# Transition-metal–Diene Complexes. Part 3.[1] Isomerization of Methyl-substituted Acyclic and Cyclic 1,3- and 1,4-Dienes Co-ordinated to Rhodium(I)

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A range of methyl-substituted acyclic and cyclic 1,4-dienes co-ordinated to Rh[I] in the complexes [Rh(cp)(diene)] (cp = cyclopentadienyl) undergo virtual quantitative isomerization when heated in non-protic solvents. Reactants and products have been characterized by chemical and physical methods, particularly by $^1H$ n.m.r. spectroscopy. Reaction products are exclusively conjugated dienes and with one exception, cis,cis-hexa-2,4-diene, are co-ordinated to Rh[I]. For the case of the acyclic 1,4-dienes the primary isomerizations, generally to mixtures of cis- and trans-1,3-isomers, are followed by a slower isomerization of the cis-primary product dienes to the trans isomers. For the isomerization of the cyclohexa-1,4-dienes, mixtures of 1,3-isomers are generally obtained in a primary process only. First-order rate constants for the decay of reactant 1,4-diene are reported. From an analysis of the kinetics of the reactions and of product distributions, a mechanism involving a ($\eta^3$-allyl)hydrido-intermediate is proposed for the primary isomerizations in which the first step is the dissociation of one double bond from the metal. For the secondary isomerization of cis- to trans-1,3-dienes a $\eta^3$–$\eta^1$–$\eta^3$ interconversion of anti and syn configurations is suggested as the key step. The primary reactions are shown to be under kinetic control. However, addition of an external proton source leads to rapid formation of the thermodynamically most stable products via a metal hydride addition–elimination mechanism.

In Part 2 [1] we described the synthesis and isomerization reactions in non-protic solvents of some rhodium(I) complexes of penta-1,4-diene, 3-methylpenta-1,4-diene, cyclohexa-1,4-diene, cis-penta-1,3-diene, and cis-3-methylpenta-1,3-diene. The reactions occurred cleanly in virtual quantitative yield under relatively mild conditions (60—110 °C) at rates that could be conveniently monitored by $^1H$ n.m.r. techniques. From a consideration of the products of isomerization (in both primary and secondary reactions), of the kinetics, and of the results of a deuterium labelling experiment, evidence was obtained in favour of a mechanism involving a $\eta^3$-allylhydridorhodium(III) intermediate and against (under the reaction conditions employed) a metal hydride addition–elimination mechanism. The rate-determining step was considered to be the carbon-to-metal hydrogen transfer and it was speculated that the transition state, for a 1,4- to 1,3-diene isomerization, might be a $\eta^1$-allyl species wherein the central saturated carbon is σ-bonded to the metal, the unco-ordinated vinyl groups being free to rotate.

This paper presents the results of an extension of the study to the isomerization of a range of methyl-substituted acyclic and cyclic 1,4-dienes and related cis-substituted 1,3-dienes complexed to rhodium(I), for which a wider range of products are anticipated, thereby providing a further test of the mechanistic proposals contained in Part 2. The isomerization of some of the dienes has been reported previously, notably by Pettit and co-workers [2] and by Birch et al.[3] In these cases the uncomplexed diene was heated in the presence of iron carbonyls and no kinetic studies were carried out. A $\eta^3$-allylic mechanism (of a somewhat different kind) [2] was also put forward for these reactions. For most other reported metal-catalysed or metal-promoted diene isomerizations a metal hydride addition–elimination mechanism has been proposed.[4]

## RESULTS AND DISCUSSION

The reactant complexes were of the type [{RhCl-(diene)}$_2$] or, more commonly [RhX(diene)] [X = pentane-2,4-dionate (pd), $\eta^5$-cyclopentadienyl (cp), or substituted $\eta^5$-cyclopentadienyl (C$_5$H$_4$R, R = CO$_2$Me or CHO)]. Isomerization of the co-ordinated reactant diene occurred on heating their solutions in chloroform, hexane, toluene, or o-dichlorobenzene (odcb) at tem-
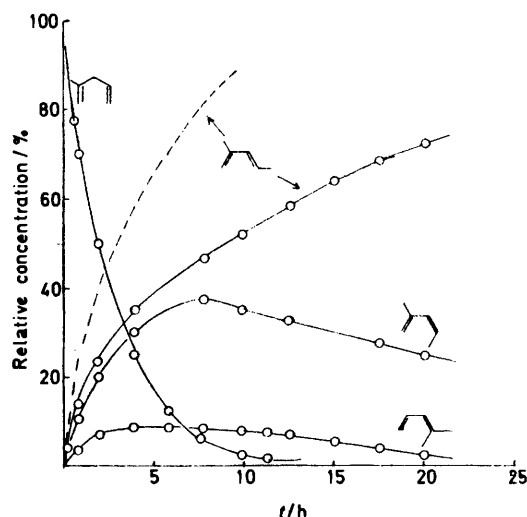


FIGURE 1 Isomerization of ($\eta^5$-methoxycarbonylcyclopentadienyl)($\eta^4$-2-methylpenta-1,4-diene)rhodium in o-dichlorobenzene at 100 °C. Formation of the trans-2-methylpenta-1,3-diene complex from the 4-methylpenta-1,3-diene complex under the same conditions (– – –)

peratures in the range 60—110 °C for periods varying from minutes to days. Complexes containing chloride or pd as counter ligand frequently gave rise to solubility or decomposition problems. The cp complexes were more soluble and more stable and these were used for the

TABLE 1

Data for the isomerization reactions [Rh(cp)(diene)] ⟶ [Rh(cp)(diene′)]

| Reactant diene | Primary product diene | Secondary product diene |
|---|---|---|
| Penta-1,4-diene [a] | trans-penta-1,3-diene<br>+<br>cis-penta-1,3-diene | trans-penta-1,3-diene |
| 3-Methylpenta-1,4-diene [a] | trans-3-methylpenta-1,3-diene<br>+<br>cis-3-methylpenta-1,3-diene | trans-3-methylpenta-1,3-diene |
| 2-Methylpenta-1,4-diene | trans-2-methylpenta-1,3-diene<br>+<br>cis-2-methylpenta-1,3-diene<br>+<br>4-methylpenta-1,3-diene | trans-2-methylpenta-1,3-diene<br><br><br>trans-2-methylpenta-1,3-diene |
| 2,4-Dimethylpenta-1,4-diene | 2,4-dimethylpenta-1,3-diene | |
| cis-Hexa-1,4-diene | cis,trans-hexa-2,4-diene<br>+<br>cis,cis-hexa-2,4-diene [b] | trans,trans-hexa-2,4-diene |
| Cyclohexa-1,4-diene [a] | cyclohexa-1,3-diene | |
| 1-Methylcyclohexa-1,4-diene | 1-methylcyclohexa-1,3-diene<br>+<br>2-methylcyclohexa-1,3-diene<br>+<br>5-methylcyclohexa-1,3-diene | |
| 1,2-Dimethylcyclohexa-1,4-diene | 1,2-dimethylcyclohexa-1,3-diene | |
| 1,4-Dimethylcyclohexa-1,4-diene | 1,4-dimethylcyclohexa-1,3-diene<br>+<br>2,5-dimethylcyclohexa-1,3-diene | |
| 2,4-Dimethylcyclohexa-1,4-diene | 1,3-dimethylcyclohexa-1,3-diene<br>+<br>1,5-dimethylcyclohexa-1,3-diene | |

[a] Ref. 1.  [b] Unco-ordinated.

kinetic studies. The reactions were monitored by [1]H n.m.r. spectroscopy as described in Part 2. The products of isomerization of the various reactant dienes are given in Table 1, while approximate rate constants at

decays in a first-order reaction (Tables 1 and 2). These are the corresponding complexes of trans-2-methylpenta-1,3-diene, cis-2-methylpenta-1,3-diene, and 4-methylpenta-1,3-diene. As shown in Figure 1, the cis- and

TABLE 2

First-order rate constants for isomerization of [RhX(diene)] complexes

| Diene | X [a] | $\theta_0/°C$ | $10^5 k$ [b]$/s^{-1}$ toluene | $10^5 k$ [b]$/s^{-1}$ odcb |
|---|---|---|---|---|
| 2-Methylpenta-1,4-diene | cp | 100 | | 6.43 |
| | mcp | 100 | | 10.0 |
| 2,4-Dimethylpenta-1,4-diene | mcp | 100 | | 2.43 |
| cis-Hexa-1,4-diene | cp | 100 | | 217 |
| 4-Methylpenta-1,3-diene | cp | 100 | | 3.22 |
| | mcp | 100 | | 8.00 |
| cis,trans-Hexa-2,4-diene | cp | 100 | | 1.05 |
| Cyclohexa-1,4-diene | cp | 60 | | 2.88 |
| | cp | 70 | 11.3 | 10.5 |
| | cp | 100 | | 400 |
| 1,2-Dimethylcyclohexa-1,4-diene | cp | 70 | 11.7 | |
| | cp | 80 | 36.6 | |
| | cp | 90 | 105 | |
| 2,4-Dimethylcyclohexa-1,4-diene | cp | 70 | 9.0 | 9.0 |
| 1,4-Dimethylcyclohexa-1,4-diene | cp | 70 | 12.0 | 12.2 |
| 1-Methylcyclohexa-1,4-diene | cp | 70 | 12.2 | |
| | cp | 90 | 127 | |

[a] mcp = $\eta^5$-Methoxycarbonylcyclopentadienyl.  [b] Estimated error $\pm 10\%$.

different temperatures for reactions carried out in toluene or odcb are collected in Table 2. As found previously, treatment of the free dienes under the same conditions of solvent and temperature did not lead to isomerization.

*Isomerization of 2-Methylpenta-1,4-diene.*—Three primary products are formed as the concentration of the reactant complex [Rh(cp)(2-methylpenta-1,4-diene)]

trans-isomers * of the 2-methyl-substituted diene are formed initially at the same rate (or, at least, very nearly the same rate) but that as reaction proceeds the rate of build-up of the cis isomer falls behind that of the trans

* In all the reactions to be described the reactant and product dienes are, with one exception, co-ordinated to the metal, in the cisoid configuration; for convenience, the prefix ' co-ordinated ' is sometimes omitted.

isomer, its concentration subsequently passing through a maximum. Co-ordinated 4-methylpenta-1,3-diene is also a primary reaction product but its initial rate of formation is less than that of the other two isomers; its concentration passes through a maximum and never exceeds *ca.* 10% of the total diene concentration.

Separate experiments showed that 4-methylpenta-1,3-diene isomerizes to *trans*-2-methylpenta-1,3-diene as sole product (Figure 1). This explains its decay after *ca.* 7 h (at 100 °C) in the isomerization of the 1,4-isomer.

to *cis* and *trans* products must be postulated. In Part 2 it was suggested (for the case of the penta-1,4-diene complex which forms the *cis* and *trans* 1,3-isomers at equal initial rates) that this transition state might be the symmetrical $\eta^1$-allyl species in which the central carbon atom $C^3$ is $\sigma$-bonded to the metal, and in which the two unco-ordinated vinyl groups are free to rotate (about $C^3$–$C^2$ or $C^3$–$C^4$) [see Scheme 4 of Part 2 [1]]. This allows $\eta^3$-allyl formation about, say $C^3$, $C^4$, and $C^5$, with either *anti* or *syn* stereochemistry according to the orientation
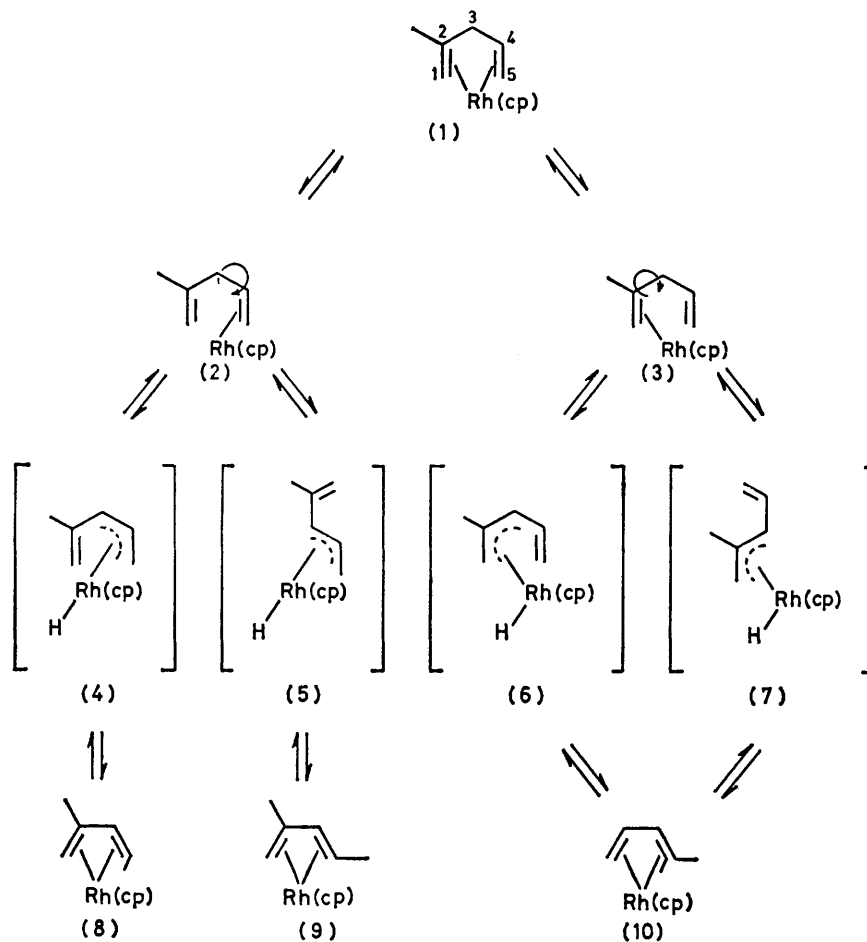


SCHEME 1

It was not possible to study the isomerization of *cis*-2-methylpenta-1,3-diene in a separate experiment. However, see below, it is proposed that this diene also isomerizes to the *trans*-1,3-isomer in a secondary process.

In considering the possible mechanisms of these reactions, two experimental observations are of particular importance: (*i*) the near equal initial rates of formation of the *cis* and *trans* isomers of 2-methylpenta-1,3-diene and the slower formation of the 4-methyl isomer. Thus, two parallel reaction pathways differing in the activation energies of the rate-determining steps are available to the reactant complex. Moreover, for one of these pathways a transition state which can lead with equal probability

of the second vinyl group at the time of formation. However, this sequence of mechanistic steps leads to difficulty when applied to the present case of the isomerization of the unsymmetrically substituted 2-methylpenta-1,4-diene since, here, an analogous transition state should lead to equal rates of formation of all three primary isomerization products. We therefore consider the alternative mechanism represented in Scheme 1. Both mechanisms involve $\eta^3$-allyls as intermediates but differ in the stage at which the stereochemical reorganization, *i.e.* unco-ordinated vinyl group rotation, occurs. This alternative mechanism (Scheme 1) is considered below in some detail for the case of 2-methyl-

penta-1,4-diene since, as will be shown, it applies equally successfully to all the other isomerization reactions which are the subject of this paper.

The first step in the reaction is seen as a de-co-ordination of one of the two double bonds in the reactant (1). Since (1) is unsymmetrically substituted two possible ' 16-electron ' mono-alkene complexes [(2) and (3)] are possible. There is ample evidence [5] that methyl substituents destabilise rhodium(I)–$\eta^2$-alkene bonds so it is expected that dissociation of the substituted double bond will be the thermodynamically preferred process. Thus, the concentration of (2) will exceed that of (3). Since one double bond is now detached from the metal it is possible for the free vinyl group to undergo free rotation about the C$^3$–C$^4$ bond in the case of (2), or about C$^2$–C$^3$ in the case of (3). The second step, considered to be rate determining, is a hydrogen transfer from C$^3$ to the metal with formation of a $\eta^3$-allylhydrido-intermediate. Two $\eta^3$-allyls, each differing in stereochemistry, are possible from each of (2) and (3) depending on the orientation of the unco-ordinated vinyl group at the moment of hydrogen transfer. These are, respectively, the anti- and syn-substituted $\eta^3$-allyls (4) and (5) generated from (2), and the anti- and syn-substituted $\eta^3$-allyls (6) and (7) generated from (3). The kinetic results (Figure 1) require that the two $\eta^3$-allylic intermediates (4) and (5) are formed at equal (or near equal) rates. This, in turn, requires equal (or near equal) concentrations of the syn and anti conformations of the unidentately co-ordinated species (2), as well as equal (or near equal) activation energies for the C$^3$-to-metal hydrogen transfer. While the different conformations of (2) are not quite equivalent (the reason why this mechanism was initially disfavoured [1]) it is probably true that whatever small barriers to free rotation about the C$^3$–C$^4$ bond there may be, these are unimportant under the reaction conditions employed. Equal (or near equal) rates of formation of (4) and (5) now lead naturally to equal (or near equal) rates of formation of the cis- and trans-2-methylpenta-1,3-diene products (8) and (9) via a reverse hydrogen transfer, this time from the metal to the terminal $\eta^3$-allylic carbon atom C$^5$.

On the other hand, the third product of the primary isomerization process, 4-methylpenta-1,3-diene (10) is formed at a slower rate. This is accounted for in Scheme 1 by the lower equilibrium concentration of the unidentately co-ordinated $\eta^2$-alkene species (3). As before, hydrogen transfer from C$^3$-to-metal gives the $\eta^3$-allyl intermediates (6) and (7) which, in this case, lead through to the same product (10). The isomerization of (10) in a secondary process to the thermodynamically more stable trans-2-methylpenta-1,3-diene (9) is also accommodated by the Scheme. However, an alternative route to (9) is that shown in Scheme 2 which involves a direct conversion of the anti-substituted $\eta^3$-allyl (6) to the syn-substituted $\eta^3$-allyl (5) via σ-bonded $\eta^1$-allylic species (11). Dynamic π–σ–π interconversions of this kind are well established, particularly for $\eta^3$-allyl complexes of Pd$^{II}$.[6]

Isomerization of 2,4-Dimethylpenta-1,4-diene.—In this case a single product, 2,4-dimethylpenta-1,3-diene, was obtained. This observation is fully consistent with the mechanism discussed above. Because of the symmetrical nature of the methyl substitution in the reactant

SCHEME 2
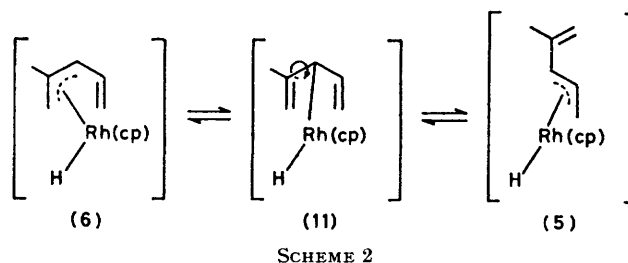
diene only one dissociation product is possible. On hydrogen transfer from C$^3$ to Rh two $\eta^3$-allyl intermediates (syn and anti) are generated which lead to the same product. The non-isomerization of the cis-substituted product in a secondary process may be apparent rather than real since it would be expected to isomerize to ' itself '.

Isomerization of cis-Hexa-1,4-diene.—The results (Tables 1 and 2, Figure 2) show that co-ordinated cis, trans-hexa-2,4-diene (17) and unco-ordinated cis, cis-hexa-2,4-diene (16) are formed together as primary reaction products but at different rates. As the reaction proceeds the concentration of the cis, trans isomer passes through a maximum subsequently decaying at the expense of the formation of co-ordinated trans,trans-hexa-2,4-diene, shown in separate experiments to come from the cis,trans isomer. Scheme 3 is proposed to account for these observations. Four possible pathways
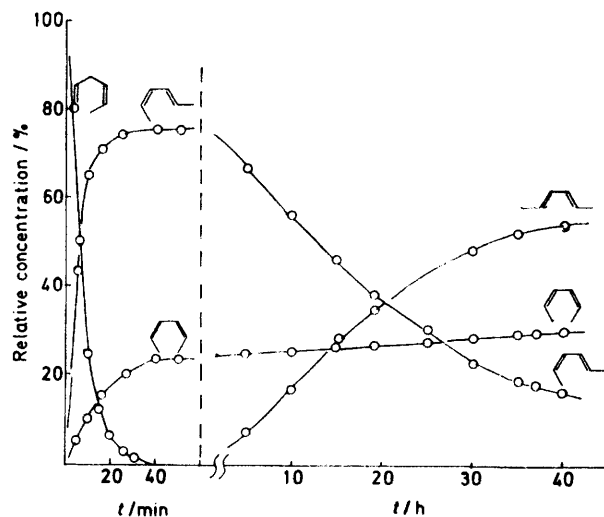
FIGURE 2  Isomerization of ($\eta^5$-cyclopentadienyl)-($\eta^4$-cis-hexa-1,4-diene)rhodium in o-dichlorobenzene at 100 °C

can be envisaged. One pair of pathways (on the left-hand side of Scheme 3) begin with the dissociation of the cis-substituted double bond from the metal in the reactant complex (12) yielding (13). This leads, on hydrogen transfer from C$^3$ to Rh, to the anti and syn

η³-allyl intermediates [(14) and (15)] and thence to the two primary products [(16) and (17)]. The very different rates of formation of (16) and (17) would seem to contravene the predictions based on the mechanism given above. However, this reaction system is unique among those studied in furnishing a product diene, cis,cis-

undue significance to the apparently slower rate of appearance of (16) compared to (17).

Scheme 3 also allows for the formation of the complexed cis- and trans-hexa-1,3-dienes [(18) and (19)]. The fact that neither of these was observed can readily be accounted for in terms of a very low equilibrium
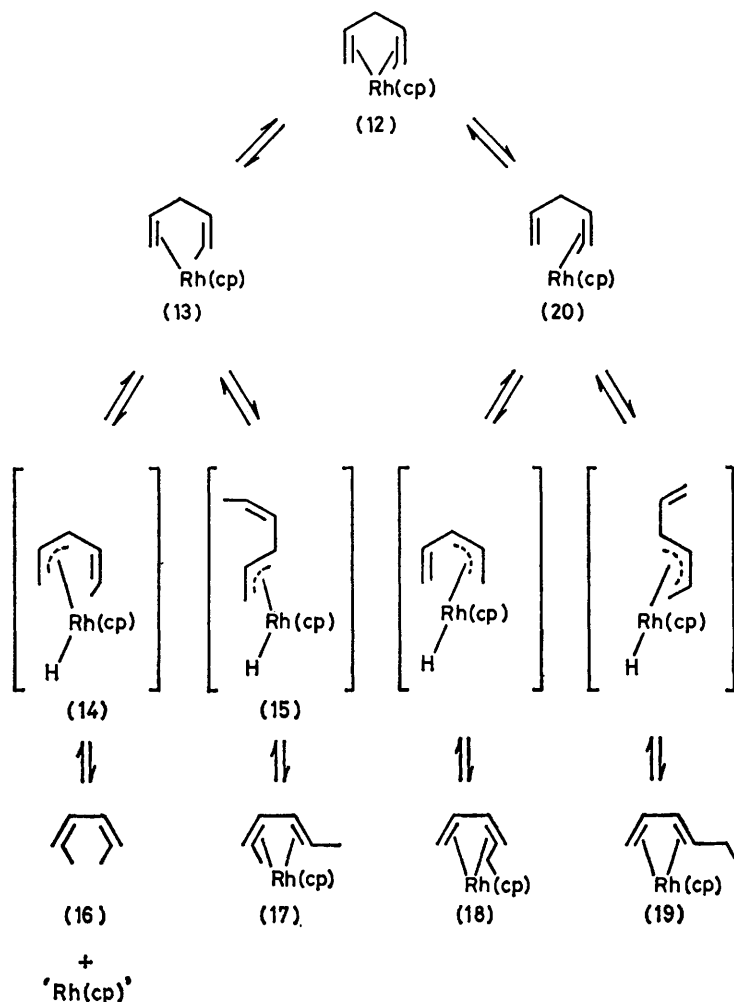


SCHEME 3

hexa-2,4-diene (16) which is unco-ordinated to the metal. There can be little doubt that this is because of the presence of the two cis-methyl substituents which render a cisoid conformation, and hence the complex, unstable. It is presumed therefore that once the complex is formed it immediately dissociates into free diene and ‘ Rh(cp) ’ fragments. Support for this view is provided by our unsuccessful attempts to isolate a chloride-bridged or pentanedionato-complex of cis, cis-hexa-2,4-diene by displacement of ethylene from [{RhCl(C₂H₄)₂}₂] or [Rh(pd)(C₂H₄)₂]; instead, it is catalytically isomerized to the cis, trans and trans,trans isomers. In addition, the isomerization of (12) was accompanied by some decomposition. For these reasons we do not attach

concentration of the unidentately co-ordinated cis-η²-alkene species (20).

It remains to account for isomerization, in a slower secondary process, of the cis,trans-hexa-2,4-diene (17) to the trans, trans isomer (Figure 2). Scheme 3 provides no route for this conversion. We suggest that this isomerization may occur via the π–σ–π mechanism analogous to that given in Scheme 2.

2,3,3-Trimethylpenta-1,4-diene.—No isomerization was observed when the complex [Rh(mcp)(2,3,3-trimethyl-penta-1,4-diene)] was heated in odcb at 100 °C even after 168 h. This is the expected result since this diene lacks a hydrogen atom on C³.

Isomerization of 1-Methylcyclohexa-1,4-diene.—We have

previously shown[1] that unsubstituted cyclohexa-1,4-diene co-ordinated to rhodium(I) isomerizes to the cyclohexa-1,3-diene complex. In the isomerization of the 1-methyl derivative (21) all three 1,3-isomers are obtained as primary reaction products, namely, the 1-methyl, 2-methyl, and 5-methyl isomers (22), (23), and (24) in Scheme 4, in the relative proportions 50, 45, and *ca.* 5%, respectively. A similar product distribution of complexed isomers (60 : 30 : 10) was obtained on reaction

dimethylcyclohexa-1,3-diene (27) at different rates, the ratio of (26) to (27) of 70 : 30 being maintained throughout the course of the reaction. The two reaction pathways arise because of the two possible carbon-to-metal hydrogen transfer processes. In one, apparently the lower activation-energy process, the hydrogen is abstracted from $C^3$ *i.e.* the carbon flanked by the two methyl substituents, and this leads through to the major product (26) (see left-hand side of Scheme 5). In the



SCHEME 4

of the free 1,4-diene with $[Fe(CO)_5]$.[3] There are four possible $\eta^3$-allyl pathways, two of which lead to the same product (22). The two left-hand side routes in Scheme 4 arise *via* dissociation of the substituted double bond while access to the two right-hand side routes requires dissociation of the unsubstituted double bond. For reasons discussed earlier the former dissociation will be preferred and thus product (23) should be formed in excess of product (24). This prediction is in accord with the observed product ratio of 45 : 5. Since the third product (22) can be formed *via* two routes we are unable to say how much is produced in one and how much in the other, though the left-hand side pathway is expected to be preferred.

*Isomerization of 2,4-Dimethylcyclohexa-1,4-diene.*—In this case the reactant 1,4-diene complex (25) isomerizes to form 1,3-dimethylcyclohexa-1,3-diene (26) and 1,5-

other route, the hydrogen is abstracted from $C^6$ leading to the minor product (27) (see right-hand side of Scheme 5). The reason for the preference is not clear. If only electronic factors are involved it can be argued that the $C^3$ hydrogens are less acidic than those on $C^6$, the implication being that the hydrogen is transferred mainly as the hydride ion.

That the observed 70 : 30 ratio of (26) : (27) is determined by kinetic and not by thermodynamic factors is demonstrated by results obtained when the reaction was carried out in the presence of acid. On exposure of an odcb solution of (25) to gaseous HCl for a few seconds and immediate recording of the $^1H$ n.m.r. spectrum (within 5 min at ambient temperature) a product ratio [(26) : (27)] of 95 : 5 was obtained which did not show further change with time. This is concluded to be the thermodynamic isomer ratio at this temperature. In

the presence of an external proton source the acid-catalysed metal hydride addition–elimination mechanism is expected to dominate.

*Isomerization of 1,4-Dimethylcyclohexa-1,4-diene.*— Once again, two products, the 1,4-dimethyl-1,3-diene and the 2,5-dimethyl-1,2-diene, are produced at relative rates 70 : 30 throughout this reaction. A product ratio of 60 : 40 was obtained by Birch *et al.*[3] on u.v. irradiation of free 1,4-dimethylcyclohexa-1,4-diene with [Fe(CO)$_5$]



(25)

(26)        (27)
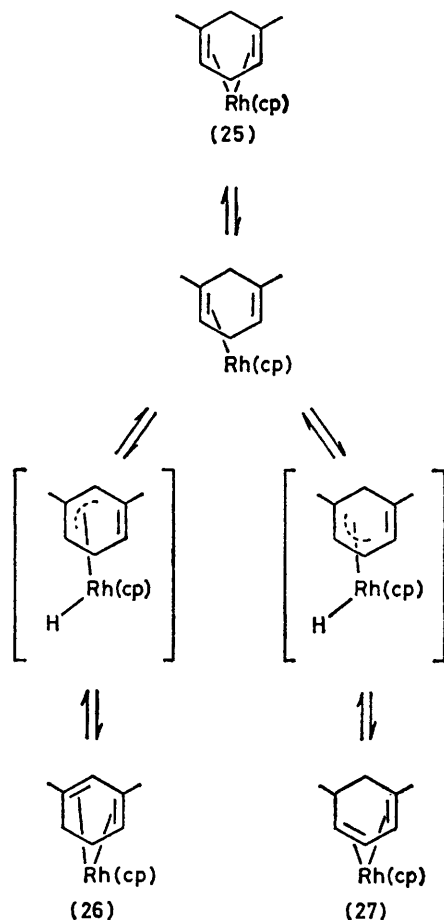
Scheme 5

in refluxing benzene. As in the previous case, the simultaneous formation of two products arises from two different hydrogen-transfer steps. As before, it appears that the lower activation-energy process is that involving transfer from a carbon atom adjacent to a co-ordinated substituted double bond.

Proof that the 70 : 30 product distribution is again due to kinetic and not thermodynamic control is provided by the results obtained when the reaction was carried out in odcb containing a trace of HCl. Here, the rate of

disappearance of the reactant complex was very much faster and only a single product (the 1,4-dimethyl isomer) was observed.

*Isomerization of 1,2-Dimethylcyclohexa-1,4-diene.*—Of the four possible 1,3-isomers only one product, 1,2-dimethylcyclohexa-1,3-diene, was observed in this reaction. Application of the $\eta^3$-allylic mechanism proposed above predicts that two of the four possible conjugated isomers could be formed, the 1,2-dimethyl isomer and the 1,6-dimethyl isomer. The mechanism further predicts that the 1,2-dimethyl isomer should be the major product. Thus, again, the results are in complete qualitative accord with predictions based on the proposed mechanism.

### EXPERIMENTAL

*Preparation and Characterization of the Complexes.*— Acyclic dienes were purchased from Aldrich, Pflatz and Bauer, Koch Light, or Phase Separations Ltd. The substituted cyclohexa-1,4-dienes were prepared by Birch reduction of the corresponding benzene precursors and were distilled prior to use. All operations were carried out under a nitrogen atmosphere using dry oxygen-free solvents.

Chloride-bridged complexes were prepared by displacement of $C_2H_4$ from [{RhCl(C$_2$H$_4$)$_2$}$_2$] as described previously.[7] $\eta^5$-Cyclopentadienyl complexes were obtained by addition of an excess of Tl(cp) to a suspension of the chloride-bridged dimer in light petroleum (b.p. 40—60 °C). After stirring for 3 h at 20 °C the mixture was filtered through silica gel and the yellow filtrate concentrated under reduced pressure. On cooling, the yellow solid product was obtained. If the product failed to crystallize the solvent was removed to give a yellow oil.

Several of the complexes have been previously characterized. Analytical, ^{1}H and [13]C n.m.r. data for the new complexes are deposited in Supplementary Publication No. SUP 22827 (13 pp.).*

The isomerization reactions were monitored as described previously.[1]

* For details see Notices to Authors No. 7, *J.C.S. Dalton,* 1979, Index issue.

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