethanol (50 ml) and water (25 ml) was refluxed for 6 h. The solution was allowed to cool and was then partitioned between water (75 ml) and dichloromethane (100 ml). The aqueous layer was extracted with dichloromethane (2 × 50 ml). The combined dichloromethane solutions were washed with water, dried ($MgSO_4$), and concentrated to 100 ml. Hexane (30 ml) was added to the residue; further concentration of the solution then gave an orange-brown precipitate of the *product* (12) (3·13 g, 90%). A portion of this was purified for analysis by differential solvent crystallisation from dichloromethane–benzene to give orange-brown needles which decomposed at 230—235° without melting (Found: C, 42·6; H, 3·5; Cl, 11·4. $C_{11}H_{10}ClO_2Rh$ requires C, 42·3; H, 3·2; Cl, 11·3%).

Cyclopentadienyl(tricyclo[6,2,1,$0^{2,7}$]*undeca-4,9-diene-3,6-dione)rhodium* (14).—A suspension of the chloro-bridged dimer (12) (0·625 g, 1 mmol) and cyclopentadienyl-thallium (0·592 g, 2·2 mmol) in dichloromethane (100 ml) was stirred at 20° for 4 h. The resulting mixture was centrifuged and the solution was filtered through cellulose to remove thallous chloride. The filtrate was concentrated to 40 ml and then diluted with pentane (60 ml). The solution was again filtered and evaporated to dryness. The residue was dissolved in benzene and transferred to a silica-gel column (40 × 2·5 cm) made up in benzene. 15% Methanol in benzene eluted an orange fraction which crystallised from dichloromethane–pentane (−78°) to give yellow-orange microcrystals of the pure *product* (14) (0·608 g, 89%), which did not melt sharply [Found: C, 56·6; H, 4·7%; *M* (mass spectrometry), 342. $C_{16}H_{15}O_2Rh$ requires C, 56·3; H, 4·4%; *M*, 342).

The deep red *bis(dinitrophenylhydrazone)* (16) had m.p. 203—204° (Found: C, 47·5; H, 3·2; N, 15·4. $C_{28}H_{23}N_8O_8Rh$ requires C, 47·3; H, 3·2; N, 15·4%).

Reactions of the Chloro-bridged Dimer (12) *with Pentane-2,4-dionatothallium and with* 1,3-*Diphenylpropane-1,3-dionatothallium*.—A suspension of the chloro-bridged dimer (12) (0·625 g, 1 mmol) and pentane-2,4-dionatothallium (0·606 g, 2 mmol) in dichloromethane (80 ml) was stirred for 4 h. The mixture was then centrifuged and the solution was filtered through cellulose to remove thallous chloride. The solution was washed with water (2 × 20 ml), dried ($MgSO_4$), and concentrated to 20 ml. Pentane (30 ml) was added; the solution when cooled to −78° precipitated orange needles of *pentane-2,4-dionato(tricyclo*[6,2,1,$0^{2,7}$]*undeca-4,9-diene-3,6-dione)rhodium* (13a) (0·524 g, 70%), m.p. 232—233° [Found: C, 51·0; H, 4·6%; *M* (mass spectrometry), 376. $C_{16}H_{17}O_4Rh$ requires C, 51·1; H, 4·7%; *M*, 376].

The reaction of the chloro-bridged dimer (0·313 g, 0·5 mmol) with 1,3-diphenylpropane-1,3-dionatothallium (0·428 g, 1 mmol) in dichloromethane similarly gave orange needles of *1,3-diphenylpropane-1,3-dionato(tricyclo*[6,2,1,$0^{2,7}$]*undeca-4,9-dien-3,6-dione)rhodium* (13b) (0·324 g, 65%), which did not melt sharply [Found: C, 61·9; H, 4·0%; *M* (mass spectrometry), 500. $C_{26}H_{21}O_4Rh$ requires C, 62·4; H, 4·0%, *M*, 500].

Sodium Borohydride Reduction of (π-C_5H_5)Rh(cq) (14).—Sodium borohydride (0·5 g) was added during 1 h to a solution of (π-C_5H_5)Rh(cq) (14) (0·648 g, 2 mmol) in methanol (75 ml) at 0°. The solution was stirred for a further hour and water (70 ml) was then added. The aqueous solution was extracted with dichloromethane and the extract was washed with water, dried ($MgSO_4$), and evaporated to dryness. The pale yellow residue was dissolved in the minimum volume of ethyl acetate and transferred to a silica-gel column (40 × 2·5 cm), made up in ethyl acetate. 5% Methanol in ethyl acetate eluted a pale yellow fraction which was evaporated to give a crystalline residue. Differential solvent crystallisation of this from dichloromethane–hexane gave pale yellow plates of *cyclopentadienyl(tricyclo*[6,2,1,$0^{2,7}$]*undeca-4,9-diene-3,6-diol)rhodium* (18) (0·307 g, 88%), m.p. 164—166° [Found: C, 55·6; H, 5·4; O, 8·7%; *M* (mass spectrometry), 346. $C_{16}H_{19}O_2Rh$ requires C, 55·5; H, 5·5; O, 9·2%; *M*, 346.

Reaction of (π-C_5H_5)Rh(cq) (14) *with Methylmagnesium Iodide*.—A solution of methylmagnesium iodide (5 ml; 1M) in ether was added to a solution of (π-C_5H_5)Rh(cq) (0·342 g, 1 mmol) in tetrahydrofuran (60 ml) at 0° under a nitrogen atmosphere. The mixture was stirred at 0° for 4 h and was then diluted with water (20 ml) followed by 2N-sulphuric acid (20 ml). The aqueous solution was extracted with dichloromethane (3 × 30 ml). The dichloromethane solution was washed with water, dried ($MgSO_4$), and evaporated to dryness. The orange-yellow residue was dissolved in benzene and transferred to a silica gel column (40 × 2·5 cm) made up in benzene. 13% Acetone in benzene eluted a yellow fraction which crystallised from dichloromethane–pentane (−78°) to give yellow needles of *cyclopentadienyl(6-hydroxy-6-methyltricyclo*[6,2,1,$0^{2,7}$]*undeca-4,9-dien-3-one)rhodium* (15) (0·279 g, 78%), m.p. 233—234° [Found: C, 56·7; H, 5·5; O, 9·2%; *M* (mass spectrometry), 358. $C_{17}H_{19}O_2Rh$ requires C, 57·0; H, 5·3; O, 9·0%; *M*, 358].

15% Acetone in benzene eluted an orange fraction, which was identified by its i.r. spectrum as (π-C_5H_5)Rh(cq) (0·046 g, 13%).

Reaction of (π-C_5H_5)Rh(cq) (14) *with Trityl Fluoroborate*.—Addition of a solution of trityl fluoroborate (0·330 g, 1 mmol) in dichloromethane (5 ml) to a solution of (π-C_5H_5)Rh(cq) (0·342 g, 1 mmol) in dichloromethane (10 ml) gave an orange precipitate. After 10 min 'wet' ether (50 ml) was added to the mixture and the orange precipitate was filtered off and washed with ether. The filtrate and washings were combined, washed with water, dried ($MgSO_4$), and evaporated to dryness. Crystallisation of the white residue from pentane gave triphenylmethanol (0·205 g), m.p. 162—164° (lit., 164—165°). The orange precipitate was dissolved in acetone. Slow addition of ether to this solution precipitated orange needles of *cyclopentadienyl(3-hydroxy-6-oxotricyclo*[6,2,1,$0^{2,7}$]*undeca-4,9-dien-3-yl)rhodium fluoroborate* (0·395 g, 92%), which decomposed at 220° without melting (Found: C, 44·3; H, 3·6. $C_{16}H_{16}BF_4O_2Rh$ requires C, 44·6; H, 3·7%).

Reaction of (π-C_5H_5)Rh(cq) (14) *with Fluoroboric Acid*.—A suspension of (π-C_5H_5)Rh(cq) (14) (0·11 g, 0·5 mmol) in ether (30 ml) was shaken with 42% fluoroboric acid (0·5 ml) for 24 h. The orange product was filtered off, washed with ether, and dissolved in acetone. Slow addition of ether to the acetone solution precipitated orange needles of *cyclopentadienyl(3-hydroxy-6-oxotricyclo*[6,2,1,$0^{2,7}$]*undeca-4,9-dien-3-yl)rhodium fluoroborate* (19a) (0·189 g, 88%) which decomposed at 220° without melting (Found: C, 44·4; H, 3·4. $C_{16}H_{16}BF_4O_2$ Rh requires C, 44·6; H, 3·7%).

Reaction of (π-C_5H_5)Rh(cq) (14) *with Fluoroboric Acid in Acetic Anhydride*.—A solution of 42% aqueous fluoroboric acid (1·0 ml) in acetic anhydride (5 ml) was added to a solution of (π-C_5H_5)Rh(cq) (0·342 g, 1 mmol) in acetic anhydride (15 ml). After 10 min ether (65 ml) was added to give an orange precipitate. This was filtered off, washed with ether, and dissolved in acetone. Slow addition of ether to this solution precipitated yellow-orange plates of

cyclopentadienyl(3-acetoxy-6-oxotricyclo[6,2,1,0^{2,7}]undeca-4,9-dien-3-yl)rhodium fluoroborate (19b) (0·420 g, 89%), m.p. 199—201° (Found: C, 45·3; H, 3·5. $C_{18}H_{18}BF_4O_3Rh$ requires C, 45·4; H, 3·8%).

Reaction of the Diol $(\pi\text{-}C_5H_5)Rh(C_{11}H_{14}O_2)$ (18) *with Hexafluorophosphoric Acid.*—Addition of 65% hexafluorophosphoric acid (0·5 ml) to a solution of the diol (0·346 g, 1 mmol) in acetone (10 ml) and ether (60 ml) gave a yellow-orange precipitate. This was filtered off, washed with ether, and dissolved in acetone. Slow addition of ether to this solution precipitated yellow-orange needles of *cyclopentadienyl(6-hydroxytricyclo[6,2,1,0^{2,7}]undeca-4,9-dien-3-yl)rhodium hexafluorophosphate* (0·352 g, 74%) which decomposed at 220° without melting (Found: C, 40·3; H, 3·9; P, 6·6. $C_{16}H_{18}F_6OPRh$ requires C, 40·5; H, 3·8; P, 6·5%).

Reaction of the Diol (18) *with 1 Mol of Trityl Fluoroborate.*—Addition of a solution of trityl fluoroborate (0·660 g, 2 mmol) in dichloromethane (10 ml) to a solution of the diol (18) (0·692 g, 2 mmol) in dichloromethane (15 ml) gave a precipitate of orange needles. This precipitate (A) was filtered off and washed with dichloromethane. The combined dichloromethane solutions were washed with water (3 × 20 ml), dried ($MgSO_4$), and concentrated to 10 ml. Addition of ether (40 ml) to this solution gave a cream precipitate (B) which was filtered off and washed with ether. The filtrate and washings were combined, dried ($MgSO_4$), and evaporated to dryness to give a white residue. This was recrystallised from pentane to give white crystals of triphenylmethanol (0·440 g), m.p. 163—165° (lit., 164—165°).

The cream precipitate (B) was dissolved in acetone. Slow addition of ether to this solution precipitated cream microcrystals of *tritylcyclopentadienyl(6-hydroxytricyclo[6,2,1,0^{2,7}]undeca-4,9-dien-3-yl)rhodium fluoroborate* (20b) (0·116 g, 15%), m.p. 141—143° (Found: C, 63·3; H, 5·1. $C_{35}H_{32}BF_4ORh$ requires C, 63·9; H, 4·9%).

The orange precipitate (A) was dissolved in acetone. Slow addition of ether to this solution precipitated yellow-orange needles of *cyclopentadienyl(6-hydroxytricyclo[6,2,1,0^{2,7}]undeca-4,9-dien-3-yl)rhodium fluoroborate* (20a) (0·482 g, 58%), m.p. 172·3° (Found: C, 46·1; H, 4·4. $C_{16}H_{18}BF_4ORh$ requires C, 46·2; H, 4·4%).

The *hexafluorophosphate* crystallised as yellow-orange needles, which decomposed at 220° without melting, from acetone (Found: C, 40·5; H, 3·9. $C_{16}H_{18}F_6OPRh$ requires C, 40·5; H, 3·8%). The i.r. spectrum of this hexafluorophosphate was identical with that of the hexafluorophosphate prepared by the reaction of $(\pi\text{-}C_5H_5)Rh(C_{11}H_{14}O_2)$ with hexafluorophosphoric acid.

Cyclopentadienyl(6-oxotricyclo[6,2,1,0^{2,7}]undeca-4,9-dien-3-yl)rhodium Hexafluorophosphate.—A solution of trityl fluoroborate (0·165 g, 0·5 mmol) in dichloromethane (5 ml) was added to a suspension of $[(\pi\text{-}C_5H_5)Rh(C_{11}H_{13}O)]BF_4$ (0·208 g, 0·5 mmol) in dichloromethane (40 ml). The mixture was stirred at 20° for 2 h; the precipitate and solution were then extracted with water (3 × 15 ml). The aqueous solutions were combined to give solution (A). The dichloromethane solution was further washed with water, dried ($MgSO_4$), and evaporated to dryness. The residue was recrystallised from pentane to give white crystals of triphenylmethane (0·109 g, 89%), m.p. 92—93° (lit., 94°).

The aqueous solution (A) was concentrated to 10 ml. Addition of 15% aqueous ammonium hexafluorophosphate solution to this gave an orange precipitate. This was dissolved in acetone. Slow addition of ether to the acetone solution precipitated orange plates of the pure *product* (0·184 g, 78%), m.p. 212—213° (Found: C, 40·6; H, 3·5; P, 6·7. $C_{16}H_{16}F_6OPRh$ requires C, 40·7; H, 3·4; P, 6·6%).

Tritylcyclopentadienyl(6-oxotricyclo[6,2,1,0^{2,7}]undeca-4,9-dien-3-yl)rhodium Fluoroborate (21a).—A solution of $[Ph_3C\cdot(C_5H_4)Rh(C_{11}H_{13}O)]BF_4$ (0·132 g, 0·2 mmol) and trityl fluoroborate (0·066 g, 0·2 mmol) in dichloromethane (15 ml) was stirred at 20° for 30 min. Addition of ether (50 ml) then gave an orange-yellow precipitate. This was filtered off and washed with ether. The combined filtrate and washings gave, on work-up, triphenylmethane (0·033 g). The orange-yellow precipitate was dissolved in acetone. Slow addition of ether to the acetone solution precipitated orange-yellow plates of the pure *product* (0·094 g, 73%), which did not melt sharply (Found: C, 64·1; H, 5·3. $C_{35}H_{30}BF_4ORh$ requires C, 64·1; H, 4·8%).

The *hexafluorophosphate* was precipitated from acetone solution by ether as orange plates which did not melt sharply (Found: C, 58·8; H, 4·9; P, 4·3. $C_{35}H_{30}F_6OPRh$ requires C, 58·8; H, 4·2; P, 4·4%).

Reaction of the Diol $(\pi\text{-}C_5H_5)Rh(C_{11}H_{14}O_2)$ *with an Excess of Trityl Fluoroborate.*—Addition of a solution of trityl fluoroborate (0·990 g, 3 mmol) in dichloromethane (10 ml) to a solution of the diol (18) (0·346 g, 1 mmol) in dichloromethane (10 ml) gave an orange precipitate. After 30 min the precipitate and solution were extracted with water (3 × 15 ml). The dichloromethane layer (A) was separated and the combined aqueous solutions were concentrated to 10 ml; 15% aqueous ammonium hexafluorophosphate solution (10 ml) was added to give an orange precipitate. This was dissolved in acetone. Slow addition of ether to the acetone solution precipitated yellow-orange microcrystals of tritylcyclopentadienyl(6-oxotricyclo[6,2,1,0^{2,7}]-undeca-4,9-dien-3-yl)rhodium fluoroborate (21a) (0·045 g, 8%) which was identified by its i.r. spectrum.

Reaction of the Alcohol $(\pi\text{-}C_5H_5)Rh(C_{12}H_{14}O_2)$ *with Hexafluorophosphoric Acid.*—Addition of 65% aqueous hexafluorophosphoric acid solution (0·5 ml) to a solution of $(\pi\text{-}C_5H_5)Rh(C_{12}H_{14}O_2)$ (15) (0·179 g, 0·5 mmol) in acetone (7 ml) and ether (50 ml) immediately gave an orange precipitate. This was filtered off and dissolved in acetone. Slow addition of ether to the acetone solution precipitated orange plates of *cyclopentadienyl(3,6-dihydroxy-6-methyltricyclo[6,2,1,0^{2,7}]undeca-4,9-dien-3-yl)rhodium hexafluorophosphate* (22) (0·212 g, 85%), m.p. 225—227° (Found: C, 40·6; H, 5·7; P, 5·9. $C_{17}H_{20}F_6O_2PRh$ requires C, 40·5; H, 3·9; P, 6·1%).

Conversion of $[(\pi\text{-}C_5H_5)Rh(C_{12}H_{15}O_2)]PF_6$ *into* $[(\pi\text{-}C_5H_5)Rh(C_{12}H_{13}O)]PF_6$.—$[(\pi\text{-}C_5H_5)Rh(C_{12}H_{15}O_2)]PF_6$ (0·100 g, 0·2 mmol) was dissolved in acetone (0·5 ml) and the solution was left at 20° for 48 h. Addition of ether to the solution then gave an orange precipitate which was filtered off and dissolved in acetone. Slow addition of ether to this solution precipitated orange plates of *cyclopentadienyl(3-methyl-6-oxotricyclo[6,2,1,0^{2,7}]undeca-4,9-dien-3-yl)rhodium hexafluorophosphate* (0·084 g, 85%), m.p. 219—220° (Found: C, 42·3; H, 3·9; P, 6·4. $C_{17}H_{18}F_6OPRh$ requires C, 42·0; H, 3·7; P, 6·4%).

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