Reactivity of Co-ordinated Ligands. Part XIX.[1] (π-Cyclopentadienyl)rhodium Complexes of some Cyclic Monoterpenoids

By **Brian F. G. Johnson, Jack Lewis,*** and **Douglas J. Yarrow,** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

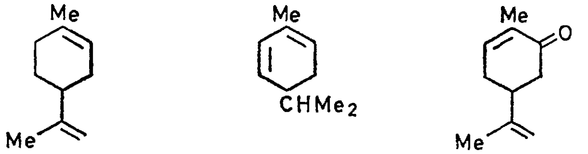
(π-Cyclopentadienyl)rhodium complexes of limonene, α-phellandrene, and carvone have been prepared by the reaction of $(C_2H_4)Rh_2Cl_2$ and the appropriate monoterpenoid followed by treatment with TlC_5H_5. The complexes undergo protonation in CF_3CO_2H to yield monocationic π-allylic species. The mechanism of proton addition is discussed and compared with that previously proposed for $C_6H_8Rh(\pi\text{-}C_5H_5)$.

We have been able to demonstrate previously[2] that for the complex (cyclohexa-1,3-diene)(π-cyclopentadienyl)rhodium in acid media proton exchange occurred at the *endo*-methylene position of cyclohexadiene *via* interaction with the metal. Further proof for *endo* addition of H^+ to co-ordinated hexadiene has been offered by Whitesides and Arhart[3] from studies of (cyclohexa-1,3-diene)(tricarbonyl)iron in acid. In both cases although ^{1}H n.m.r. spectroscopic data was fully compatible with these conclusions the main evidence came from reactivity considerations and depended on the assumption that attack by Ph_3C^+ always occurred on the *exo* side of the ring system and that attack by H^- also always occurs *exo*. This is not necessarily a correct assumption.[4] In this paper we report observations on the protonation of some complexes of (π-cyclopentadienyl)rhodium with limonene, α-phellandrene, and carvone which indicate that specific *endo* protonation occurs. These molecules were chosen for these studies because they permitted a clear differentiation between the *endo* and *exo* faces of the co-ordinated diene.

$$(C_2H_4)_2Rh_2Cl_2 \xrightarrow{(i)} (\text{diene})_2Rh_2Cl_2 \xrightarrow{(ii)} (\text{diene})Rh(\pi\text{-}C_5H_5)$$

diene = (I), limonene; (II), α-phellandrene; (III), carvone

(i), Reaction with terpenoid; (ii), reaction with TlC_5H_5

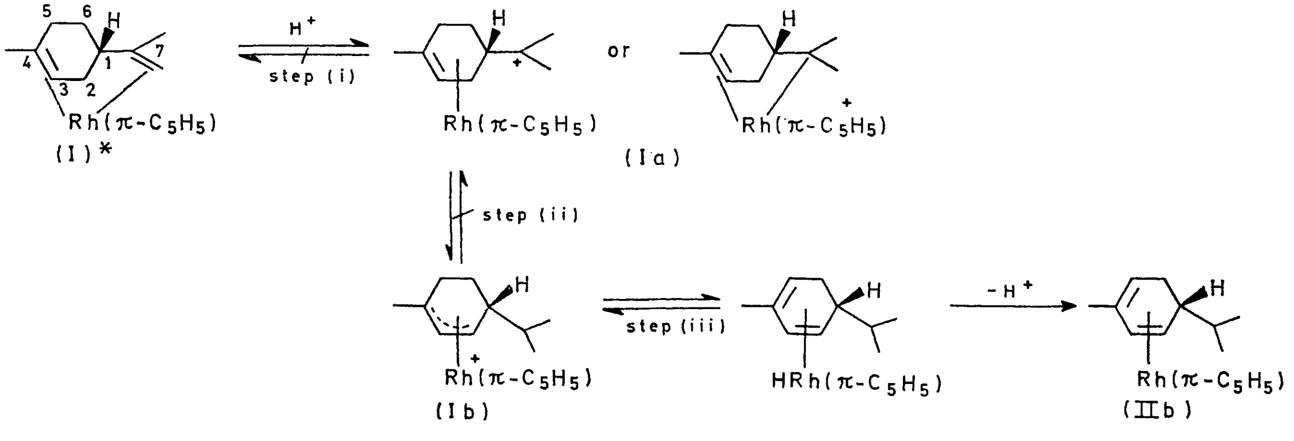


Limonene α-Phellandrene Carvone

Scheme 1 Preparation of complexes (I)—(III)

Preparation of Complexes.—The (π-cyclopentadienyl)rhodium complexes employed in the work were prepared by the route shown in Scheme 1. All were obtained as orange oils and were characterised from their ^{1}H n.m.r., mass spectroscopic, and analytical data.

In the reaction with α-phellandrene two isomeric forms of complex (II) were obtained; these were characterised, on the basis of their n.m.r. spectrum, as the *exo* and *endo* forms (IIa) (^{1}H, τ 8·34) and (IIb) (^{1}H, τ *ca.* 8·7). The amount of (IIb) (which we consider to be the *endo* derivative) produced was small; an observation consistent with the view that co-ordination of $(\pi\text{-}C_5H_5)Rh$ is expected to occur preferentially on the least sterically crowded face of the oligo-olefin.



Scheme 2 The protonation of complex (I)

* In this Scheme, and throughout the paper, the numbering of the menthane system does not conform to the I.U.P.A.C. system.

---

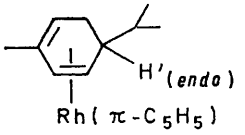
[1] Part XVIII, R. R. Schrock, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1974, 951.

[2] B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J.C.S. Dalton*, 1972, 2084.

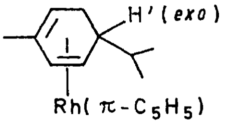
[3] T. M. Whitesides and R. W. Arhart, *J. Amer. Chem. Soc.*, 1971, **93**, 5296.

[4] A. J. Birch, K. B. Chamberlain, M. A. Haas, and D. J. Thompson, *J.C.S. Perkin I*, 1973, 1882.

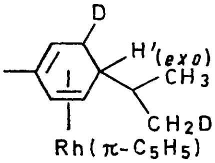
Protonation of the Complexes.—(a) *Limonene complex* (I). The ^{1}H n.m.r. spectrum of complex (I) was in agreement with the structure shown in Scheme 2. The n.m.r. spectra show radical changes on dissolution of the complex in trifluoroacetic acid. Thus, in an excess of CF_3CO_2H, under ambient conditions, the following features were observed: a multiplet at τ 4·66 (2H), a multiplet at τ 7·48 (2H), a singlet at τ 7·78 (3H), a multiplet at τ 8·78 (1H), a multiplet at τ 8·96 (1H), a doublet at τ 9·06 (6H), and a multiplet at τ 13·9 (2H). In addition a π-C_5H_5 resonance was observed as a singlet at τ 4·26. A similar spectrum was obtained for complex (I) in CF_3CO_2D except that the signal at τ 13·9 which initially corresponded to two protons decreased in intensity with time until after 30 min under ambient conditions, it had completely disappeared. In addition, the multiplet at τ 4·66 resolved into a doublet and the signal at τ 7·48 sharpened. Neutralisation of the solution of (I) in CF_3CO_2H with aqueous $NaHCO_3$ produced an orange oil which was readily identified from its spectroscopic properties, and by comparison with an authentic sample as complex (IIb). Neutralisation of the corresponding solution in CF_3CO_2D gave [^{2}H](IIb) on the basis of its mass spectrum. The ^{1}H n.m.r. of this derivative also indicated the incorporation of two deuterium atoms although a precise determination of the relative intensities was impossible because of the close proximity of neighbouring upfield resonances.



(IIa)



(IIb)

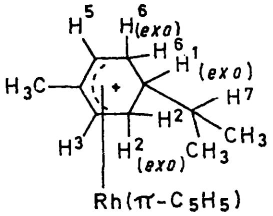


[$^{2}H_2$](IIb)

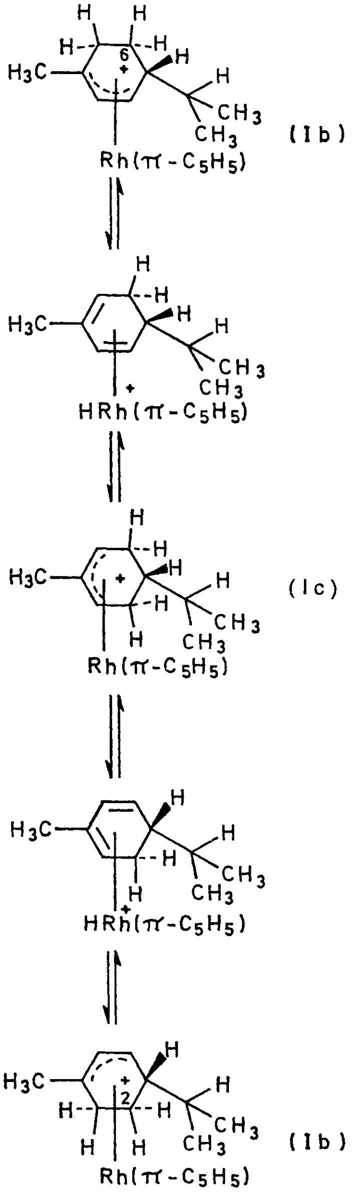
These observations were rationalised according to Schemes 2 and 3 and the above time-averaged spectrum assigned in terms of the symmetrical cationic complex (Ic) as follows: τ 4·66 (m, $H^3 + H^5$), τ 7·48 (m, $H^2{}_{exo} + H^6{}_{exo}$), τ 7·78 (s, CH_3), τ 8·78 (m, $H^1{}_{exo}$), τ 8·96 (m, H^7), and τ 9·06 [d, $C(CH_3)_2$; $J(CH_3$–$H^7)$ 5·8 Hz]. The resonance at τ 13·9 is assigned to the protons $H^2{}_{endo}$ and $H^6{}_{endo}$ which we conclude are in rapid equilibrium with a rhodium hydride species (see Scheme 3). It is very similar in appearance to its analogue in the spectrum of protonated (cyclohexa-1,3-diene)(π-cyclopentadienyl)-rhodium.[2]

The mechanism postulated in Scheme 2 involves the following steps:

(i) This involves the protonation of complex (I) at the exocyclic co-ordinated double bond, although it is not possible to decide whether or not this initial proton addition goes *via* the metal. By this means the cationic intermediate (Ia) is produced and which may be stabilised by σ-donation from the metal as has been previously observed in other cationic π-cyclopentadienylrhodium



(Ib)



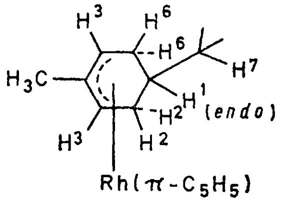
SCHEME 3 Proton exchange in cation (Ib)

complexes.[5] The isolation of [$^2H_2$](IIb), which apparently contains D in the $C(CH_3)$ position, is consistent with this view although definitive proof is lacking for the reasons stated above.

(ii) In the second step the transfer of a hydrogen from the ring system to carbon atom C^7 is envisaged. Since the configuration about carbon atom C^1 is maintained [because neutralisation leads to complex (IIb)] this transfer most probably involves a 1,3-hydrogen shift of H^2_{endo} (or H^6_{endo}) *via* interaction with the metal to form the cationic π-allyl complex (Ib) although we cannot exclude the alternative possibility of a $H^1 \longrightarrow H^7$ shift followed by an H^2_{exo} (or H^6_{exo}) shift to C^1.

(iii) The species (Ib) generated in step (ii) is similar to that obtained in the protonation of (1,3-cyclohexadiene)(π-cyclopentadienyl)rhodium [2] except that whereas the cyclohexadiene species has three *endo* protons available for exchange *via* the metal, cation (Ib) has only two (H^5_{endo}, H^6_{endo}). Thus the ^1H n.m.r. spectrum may be interpreted on the basis of the rapidly equilibrating system depicted in detail in Scheme 3. This Scheme indicates that the two *endo*-methylene protons of the transient π-allylic species are equilibrated by a series of 1,4-hydrogen transfers across the six-membered ring *via* protonated metal intermediates. This phenomenon accounts for the high-field signal at τ 13·9 of relative intensity equivalent to two protons. Tautomerism of the π-allyl system around the complete ring system, as observed with $C_6H_8Rh(\pi\text{-}C_5H_5)$ in acid, is inhibited by the *endo*-isopropyl substituent at C^1 and the inability of the resultant *exo* proton (H^1) to transfer to the metal. This tautomerism produces a ' windscreen-wiper ' effect within the molecular system. The appearance of the singlet methyl resonance attributed to the methyl group on C^4 indicates that the C^4 centre is never protonated. Furthermore the degeneracy of the methyl resonances of the isopropyl group indicates that C^1 is not an asymmetric centre and infers that a plane of symmetry is generated through the ring system and is consistent with our proposed mechanism. The observation that the high-field signal decreases in intensity in CF_3CO_2D may be interpreted in terms of D^+ exchange between the solvent and the metal hydride intermediate.

(b) *The α-phellandrene complex* (II). As stated above two isomers of this complex were obtained. The two isomers could not be separated but the amount of complex (IIb) present was small (*ca.* 5%). In contrast to isomer (IIb) (*vide supra*), isomer (IIa) has the proton H^1 in the *endo* conformation and hence is available for transfer to the metal centre. In agreement isomer (IIa) exhibits different behaviour on protonation to that of isomer (IIb). Thus, protonation of the mixture of isomers (IIa) and (IIb) in CF_3CO_2H produced *predominantly* a species which exhibited the following ^1H n.m.r. spectrum: τ 4·32 (s, π-C_5H_5), τ 6·28 (m, H^2_{exo} + H^6_{exo}), τ 6·74 (m, H^3_{exo} + H^5_{exo}), τ 8·46 (d, CH_3), τ 8·80 (m, H^7), τ 8·88 [d, $C(CH_3)_2$; $J(CH_3\text{-}H^7)$ 7 Hz], τ 11·7 (m, H^2_{endo} and H^6_{endo}), and τ 12·5 (m, H^1_{endo}) [*i.e.* corresponding to the protonation of complex (IIa)]:



This spectrum may be interpreted in terms of the equilibrating system given in Scheme 4 which is analogous to the mechanism of proton exchange established for $C_6H_8Rh(\pi\text{-}C_5H_5)$.[2] Of particular interest is the observation of two high field resonances as two multiplets of relative intensities 2 : 1. This is in accord with the illustrated pattern of intramolecular 1,4-hydrogen shifts equilibrating the metal–hydrogen system with either one *endo* proton (H^1) between the two carbon atoms C^1 and C^4 or the two *endo* protons H^2 and H^6 through the environments $C^2 \rightleftharpoons C^5$ and $C^3 \rightleftharpoons C^6$. The observation that the C^4-methyl resonance is split into a doublet confirms that carbon atom C^4 is involved in the equilibration process ($C^1 \rightleftharpoons C^4$) and is in contrast to its appearance as a singlet in the protonation of complex (I) which is known to involve species (IIb). In CF_3CO_2D this doublet resonance collapses to a singlet and the signals due to H^2, H^6, H^3, and H^5 permanently bound to the ring are resolved into doublets $J(H^2,H^3) = J(H^5,H^6) = 4{\cdot}5$ Hz. The resonances at high field disappeared after 5 min indicating that exchange with the solvent had occurred.

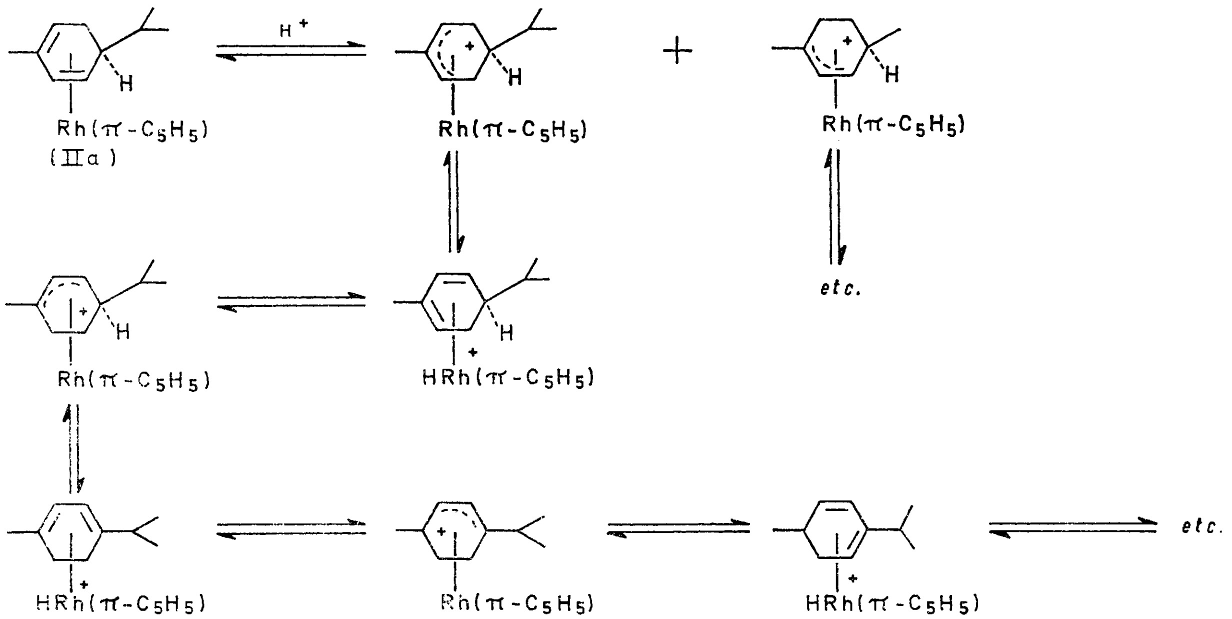
The behaviour of (IIb) in $CD_2Cl_2\text{–}CF_3CO_2H$ at low temperatures was also examined. On cooling the acid solution all resonances broadened until at −35 °C the absorption at τ 11·7 due to two protons, was no longer observed. At −40 °C the signal at τ 12·5 collapsed and the only observable peaks in the spectrum were those ascribed to the resonances of the π-cyclopentadienyl, the isopropyl side-chain, and the C^4-methyl hydrogens. No further change in the spectrum occurred even at −70 °C. These results indicate that the equilibrations $C^2 \rightleftharpoons C^5$ and $C^3 \rightleftharpoons C^6$ take place at a different rate to the equilibration $C^1 \rightleftharpoons C^4$ and that the most labile proton is that associated with the substituted carbon centres C^1 and C^4.

Neutralisation of the acid solution generated an orange oil. The molecular formula of this product corresponded to $C_{10}H_{16}Rh(\pi\text{-}C_5H_5)$, from elemental analysis and mass spectrometry. The ^1H n.m.r. spectrum revealed three separate resonances ascribed to cyclopentadienyl ring protons in the ratio 2 : 1 : 1, indicating that three isomers of $C_{10}H_{16}Rh(\pi\text{-}C_5H_5)$ had been formed. Comparison of the spectrum with that of pure (IIa) revealed that this α-phellandrene complex had been produced as one of the minor products. The proposed mechanism leads to the prediction that

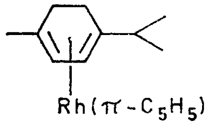
---

[5] J. Evans, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1972, 2668.

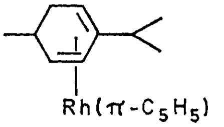
deprotonation will yield a mixture of the three isomers (IIa), (IIc), and (IId). The n.m.r. spectrum is largely consistent with this mixture of isomers and the observation of a singlet methyl resonance at τ 8·52 of the same intensity as the C^4-methyl resonance at τ 8·06 in (IIa) is assigned to the vinylic absorption of the α-terpinene complex (IIc). The expected doublet resonance of the C^4-methyl group of (IId) is not identifiable as it is degenerate with the other resonances at higher field. These results indicate that the isomers (IId) : (IIc) : (IIb) are formed in the ratio 2 : 1 : 1. The mass spectrum of the oil recovered on neutralisation of the CF_3CO_2D solution indicated that the incorporation of two deuterium atoms in the complexes had occurred, in agreement with the proposed mechanism of proton addition and solvent exchange.



Scheme 4 The protonation of complex (IIa)

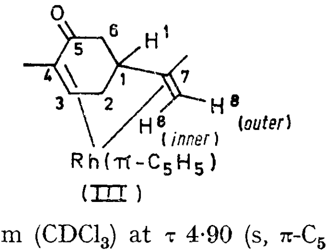


(IIc)



(IId)

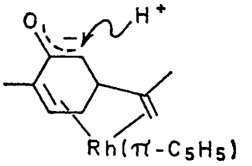
The Carvone Complex (III).—(a) *Characterisation.* The carvone complex (III) showed resonances in the n.m.r. spectrum ($CDCl_3$) at τ 4·90 (s, π-C_5H_5), 5·30 (m, H^3), 6·68 (d, H^8 outer, J_{gem} 2 Hz), 7·20 [dt, A part of AB system, H^2_{endo}, J_{gem} 14 Hz, $J(H^2_{endo}, H^3) = J(H^2_{endo}, H^1) = 4{\cdot}5$ Hz], 7·58 (d, B part of AB system, J_{gem} 14 Hz), 7·76 (d, H^8 inner, J_{gem} 2 Hz), 8·08 (m, H^1), 8·32 (s, CH_3), 8·42 [dd, a part of AB system, H^6_{endo}, J_{gem} 18 Hz, $J(H^6_{endo}, H^1)$ 3 Hz, 8·58 (s, CH_3), 8·70 [dd, B part of AB system, H^6_{exo}, J_{gem} 18 Hz, $J(H^6_{exo}, H^1)$ 3 Hz]. The contact shifts produced in the n.m.r. of the complex on treatment with small amounts of the lanthanide shift reagent, $Pr(fod)_3$, confirm the assignment of the spectrum given above. In particular the large shift induced in the higher field AB system demonstrates that these resonances arise from the α-methylene group, and the greater shift of the methyl resonance observed at τ 8·32 over that at τ 8·58 allows the former resonance to be ascribed to the hydrogens of the β-methyl group. The assignment of the lower-field components of the AB methylene systems to the *endo* hydrogens is based on the relative chemical shifts of the methylene protons of C_6H_8Rh-(π-C_5H_5) and its *endo*-dideuterio-derivative described in a previous paper. Also it has been observed that the *endo* proton H^1 of the α-phellandrene complex (IIb) resonates at lower field than the corresponding proton in the isomeric complex (I) where H^1 is constrained in an *exo* environment.



(III)

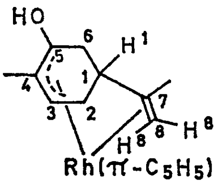
(b) *Reaction with base.* The n.m.r. spectrum of (III) in CD_3ONa–CD_3OD was monitored over a period of hours and the signal at highest field was observed to decrease in intensity until after 24 h it could no longer be detected. The rest of the spectrum was unchanged apart from the collapse of the resonance at τ 8·42 into a doublet. The mass spectrum of the complex recovered from this basic solution revealed mono-deuterium incorporation and the n.m.r. spectrum indicated specific incorporation at H^6_{exo}. The reaction presumably proceeds by proton abstraction to give the enolate anion

(IV) followed by addition of D^+ to the least hindered side of the molecule. Treatment of tricarbonylcycloheptatrieneiron with CH_3O^- in CD_3OD has been reported[6] to yield *exo*-tricarbonyl[7-$^2H_1$]cycloheptatrieneiron in a similar fashion.



(IV)

(c) *Protonation studies.* Addition of 65% aqueous HPF_6 to an ethereal solution of (III) precipitated a yellow salt. The n.m.r. spectrum of this salt (liq. SO_2) exhibited resonances at τ 3·88 (s, OH), 4·50 (s, π-C_5H_5), 4·61 (m, H^3), 5·46 (d, H^8 outer, J_{gem} 1 Hz), 6·40 (d, H^8 inner, J_{gem} 1 Hz), 7·26 [dt, A part of AB system, H^2_{endo}, J_{gem} 14 Hz, $J(H^2_{endo}, H^3) = J(H^2_{endo}, H^1) = 4{\cdot}5$ Hz], 7·7 (m, $H^2_{exo} + H^1$), 7·96 (s, CH_3), 8·04 (s, CH_3), 8·20 (d, A part of AB system, H^6_{endo}, J_{gem} 16 Hz), 8·42 (d, B part of AB system, H^6_{exo}, J_{gem} 16 Hz), indicating protonation had occurred at the ketonic oxygen to generate the illustrated π-allyl olefin bonded cation (V). The formation of an OH group was confirmed by a band at 3490 cm^{-1} in the i.r. spectrum.



(V)

The n.m.r. spectrum of (III) in CF_3CO_2H exhibited a spectrum similar to that described above. It is interesting to note that from a comparison of this spectrum of (V) with that of (Ib) in the same solvent it is apparent that co-ordination of the exocyclic double bond in complex (V) produces a co-ordinately saturated system which does not undergo hydrogen migration to the metal.

EXPERIMENTAL

Preparation of Monoterpenoid Complexes (I)—(III).—The complexes were prepared by the general method described previously for the synthesis of $C_6H_8Rh(\pi$-$C_5H_5)$.[2] However complexes (I) and (II) were purified by chromatography on Alumina ' O.' Pentane eluted an orange band in both cases, and evaporation *in vacuo* yielded the products as orange oils.

π-Cyclopentadienyl(limonene)rhodium, (I) (Found: C, 59·6; H, 6·95. $C_{15}H_{21}Rh$ requires C, 59·21; H, 6·91%). The mass spectrum showed peaks at *m/e* 304(*P*) and 233[$Rh(C_5H_5)_2$].

π-Cyclopentadienyl(α-phellandrene)rhodium (IIa) *and* (IIb) (Found: C, 59·85; H, 7·0. $C_{15}H_{12}Rh$ requires C, 59·21; H, 6·91%). The mass spectrum showed peaks at *m/e* 304(*P*), 289($P - CH_3$), 261($P - C_3H_7$), 259($P - C_3H_9$), and 233[$Rh(C_5H_5)_2$].

Carvone(π-cyclopentadienyl)rhodium (III) was purified by chromatography on silica with toluene as eluant. The solvent eluted an orange band which on evaporation *in vacuo* yielded the *product* as orange crystals (Found: C, 56·35; H, 5·65. $C_{15}H_{19}ORh$ requires C, 56·61; H, 5·97%), m.p. 179—181 °C, ν_{CO} (Nujol) 1664 cm^{-1}. The mass spectrum showed peaks at *m/e* 318(*P*), 303($P - CH_3$), 289($P - C_2H_5$), and 232[$Rh(C_5H_5)_2$].

Protonation of Complexes (I)—(III).—The complexes were protonated by dissolution in CF_3CO_2H. Low temperature n.m.r. spectra were obtained by dissolving the appropriate complex in CD_2Cl_2 and adding a slight molar excess of CF_3CO_2H. The complex (III) was also protonated by adding 65% aqueous HPF_6 to an ethereal solution of (III). The yellow precipitate that formed was filtered and washed with ether to give the *product*, (V), in quantitative yield (Found: C, 38·6; H, 4·3. $C_{15}H_{20}F_6ORh$ requires C, 38·80; H, 4·31%), ν_{OH} (Nujol) 3490 cm^{-1}.

Deprotonation of Acid Solutions.—In general the acid solution was diluted with H_2O or D_2O as appropriate, and $NaHCO_3$ added until neutral. The solution was then extracted with ether. The ether was dried ($MgSO_4$) and evaporated *in vacuo* and the residue chromatographed as described above.

From (I) in CF_3CO_2H was recovered an orange oil (Found: C, 59·35; H, 6·95. $C_{15}H_{21}Rh$ requires C, 59·21; H, 6·91%), *M* (mass spectrum) 304.

From (II) in CF_3CO_2H was recovered an orange oil (Found: C, 59·65; H, 7·1. $C_{15}H_{21}Rh$ requires C, 59·21; H, 6·91%), *M* (mass spectrum) 304.

From (III) in CF_3CO_2H were recovered orange crystals, characterised by m.p., n.m.r., i.r., and mass spectrum and shown to be identical to the original material (III).

We thank the S.R.C. for a Fellowship (D. J. Y.) and Johnson, Matthey and Co. Ltd. for their generous loan of rhodium salts.

[3/254 *Received, 5th February,* 1973]

---

[6] H. Maltz and B. A. Kelly, *Chem. Comm.*, 1971, 1390.