Protonation of η-Cyclo-octa-1,5-diene(η-cyclopentadienyl)-cobalt(I), -rhodium(I), and -iridium(I)

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The protonation of the title complexes is reported. The cobalt system yields two, and the rhodium three, cationic species. In [$^2H_1$]trifluoroacetic acid, deuteriation of both rings in the rhodium complex occurs. Protonation of the iridium complex gives a cationic metal hydride in which the eight-membered ring has isomerised to the 1,3-diene; the reaction is readily reversed with weak bases. Labelling experiments have been used to investigate the mechanism of these processes. η-Cyclopentadienyl(η-norbornadiene)rhodium also undergoes protonation in CF_3CO_2H, to form a σ,η-olefin complex.

AN investigation into the reactivity of complexes of cyclic olefins with cobalt(I), rhodium(I), and iridium(I) has demonstrated that these complexes are nucleophilic.[1-4] Stable cationic species have been obtained previously by protonation of the non-conjugated diene complexes of limonene[3] and cyclo-octa-1,5-diene with cyclopentadienylrhodium(I).[5] We report a study of the protonation of cyclo-octa-1,5-diene(cyclopentadienyl)-cobalt(I),rhodium(I), and -iridium(I).

RESULTS

Protonation of Cyclo-octadiene Complexes.—(a) [Co(η-C_5H_5)(η-C_8H_{12})]. Protonation of η-cyclo-octa-1,5-diene(η-cyclopentadienyl)cobalt(I) (1) was attempted by several means but in each case rapid decomposition occurred. However, the ^{1}H n.m.r. spectrum of a solution of (1) in trifluoroacetic acid indicated the formation of two cationic species. Initially a cation, which exhibited a cyclopentadienyl singlet at τ 4.4, was produced; this was slowly converted into a second species which exhibited a singlet at τ 4.2. All the other peaks present were broad and the spectrum could not readily be assigned.

(b) [Rh(η-C_5H_5)(η-C_8H_{12})]. η-Cyclo-octa-1,5-diene(η-cyclopentadienyl)rhodium(I) (2) formed a yellow solution in CF_3CO_2H which is stable over long periods in the absence of air. The ^{1}H n.m.r. spectrum of a freshly prepared solution is listed in the Table. Apart from the cyclopentadienyl singlet, all the resonances were broad suggesting that the protons of the eight-membered ring are involved in some exchange process. This spectrum changed with time and the formation of a second cation (4) was indicated ($t_{\frac{1}{2}}$ *ca.* 40 min at 29.5 °C). The ^{1}H n.m.r. of this second species was well defined (Table) and if any exchange process is occurring it must be slow. Cation (4) appeared to be in equilibrium with a third cation (5) (*ca.* 10%) which, on the basis of its ^{1}H n.m.r. spectrum (Table), was considered to be an η-cyclo-octenyl complex. The absence of resonances in the τ 10—30 region confirmed that no stable Rh–H species were produced during the course of this reaction. Addition of aqueous HPF_6 to a diethyl ether solution of (2) caused slow precipitation of an unstable yellow salt. The ^{1}H n.m.r. spectrum of this salt in [$^2H_6$]acetone indicated the presence of a co-ordinated η-allylic group (Table).

These observations are best explained as follows. Species (2) undergoes protonation of a co-ordinated olefinic bond; this is followed by isomerisation of the C_8H_{13} moiety (Scheme 1) by a proton-shift mechanism first to (4) and then to (5). The ^{1}H n.m.r. spectrum of compound (4) allows it to be identified as the 1-σ,3—4-η-cyclo-octenyl(cyclopentadienyl)rhodium cation. A further prototropic shift yields cation (5). The spectra observed in the cobalt system might be taken to be consistent with structures (3) and (4). Possibly, protonation of (1) follows a similar path but the cations formed are less stable. Treatment of cation (5) with triethylamine regenerated (2) in *ca.* 30% yield.

Proton-decoupled ^{13}C n.m.r. spectra were obtained for

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

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

[3] B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J.C.S. Dalton*, 1974, 1054.

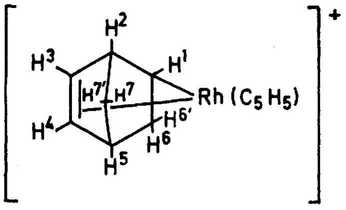
[4] J. Evans, B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J.C.S. Dalton*, 1974, 2375.

[5] J. Evans, B. F. G. Johnson, and J. Lewis, *Chem. Comm.*, 1971, 1252.

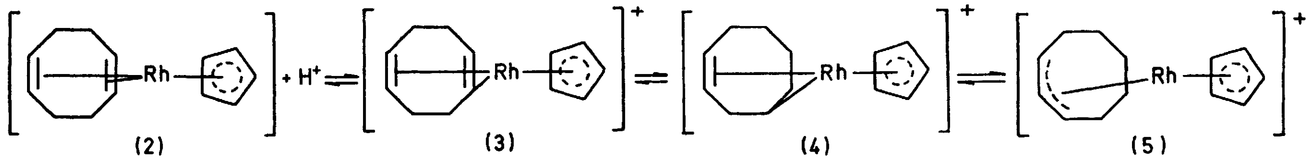
cations (3) and (4). These data are consistent with the structures suggested (Scheme 1). Complex (3) in CF_3CO_2H exhibited peaks at 5 °C at δ 91.9 (C_5H_5), 84.0 (olefinic carbon, *J* 15 Hz), 75.5 (olefinic carbon), 31.8 (multiplet of methylene carbons), and 26.4 p.p.m. (σ-bonded carbon *J* 28 Hz), whilst (4) in CF_3CO_2H at 35 °C gave peaks at δ 87.0 (*J* 5 Hz), 80.3 (*J* 15 Hz), and 23—31 p.p.m. (sp^3 carbon atoms). The isomerisation (3) $\rightleftharpoons$ (4) $\rightleftharpoons$ (5) was also followed in $[^2H]$trifluoroacetic acid and occurred at a slower rate. The cyclopentadienyl singlet of (3) was rapidly reduced to less than 10% of its initial intensity, but then did not alter significantly over long periods. The ^1H resonances arising from the eight-membered ring were broader than those observed for (3) in the $[^1H]$acid and the signal at τ 7.3 was considerably reduced in intensity. By the time complex (4) had become the major species, random deuteriation of the C_8 ring was evident. After several days, *ca.* 75% deuteriation had occurred.

Hydrogen-1 n.m.r. data

Complex	Proton	Chemical shift (τ)
(3) in CF_3CO_2H	2 vinyl	5.1 (br)
	$11CH_2$ + σ-bonded	7.1—7.9 (m)
	CH C_5H_5	4.21 (s)
(4) in CF_3CO_2H	2 vinyl	5.6 (br)
	$11CH_2$ + σ-bonded	7.2 (m)
	CH	7.9—8.4 (m)
	C_5H_5	4.10 (s)
(5) in $(CD_3)_2CO$	allyl	4.1—4.5 (m)
	CH_2	7.6—8.2 (m)
		8.5 (m)
	C_5H_5	3.97 (s)
(7) in CF_3CO_2H	2 inner diene	4.6 (m)
	2 outer diene	5.4 (m)
	8 CH_2	7.3—7.7 (m)
	Ir–H	21.7 (s, br)
	C_5H_5	4.10 (s)
(11) in CF_3CO_2D	2 inner diene	4.64 (asym. d, *J* 9 Hz)
	2 outer diene	5.44 (asym. d, *J* 9 Hz)
	4 CH_2	7.5 (s)
		7.7 (s)
	Ir–H	21.7 (s, br)
	C_5H_5	4.10 (s)
(10) in $CDCl_3$	4 vinyl	6.24 (s)
	4 CH_2	8.26 (s)
	C_5H_5	4.86 (s)
(13) in CF_3CO_2H	H^4	4.44 (m)
	H^3 + H^5	5.16 (m)
	H^1 or H^6	6.07 (asym, d, *J* 8 Hz)
	$H^{6'}$	6.35 (m)
	H^2	6.5 (m)
	H^1 or H^6	7.00 (asym. d, *J* 13 Hz)
	H^7 + $H^{7'}$	8.84 (m)
	C_5H_5	4.20 (s)



(13) in CF_3CO_2H



Scheme 1

The reactions of (2) in CF_3CO_2H are obviously complex. The equilibria illustrated (Scheme 1) do not fully explain the deuteriation results. For deuteriation of the olefinic protons to occur, exchange with solvent protons must occur on both sides of the ring (*exo* and *endo*).

(c) $[Ir(\eta\text{-}C_5H_5)(\eta\text{-}C_8H_{12})]$. η-Cyclo-octa-1,5-diene(η-cyclopentadienyl)iridium(I) (6) readily formed a colourless solution in CF_3CO_2H and a white stable salt $[Ir(\eta\text{-}C_5H_5)(\eta\text{-}C_8H_{12})H][PF_6]$ on addition of aqueous HPF_6 to a solution in diethyl ether. The ^1H n.m.r. spectrum of this salt in liquid sulphur dioxide was the same as that observed for (6) in CF_3CO_2H (Table). The formation of an Ir–H species was apparent from the high-field singlet at τ 21.7 (br); the remainder of the spectrum was assigned, on the basis of double-irradiation experiments, to the cation (7) (Scheme 2). Both acetone and acetonitrile were sufficiently basic to deprotonate (7), reforming (6). The preference of the $[Ir(\eta\text{-}C_5H_5)H]^+$ unit for bonding to conjugated rather than chelating diene units has previously been noted for both the cyclo-octatetraene [4] and cyclo-octa-1,3,5-triene complexes.[2]

This rapid and reversible protonation was also followed in CF_3CO_2D; these results are summarised in Scheme 2. The only difference between a spectrum of (6) in CD_3CO_2H and that of (7) was the absence of the high-field resonance. Thus the isomerisation of the octadiene ligand must occur without the incorporation of D^+. This was also demonstrated for the reverse reaction. On addition of $(CD_3)_2CO$ to a solution of the cation (8) in $[^2H]$trifluoroacetic acid complex (6) was quantitatively regenerated. However, over much longer periods of time, the incorporation of D^+ occurred. The ^1H n.m.r. spectrum of a solution of (8) in $[^2H]$trifluoroacetic acid slowly changed with time, until after 133 h the relative intensity of the methylene protons had decreased from 8 to 4. The resonance due to the outer diene protons simplified from a multiplet to half an AB quartet, indicating loss of at least one adjacent methylene proton. Both η-cyclohexa-1,3-diene(η-cyclopentadienyl)-rhodium(I) [1,6] and -iridium(I) [1] undergo exchange of their *endo*-methylene protons in $[^2H]$trifluoroacetic acid. The same mechanism is considered to operate here. The D atom bonded to the metal is transferred to the C_8H_{12} ligand, yielding an η-allyl complex. The cyclo-octadiene ligand can then be regenerated by transfer of H^+ or D^+ from one of two carbon atoms, either regenerating (8) or leading to deuterium substitution. Eventually this leads to exchange of the four *endo*-protons. The $[^2H_5]$cation observed is considered to be (9). The compound (9) was deprotonated to yield $[^2H_4]$cyclopentadienylcyclo-octa-1,5-dieneiridium(I). The ^1H n.m.r. spectrum of this complex (Table) consisted of three singlets of

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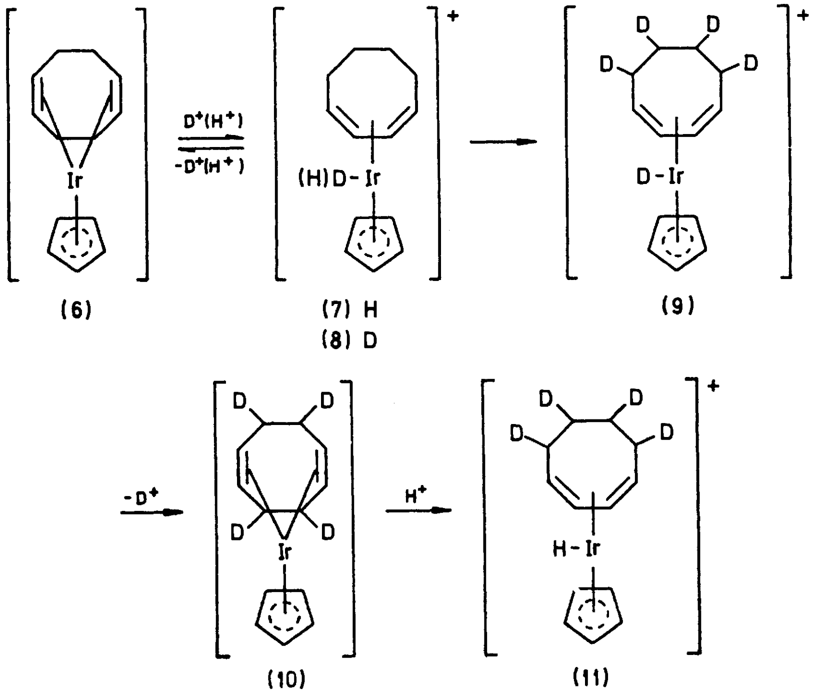
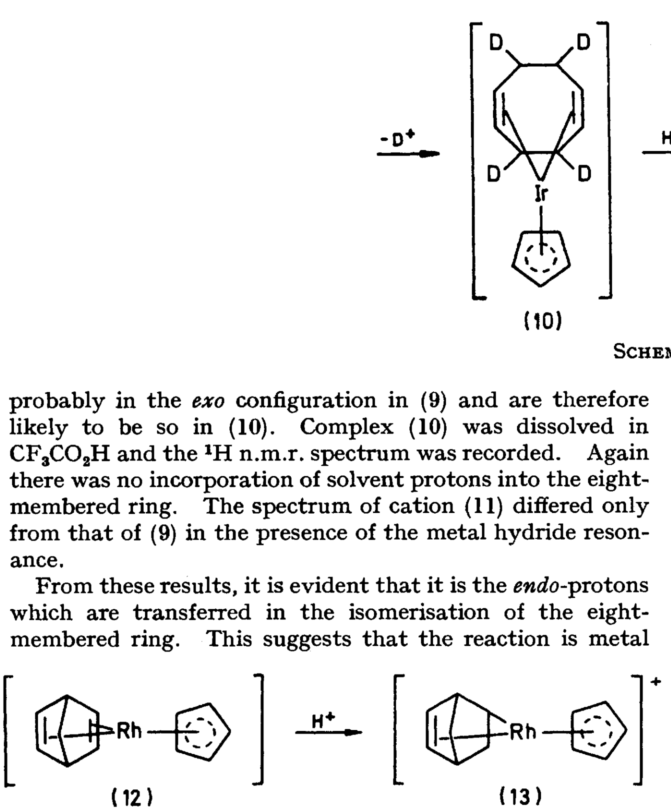
[6] B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J.C.S. Chem. Comm.*, 1972, 235.

relative intensity 5 : 4 : 4. Since the cyclopentadienyl and vinyl protons are still present, the four deuterium atoms must have been incorporated in methylene positions. The magnetic equivalence of the residual four methylene protons indicates that they are in the same chemical environment, *i.e.* on the same side of the ring. These protons are probably in the *exo* configuration in (9) and are therefore likely to be so in (10). Complex (10) was dissolved in CF$_3$CO$_2$H and the ^{1}H n.m.r. spectrum was recorded. Again there was no incorporation of solvent protons into the eight-membered ring. The spectrum of cation (11) differed only from that of (9) in the presence of the metal hydride resonance.



Scheme 2

From these results, it is evident that it is the *endo*-protons which are transferred in the isomerisation of the eight-membered ring. This suggests that the reaction is metal assisted in a manner which distinguishes between the protons of the ring and the incoming proton. The following mechanism is therefore proposed. First the incoming H$^+$ interacts with the metal and brings about a 1,3-suprafacial hydrogen shift to give a cyclo-octa-1,4-diene species. A second suprafacial shift during the formation of the metal-hydride bond results in the η-cyclo-octa-1,3-diene(cyclopentadienyl)hydrido-cation (7).



Scheme 3

Protonation of [Rh(η-C$_5$H$_5$)(nbd)] (12).—By protonation of a more rigid ligand than cyclo-octa-1,5-diene, *i.e.* norbornadiene (nbd), it was hoped to obtain some simplification of the exchange processes involved in the [Rh(η-C$_5$H$_5$)(η-C$_8$H$_{12}$)]–CF$_3$CO$_2$H system. A stable protonated species (13) (Scheme 3) was observed in neat CF$_3$CO$_2$H. The ^{1}H n.m.r. spectrum (Table) of this solution indicated that H$^+$ addition to the co-ordinated olefinic bond had occurred. No change in the spectrum of this solution was observed over a period of 24 h. In the ^{1}H n.m.r. spectrum of (12) in [^{2}H$_2$]trifluoroacetic acid, the cyclopentadienyl singlet integrated for *ca.* 1 proton and a rapid exchange of the protons of the cyclopentadienyl ring must have occurred. Other differences in this spectrum [compared to that of (13)] indicated that one deuterium atom had been specifically introduced into the bicyclic ligand. It is interesting that both (2) and (12) undergo exchange of the cyclopentadienyl ring protons in [^{2}H]acid. The presence of conjugated double bonds in a complex prevents this, even if the metal is not co-ordinated to them in the neutral complex, *e.g.* η-cyclo-octa-1,3,5-triene(η-cyclopentadienyl)rhodium(I).

Other Reactions of [Rh(η-C$_5$H$_5$)(η-C$_8$H$_{12}$)].—(a) *With the* [OEt$_3$]$^+$ *cation.* Complex (2) reacts readily with trityl tetrafluoroborate. Trityl substitution on the cyclopentadienyl ring occurs with the first mole of the reagent and hydride abstraction from the eight-membered ring with the second, giving the cyclo-octa-2,5-dienium(tritylcyclopentadienyl)rhodium cation.[7] Triethyloxonium tetrafluoroborate has previously been used as a hydride-abstracting reagent to convert tricarbonyl(cycloheptatriene)chromium into the tropylium salt.[8] However, no reaction occurred on treating (2) with the oxonium salt. Indeed, both (1) and tricarbonyl(cyclo-octa-1,3,5-triene)iron(0) are also inert to this reagent.

(b) *With sodium methoxide.* When (2) was stirred overnight as part of a charge also containing sodium methoxide, [^{2}H$_4$]methanol, and diethyl ether, it was recovered unchanged with no evidence of nucleophilic addition or deuterium incorporation.

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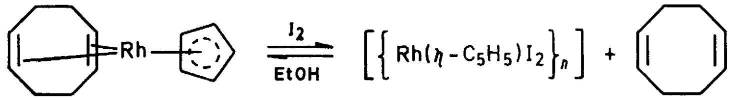
[7] J. Lewis and A. W. Parkins, *J. Chem. Soc.* (*A*), 1967, 1150.

[8] J. A. Connor and E. J. Rasburn, *J. Organometallic Chem.*, 1970, **24**, 441.

(c) *Ligand displacement.* If organometallic complexes of rhodium were to be used for synthetic organic purposes, ligand displacement would be essential. Recovery of the metal would also be advantageous. Both these requirements can be met. Addition of a solution of iodine in dichloromethane to a solution of (2) in the same solvent produced a quantitative yield of $[\{Rh(\eta\text{-}C_5H_5)I_2\}_n]$ (14).[9] After removing this dark brown solid by filtration, pure cyclo-octa-1,5-diene could be obtained. This reaction is probably the real cause of the reported [10] ring-contraction reaction of μ-dichloro-bis(cyclo-octa-1,5-dienerhodium) and iodine forming (14) which could not be repeated.[11] Refluxing (14) with excess of cyclo-octa-1,5-diene in alkaline alcohol regenerates (2) in high yield. This method has been used to produce $[Rh(\eta\text{-}C_5Me_5)(nbd)]$ from $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ and the free ligand (Scheme 4).[12]



(2) (14)

SCHEME 4

DISCUSSION

Considering the cobalt triad, it is apparent that the neutral diene complexes studied are susceptible to electrophilic rather than nucleophilic attack. On protonation, no stable 16-electron cobalt cations have been observed. However, rhodium and iridium provide a balance of stability: $[M(C_5H_5)(\eta^3\text{-enyl})]^+ \simeq [M(C_5H_5)(\eta^4\text{-diene})H]^+ \leqslant [M(C_5H_5)(\eta^5\text{-dienyl})]^+$. The 16-electron η^3-enyl cations are more favoured by rhodium, and the 18-electron dienehydrido-cations more so by iridium. When available, a lower-energy form appears to be the dienyl cation (either fully conjugated or as η^3-allylic η^2-olefin fragments). The energy differences between these first two co-ordination types are relatively small for rhodium and iridium complexes and this fact facilitates the various prototropic rearrangements that have been observed.

Two questions arise. First, why are these complexes susceptible to electrophilic rather than nucleophilic attack? This must in part be due to the auxiliary ligands present. *X*-Ray photoelecton studies [13] indicate that the cyclopentadienyl ligand is primarily an electron donor, while carbonyl groups have both donor and acceptor properties. Thus the electron density available to the dienemetal fragment may be similar in both the tricarbonyliron and cyclopentadienylcobalt triads. Secondly, it is interesting that, whereas in the neutral diene complexes the metals prefer to bond to 1,3- rather than 1,5-dienes, in the cationic iridium(III) hydrides this trend is reversed. Both the energies and forms of the π orbitals of conjugated dienes make them better donors and acceptors than two isolated olefins.[14] Thus they can better compensate the iridium atom for the loss of electron density on forming a cationic hydride.

EXPERIMENTAL

The following known compounds were all prepared by procedures similar to those published: η-cyclo-octa-1,5-diene(η-cyclopentadienyl)-cobalt(I),[7] -rhodium(I),[15,16] and -iridium(I);[17] η-bicyclo[2.2.1]hepta-2,5-diene(η-cyclopentadienyl)rhodium(I);[15,16] and triethyloxonium tetrafluoroborate.[18]

Protonations.—These were carried out as primarily described.[2] Satisfactory analytical data were not obtained for the yellow solid $[C_{13}H_{18}Rh][PF_6]$, whose i.r. spectrum included ν(CH) at 3 130m cm^{-1} and $[PF_6]^-$ absorptions at 835vs,br cm^{-1}. The iridium analogue was obtained as a stable white solid (Found: C, 30.2; H, 3.90. $C_{13}H_{16}F_6IrP$ requires C, 30.5; H, 3.50%), ν(CH) at 3 130m cm^{-1}, ν(IrH) at 2 165w and 2 154w cm^{-1}, and $[PF_6]^-$ absorption at 840vs,br cm^{-1}.

Neutralisations.—(*i*) The reaction of $[Rh(\eta\text{-}C_5H_5)(\eta\text{-}C_8H_{13})][PF_6]$ was carried out as described in ref. 2, yielding η-cyclo-octa-1,5-diene(η-cyclopentadienyl)rhodium(I) (2) in 30% yield.

(*ii*) A solution of (9) (30 mg) in [^{2}H]trifluoroacetic acid (0.4 cm^3) was reduced in volume to 0.1 cm^3. [$^2H_6$]Acetone (0.4 cm^3) was added, forming a white crystalline solid. The mixture was extracted into D_2O (5 cm^3) and diethyl ether (5 cm^3), the D_2O layer was extracted with diethyl ether (3 × 5 cm^3), and the ether extracts were washed with D_2O (2 × 2.5 cm^3) and dried over Mg[SO$_4$]. The solution yielded the *product* as a white crystalline solid (10), ν(CD) at 2 180 and 2 160 cm^{-1}. Mass spectrum: [P]$^+$ 370 corresponds to $C_{13}H_{13}D_4{}^{193}Ir$.

Reaction of (2) *with Iodine*.—Complex (2) (552 mg) in dry dichloromethane (8 cm^3) was treated with a solution of iodine (508 mg) in dichloromethane (30 cm^3). The brown precipitate produced (800 mg) was washed with pentane until the iodine was removed from the washings. The *product* (Found: C, 14.7; H, 1.4. $C_5H_5{}^{127}I_2{}^{103}Rh$ requires C, 14.2; H, 1.2%) had a similar i.r. spectrum to that reported for $[Rh(\eta\text{-}C_5H_5)I_2]$.[9] The brown filtrate and washings were washed with 10% aqueous sodium thiosulphate solution (2 × 25 cm^3) and water (3 × 25 cm^3) and dried over Mg[SO$_4$]. The solvent was removed to yield a pale oil (94 mg). Thin-layer chromatography on a silica plate with pentane as eluant separated unchanged (2) (8 mg) from cyclo-octa-1,5-diene (39 mg). The liquid-film i.r. spectrum was identical to that of the authentic diene.

Reaction of $[\{Rh(\eta\text{-}C_5H_5)I_2\}_n]$ *with Cyclo-octa-*1,5-*diene*.—

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The complex (600 mg), cyclo-octa-1,5-diene (1 cm^3), and sodium carbonate (600 mg) were heated under reflux in absolute ethanol (50 cm^3) for 20 h. The mixture was cooled, filtered, and the solvent removed. The residue was extracted into diethyl ether, and the ether was removed from the extracts. The resulting solid was dissolved in toluene and chromatographed on a silica column (10 × 2 cm) and eluted with toluene. A faster moving yellow band was collected and yielded complex (2) as *product* (270 mg, 70% on Rh).

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