Cationic Transition-metal Complexes. Part II.[1] The Reaction of Arenes and Olefins with Bis(cyclo-octa-1,5-diene or norbornadiene)rhodium Tetrafluoroborate

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Treatment of $[Rh(nbd)_2]^+BF_4^-$ or $[Rh(cod)_2]^+BF_4^-$ (nbd = norbornadiene, cod = cyclo-octa-1,5-diene) with arenes leads to the displacement of nbd or cod and the formation of $[Rh(nbd)(arene)]^+BF_4^-$ (arene = C_6Me_6, 1,3,5-$C_6H_3Me_3$, 1,3-$C_6H_4Me_2$, C_6H_5Me, C_6H_6, C_6H_5OH, or C_6H_5OMe) and $[Rh(cod)(arene)]^+BF_4^-$ (arene = C_6Me_6, 1,3,5-$C_6H_3Me_3$, 1,3-$C_6H_4Me_2$, or C_6H_5Me). Analogous reactions with benzonitrile and aniline gave instead the complexes $[Rh(nbd)(C_6H_5CN)_2]^+BF_4^-$ and $[Rh(nbd)(C_6H_5NH_2)_2]^+BF_4^-$; dimethyl sulphoxide reacts similarly to give $[Rh(cod)(Me_2SO)_2]^+BF_4^-$. Reaction of $[Rh(C_2H_4)_2(acac)]$ with $Ph_3C^+BF_4^-$ and an arene affords $[Rh(C_2H_4)_2(arene)]^+BF_4^-$ (arene = C_6Me_6, 1,3-$C_6H_4Me_2$, or C_6H_6).

Bicyclo[2,2,1]heptadiene is dimerised and trimerised catalytically by $[Rh(nbd)_2]^+BF_4^-$; the mechanism of this reaction is discussed. Cycloheptatriene (cht) displaces nbd or cod to form $[Rh(nbd)(cht)]^+BF_4^-$ and $[Rh(cod)(cht)]^+BF_4^-$, which are considered to involve cht bonded in the $\pi(h^6)$ form. Cyclohexa-1,3-diene is disproportionated by $[Rh(nbd)_2]^+BF_4^-$ to cyclohexene and benzene; the 1,4-diene undergoes isomerisation before disproportionation. Sodium benzoate and acetate form bridged carboxylates $[Rh(nbd)(rco_2)]_2$ on reaction with $[Rh(nbd)_2]^+BF_4^-$.

WE recently[1] described the synthesis of the cationic complexes $[M(diene)_2]^+BF_4^-$ (M = Rh or Ir; diene = bicyclo[2,2,1]heptadiene or cyclo-octa-1,5-diene). These co-ordinatively unsaturated systems react with both σ-donor and π-acceptor ligands, as exemplified[1] by the formation of the cations $[M(diene)(CH_3CN)_2]^+$, $[M(diene)L_2]^+$, and ML_4^+ on reaction with acetonitrile or phosphines (L). As previously indicated one of the diene molecules is also readily displaced by arenes, dienes, or trienes, and in this paper we describe our results in this area. The new compounds described were characterised by elemental analysis and i.r. and ^1H n.m.r. spectroscopy.

Bis(bicyclo[2,2,1]heptadiene)rhodium tetrafluoroborate readily undergoes an exchange reaction at room temperature on treatment with a methylene chloride solution of hexamethylbenzene, 1,3,5-trimethylbenzene, *m*-xylene, toluene, benzene, phenol, or anisole to form respectively the crystalline cationic arene complexes (I), (II), (III), (IV), (V), (VI), and (VII). The corresponding reactions with bis(cyclo-octa-1,5-diene)rhodium tetrafluoroborate proceeded more slowly, but in this way the complexes (VIII), (IX), (X), and (XI) were formed as crystalline compounds. The formation of these new arene complexes involves a reversible reaction and treatment of the complexes (I)—(XI) with an excess of the respective diene, *i.e.* either bicyclo[2,2,1]heptadiene (norbornadiene = nbd) or cyclo-octa-1,5-diene (cod) resulted in the regeneration of the $[Rh(diene)_2]^+BF_4^-$ complexes. It was also found that the formation of the complexes $[Rh(diene)(arene)]^+$ occurred more readily if the arene carries electron donating substituents, *i.e.* the reactivity sequence $C_6Me_6 > 1,3,5\text{-}C_6H_3Me_3 > 1,3\text{-}C_6H_4Me_2 > C_6H_5Me > C_6H_6$ was qualitatively observed.

As noted above bicyclo[2,2,1]heptadiene is displaced by arenes more readily from $[Rh(nbd)_2]^+BF_4^-$ than is cyclo-octa-1,5-diene displaced from $[Rh(cod)_2]^+BF_4^-$. Since it has been shown[2] that bicyclo[2,2,1]heptadiene has stronger π-back bonding capabilities than cyclo-octa-1,5-diene the difference in reactivity may be explained if it is assumed that a five-co-ordinate intermediate is involved; the increased positive charge on the rhodium in $[Rh(nbd)_2]^+$ relative to that in $[Rh(cod)_2]^+$ facilitating the reaction with the arene.

Recently, Osborn and Schrock in a preliminary communication[3] have described the formation of the hexafluorophosphate salts of these cationic arene complexes. Previously, the possibly related cations $[Rh(\pi\text{-}C_6Me_6)_2]^+$ (ref. 4) and $[Co(\pi\text{-}C_4Ph_4)(C_6H_6)]^+$ (ref. 5) have been reported.

The ^1H n.m.r. spectra of compounds (I)—(XI) are temperature invariant (−80 to +50°), showing, for example, in the case of (I) typical co-ordinated bicyclo-

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[1] M. Green, T. A. Kuc, and S. H. Taylor, *Chem. Comm.*, 1970, 1553; Part I, M. Green, T. A. Kuc, and S. H. Taylor, *J. Chem. Soc.* (*A*), 1971, 2334.

[2] H. C. Volger, M. M. P. Gaasbeek, H. Hogeveen, and K. Vrieze, *Inorg. Chem. Acta*, 1969, **3**, 145, and references therein.

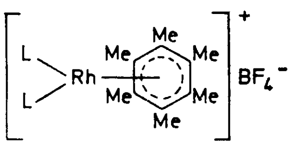
[3] R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc.*, 1971, **93**, 3089.

[4] E. O. Fischer and H. H. Lindner, *J. Organometallic Chem.*, 1964, **1**, 307.

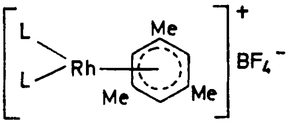
[5] A. Efraty and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1967, **89**, 3744.

[2,2,1]heptadiene resonances and one sharp singlet aromatic methyl resonance. For (V) the aromatic hydrogens appeared as one sharp resonance shifted upfield from unco-ordinated benzene. This suggests that these complexes are 18-electron systems in which the arene ring is bonded in the $\pi(h^6)$ form. Such a mode of bonding has in fact been identified[6,7] in the Rh^I complexes [RhL_2BPh_4] [where L = $P(OMe)_3$, PPh_3, or 1,5-C_8H_{12}] where the tetraphenylborate is co-ordinated to the metal *via* a $\pi(h^6)$ interaction of an arene ring. However, it is interesting that an *X*-ray crystallographic study[6] of {$Rh[P(OMe)_3]_2BPh_4$} showed that the co-ordinated ring is slightly puckered into a boat form.

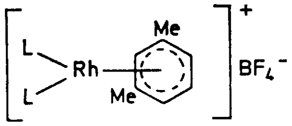
However, in contrast with the species [RhL_2BPh_4] (L_2 = nbd), which is reported not to react with carbon monoxide, the complexes $[Rh(diene)(arene)]^+BF_4^-$ readily undergo ligand exchange on treatment with both π-acceptor ligands such as nbd or cod, and with σ-donor ligands such as acetonitrile or dimethyl sulphoxide, *viz.* $[Rh(diene)(arene)]^+ + 2L \longrightarrow [Rh(diene)L_2]^+$. Although this difference could be ascribed to steric factors it is possible that the complexes (I)—(XI) are co-ordinatively unsaturated 16-electron species where the arene is bonded in the $\pi(h^4)$ form, or alternatively that the mode of bonding can very easily change from $\pi(h^6)$ to $\pi(h^4)$ on interaction of the rhodium with an incoming ligand. If the first alternative is correct then the low-temperature ^1H n.m.r. results require that the complexes are undergoing a very ready valence tautomerism. A crystal-structure determination is required to clarify this question. In this connection it is interesting that a $\pi(h^4)$-bonded arene ring is present[8] in the fluxional molecule [$Ru(C_6Me_6)_2$].



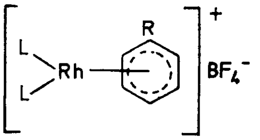
(I) L_2 = nbd
(VIII) L_2 = cod
(XII) L = C_2H_4



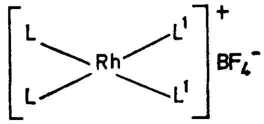
(II) L_2 = nbd
(IX) L_2 = cod



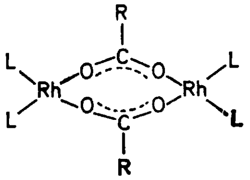
(III) L_2 = nbd
(X) L_2 = cod
(XIII) L = C_2H_4



(IV) L_2 = nbd, R = Me
(V) L_2 = nbd, R = H
(VI) L_2 = nbd, R = OH
(VII) L_2 = nbd, R = OMe
(XI) L_2 = cod, R = Me
(XIV) L = C_2H_4, R = H



(XVII) L_2 = nbd, L_2^1 = cyclohexa-1,3-diene
(XVIII) L_2 = nbd, L_2^1 = cyclohexa-1,4-diene
(XIX) L_2 = nbd, L^1 = C_6H_5CN
(XXI) L_2 = cod, L^1 = C_6H_5CN
(XX) L_2 = nbd, L^1 = $C_6H_5NH_2$
(XXII) L_2 = cod, L^1 = Me_2SO



(XXIII) L_2 = nbd, R = C_6H_5
(XXIV) L_2 = nbd, R = Me

The complexes (I) and (VIII) can also be synthesised by reaction of [Rh(diene)(acac)] (diene = nbd or cod) with triphenylmethyl tetrafluoroborate in the presence of an excess of hexamethylbenzene. This approach was extended to include the synthesis of (XII), (XIII), and (XIV) by the corresponding reaction of [$Rh(C_2H_4)_2$(acac)]. The cations (XII), (XIII), and (XIV) are stable crystalline materials.

The ^1H n.m.r. spectrum of (XII), which was sufficiently soluble for low-temperature measurements, showed a temperature-invariant single methyl resonance for the co-ordinated hexamethylbenzene; the chemical shift being close to that observed for (I). The resonances of the co-ordinated ethylenes showed temperature dependence. At 65° ($CDCl_3$) resonances at τ 7·51 (broad s, 8H, CH_2=CH_2) and 7·71 (s, 18H, CH_3) were observed. On cooling to 31° the ethylene resonances appeared as two broad singlets at τ 7·43 (outer) and 7·61 (inner). At 0° the inner and outer ethylene resonances appeared as approximately two doublets caused by coupling with ^{103}Rh (J_{RhH} 2·1 Hz). This temperature dependence possibly indicates rotation of the co-ordinated ethylenes about the rhodium–ethylene axes; the coalescence temperature is similar to that reported[9] for $Rh(C_5Me_5)(C_2H_4)_2$ and higher than for $Rh(C_5H_5)(C_2H_4)_2$.[10] However, it is not possible to exclude completely the possibility of arene dissociation at higher temperature, and this and related systems are being investigated further.

An attempt to extend the arene exchange reaction to the formation of $\pi(h^6)$-bonded benzonitrile or aniline led

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[6] H. J. Holte, G. Gafner, and L. M. Haines, *Chem. Comm.*, 1969, 1406.

[7] R. R. Schrock and J. A. Osborn, *Inorg. Chem.*, 1970, **9**, 2339.

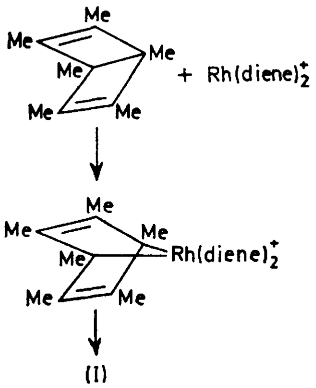
[8] G. Huttner, S. Lange, and E. O. Fischer, *Angew. Chem. Internat. Edn.*, 1971, **10**, 556.

[9] K. Moseley, J. W. King, and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1970, 2875.

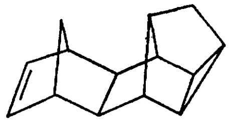
[10] R. Cramer, J. B. Kline, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 2519.

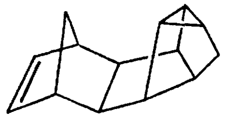
to the synthesis of (XIX), (XX), and (XXI), which are depicted as σ-donor complexes analogous to the bis-acetonitrile compounds[1] $[M(diene)(CH_3CN)_2]^+BF_4^-$ (M = Rh or Ir). The aromatic ^1H n.m.r. resonances for these complexes were not shifted upfield as observed with (I)—(XI). Dimethyl sulphoxide also reacts with $[Rh(cod)_2]^+BF_4^-$ to form an analogous σ-donor complex (XXII), in which one cyclo-octa-1,5-diene is replaced by two dimethyl sulphoxide ligands.

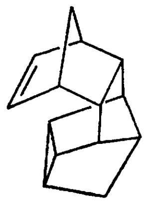
Hexamethylbicyclo[2,2,0]hexadiene reacts at room temperature with both bis(bicyclo[2,2,1]heptadiene)-rhodium tetrafluoroborate and bis(cyclo-octa-1,5-diene)-rhodium tetrafluoroborate to form respectively (I) and (VIII). If this reaction is concerted it involves an apparent violation of the principle of the conservation of orbital symmetry.[11] A similar observation is the report[12] that the disrotatory cyclobutene ring opening of hexamethyl bicyclo[2,2,0]hexadiene to hexamethylbenzene is catalysed by di-μ-chloro-di(hexamethylbicyclo[2,2,0]hexadiene)dirhodium in the temperature range 60—70°. This reaction has been interpreted by Mango[13] as a concerted reaction which by involvement of metal *d* orbitals becomes a symmetry-allowed process. While this rationale may be extended to explain the ready formation of (I) and (VIII), recent experiments on the reaction of $[Rh(CO)_2Cl]_2$ with strained cycloalkanes such as cyclopropane,[14] quadricyclene,[15] and cubanes,[16] suggest that the reaction of hexamethylbicyclo[2,2,0]hexadiene with $[Rh(nbd)_2]^+$ or $[Rh(cod)_2]^+$ may involve an essentially oxidative reaction initiated by interaction of the bonding electrons of the central C–C single bond of the hexamethylbicyclo[2,2,0]hexadiene with the rhodium, *i.e.*

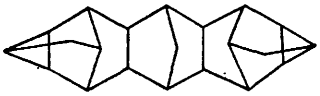


In the synthesis of bis(bicyclo[2,2,1]heptadiene)rhodium tetrafluoroborate it was found that if the reaction mixture (containing an excess of diene) was allowed to stand for prolonged periods then appreciable quantities of hydrocarbons were formed. Re-investigation of this system showed that $[Rh(nbd)_2]^+BF_4^-$ is a catalyst for the dimerisation and trimerisation of bicyclo[2,2,1]-heptadiene, and comparison of ^1H n.m.r. data demonstrated that the products were the same as those obtained by Katz and Mrowca[17] on refluxing bicyclo[2,2,1]-heptadiene over 5% rhodium on carbon. In a typical reaction (60 hr. at room temperature in CH_2Cl_2) the dimers (XXVI) (60% yield) and (XXVII) (10%) were formed together with a trimer (XXVIII) (25%). Very recently[3] the catalytic dimerisation of nbd by $[Rh(nbd)_2]^+PF_6^-$ has been briefly described.

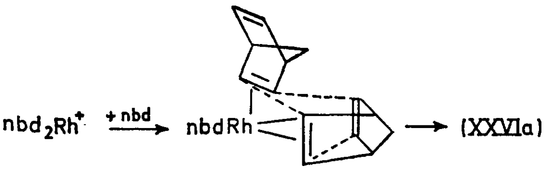

(XXVIa)


(XXVIb)


(XXVII)


(XXVIII)

The ease with which these reactions occur suggests that the dimerisation and trimerisation reactions involve the occupancy of the vacant co-ordination site in $[Rh(nbd)_2]^+BF_4^-$ by a third molecule of bicyclo[2,2,1]-heptadiene, bonding as a mono-olefin. Since such coordination would occur preferentially on the less hindered *exo*-side the formation of the major dimer is readily explained. The reaction which is illustrated for the formation of (XXVIa), then involves what is essentially a $\pi^2s + \pi^2s + \pi^2s$ concerted reaction:



SCHEME 1

However, $\pi^2s + \pi^2s + \pi^2s$ reactions are symmetry-allowed[11] for a thermal reaction and a number[18] of such reactions have been investigated, which suggests that if this is the mechanism, then the metal merely functions as a template, although considerations similar to

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[11] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie GmbH, 1970.

[12] H. C. Volger and H. Hogeveen, *Rec. Trav. chim.*, 1967, **86**, 830.

[13] F. D. Mango, *Adv. Catalysis*, 1969, **20**, 291.

[14] D. M. Roundhill, D. N. Lawson, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 845.

[15] L. Cassar and J. Halpern, *Chem. Comm.*, 1970, 1182.

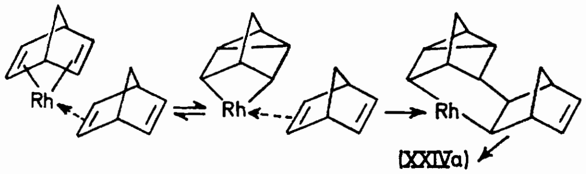
[16] L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, 1970, **92**, 3515.

[17] J. J. Mrowca and T. J. Katz, *J. Amer. Chem. Soc.*, 1966, **88**, 4012.

[18] A. T. Blomquist and Y. C. Meinwald, *J. Amer. Chem. Soc.*, 1959, **81**, 667; R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *Tetrahedron Letters*, 1962, 615; H. K. Hall, *J. Org. Chem.*, 1960, **25**, 42.

those of Mango suggest that the symmetry requirements would be considerably altered by co-ordination.

An alternative and possibly more likely mechanism involves a reversible oxidation-reduction step:



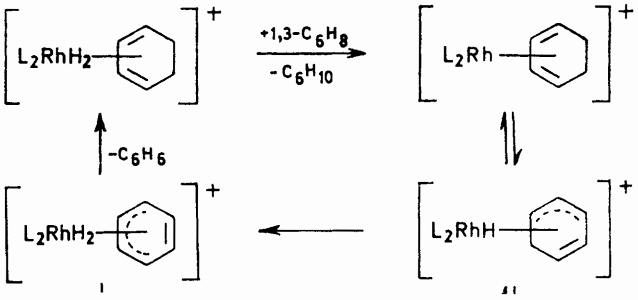
SCHEME 2 (third C_7H_8 omitted for clarity)

Co-ordination of a third bicyclo[2,2,1]heptadiene molecule causes the formation of two σ-carbon to rhodium bonds; the resultant intermediate corresponding to that postulated [15] in the Rh^I-catalysed conversion of quadricyclene to bicyclo[2,2,1]heptadiene. Olefin insertion into a σ-carbon rhodium bond then leads to the formation of the dimer.

Cycloheptatriene rapidly reacts with both bis(bicyclo-[2,2,1]heptadiene)rhodium tetrafluoroborate and bis-(cyclo-octa-1,5-diene)rhodium tetrafluoroborate to give respectively the crystalline cycloheptatriene complexes (XV) and (XVI); a reaction which involves displacement of a diene by a triene. The same complexes are obtained on reaction of cycloheptatriene with the bis-acetonitrile complexes $[Rh(diene)(CH_3CN)_2]^+BF_4^-$; a reaction which proceeds more slowly than the diene displacement. The ^1H n.m.r. spectra of (XV) and (XVI) showed resonances compatible with normally co-

Both cyclohexa-1,3-diene and the 1,4-isomer reacted with $[Rh(nbd)_2]^+BF_4^-$ to form respectively the complexes (XVII) and (XVIII). These complexes, whose ^1H n.m.r. spectra could not be recorded due to decomposition in solution, were differentiated by decomposition with aqueous potassium cyanide to give nbd and respectively cyclohexa-1,3-diene and cyclohexa-1,4-diene (v.p.c.). In methylene chloride at room temperature (XVII) readily catalysed the disproportionation of cyclohexa-1,3-diene to benzene and cyclohexene; the reaction being followed by removing aliquot portions and analysing the volatile components by v.p.c. In contrast, cyclohexa-1,4-diene was only slowly disproportionated in the presence of (XVII) or (XVIII).

It is possible, as illustrated in Scheme 3, that the disproportionation of both cyclohexadienes proceeds *via* a common intermediate, and that carbon to rhodium H-migration from the 1,4-isomer occurs much more slowly than for the 1,3-isomer.



interesting that in the absence of a metal the disproportionation of cyclohexa-1,3-diene by a similar concerted transfer of two hydrogen atoms is a symmetry-allowed process; whereas, the corresponding reaction for cyclohexa-1,4-diene is symmetry-forbidden.[11]

The disproportionation of cyclohexene, cyclohexa-1,3-diene, and cyclohexa-1,4-diene to benzene and cyclohexene on palladium has been known for a number of years.[21] Recently, Lyons[22] observed disproportionation of cyclohexa-1,4-diene using *trans*-$\mathrm{IrCl(CO)(PPh_3)_2}$ as a catalyst, and Moseley and Maitlis[23] have suggested the involvement of rhodium hydrides in the disproportionation of the 1,3-isomer on reaction of $\mathrm{[Rh(\pi\text{-}C_5Me_5)Cl_2]_2}$ with the diene and alcohol–base. However, the system described here is the simplest observed to date and a detailed mechanistic study is being undertaken.

Treatment of $\mathrm{[Rh(nbd)_2]^+BF_4^-}$ with $\mathrm{NaBPh_4}$ afforded the known complex $\mathrm{[Rh(C_7H_8)BPh_4]}$.[7] An attempt to obtain a similar zwitterionic compound with sodium benzoate gave the binuclear bridged carboxylate species (XXIII); a similar compound (XXIV) was obtained from the corresponding reaction of sodium acetate. In these reactions there was no evidence for nucleophilic attack by the carboxylate anion on the carbon–carbon double bond of the co-ordinated bicyclo[2,2,1]heptadiene, which provides an interesting contrast with the analogous d^8 $\mathrm{Pd^{II}}$ chemistry. It is worth noting that a similar preferential attack by a hard base on the metal was observed[1] in the formation of $\mathrm{[Ir(1,5\text{-}C_8H_{12})OMe]_2}$ from $\mathrm{[Ir(1,5\text{-}C_8H_{12})_2]^+BF_4^-}$ and methoxide anion.

Sodium cyclopentadienide reacted with bis(bicyclo[2,2,1]heptadiene)rhodium tetrafluoroborate to give (XXV) bicyclo[2,2,1]heptadiene(π-cyclopentadienyl)rhodium, again there being no evidence for attack by the carbanion on the co-ordinated olefin.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded at 100 MHz on a Varian Associates HA 100 spectrometer. Chemical shifts are relative to $\mathrm{Me_4Si}$ (τ 10·00). I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer. Bis(bicyclo[2,2,1]hepta-2,5-diene)rhodium tetrafluoroborate and bis(cycloocta-1,5-diene)rhodium tetrafluoroborate were prepared as previously described.[1] All reactions were conducted in a oxygen-free nitrogen atmosphere.

Preparation of Arene Complexes

Reactions of Bis(*bicyclo*[2,2,1]*hepta*-2,5-*diene*)*rhodium Tetrafluoroborate*.—(a) *With hexamethylbenzene*. An excess of hexamethylbenzene (0·30 g., 1·9 mmoles) was added to a solution of bis(bicyclo[2,2,1]hepta-2,5-diene)rhodium tetrafluoroborate (0·10 g., 0·27 mmole) in methylene chloride (10 ml.). After 10 min. at room temperature, diethyl ether (60 ml.) was added to the pale yellow solution, and the precipitated solid recrystallised from methylene chloride–diethyl ether to give white *crystals* of (I) (0·11 g., 89%), m.p. >270° (Found: C, 51·4; H, 6·2. $\mathrm{C_{19}H_{26}BF_4Rh}$ requires C, 51·3; H, 5·9%). The ^{1}H n.m.r. spectrum ($\mathrm{CDCl_3}$) showed resonances at τ 6·54 (s, 2H, CH), 6·63 (q, 4H, CH=CH, J_{RhH} 2·4 Hz), 7·73 (s, 18H, $\mathrm{CH_3}$), and 8·90 (t, 2H, $\mathrm{CH_2}$, J_{HH} 1·2 Hz).

(b) *With hexamethyl*(*dewar benzene*). Treatment of a solution of bis(bicyclo[2,2,1]hepta-2,5-diene)rhodium tetrafluoroborate (0·10 g., 0·27 mmole) in methylene chloride (10 ml.) with hexamethyl(dewar benzene) (0·30 g., 1·9 mmoles) gave after 1 hr. at room temperature and addition of diethyl ether, white crystals of (I) (0·10 g., 85%).

(c) *With* 1,3,5-*trimethylbenzene*. In a similar way, addition of 1,3,5-trimethylbenzene (1·0 g., excess) to a methylene chloride (10 ml.) solution of bis(bicyclo[2,2,1]heptadiene)rhodium tetrafluoroborate (0·17 g., 0·45 mmole) gave after 1 min. at room temperature a pale yellow solution. Addition of diethyl ether (60 ml.) followed by recrystallisation from methylene chloride–diethyl ether gave fine pale cream *needles* of (II) (0·18 g., 95%), m.p. 235—237° (Found: C, 48·0; H, 5·0. $\mathrm{C_{16}H_{20}BF_4Rh}$ requires C, 47·8; H, 5·0%). The ^{1}H n.m.r. spectrum ($\mathrm{CDCl_3}$) showed resonances at τ 3·39 (s, 3H, aromatic), 6·06 (q, 4H, CH=CH, J_{RhH} 2·2 Hz) 6·50 (broad s, 2H, CH), 7·63 (s, 9H, $\mathrm{CH_3}$), and 8·83 (t, 2H, $\mathrm{CH_2}$).

(d) *With* m-*xylene*. An excess of *m*-xylene (1·0 g., excess) was added to a solution of bis(bicyclo[2,2,1]hepta-2,5-diene)rhodium tetrafluoroborate (0·10 g., 0·27 mmole) in methylene chloride (10 ml.). After 5 min. at room temperature diethyl ether was added to the pale yellow solution to give a solid, which on recrystallisation afforded yellow *crystals* of (III) (0·09 g., 82%), m.p. 88—90° (Found: C, 46·3; H, 4·7. $\mathrm{C_{15}H_{18}BF_4Rh}$ requires C, 46·4; H, 4·6%). The ^{1}H n.m.r. spectrum ($\mathrm{CDCl_3}$) showed resonances at τ 3·13—3·41 (m, 4H, aromatic), 5·92 (q, 4H, CH=CH, J_{RhH} 2·3 Hz), 6·44 (broad, s, 2H, CH), 7·59 (s, 6H, $\mathrm{CH_3}$), and 8·80 (t, 2H, $\mathrm{CH_2}$, J_{HH} 1·2 Hz).

(e) *With toluene*. Similarly, toluene (1·0 g., excess) was added to bis(bicyclo[2,2,1]hepta-2,5-diene)rhodium tetrafluoroborate (0·10 g., 0·27 mmole) in methylene chloride (10 ml.). After 10 hr. at room temperature, diethyl ether was added, and the resultant solid recrystallised to give pale yellow *crystals* of (IV) (0·09 g., 86%), m.p. 132—134° (Found: C, 44·8; H, 4·4. $\mathrm{C_{14}H_{16}F_4BRh}$ requires C, 44·9; H, 4·3%). The ^{1}H n.m.r. spectrum ($\mathrm{CDCl_3}$) showed resonances at τ 3·15 (s, 5H, aromatic), 5·80 (q, 4H, CH=CH, J_{RhH} 2·0 Hz), 6·51 (broad s, 2H, CH), 7·60 (s, 3H, $\mathrm{CH_3}$), and 8·82 (t, 2H, $\mathrm{CH_2}$, J_{HH} 1·4 Hz).

(f) *With benzene*. In a similar way, after 16 hr. at room temperature diethyl ether was added to a solution of benzene (1·0 g., excess) and bis(bicyclo[2,2,1]hepta-2,5-diene)rhodium tetrafluoroborate (0·27 mmole) in methylene chloride (10 ml.). Recrystallisation of the precipitated solid gave pale yellow *crystals* of (V) (0·08 g., 84%), m.p. 166—169° (dec.) (Found: C, 42·8; H, 3·3. $\mathrm{C_{13}H_{14}BF_4Rh}$ requires C, 42·3; H, 3·8%). The ^{1}H n.m.r. spectrum ($\mathrm{CDCl_3}$) showed resonances at τ 3·02 (s, 6H, aromatic), 5·65 (q, 4H, CH=CH, J_{RhH} 2·2 Hz), 6·53 (broad s, 2H, CH), and 8·82 (t, 2H, $\mathrm{CH_2}$).

(g) *With phenol*. A solution of phenol (0·20 g., 2·1 mmoles) and bis(bicyclo[2,2,1]hepta-2,5-diene)rhodium tetrafluoroborate (0·07 g., 0·19 mmole) in methylene chloride (10 ml.) was stirred at room temperature for 30 min. Diethyl ether was added and the resultant solid recrystallised from methylene chloride–diethyl ether to give cream *crystals* of (VI) (0·06 g., 88%), m.p. 120° (dec.) (Found: C, 41·2; H,

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4·0. $C_{13}H_{14}BF_4ORh$ requires C, 41·5; H, 3·7%). The ^1H n.m.r. spectrum (CH_2Cl_2) showed resonances at τ 3·2—3·3 (m, 5H, aromatic), 5·86 (q, 4H, CH=CH, J_{RhH} 2·0 Hz), 6·12 (s, 1H, OH), 6·51 (broad s, 2H, CH), and 8·79 (t, 2H, CH_2, J_{HH} 1·2 Hz).

(h) *With anisole.* A solution of anisole (0·5 g., 4·6 mmoles) and bis(bicyclo[2,2,1]hepta-2,5-diene)rhodium tetrafluoroborate (0·07 g., 0·19 mmole) in methylene chloride was stirred for 30 hr. at room temperature, slowly becoming yellow in colour. Diethyl ether gave, after recrystallisation, pale yellow *crystals* of (VII) (0·063 g., 86%), m.p. 150—153° (Found: C, 43·9; H, 4·1. $C_{14}H_{16}F_4BORh$ requires C, 43·2; H, 4·1%). The ^1H n.m.r. spectrum (CH_2Cl_2) showed resonances at τ 3·17—3·24 (m, 5H, aromatic), 5·79 (q, 4H, CH=CH, J_{RhH} 2·0 Hz), 6·01 (s, 3H, CH_3), 6·51 (broad, s, 2H, CH), and 8·77 (t, 2H, CH_2, J_{HH} 1·5 Hz).

*Reactions of Bis(cyclo-octa-*1,5-*diene)rhodium Tetrafluoroborate.*—(a) *With hexamethylbenzene.* An excess of hexamethylbenzene (0·30 g.), was added to a methylene chloride solution of bis(cyclo-octa-1,5-diene)rhodium tetrafluoroborate (0·06 g., 0·15 mmole). After 1 hr. at room temperature, diethyl ether (60 ml.) was added to the pale yellow solution and the resultant solid recrystallised to give white *crystals* of (VIII) (0·06 g., 93%), m.p. >270° (Found: C, 52·4; H, 6·6. $C_{20}H_{30}BF_4Rh$ requires C, 52·2; H, 6·5%). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 6·35 (s, 4H, CH=CH), 7·79 (s, 18H, CH_3), and 7·6—8·2 (complex m, 8H, CH_2CH_2).

(b) *With hexamethyl(dewar benzene).* Similarly, hexamethyl(dewar benzene) (excess), after 1 hr. at room temperature, gave white crystals (86%) of (VIII).

(c) *With* 1,3,5-*trimethylbenzene.* In a similar way, reaction of 1,3,5-trimethylbenzene (1·0 g., excess) with bis(cyclo-octa-1,5-diene)rhodium tetrafluoroborate (0·10 g., 0·25 mmole) in methylene chloride (10 ml.) gave after 3 hr. at room temperature, and addition of diethyl ether, a solid, which on recrystallisation afforded pale yellow *crystals* of (IX) (0·09 g., 83%), m.p. 230° (dec.) (Found: C, 48·8; H, 5·6. $C_{17}H_{24}BF_4Rh$ requires C, 48·8; H, 5·7%). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 3·43 (s, 3H, aromatic), 5·66 (broad s, 4H, CH=CH), 7·66 (s, 9H, CH_3), and 7·56—7·96 (m, 8H, CH_2CH_2).

(d) *With* m-*xylene.* Reaction of *m*-xylene (1·0 g., excess) and bis(cyclo-octa-1,5-diene)rhodium tetrafluoroborate (0·07 g., 0·17 mmole) in methylene chloride (10 ml.) gave after 2 hr. at room temperature and addition of diethyl ether pale yellow *crystals* of (X) (0·06 g., 85%), m.p. 168—170° (Found: C, 47·3; H, 5·4. $C_{16}H_{22}F_4BRh$ requires C, 47·6; H, 5·5%). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 3·29 (s, 4H, aromatic), 5·46 (broad s, 4H, CH=CH), 7·61 (s, 6H, CH_3), and 7·42—7·95 (m, 8H, CH_2CH_2).

(e) *With toluene.* Similarly, reaction of toluene (1·0 g., excess) with bis(cyclo-octa-1,5-diene)rhodium tetrafluoroborate (0·07 g., 0·17 mmole) in methylene chloride gave after 24 hr. at room temperature pale yellow *crystals* of (XI) (0·06 g., 89%), m.p. 174—175° (Found: C, 45·8; H, 5·4. $C_{15}H_{20}BF_4Rh$ requires C, 46·1; H, 5·1%). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 3·28 (s, 5H, aromatic), 5·41 (broad s, 4H, CH=CH), 7·66 (s, 3H, CH_3), and 7·51—7·91 (m, 8H, CH_2CH_2).

Preparation of Bis(ethylene)(arene)rhodium Tetrafluoroborate Complexes

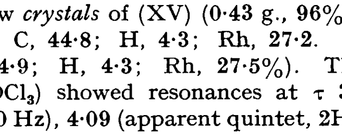
(a) *Bis(ethylene)(hexamethylbenzene)rhodium Tetrafluoroborate.*—A solution of triphenylmethyl tetrafluoroborate (0·127 g., 0·38 mmole) in methylene chloride (6 ml.) was added dropwise with stirring to a solution of acetylacetonatobis(ethylene)rhodium (0·10 g., 0·38 mmole) and hexamethylbenzene (0·35 g., 2·0 mmoles). After 24 hr. at room temperature, diethyl ether was added to the yellow solution and the precipitated solid recrystallised from methylene chloride–diethyl ether to give cream *crystals* of (XII) (0·14 g., 89%), m.p. 200—201° (dec.) (Found: C, 47·3; H, 6·6. $C_{16}H_{26}BF_4Rh$ requires C, 47·0; H, 6·4%). The ^1H n.m.r. spectrum ($CDCl_3$) at 65° showed resonances at τ 7·51 (broad s, 8H, CH_2=CH_2) and 7·71 (s, 18H, CH_3); the low temperature n.m.r. spectra are described in the text.

(b) *Bis(ethylene)*(m-*xylene)rhodium Tetrafluoroborate.*—By an identical procedure using *m*-xylene instead of hexamethylbenzene, cream *crystals* were obtained of (XIII) (0·104 g., 76%), m.p. 170—171° (Found: C, 40·4; H, 4·9. $C_{12}H_{18}F_4BRh$ requires C, 40·9; H, 5·1%). The ^1H n.m.r. spectrum (CH_2Cl_2) at 31° showed resonances at τ 3·23 (s, 4H, aromatic), 6·57 (s, 4H, CH_2=CH_2), 7·62 (s, 6H, CH_3), and 7·87 (s, 4H, CH_2=CH_2).

(c) *Bis(ethylene)(benzene)rhodium Tetrafluoroborate.*—Similarly, benzene reacted with acetylacetonatobis(ethylene)rhodium in the presence of triphenylmethyl tetrafluoroborate to give yellow *crystals* of (XIV) (0·09 g., 72%), m.p. 133—134° (dec.) (Found: C, 36·8; H, 4·4. $C_{10}H_{14}BF_4Rh$ requires C, 37·1; H, 4·3%). The ^1H n.m.r. spectrum (CH_2Cl_2) at 31° showed resonances at τ 3·06 (s, 6H, aromatic), 6·58 (s, 4H, CH_2=CH_2), and 7·88 (s, 4H, CH_2=CH_2).

Preparation of (diene′)(diene″)rhodium Tetrafluoroborate Complexes

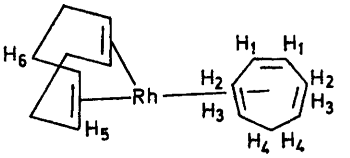
(a) (*Bicyclo*[2,2,1]*hepta*-2,5-*diene*)(*cyclohepta*-1,3,5-*triene*)-*rhodium Tetrafluoroborate.*—Cyclohepta-1,3,5-triene (2·0 g., 2·2 mmoles) was added to a stirred solution of bis(bicyclo-[2,2,1]hepta-2,5-diene)rhodium tetrafluoroborate (0·45 g., 1·2 mmoles) in methylene chloride (15 ml.). After 5 min. at room temperature diethyl ether (60 ml.) was added to the yellow solution to give a solid which on recrystallisation afforded yellow *crystals* of (XV) (0·43 g., 96%), m.p. 209—211° (Found: C, 44·8; H, 4·3; Rh, 27·2. $C_{14}H_{16}BF_4Rh$ requires C, 44·9; H, 4·3; Rh, 27·5%). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 3·06 (d of d, 2H, H_1, J_{12} 4·0 Hz), 4·09 (apparent quintet, 2H, H_2) 5·56 (q, 4H, H_5, J_{RhH} 2·1 Hz), 5·60 (broad s, 2H, H_6), 6·46 (broad s, 2H, H_3), 8·06—8·25 (m, 2H, H_4) and 8·74 (t, 2H, H_7, J_{HH} 1·4 Hz). Double irradiation of the signal at τ 4·09 caused the resonance at τ 3·06 to collapse into a singlet; irradiation at 3·06 caused the resonance at τ 4·09 to collapse into a doublet (J_{HH} 8·0 Hz); irradiation at τ 6·46 caused the partial collapse of the resonance at τ 4·09 into a broad singlet.



The complex (XV) was also prepared by refluxing a chloroform solution of bis(acetonitrile)(bicyclo[2,2,1]hepta-2,5-diene)rhodium tetrafluoroborate and cyclohepta-1,3,5-triene.

(b) (*Cyclo-octa*-1,5-*diene*)(*cyclohepta*-1,3,5-*triene*)*rhodium Tetrafluoroborate.*—A solution of cyclohepta-1,3,5-triene

(1·5 g., 1·6 mmole) and bis(cyclo-octa-1,5-diene)rhodium tetrafluoroborate (0·10 g., 0·25 mmole) in methylene chloride (10 ml.) was stirred at room temperature for 10 min. Addition of diethyl ether (100 ml.) to the yellow solution followed by recrystallisation gave yellow *crystals* of (XVI) (0·09 g., 95%), m.p. 210—212° (Found: C, 46·0; H, 5·1. $C_{15}H_{20}BF_4Rh$ requires C, 46·2; H, 5·1%). The ^{1}H n.m.r. spectrum ($^2H_6$ acetone) showed resonances at τ 3·17 (m, 2H, H_1), 3·94 (m, 2H, H_2), 5·14 (broad s, 4H, H_5), 5·92 (broad s, 2H, H_3), and 7·50—8·35 (complex m, 10H, H_4 and H_6).



(c) (*Bicyclo*[2,2,1]*hepta*-2,5-*diene*)(*cyclohexa*-1,3-*diene*)-*rhodium Tetrafluoroborate*.—Addition of cyclohexa-1,3-diene (0·5 g., excess) to a solution of bis(bicyclo[2,2,1]hepta-2,5-diene)rhodium tetrafluoroborate (0·10 g., 0·27 mmole) in methylene chloride (10 ml.) gave after 20 min. at room temperature a yellow solution. The solid precipitated by diethyl ether was recrystallised from methylene chloride–diethyl ether to give pale yellow *crystals* of (XVII) 0·08 g., 83%), m.p. 126—128° (Found: C, 43·4; H, 4·2. $C_{13}H_{16}F_4BRh$ requires C, 43·2; H, 4·4%).

(d) (*Bicyclo*[2,2,1]*hepta*-2,5-*diene*)(*cyclohexa*-1,4-*diene*)-*rhodium Tetrafluoroborate*.—Similarly, cyclohexa-1,4-diene reacted during 40 hr. at room temperature to give yellow-brown *crystals of* (XVIII) (0·07 g., 79%), m.p. 151—153° (Found: C, 43·7; H, 4·2. $C_{13}H_{16}BF_4Rh$ requires C, 43·2; H, 4·4%).

Reactions of Bis(*bicyclo*[2,2,1]*hepta*-2,5-*diene*)*rhodium Tetrafluoroborate with σ-Donor Ligands*.—(a) *With benzonitrile*. Bis(bicyclo[2,2,1]hepta-2,5-diene)rhodium tetrafluoroborate (0·07 g., 0·19 mmole) was dissolved in benzonitrile (5 ml.) giving a bright yellow solution. Addition of diethyl ether gave yellow crystals of (XIX) *bis*(*benzonitrile*)(*bicyclo*[2,2,1]*hepta*-2,5-*diene*)*rhodium tetrafluoroborate* (0·073 g., 84%), m.p. 188—190° (Found: C, 52·0; H, 3·9; N, 5·9. $C_{21}H_{18}F_4BN_2Rh$ requires C, 51·6; H, 3·7; N, 5·7%). The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·23—2·61 (complex m, 10H, aromatic), 5·57 (q, 4H, CH=CH, J_{RhH} 2·0 Hz), 6·08 (broad s, 2H, CH), and 8·68 (s, 2H, CH_2). The infrared spectrum (Nujol) showed bands at 3080m, 2267s, 1599w, 1313m, 1182m, 1096s, 1053s, 767s, and 682s cm^{-1}.

(b) *With aniline*. An excess of aniline (1 g.) was added

borate with σ-Donor Ligands.—(a) *With benzonitrile*. Dissolution of bis(cyclo-octa-1,5-diene)rhodium tetrafluoroborate (0·05 g., 0·12 mmole) in benzonitrile (5 ml.) gave a bright yellow solution which on addition of diethyl ether gave fine yellow needles of (XXI) *bis*(*benzonitrile*)(*cyclo-octa*-1,5-*diene*)*rhodium tetrafluoroborate* (0·05 g., 78%), m.p. 144—146° (Found: C, 52·7; H, 4·6; H, 5·4. $C_{22}H_{22}N_2F_4BRh$ requires C, 52·4; H, 4·4; N, 5·6%). The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·21—2·56 (complex, m, 10H, aromatic), 5·52 (broad s, 4H, CH=CH), 7·49 (m, 4H, CH_2), and 8·10 (m, 4H, CH_2). The infrared spectrum (Nujol) showed bands at 2260s, 1596w, 1334s, 1269m, 1180m, 1092s, 1051s, 996m, 760s, 718m, and 680m cm^{-1}.

(b) *With dimethyl sulphoxide*. An excess of dimethyl sulphoxide (1 ml.) was added to a solution of bis(cyclo-octa-1,5-diene)rhodium tetrafluoroborate (0·06 g., 0·14 mmole) in methylene chloride (10 ml.). Addition of diethyl ether to the bright yellow solution gave, after a few hours, fine yellow needles of (XXII) *bis*(*dimethyl sulphoxide*)-(*cyclo-octa*-1,5-*diene*)*rhodium tetrafluoroborate* (0·04 g., 60%), m.p. 103—104° (Found: C, 31·3; H, 5·1; S, 13·7. $C_{12}H_{24}F_4BO_2RhS_2$ requires C, 31·7; H, 5·3; S, 14·1%). The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 6·02 (broad s, 4H, CH=CH), 7·20 (s, 12H, CH_3), 7·51 (m, 4H, CH_2), and 8·31 (m, 4H, CH_2). The infrared spectrum (nujol) showed bands at 1425m, 1324w, 1112s, 1051s, 993m, 972m, 956m, and 925m cm^{-1}.

Reactions of Bis(*bicyclo*[2,2,1]*hepta*-2,5-*diene*)*rhodium Tetrafluoroborate with Anionic Species*.—(a) *With sodium benzoate*. An excess of sodium benzoate (0·30 g.), was added to a solution of bis(bicyclo[2,2,1]hepta-2,5-diene)-rhodium tetrafluoroborate (0·05 g., 0·14 mmole) in methylene chloride. After 5 min. of stirring at room temperature, diethyl ether (60 ml.) was added; the solution was filtered and the solvent removed from the orange filtrate. The residue was recrystallised from methylene chloride–hexane to give orange crystals of (XXIII) di-μ-benzoato-bis(bicyclo[2,2,1]hepta-2,5-diene)-dirhodium (0·04 g., 90%), m.p. 243—245° (dec.) [Found: C, 52·4; H, 4·0%; *M*(isopiestic in $CHCl_3$) 623. $C_{28}H_{26}O_4Rh_2$ requires C, 52·2; H, 4·1%; *M*, 632]. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·28 (m, 4H, aromatic), 2·76 (m, 6H, aromatic), 5·78 (broad s, 12H, CH=CH and CH), and 8·64 (s, 4H, CH_2). The infrared spectrum (Nujol) showed bands at 1603s, 1564s, 1399s, 1303m, 1171m, 1024m, 713s, and 675m cm^{-1}.

(b) *With sodium acetate*. In an identical manner sodium acetate reacted to give orange crystals of (XXIV) di-μ-acetato-bis(bicyclohepta-2,5-diene)dirhodium (64%), m.p. 198—200° [Found: C, 42·7; H, 4·3%; *M*(isopiestic in $CHCl_3$) 510. $C_{18}H_{22}O_4Rh_2$ requires C, 42·5; H, 4·3%; *M*, 508]. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances

$C_{12}H_{13}Rh$ requires C, 55·4; H, 5·0%). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 4·80 (s, 5H, C_5H_5), 6·73 (m, 6H, CH=CH and CH), and 9·02 (s, 2H, CH_2).

Dimerisation of Bicyclo[2,2,1]*heptadiene*.—A solution of $[Rh(NBD)_2]^+BF_4^-$ (0·110 g., 0·3 mmole) and bicyclo[2,2,1]-heptadiene (8 ml., excess) in methylene chloride (10 ml.) was stirred (60 hr.) at room temperature. Pentane was added, the mixture filtered, and the solvent removed *in vacuo*. The residue was shown by v.p.c. and ^1H n.m.r. spectroscopy to consist of (XXVI) (65%), (XXVII) (10%), and (XXVIII) (25%).

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