Pentamethylcyclopentadienyl-rhodium and -iridium Halides. Part III.[1] Reactions with Cyclohexadienes

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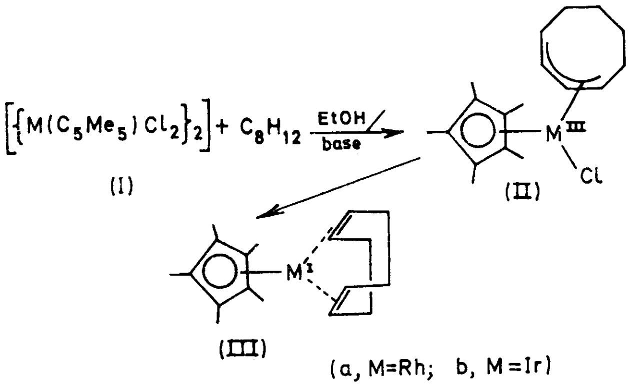
The dimeric dichloropentamethylcyclopentadienyl-rhodium and -iridium complexes (I) react with both cyclohexa-1,3- and 1,4-diene to give the π-cyclohexa-1,3-diene-(pentamethylcyclopentadienyl)-rhodium and -iridium complexes, (IV). During this reaction, isomerisation of the uncomplexed cyclohexa-1,4- to the -1,3-diene occurred. The rhodium complex (IV) was a catalyst for the disproportionation of cyclohexa-1,3-diene to cyclohexene and benzene. This reaction was strongly assisted by the presence of ethanol and base. Mechanisms for the complex formation, isomerisation, and disproportionation are suggested.

In the preceding paper we discussed the reactions of the rhodium and iridium complexes, $[\{M(C_5Me_5)Cl_2\}_2]$, (I) with olefins in ethanol in the presence of base. The simplest type of reaction involves the addition of M–H [as in C_5Me_5MHCl(solv.), arising from (I) and ethoxide ion] to a 1,3-diene. In the case of butadiene, the π-1-methylallyl-complex was formed.[1] A similar reaction occurred with cyclo-octa-1,3-diene and the resultant chloro-(π-cyclo-oct-2-enyl)pentamethylcyclopentadienyl-rhodium and -iridium complexes (II) have been shown to be intermediates in the formation of π-cyclo-octa-1,5-diene-(pentamethylcyclopentadienyl)-rhodium and -iridium, (III).[2]



We now present our results on the reactions of (I) with both cyclohexa-1,3- and -1,4-diene (1,3-chd and 1,4-chd); a brief account has already been communicated.[3]

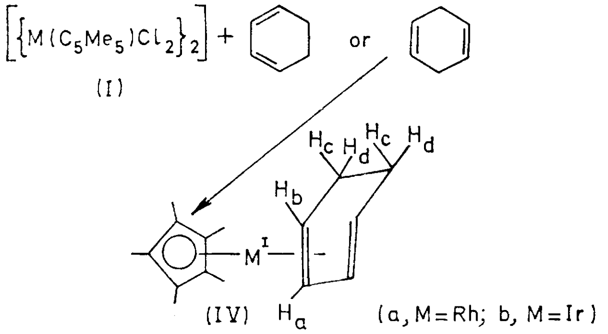
Metal complexes of cyclohexa-1,3-diene have been known for a number of years;[4] King *et al.* prepared π-cyclohexa-1,3-diene-(cyclopentadienyl)cobalt by heating dicarbonylcyclopentadienylcobalt with 1,3-chd in ethylcyclohexane.[5] The formation of this complex and of the rhodium analogue by a similar reaction involving irradiation has been mentioned by Fischer and Werner.[6] Winkhaus and Singer[7] have reported the formation of $[\{Rh(1,3\text{-chd})Cl\}_2]$ and $[Ir(1,3\text{-chd})_2Cl]$, from 1,3-chd and rhodium trichloride and hexachloroiridate(IV) respectively, in alcohol solution.

Arnet and Pettit[8] observed that tricarbonylcyclohexa-1,3-dieneiron was formed from pentacarbonyliron and 1,4-chd as well as 1,3-chd. A fairly extensive study of the reactions of various substitued cyclohexa-1,4-dienes with iron carbonyls to give substituted cyclohexa-1,3-dienetricarbonyliron complexes has been reported by Birch *et al.*[9] who also suggested a possible mechanism of formation of the complexes. Organic by-products do not appear to have been investigated.

Complexes of 1,4-chd are not known.

RESULTS

As in the reactions already described,[1,2] both the rhodium and iridium complexes (I) reacted readily with 1,3-chd in ethanol in the presence of sodium carbonate to give somewhat air-sensitive crystals of π-cyclohexa-1,3-diene-(pentamethylcyclopentadienyl)-rhodium (IVa) and -iridium (IVb) respectively.



The complexes were isolated by sublimation *in vacuo*, and were characterised by analysis, molecular weight, and n.m.r. spectroscopy. The 100 MHz n.m.r. spectrum in benzene of the iridium complex, (IVb), showed resonances at τ 5·36 (2H, dd, H_a), 7·14 (2H, unresolved m, H_b), 8·04 (15H, s, C_5Me_5), and 8·48 (4H, unresolved asymmetric d, H_c and H_d). The assignments agree with those reported for other π-cyclohexa-1,3-diene complexes.[6,7,10] Decoupling experiments indicated that H_a was significantly coupled only to H_b ($J_{a\text{-}b}$ 4·5 Hz; $J_{a\text{-}b'}$ 2·0 Hz), and that H_b was again only significantly coupled to H_a;

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[1] Part II, K. Moseley, J. W. Kang, and P. M. Maitlis, preceding paper.

[2] K. Moseley, J. W. Kang, and P. M. Maitlis, *Chem. Comm.*, 1969, 1155.

[3] K. Moseley and P. M. Maitlis, *Chem. Comm.*, 1969, 1156.

[4] B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 1958, 642.

[5] R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 3593.

[6] E. O. Fischer and H. Werner, 'Metal π-Complexes,' Elsevier, Amsterdam, 1966, p. 67.

[7] G. Winkhaus and H. Singer, *Chem. Ber.*, 1966, **99**, 3602, 3610.

[8] J. E. Arnet and R. Pettit, *J. Amer. Chem. Soc.*, 1961, **83**, 2954.

[9] A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc.* (*A*), 1968, 333.

[10] R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1961, 594.

there was only a slight sharpening of the resonances of H_c and H_d on irradiation at the resonance frequency for H_b.

The n.m.r. spectrum of the rhodium complex (IVa) was similar, except that H_a was now observed as a complex multiplet, owing to coupling to ^{103}Rh (I 1/2). Resonances were observed at τ 5·46 (2H, m, H_a), 7·16br (2H, H_b), 8·07 (15H, s, C_5Me_5), and 8·50 (4H, m, H_c and H_d). Decoupling experiments again showed that H_a and H_b were coupled but that interaction with H_c and H_d was only small.

The mass spectra of the complexes were also of interest; both showed strong molecular ion peaks, at *m*/*e* 318 for (IVa), and 406 and 408 for $(C_{16}H_{23}\,^{191}Ir)^+$ and $(C_{16}H_{23}\,^{193}Ir)^+$ (IVb) respectively. The *m*/*e* 406 peak was the base peak for the latter, and that at 238 $(C_5Me_5Rh)^+$ was the base peak for (IVa). The formation of $(C_5Me_5Ir)^+$ (*m*/*e* 326 and 328) was an important fragmentation in (IVb) too. Both complexes showed significant peaks corresponding to $(C_5Me_5MC_6H_6)^+$ [*m*/*e* 316 (Rh); 404 and 406 (Ir)] and $C_5Me_5MC_6H_6)^{2+}$ [*m*/*e* 158 (Rh); 202 and 203 (Ir)]. A metastable peak at *m*/*e* *ca.* 314 corresponds to the fragmentation $(C_5Me_5RhC_6H_8)^+$ (318) $\longrightarrow$ $(C_5Me_5RhC_6H_6)^+$ (316). Loss of CH_3 from the parent ion was observed in each case and was probably due, in part at least, to a ring contraction to $(C_5Me_5MC_5H_5)^+$ [*m*/*e* 303 (Rh); 391 and 393 (Ir)].

Complexes (IVa) and (IVb) were also obtained in similar yields from reaction of (Ia) and (Ib) with 1,4-chd. We therefore investigated all these reactions in detail particularly to establish which organic products were also formed.

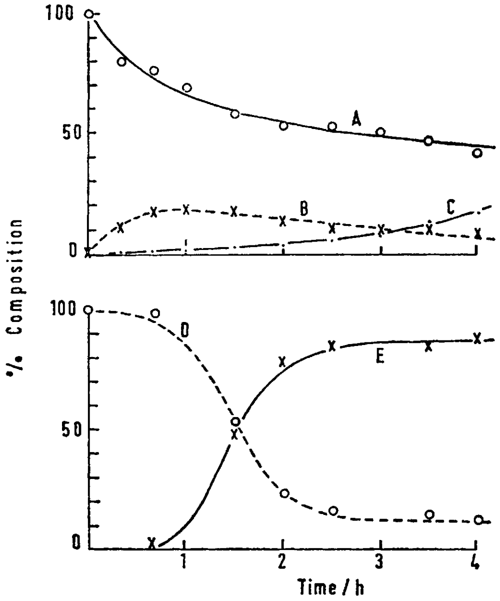
The rhodium complex (Ia) was treated with excess of 1,3-chd in ethanol in the presence of sodium carbonate. The complex was isolated in the usual manner and the solvent and volatile materials were distilled and analysed by v.p.c. with two different columns. Acetaldehyde was again detected, as well as a small amount of 1,3-chd. No cyclohexane or 1,4-chd was observed. In this particular reaction, 90% of the uncomplexed C_6 hydrocarbons were present as benzene and cyclohexene. A series of reactions of this type showed that the degree of disproportionation of 1,3-chd to benzene and cyclohexene depended on the reaction time.

Isomerisation and disproportionation of cyclohexadienes catalysed by $[Rh(C_5Me_5)(C_6H_8)]$ (IVa)

Diene	Conditions	(IVa) recovered (%)	Cyclohexene (%)	Benzene (%)	Cyclohexa-1,3-diene (%)	Cyclohexa-1,4-diene (%)
Cyclohexa-1,3-diene	Na_2CO_3/EtOH/55°/5 h	85	41	48	trace	0
	EtOH/55°/4 h	85	15	17	75	0
	n-Hexane/66°/6·5 h	100	0	0	100	0
	Et_3N/n-hexane/66°/3·5 h	95	0	0	100	0
	THF/65°/21 h	95	6	6	85	0
Cyclohexa-1,4-diene	Na_2CO_3/EtOH/60°/4 h	85	5	6	11	65
None	Na_2CO_3/EtOH/60°/3 h	80	4	5	0	0

The reaction of $[\{Rh(C_5Me_5)Cl_2\}_2]$, (Ia) with excess of 1,4-chd under similar conditions gave, apart from (IVa), acetaldehyde, 1,4-chd, 1,3-chd, benzene, and cyclohexene. In one reaction, disproportionation of uncomplexed diene amounted to 26% and isomerisation to 4%.

A typical reaction of (Ia) with 1,4-chd was followed by removing aliquot portion at regular intervals and analysing the volatile components by v.p.c. and the solid residues by n.m.r. spectroscopy. These results are summarised in the Figure; they show that disproportionation does not become significant until the formation of the 1,3-chd complex (IVa) is almost complete. This complex therefore appears to be the active catalyst for the disproportionation.



Variation in the composition of the reaction of 1,4-chd (A) with $[Rh(C_5Me_5)Cl_2]$ (D) in ethanol–sodium carbonate at 44—48°, giving $[Rh(C_5Me_5)(1,3\text{-chd})]$ (E), 1,3-chd (B), cyclohexene plus benzene (C)

The results for a number of experiments with $[Rh(C_5Me_5)(1,3\text{-chd})]$ (IVa) (Table) show that (IVa) does catalyse the disproportionation but that ethanol and base are necessary co-catalysts, and also that 1,4-chd undergoes disproportionation much more slowly than 1,3-chd, probably *via* primary isomerisation to 1,3-chd.

The reliability of the results in the Table is ±5%. There was also some indication that a little more benzene than cyclohexene was formed, but this may arise from analytical inaccuracies.

The iridium complex $[\{Ir(C_5Me_5)Cl_2\}_2]$ (Ib) also reacted with both 1,3- and 1,4-chd, and at a rather lower temperature (35°; 4 h) than the rhodium complex (Ia) to give (IVb). Analysis of the uncomplexed C_6 hydrocarbons from the reaction with 1,3-chd showed that no isomerisation, and only a small amount of disproportionation, occurred at this temperature. In the reaction with the 1,4-chd, on the other hand, considerable isomerisation of 1,4- to 1,3-chd occurred. Again, little disproportionation was observed at this temperature, but it became appreciable at 75° during 6 h. It also appears that disproportionation only occurs after isomerisation. When heated in ethanolic sodium carbonate in the absence of added cyclohexadiene, the rhodium complex (IVa) was recovered (80%). No metal, but a small amount of a purple oil,* and *ca.* 5% of both cyclohexene and benzene was obtained.

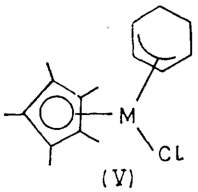
The iridium complex (IVb) was heated with a five-fold excess of both 1,3- and 1,4-chd in ethanol in the presence of sodium carbonate at 50° for 21 h. In neither case was any isomerisation or disproportionation detected, and the reactants were recovered. This result also indicates that ethanol and sodium carbonate alone are not responsible for the disproportionations or isomerisations.

The rhodium complex (IVa) was also heated with cyclo-octa-1,3- and -1,5-diene in ethanol in the presence of sodium carbonate. In the first case, 12% of the π-cyclo-octa-1,5-diene-(pentamethylcyclopentadienyl)rhodium[2] and some cyclo-octene were obtained in addition to traces of 1,3-chd, cyclohexene, and benzene. In the reaction with cyclo-octa-1,5-diene, *ca.* 50% of π-cyclo-octa-1,5-diene-(pentamethylcyclopentadienyl)rhodium was obtained. Cyclo-octa-1,3- and -1,4-diene, cyclo-octene, and 1,3-chd but only a trace of cyclohexene were found.

DISCUSSION

The main features revealed by these reactions are: (i) The 1,3-chd complexes (IV) are formed with approximately equal facility from both 1,3- and 1,4-chd. (ii) A substantial amount of isomerisation of 1 4- to 1,3-chd has to occur before formation of the 1,3-chd rhodium complex (IVa) can begin. Presumably a similar consideration holds for the iridium reactions where this isomerisation appears to be faster. (iii) The 1,3-chd is disproportionated to benzene and cyclohexene largely by the rhodium complex (IVa). In addition, a small degree of disproportionation during the formation of (IV) cannot be ruled out, particularly for the iridium complex (IVb). This does not disproportionate or isomerise under the conditions used here.

By contrast to the reactions of (I) with cyclo-octadienes,[2] no stable π-en-yl complex, *i.e.* chloro-π-cyclohex-2-enyl-(pentamethylcyclopentadienyl)-rhodium or -iridium (V) corresponding to the chloro-π-cyclo-oct-2-enyl-(pentamethylcyclopentadienyl)-complexes (II) was formed here as an intermediate.

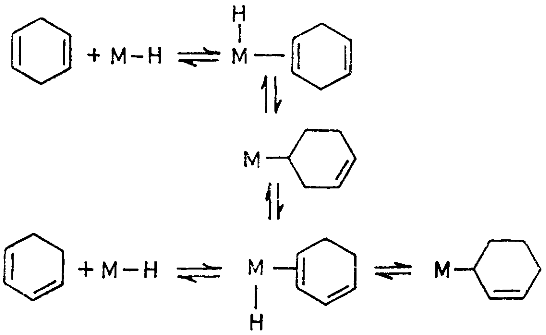


(V)

This fact emerges clearly from the results in the Figure, which show that there was no detectable change in the concentration of (Ia) over the first 40 min of reaction despite the occurrence of a substantial amount (17%, corresponding to *ca.* 2/3 of a mol per g atom of rhodium) of isomerisation of 1,4- to 1,3-chd. This suggests, by analogy with our other work,[1,2] that a hydrido-species, [$(C_5Me_5)HCl(solv.)$], was formed in low concentration which caused the isomerisation by a 1,2-hydride shift[11] as shown in Scheme 1. The detection

$$[\{M(C_5Me_5)Cl_2\}_2] + EtOH + base \longrightarrow [M(C_5Me_5)HCl\ solv.)] + MeCHO + base\ hydrochloride$$

of acetaldehyde in the reaction mixture is in agreement with this hypothesis.



SCHEME 1 (M = C_5Me_5MCl)

Since, under comparable conditions, other 1,3-dienes reacted with [$\{Rh(C_5Me_5)Cl_2\}_2$] to give π-en-yl complexes,[1,3] and since π-cyclohex-2-enyl complexes are known for other metals, *e.g.* palladium(II),[12–14] this suggests that the complex (Va) is not particularly stable. The possibility that the π-cyclohex-2-enyl complex (Va) is not detected because it is rapidly transformed into the 1,3-chd complex (IVa) is unlikely too, since this hypothesis does not account for the long induction period (during which 1,3-chd is formed) before appreciable amounts of (IVa) are detected.

The simplest explanation of these results is that the [$\{Rh(C_5Me_5)Cl_2\}_2$] (Ia) is transformed in a slow reaction into the reactive species. The latter is unlikely to be [$Rh(C_5Me_5)HCl(solv.)$], since this must be formed quite readily under our conditions to account for the isomerisation. The most likely intermediate here is solvated [$Rh^I(C_5Me_5)$], arising from the hydridochloride, [$Rh^{III}(C_5Me_5)HCl(solv.)$], by a slow, base-assisted, loss of hydrogen chloride. This can then react with 1,3-chd to give (IVa). It is possible that the 'solvent' here is

$$[Rh(C_5Me_5)HCl(solv.)] \xrightarrow{base} [Rh(C_5Me_5)(solv.)] \xrightarrow{1,3\text{-}chd} [Rh(C_5Me_5)(1,3\text{-}chd)]$$

partly, or even largely, 1,3-chd.

A similar rationalisation probably applies to the iridium reactions, except that here isomerisation of 1,4- to 1,3-chd appears to be faster.

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* A similar material, with analysis corresponding to $(C_5Me_5Rh)_n$, was isolated from some decompositions of the π-cyclo-octenyl complex (IIa).

[11] R. Cramer, *J. Amer. Chem. Soc.*, 1966, **88**, 2272.

[12] D. Jones, G. W. Parshall, L. Pratt, and G. Wilkinson, *Tetrahedron Letters*, 1961, **48**.

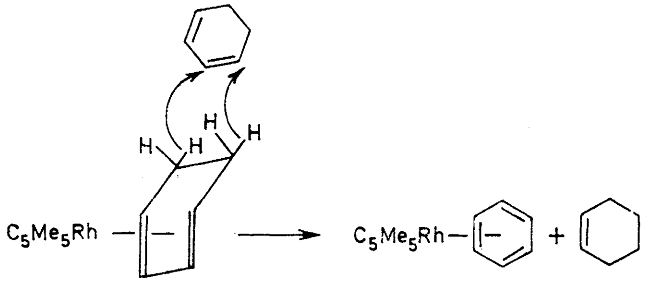
[13] R. Hüttel, H. Dietl, and H. Christ, *Chem. Ber.*, 1964, **97**, 2037.

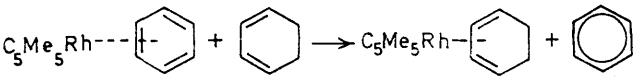
[14] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1964, 5002.

This mechanism is rather different to that proposed by Birch *et al.*[9] for the formation of tricarbonyliron complexes of substituted cyclohexa-1,3-dienes from the cyclohexa-1,4-dienes. In their case, however, solvent participation was minimal and their postulate that the isomerisation occurs *via* hydride abstraction from the diene and a hydrido-π-cyclohexadienyl-iron complex may well be correct.

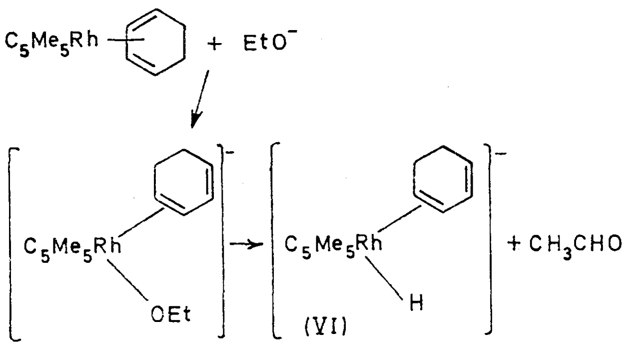
The most significant disproportionation is that catalysed by (IVa). Disproportionations of this type on solid noble-metal catalysts have been known for many years. Zelinsky and Pavlov showed that cyclohexene, 1,3-chd and 1,4-chd were disproportionated to benzene and cyclohexane on palladium.[15] Carrà *et al.*[16,17] investigated this disproportionation of cyclohexene and showed that it probably proceeded *via* 1,3-chd. Lyons[18] has recently reported that 1,4-chd was disproportionated to cyclohexene and benzene but that 1,3-chd was not affected. He used a variety of soluble iridium(I) and iridium(III) catalysts and found that disproportionation was significant only with [Ir(Ph$_3$P)$_2$-(CO)halide] at 80° during long times (90—180 h). No co-catalysts were used.

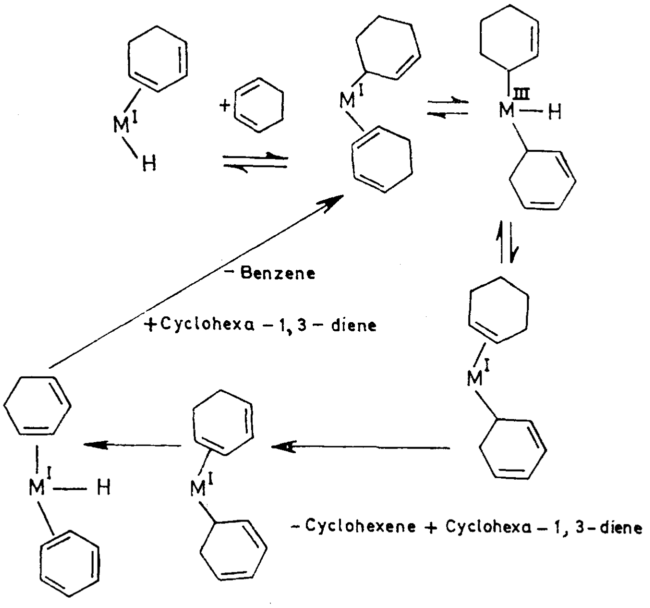
A tempting hypothesis to account for our initial results was that direct transfer of two hydrogen atoms from complexed to uncomplexed (or loosely complexed) 1,3-chd occurred, to give cyclohexene and a weak π-benzene complex. Further studies (Table) showed that this could not be the main process, if indeed it occurred at all, since the reaction was strongly co-catalysed by alcohol and base, and was virtually non-existent in other solvents. In addition, we detected acetaldehyde in the ethanol–base reactions. This result again points to the intermediacy of a rhodium hydride species in the reactions. In the absence of an external source of hydride ion and at higher temperatures a reaction involving direct transfer between two C$_6$ rings is still plausible.





While conclusive evidence is lacking, we are tempted to suggest a mechanism involving an anionic hydride (VI). A series of reactions illustrated in Scheme 2 rationalises the observed results. In this scheme two C$_6$ rings are co-ordinated to the metal and a series of hydride transfers (probably with assistance of the metal) from one to another takes place. No hydrogenation of cyclohexene is observed, probably because it is too weakly complexed and is displaced immediately on formation. This is in agreement with other observations.[7]





SCHEME 2 (M = C$_5$Me$_5$Rh$^-$)

Cyclohexa-1,4-diene also undergoes isomerisation and disproportionation with (IVa) under these conditions, but much more slowly. It is likely that this diene too complexes only weakly to the metal. By contrast, the iridium complex (IVb) does not catalyse these reactions at 50°, though we have evidence that disproportionation as well as isomerisation occurs at higher temperature (75°).

The reactions of the 1,3-chd complex (IVa) with cyclo-octa-1,3- and -1,5-diene also show that simple hydrogen-transfer does not occur. The results can be accommodated in similar terms to the Scheme 2, but with

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[15] N. D. Zelinsky and G. S. Pavlov, *Ber.*, 1933, **66**, 1420.

[16] S. Carrà, P. Beltrame, and V. Ragaini, *J. Catalysis*, 1964, **3**, 353.

[17] S. Carrà and V. Ragaini, *Tetrahedron Letters*, 1967, 1079.

[18] J. E. Lyons, *Chem. Comm.*, 1969, 564.

some replacement of complexed 1,3-chd by cyclo-octa-1,5-diene. Similar reactions catalysed by the cyclooctadiene complex (IIIa) are also known[2] and will be described soon.

EXPERIMENTAL

The two cyclohexadienes were obtained from Aldrich. Cyclohexa-1,4-diene was purified by preparative v.p.c.; the 1,3-diene was sufficiently pure and was redistilled before use. Both dienes were stored at 0° under nitrogen. The volatile products were analysed by v.p.c. on a 10 ft column of 20% Carbowax (75°) and a 5 ft column of 5% SE30 (45°). The products were identified by comparison of their retention times on both columns with those of authentic samples. N.m.r. spectra were determined with a Varian HA-100 instrument and mass spectra with a Hitachi–Perkin-Elmer RMU-6A spectrometer. The complexes were introduced into the latter by means of a sample injection probe at the minimum temperature which gave an adequate vapour pressure. V.p.c. analyses were carried out on a Varian Aerograph 204B, and preparative-scale separations on a Varian Aerograph A90-P3 chromatograph. All reactions were carried out under nitrogen.

*π-Cyclohexa-*1,3-*diene(pentamethylcyclopentadienyl)rhodium* (IVa).—A mixture of the dichloro-rhodium complex (Ia) (150 mg, 0·24 mmol), anhydrous sodium carbonate (150 mg), and cyclohexa-1,3-diene (115 mg, 1·44 mmol) in absolute ethanol was heated and stirred at 48° for 3·5 h. The solution was cooled, and the solvent and volatile products were removed *in vacuo* and analysed separately; the greenish orange solid residue was extracted with ether. Removal of the solvent gave a pale brown oil. A crystalline solid, cyclohexa-1,3-diene(pentamethylcyclopentadienyl)-rhodium (IVa) (110 mg, 0·36 mmol, 75%), m.p. 47—48°, was sublimed out of this at 25° at 10^{-3} mmHg. [Found: C, 60·35; H, 7·35%; *M* (mass spectrum), 318. $C_{16}H_{23}Rh$ requires C, 60·4; H, 7·3%; *M*, 318]. V.p.c. analysis of the volatile products showed the presence of acetaldehyde, 1,3-chd (8 μl, 0·08 mmol), cyclohexene (40 μl, 0·40 mmol), and benzene (40 μl, 0·44 mmol).

The same complex (64%) was obtained similarly from (Ia) (0·25 mmol) and cyclohexa-1,4-diene (0·72 mmol). V.p.c. analysis of the volatile products showed the presence of acetaldehyde, 1,4-chd (15 μl, 0·16 mmol), 1,3-chd (1 μl, 0·01 mmol), cyclohexene (3 μl, 0·03 mmol), and benzene (3 μl, 0·03 mmol).

Detailed Reaction Study.—A mixture of the complex (Ia) (500 mg, 0·81 mmol), sodium carbonate (500 mg), and cyclohexa-1,4-diene (400 μl, 5·0 mmol) in ethanol (20 ml) were heated for 4 h at 44—48°. Aliquot portions (0·5 ml) were removed at intervals from the flask *via* a rubber cap with a syringe. The volatile material from each portion was distilled off and analysed by v.p.c.; the solid residues were dissolved in deuteriochloroform and analysed by n.m.r. spectroscopy. The results are presented in the Figure.

*Disproportionation of Cyclohexa-*1,3-*diene to Benzene and Cyclohexene.*—A freshly sublimed sample of the cyclohexa-1,3-diene complex (IVa) (104 mg, 0·33 mmol), cyclohexa-1,3-diene (50 μl, 0·53 mmol), and sodium carbonate (100 mg) in ethanol (3 ml) were heated at 55° for 4 h. Ethanol and hydrocarbons were distilled off and analysed by v.p.c.; the complex was recovered by sublimation *in vacuo*.

The results for a series of reactions with similar quantities of reactants are presented in the Table.

Reaction of Complex (IVa) *with Cyclo-octa-*1,3- *and* -1,5-*diene.*—The cyclohexa-1,3-diene complex (IVa) (100 mg, 0·32 mmol), cyclo-octa-1,5-diene (80 μl, 0·65 mmol), and sodium carbonate (100 mg) were heated in ethanol for 2·5 hr at 60°. The solvent and hydrocarbons were distilled off and analysed by v.p.c. Apart from ethanol and acetaldehyde, the volatile materials were: cyclo-octa-1,5-diene (54 μl), cyclo-octa-1,3-diene (5 μl), cyclo-octa-1,4-diene (3 μl), cyclo-octene (3 μl), cyclohexa-1,3-diene (12 μl), and a trace of cyclohexene. The solid residue, extracted with chloroform and analysed by n.m.r. spectroscopy, was shown to contain (IVa) (*ca.* 50%) and cyclo-octa-1,5-diene(pentamethylcyclopentadienyl)rhodium (IIIa) (50%).

A similar reaction in which cyclo-octa-1,3-diene (106 μl, 0·85 mmol) was treated for 3·5 h with complex (IVa) (135 mg, 0·43 mmol) gave a mixture containing (IVa) (88%) and the cyclo-octa-1,5-dienerhodium complex (IIIa) (12%). The volatile hydrocarbons were cyclo-octa-1,3-diene (72 μl), cyclo-octene (7 μl), cyclohexa-1,3-diene (1 μl), benzene (1 μl), and cyclohexene (1 μl).

*π-Cyclohexa-*1,3-*diene(pentamethylcyclopentadienyl)iridium* (IVb).—A mixture of the dichloro-iridium complex (Ib) (190 mg, 0·24 mmol), sodium carbonate (200 mg), and cyclohexa-1,3-diene (115 mg, 1·4 mmol) was heated for 3·5 h at 35°. The pale yellow solution was worked up in the same manner as described for (IVa) above, to yield the white crystalline iridium complex (IVb) (160 mg, 0·4 mmol, 83%), m.p. 65—67°. [Found: C, 47·25; H, 5·45%; *M*, 406 and 408 (mass spectrum). $C_{16}H_{23}Ir$ requires, C, 47·15; H, 5·7%; *M*, 406 and 408]. V.p.c. analysis of the volatile components showed the presence of acetaldehyde, 1,3-chd (20 μl, 0·2 mmol), cyclohexene (trace; <1 μl, 0·01 mmol) and benzene (trace; <1 μl, 0·01 mmol).

The same complex was obtained (66%) from (Ib) (0·24 mmole) and cyclohexa-1,4-diene (0·72 mmol) at 35°. V.p.c. analysis of the volatile products indicated the presence of acetaldehyde, 1,3-chd (18 μl, 0·18 mmol) 1,4-chd (22 μl, 0·24 mmol), cyclohexene (<2 μl), and benzene (<2 μl). A similar reaction at 75° for 6 h gave (IVb) (72%) together with acetaldehyde, 1,3-chd (7·5 μl, 0·08 mmol), 1,4-chd (6 μl, 0·07 mmole), cyclohexene (6·5 μl, 0·065 mmol), and benzene (10 μl, 0·11 mmol).

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