Transition Metal–Diene Complexes. Part II.[1] Isomerization of Rhodium-complexed Penta-1,4- and *cis*-Penta-1,3-dienes

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Several 1,4-dienes and *cis*-methyl-substituted 1,3-dienes co-ordinated to Rh^{I} in the complexes [(diene)RhX] [X = η-cyclopentadienyl (cp), pentane-2,4-dionate (pd), or bridging Cl] undergo virtually quantitative isomerization when heated in inert solvents. Co-ordinated *cis*-penta-1,3-diene and *cis*-3-methylpenta-1,3-diene yield complexes of the *trans*-isomers as sole products. Co-ordinated cyclohexa-1,4-diene gives co-ordinated cyclohexa-1,3-diene; a 1,3-hydrogen shift has been demonstrated for this reaction by means of deuterium labelling. Co-ordinated penta-1,4-diene and 3-methylpenta-1,4-diene isomerize to the corresponding co-ordinated *cis*- and *trans*-1,3-isomers at equal rates, the *cis* product subsequently converting into the *trans* in a secondary process. First-order rate constants and activation parameters for some of the reactions in *o*-dichlorobenzene are derived. Reaction rates increase with increase in the electron-withdrawing nature of the counter ligand X. The results are examined in relation to current theories concerning the mechanism of metal-assisted alkene isomerization. A new mechanism is proposed in which the rate-determining step is formation of a symmetrical σ-allyl complex, this being a common transition state for the isomerization of the acyclic 1,4-dienes and the η–σ–η interconversion of *anti*- and *syn*-η-allyls, the key step in the isomerization of *cis*- to *trans*-1,3-dienes. An important conclusion which probably has general significance is that the conversion of an η-alkene to a η-allyl complex involves prior formation of an σ-allyl complex.

In Part I[1] we described the synthesis and structure of a series of rhodium(I) complexes of 1,3-dienes. Subsequent work has shown that several of these dienes, together with some recently investigated 1,3- and 1,4-dienes, undergo isomerization under fairly mild conditions when co-ordinated to Rh^{I}. Requirements for isomerization appear to be (*i*) (for 1,3-dienes) the presence of a methyl group in a *cis* (*anti*) position, and (*ii*) (for 1,4-dienes) the presence of a hydrogen atom on the central saturated carbon atom. In the case of (*i*) the ultimate products of isomerization generally, though not always, contain no *cis*-methyl substituent, and in (*ii*) the 1,4-dienes rearrange to 1,3-dienes. Thus, a reasonable hypothesis is that the thermodynamic driving force for isomerization is [in (*i*)] the relief of repulsion between *anti* substituents and the metal and between the *anti* substituents themselves, and [in (*ii*)] the increase in stability associated with gaining a conjugated structure.

Precisely these arguments have been used by Pettit and his co-workers[2] to account for the isomerization of various dienes when heated with Fe(CO)$_5$ to give *trans*-conjugated products, and for which they proposed a mechanism involving hydrogen transfer from an (η-allyl)hydrido-intermediate to a terminal olefinic carbon atom. Birch *et al.*[3] similarly found that reaction of several methyl- and methoxy-substituted cyclohexa-1,4-dienes with Fe(CO)$_5$ or Fe$_3$(CO)$_{12}$ yielded complexes of cyclohexa-1,3-diene. Evidence for the intermediacy of an (η-allyl)hydrido-species was obtained by Alper *et al.*[4] from deuterium-labelling experiments for the case of the unsubstituted cyclohexa-1,4-diene reaction. However, Moseley and Maitlis[5] suggested a metal-hydride addition–elimination mechanism for the isomerization of the same diene by di-μ-chloro-dichloro-bis(η-pentamethylcyclopentadienyl)dirhodium(III) in ethanol. The isomerization of penta-1,4- to penta-1,3-diene in the presence of a nickel hydride catalyst was noted by Tolman,[6] and the isomerization of hexa-1,4- to hexa-2,4-dienes by [{(H$_4$C$_2$)$_2$RhCl}$_2$] in methanolic HCl was briefly studied by Cramer.[7] Very recently, Miller *et al.*[8] described two types of skeletal rearrangement of 1,4-dienes when treated with dihalogenobis(trialkylphosphine)nickel(II) and di-isobutylaluminium chloride. In all the latter systems the mechanism is believed to involve addition of metal hydride to a double bond.

Our observations on the rhodium systems parallel those of Pettit and his co-workers[2] in some respects but there are also important differences which necessitate a re-examination of possible mechanisms. Principal among the differences in behaviour are variations in the nature and distribution of products and the fact that certain dienes isomerize in the presence of Fe(CO)$_5$ and not when co-ordinated to Rh^{I} and *vice versa* in the case of others. A further point of difference of practical importance is that the Rh-promoted isomerizations occur in high yield, often quantitative, and generally under milder conditions. They are, therefore, better suited to detailed investigation. In this paper we describe the results obtained for the isomerization of co-ordinated *cis*-penta-1,3-diene, *cis*-3-methylpenta-1,3-diene, penta-1,4-diene, 3-methylpenta-1,4-diene, and cyclohexa-1,4-diene. A new mechanism is proposed which retains the intermediacy of (η-allyl)hydrido-species, formed *via* σ-bonded allyls, and in which the key

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[1] Part I, S. M. Nelson, M. Sloan, and M. G. B. Drew, *J.C.S. Dalton*, 1973, 2195.

[2] J. E. Mahler, R. Kochlar, and R. Pettit, *J. Org. Chem.*, 1964, **29**, 3620; R. Pettit, G. F. Emerson, and J. E. Mahler, *J. Chem. Educ.*, 1963, **40**, 175.

[3] A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc.* (*A*), 1968, 332.

[4] H. Alper, P. C. LePort, and S. Wolfe, *J. Amer. Chem. Soc.*, 1969, **91**, 7553.

[5] K. Moseley and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1970, 2884.

[6] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 6777, 6785.

[7] R. Cramer, *J. Amer. Chem. Soc.*, 1967, **89**, 1633.

[8] R. G. Miller, P. A. Pinke, R. D. Stauffer, H. J. Golden, and D. J. Baker, *J. Amer. Chem. Soc.*, 1974, **96**, 4211, 4221.

step responsible for isomerization, in the case of acyclic dienes, is a η–σ–η rearrangement. The mechanism is supported by results obtained for reactions of other substituted 1,3- and 1,4-dienes under current investigation. These reactions display a rather more elaborate pattern of reactivity and will be considered separately in a forthcoming paper in this series.

RESULTS

The reactant complexes were of the type [{(diene)RhCl}$_2$] or [(diene)RhX] [X = pentane-2,4-dionate (pd), η-cyclopentadienyl (cp), or substituted η-cyclopentadienyl (R = CO$_2$Me or CHO)]. The preparation and characterization of the reactant complexes and of the isomerized products are given in Part I [1] or in the Experimental section of this paper. In all the complexes used in the isomerization studies the diene functions as a bidentate ligand, *i.e.* using both double bonds, though under certain conditions in solution *cis*-penta-1,3-diene may co-ordinate in a unidentate manner.[1,9]

Treatment of the complexes in solution in chloroform, hexane, light petroleum, or *o*-dichlorobenzene for periods varying from hours to days at temperatures in the range 60—110 °C yielded complexes of the isomerized dienes shown in Table 1. In the case of complexes having chloride or pd as counter ligand the isomerization was usually accompanied by some decomposition. When chlorides were used the isomerized co-ordinated diene was isolated by conversion into the corresponding cp complex on treatment with thallium(I) cyclopentadienide and purification by vacuum sublimation. Despite slower reaction rates the cp complexes reacted more cleanly to essentially quantitative conversion in most cases. For these the course of the reaction was monitored by ^{1}H n.m.r. spectroscopy making use of the known spectra of the reactants and products. Approximate rate constants at different temperatures and activation parameters for reactions carried out in *o*-dichlorobenzene are collected in Table 2. The nature of the products and, as far as could be ascertained, the product distribution, were independent of the nature of the counter ligand. The isomerization is not simply a

TABLE 1

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

Reactant diene	*X* [a]	Product diene
cis-Penta-1,3-diene	cp, mcp, Cl,[b] pd	*trans*-penta-1,3-diene
cis-3-Methylpenta-1,3-diene	cp, mcp, Cl,[b] pd	*trans*-3-methylpenta-1,3-diene
Penta-1,4-diene	cp, mcp	*trans*-penta-1,3-diene + *cis*-penta-1,3-diene ⟶ *trans*-penta-1,3-diene [c]
3-Methylpenta-1,4-diene	cp, mcp	*trans*-3-methylpenta-1,3-diene + *cis*-3-methylpenta-1,3-diene ⟶ *trans*-3-methylpenta-1,3-diene [c]
Cyclohexa-1,4-diene	cp, mcp, fcp	cyclohexa-1,3-diene

[a] cp = η-Cyclopentadienyl; mcp and fcp = η-methoxycarbonyl- and η-formyl-cyclopentadienyl. [b] [{(diene)RhCl}$_2$] complex. Secondary isomerization product.

TABLE 2

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

Diene	X	°C	10^4k * min^{-1}	$\Delta G^{\ddagger}_{100}$ kJ mol^{-1}	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J K^{-1} mol^{-1}
cis-Penta-1,3-diene	cp	70	0.07	139 ± 3	149 ± 3	28 ± 3
		90	1.2			
		100	4.8			
		110	18.8			
	mcp	100	7.9			
cis-3-Methylpenta-1,3-diene	cp	100	3.1			
	mcp	100	4.2			
Penta-1,4-diene	cp	70	0.70	129 ± 3	136 ± 3	20 ± 2
		90	7.6			
		100	30.5			
		110	135			
	mcp	100	97			
3-Methylpenta-1,4-diene	mcp	100	14.2			
Cyclohexa-1,4-diene	cp	60	17.3	110 ± 3	115 ± 3	13 ± 2
		70	63.0			
		80	200			
		100	24			
	mcp	60	46.2	109 ± 3	112 ± 3	9 ± 2
		70	157			
		80	501			
		100	3 980			
		60	85.0	107 ± 3	110 ± 3	8 ± 2
	fcp	70	275			
		75	478			
		80	888			
		100	6 600			
3,3,6,6-Tetradeuteriocyclohexa-1,4-diene	fcp	75	283			

* Estimated error ±8%.

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[9] M. G. B. Drew, S. M. Nelson, and M. Sloan, *J.C.S. Dalton*, 1973, 1484.

thermal process since treatment of the free dienes under the same conditions of solvent and temperature did not lead to isomerization.

The two co-ordinated conjugated dienes *cis*-penta-1,3-diene and *cis*-3-methylpenta-1,3-diene underwent a simple first-order isomerization to the co-ordinated *trans* isomer. Cyclohexa-1,4-diene complexes similarly yielded a single product, the conjugated isomer, again in a first-order process. The two acyclic 1,4-dienes, on the other hand, gave two primary products, the *cis* and *trans* isomers of the corresponding conjugated diene, the former then isomerizing in a secondary step to the latter. That the *cis*- and *trans*-dienes are formed together in primary parallel reactions from the parent 1,4-diene is clearly shown in Figures 1 and 2, which also demonstrate the important result that they are formed at equal initial rates. Thus, for the case of co-ordinated penta-1,4-diene [complex (IV)], the broken curve (Figure 1) represents the formation of the *trans*-1,3-diene complex (III) from the *cis* complex (I) based on data derived from a separate experiment carried out under the same conditions. It is clear that this reaction is too slow to account for the relatively rapid build-up of the *cis* from the penta-1,4-diene complex. It is noteworthy that the rate constants found for direct isomerization of co-ordinated *cis*-penta-1,3-diene are the same as those derived for the secondary isomerization in the reaction of co-ordinated penta-1,4-diene for a given temperature. Exactly similar behaviour was found for reactions of complexes of 3-methylpenta-1,4-diene and *cis*-3-methylpenta-1,3-diene.

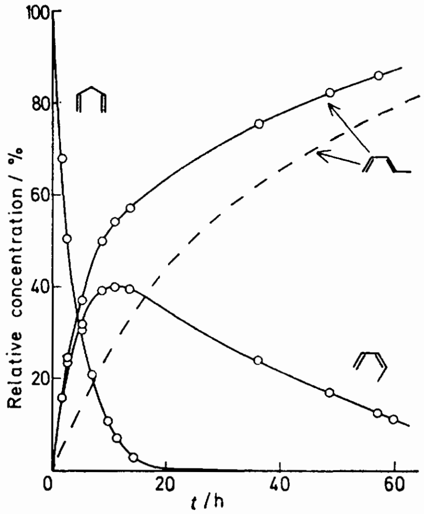


FIGURE 1 Isomerization of (η-cyclopentadienyl)(η-penta-1,4-diene)rhodium in *o*-dichlorobenzene at 100 °C. (— — —), Formation of (η-cyclopentadienyl)(*trans*-penta-1,3-diene)- from (η-cyclopentadienyl)(η-*cis*-penta-1,3-diene)-rhodium under the same conditions

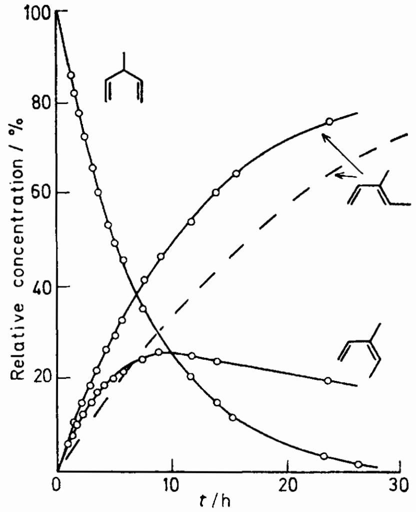
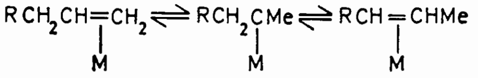


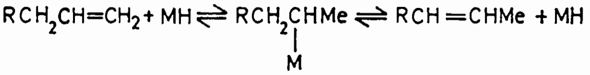
FIGURE 2 Isomerization of (η-methoxycarbonylcyclopentadiene)-(η-3-methylpenta-1,4-diene)rhodium in *o*-dichlorobenzene at 100 °C. (— — —), Formation of the *trans*- from the *cis*-3-methylpenta-1,3-diene complex under the same conditions

DISCUSSION

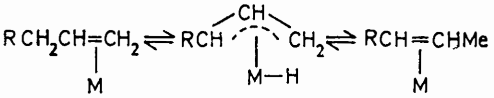
Three different mechanisms have been proposed for metal-assisted alkene isomerization: (*i*) a 1,2-hydrogen transfer *via* a carbene intermediate,[10] (1); (*ii*) an intermolecular metal-hydride addition–elimination process,[6,7,8,11] (2); and (*iii*) a 1,3-hydrogen transfer *via* a (η-allyl)hydrido-intermediate,[2,4,12] (3). While all mechanisms have been suggested for different catalytic systems it is often difficult to obtain conclusive proof for one mechanism as against another. An often used experimental distinction between mechanisms involves the use of labelled alkenes. The results of experiments involving 3,3,6,6-tetradeuteriocyclohexa-1,4-diene are therefore pertinent. The η-formylcyclopentadienyl (fcp) complex of this diene was heated at 75 °C in *o*-dichlorobenzene. The ^1H n.m.r. spectrum of the co-ordinated reactant diene, complex (V), consisted of a doublet at τ 6.92 attributable to the four olefinic protons [J(HH) 2.4 Hz]. As reaction proceeded these resonances showed a first-order decay [$k_D = (2.8 \pm 0.4) \times 10^{-2}$ min^{-1}; *cf.* $k_H = (4.8 \pm 0.3) \times 10^{-2}$ min^{-1}] at the expense of the growth of new resonances at τ 5.0 (double doublet), 5.8 (broad doublet), and 9.1 (broad singlet) in the integrated intensity ratio of 1 : 2 : 1. These are assigned to H_A, $H_B + H_C$, and H_D, respectively, of the co-ordinated cyclohexa-1,3-diene [complex (VII)]. No evidence for any other product was found. This result demonstrates the occurrence of a 1,3-hydrogen shift and therefore constitutes support for a mechanism involving



$$\underset{M}{RCH_2CH{=}CH_2} \rightleftharpoons RCH_2\underset{M}{C}Me \rightleftharpoons \underset{M}{RCH{=}CHMe} \quad (1)$$



$$RCH_2CH{=}CH_2 + MH \rightleftharpoons RCH_2\underset{M}{C}HMe \rightleftharpoons RCH{=}CHMe + MH \quad (2)$$



$$\underset{M}{RCH_2CH{=}CH_2} \rightleftharpoons \underset{M-H}{RCH\overset{CH}{\cdots}CH_2} \rightleftharpoons \underset{M}{RCH{=}CHMe} \quad (3)$$

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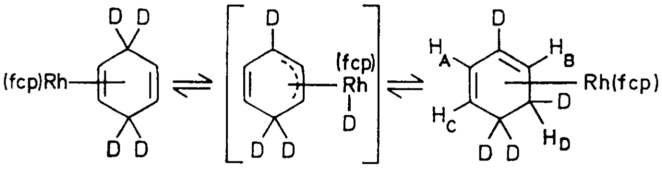
[10] N. R. Davies, *Nature*, 1964, **201**, 490; **205**, 281.

[11] R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, 1961, **83**, 4023; J. F. Harrod and A. J. Chalk, *ibid.*, 1964, **86**, 1776; R. Cramer and R. V. Lindsay, *ibid.*, 1966, **88**, 3534.

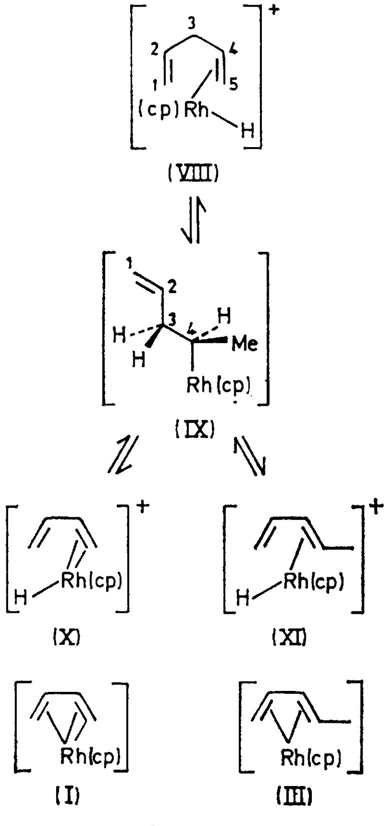
[12] W. T. Hendrix, F. G. Cowherd, and J. L. von Rosenberg, *Chem. Comm.*, 1968, 97; T. A. Manuel, *J. Org. Chem.*, 1962, **27**, 3941.

the intermediacy of a (η-allyl)hydrido-species, (VI). It is not compatible with a carbene mechanism nor with a metal-hydride addition–elimination sequence, though this mechanism will be reconsidered below for the case of acyclic dienes.



(V) (VI) (VII)

The observation that the two acyclic penta-1,4-diene systems react to form the corresponding *cis*- and *trans*-penta-1,3-dienes at equal initial rates is of key significance and must be accounted for in whatever mechanism is adopted. It requires that the rate-determining step involves a transition state which can lead with equal probability to the *cis*- and *trans*-primary products. With this requirement in mind we now examine, in turn, the applicability of the metal-hydride addition–elimination mechanism, (2), and the η-allyl mechanism, (3), to isomerization of acyclic 1,4-dienes.



(VIII) (IX) (X) (XI) (I) (III)

Scheme 1

Metal-hydride Addition–Elimination Mechanism.—Scheme 1 outlines a possible reaction sequence for isomerization of penta-1,4-diene. For this mechanism to apply it is first necessary that a metal hydride be formed[13] (see below). Dissociation of one of the alkene groups of the 1,4-diene gives the (η-alkene)hydrido-complex, (VIII). The metal alkyl (IX) is formed by addition of Rh–H across the co-ordinated double bond. Free rotation of the vinyl group about C^3–C^4 brings the two C^3 hydrogen atoms into *cis* relation with the Rh–C^4 bond in turn. Depending on which hydrogen is abstracted by the metal in the β-elimination step, we expect the two products, (I) and (III), to be produced *via* the singly co-ordinated alkene species (X) and (XI).

This mechanism requires prior formation of a metal hydride. Isomerization systems for which the hydride addition–elimination sequence has been shown to apply usually contain an acid co-catalyst, or are, at least, carried out in protic solvents. In the present systems there is no obvious proton source. The reactions which are stoicheiometric, not catalytic, were carried out in dry non-protic solvents using pure reactants. An argument against the involvement of an ' acid ' impurity acting as a catalyst is the fact that acceptable reproducibility of rate constants was obtained for reactions carried out in *o*-dichlorobenzene. Moreover, good agreement in rate constants for selected systems in *o*-dichlorobenzene and in decalin was also observed. While no quantitative measurements of reaction rate in chloroform or in hexane were made, it was clear that there was no gross solvent effect. However, these observations alone do not eliminate the possibility of a metal-hydride addition–elimination process. A more compelling argument against this mechanism is given below.

While the metal-alkyl species can lead to the two observed products of reaction, they are not expected to be formed at equal rates. This is because the two possible conformations having C^3–H in *cis* relation with C^4–Rh are not equivalent; in one the vinyl group is *cis* to the methyl group while in the other it is *trans*. An even greater specificity is expected for isomerization of 3-methylpenta-1,4-diene. If it is accepted that the sterically preferred conformation of the co-ordinated reactant diene is that in which the methyl group on C^3 is directed away from the metal, then elimination of the (single) C^3 hydrogen, when *cis* to C^4–Rh, will lead only to the *cis*-1,3-diene. For these reasons, and others to be considered below, we prefer an isomerization mechanism based on an η-allyl intermediate.

(η-Allyl)hydrido-mechanisms.—The $Fe(CO)_5$-promoted isomerizations of several 1,3- and 1,4-dienes first studied by Pettit and his co-workers [2] have already been referred to. The essential features of the mechanism proposed [2] for these isomerizations are summarized briefly. The diene displaces two molecules of CO from $Fe(CO)_5$ to give a metal–diene complex, (I) (see Scheme 2 for the illustrative case of *cis*-penta-1,3-diene). The metal atom abstracts an allylic hydrogen atom from the *anti*-methyl group to form an (η-allyl)hydrido-intermediate, (II). The double bond, being no longer co-ordinated, is not required to lie in the plane of the other carbon atoms.

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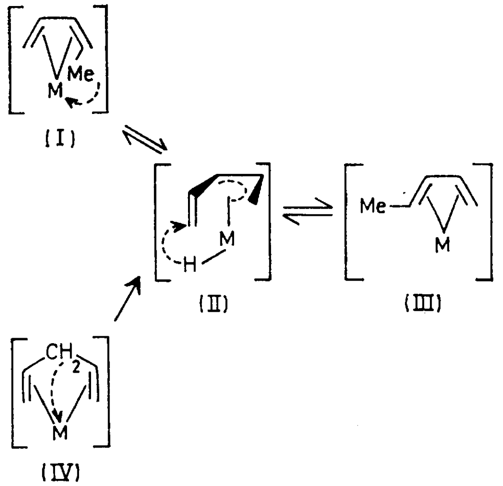
[13] C. A. Tolman, in ' Transition Metal Hydrides,' ed. E. L. Meutterties, Marcel Dekker Inc., New York, 1971, p. 271.

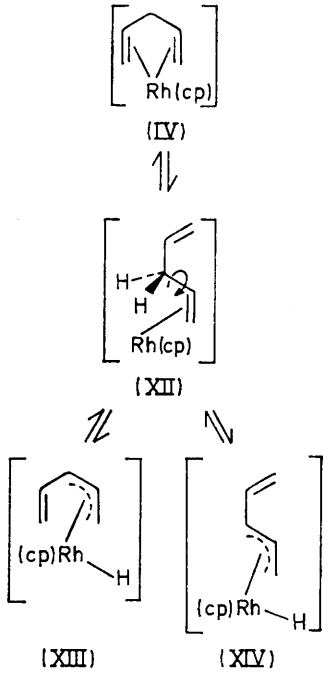
A reverse metal-to-carbon hydrogen transfer, this time to the terminal olefinic carbon atom, coupled with rotation of the vinyl group away from the metal, yields the thermodynamically more stable isomer, (III). The overall reaction corresponds to a 1,5-hydrogen shift. A similar mechanism was presumed to apply to isomerization of a 1,4-diene, the only difference being that the metal abstracts hydrogen from the allylic carbon C^3. Thus for the case of penta-1,4-diene [complex (IV)] the intermediate is identical to (II). Here the overall reaction corresponds to a 1,3-hydrogen shift.

This mechanism is inadequate in that it fails to account for the equal rates of formation of the *cis* and *trans* isomers of penta-1,3-diene. An alternative isomerization route, which retains the intermediacy of an (η-allyl)hydride, is for the hydrogen on the metal to add to an allylic carbon atom, *i.e.* the same kind of carbon atom from which it originally came. In the case of isomerizations involving *cis*- to *trans*-1,3-dienes the hydrogen would return to the same carbon atom. This requires that some molecular rearrangement capable of leading to different products must occur before the metal-to-carbon hydrogen transfer. Two reaction paths by which this could occur are now considered; as will be seen, only the second satisfies all the experimental observations.

The simpler of the two routes is represented in Scheme 3. Taking co-ordinated penta-1,4-diene [complex (IV)] as an example, once again, the first step is dissociation of one of the alkene groups giving the η-alkene complex, (XII). Hydrogen abstraction from C^3 will yield either the *anti*-, (XIII), or *syn*-substituted η-allyl, (XIV), depending on which hydrogen atom is eliminated. Transfer of hydrogen from the metal to the unsubstituted η-allylic carbon atom now yields the primary products, (I) and (III). For these to form at equal rates requires either (*i*) that the η-alkene complex, (XII), is itself a transition state, *i.e.* that it can pass to the *syn*- and *anti*-η-allyls without activation energy, or (*ii*) that the activation barriers connecting (XII) to (XIII) and (XII) to (XIV) are of equal height. Requirement (*i*) means that the η-alkene complex must be the highest-energy species involved in the overall reaction.



Scheme 2



Scheme 3

This seems very unlikely in view of the stability of unidentate dienes in, for example, di-μ-chloro-bis[(4-methylpenta-1,3-diene)rhodium].[1,9] Moreover, the observation of a deuterium-isotope effect ($k_H/k_D = 1.7 \pm 0.3$) on the rate of isomerization of co-ordinated cyclohexa-1,4-diene suggests that the rate-determining step involves cleavage of a C–H bond. The alternative requirement, (*ii*), is clearly not satisfied because of the non-equivalence of the conformations of the two transition states relating (XII) and (XIII) and (XII) and (XIV). Moreover, when co-ordinated 3-methylpenta-1,4-diene is considered, only *cis*-3-methylpenta-1,3-diene would be expected as primary product for analogous arguments to those given earlier for the metal-hydride addition–elimination mechanism. Once again this model fails in that it does not contain a transition state capable of leading with equal probability to the two observed reaction products.

We propose that the transition state is the symmetrical σ-allyl species, (XV), shown in Scheme 4. Since, in the case of η-cyclopentadienyl derivatives, the effective number of valence electrons (n.v.e.) of the metal would otherwise exceed 18, it is necessary that at least one of the alkene groups is unco-ordinated. If both vinyl groups are free to rotate (n.v.e. = 16) in the transition state,[*] the η^3 group can form about either C^1, C^2, and

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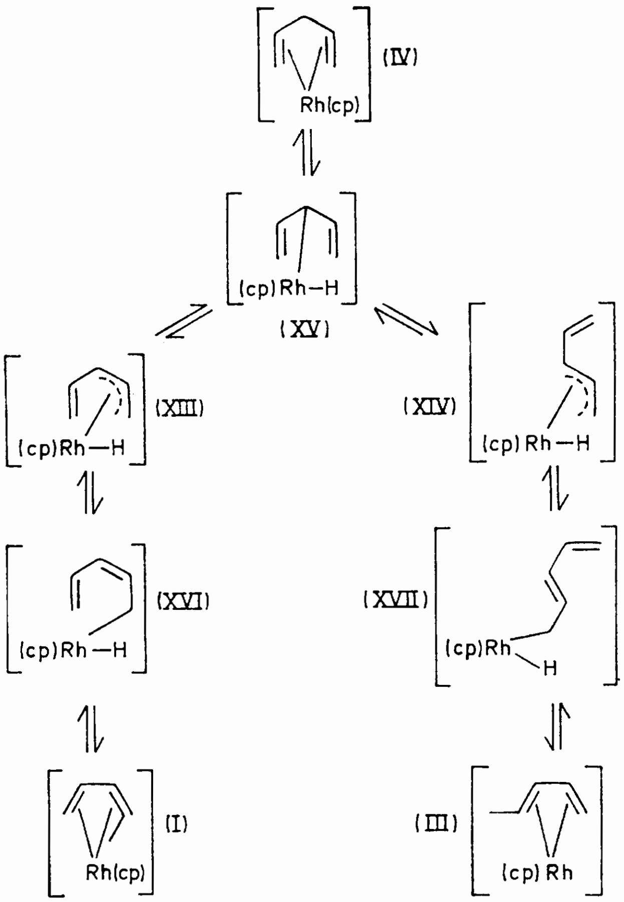
[*] In view of the requirement that the σ complex should have a lifetime great enough for vinyl-group rotation to occur it is probably more realistic to think of it as an intermediate having small activation barriers of equal height. However, the term ' transition state ' will be retained in the discussion to avoid confusion with more stable η-allyl intermediates.

C^3 or C^3, C^4, and C^5 and can have either *syn* or *anti* stereochemistry according to the orientation of the second vinyl group at the time of formation. The argument applies equally to the case of 3-methylpenta-1,4-diene.



SCHEME 4

The transition state, (XV), occupies a pivotal position in the overall reaction scheme. It relates not only the unconjugated diene complex to the conjugated *cis* and *trans* isomers, but also provides a path for isomerization of the *cis* to the *trans* compound. The responsibility for the latter transformation now lies in the *anti* to *syn* [(XIII) to (XIV)] η–σ–η rearrangement. Dynamic *syn* $\rightleftharpoons$ *anti* exchange–isomerization is particularly well established for palladium(II) complexes [14] but is also known for rhodium.[15]

An important feature of the mechanism outlined in Scheme 4 is the intermediacy of a σ-allyl complex, (XV), in the formation of a η-allyl, (XIII) or (XIV), from a η-alkene complex, (IV). If this is a requirement for one η-alkene to η-allyl conversion it must logically apply to others in the Scheme. Thus, we propose that the *cis*- and *trans*-penta-1,3-diene complexes, (I) and (III), are also related to the corresponding η-allyls by σ-allyl transition states, (XVI) and (XVII). In these the σ bond is to the terminal allylic carbon atom. The proposal that the formation of a σ-bonded allyl complex is a necessary step in the formation of a η-allyl from a η-alkene, and *vice versa*, is new; we believe it may have general validity.

Reaction Rates and Activation Parameters.—Figure 3 is a free-energy reaction profile for the isomerizations of penta-1,4-diene and *cis*-penta-1,3-diene. It is seen that the σ-allyl transition state, (XV), is the highest-energy species in the overall process, higher in energy than the two terminally bonded σ-allyls, (XVI) and (XVII). This relative energy order is required by the kinetic results but it is also to be expected for two reasons. First, the 'terminal' σ-allyls are conjugated structures whereas the symmetrical σ-allyl, (XV), is not. Secondly, there is evidence from studies on dynamic *syn* $\rightleftharpoons$ *anti* equilibria in unsymmetrical palladium η-allyls that the preferred σ-bonded allylic intermediate is that in which the metal is σ bonded to the less substituted carbon atom.[14] Also studies on metal-hydride addition to alkenes have shown that the metal prefers to bond to the least substituted carbon.[11,16] These considerations also suggest a reason why penta-1,4-diene and *cis*-penta-1,3-diene isomerize faster than the corresponding 3-methyl-substituted derivatives (see Table 2). For the latter compounds the metal is σ bonded to a tertiary carbon atom in the transition state governing the rate-controlling steps.

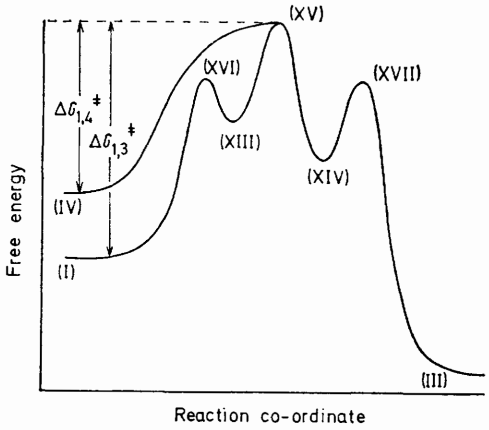


FIGURE 3 Free energy–reaction co-ordinate for isomerization of co-ordinated penta-1,4-diene, (IV), to *cis*- and *trans*-penta-1,3-dienes, (I) and (III), and of co-ordinated *cis*-penta-1,3-diene, (I), to *trans*-penta-1,3-diene, (III)

The lower activation free energy for the isomerization of the penta-1,4-diene complexes *vis-a-vis* those of co-ordinated *cis*-penta-1,3-diene is due to a smaller enthalpy of activation; the $\Delta S^{\ddagger}$ term is actually slightly less favourable in the case of the unconjugated reactant. Since the two reactions have a common transition state

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[16] J. F. Nixon and B. Wilkins, *J. Organometallic Chem.*, 1972, **44**, C25.

it is concluded that co-ordinated *cis*-penta-1,3-diene has a lower enthalpy, by *ca.* 13 kJ mol^{-1}, than co-ordinated penta-1,4-diene. This enthalpy difference may be compared with the difference of 27.2 kJ mol^{-1} in the gas-phase heats of formation (298 K) of the uncomplexed isomers.[17] The positive $\Delta S^{\ddagger}$ terms for both reactions are consistent with the greater degree of conformational freedom expected for the dienes in the transition state.

The lower enthalpy of activation for isomerization of co-ordinated cyclohexa-1,4-diene *vis-a-vis* that for the ayclic system could be due to lower enthalpy for the transition state or a higher enthalpy for the reactant state. The latter possibility seems the more likely and is consistent with the ease of isomerization noted for this diene in other metal-containing systems.[3] In fact, few metal complexes of cyclohexa-1,4-diene have hitherto been reported. A Pd^{I} acetate complex is known and Birch *et al.*[18] noted the coexistence in equilibrium of the 1,4- and 1,3-isomers of the iron tricarbonyl complex of 1-methoxycyclohexadiene. The uncomplexed isomers of cyclohexadiene have similar stabilities, the conjugated isomer having a free-energy stabilization over the 1,4-compound of only 2.4 kJ mol^{-1}.[19] Clearly, this stability advantage is enhanced on co-ordination to Rh^{I}. The significantly less positive $\Delta S^{\ddagger}$ term for the cyclohexa-1,4-diene reaction, compared to the acyclic 1,4-diene, is easily understood in terms of the smaller degree of conformational freedom in the transition state of the cyclic system.

Effect of Counter Ligands.—Although no rate constants were measured for the isomerization of chloride-bridged or pd complexes, it was clear that these reacted faster than those of cp. Also, the data in Table 2 show that the effect of electron-withdrawing substituents on the cp ring is to increase the rate of isomerization. These observations suggest that reaction is aided by a decrease in the degree of back co-ordination of metal *d*-electron density in the metal–diene bond. This conclusion is in accord with the results of Cramer and Mrowca [20] who found that the activation energy for ethylene rotation in bis(ethylene)rhodium(I) complexes of substituted η-cyclopentadienyls decreased with increase in the electron-withdrawing nature of the substituent.

EXPERIMENTAL

All operations were carried out under an atmosphere of nitrogen and all solvents were dried and freed from oxygen before use. Dienes were purchased from Pfaltz and Bauer, Koch–Light, R. Emmanuel, or Phase Separations Ltd.

Preparation of Cyclopentadienide Salts.—Thallium(I) cyclopentadienide was prepared as described by Hunt and Doyle.[21] Dicyclopentadienedicarboxylic acid was prepared by a modification of Peters' method.[22] The initial preparation of ethylmagnesium bromide was carried out in diethyl ether after which half the ether was replaced by benzene. The cyclopentadienylmagnesium bromide was treated with an excess of solid CO$_2$. Work-up of the reaction gave dicyclopentadienedicarboxylic acid in 60% yield (Found: C, 65.2; H, 5.5. $C_{12}H_{12}O_4$ requires C, 65.4; H, 5.4%).

The methyl ester of dicyclopentadienedicarboxylic acid (19 g), prepared as described by Peters,[22] was cracked at 20 mmHg and 220 °C directly into a solution (200 cm^3) of thallium(I) acetate (41 g) and KOH (10 g) in water.* The resulting white precipitate was washed with water and vacuum dried. Recrystallization of 5 g portions from acetonitrile (250 cm^3) gave white needles (*ca.* 4 g) melting with decomposition at 140—142 °C (Found: C, 25.6; H, 2.1. $C_6H_7O_2Tl$ requires C, 25.6; H, 2.1%). The ν(CO) stretching vibration occurred at 1 680 cm^{-1} and the ^{1}H n.m.r. spectrum in $(D_3C)_2SO$ showed two pseudo-triplets at τ 3.71 and 4.34 and a singlet at 6.40 (with respect to DSS as internal standard).

(Formylcyclopentadienyl)potassium was prepared by a modification of the method of Hafner *et al.*[23] Potassium cyclopentadienide was prepared by stirring KOH and cyclopentadiene in 1,2-dimethoxyethane for 2 h. Excess of ethyl formate was added to the filtrate and the mixture heated under reflux for 1 h. The white hygroscopic solid which separated was washed with diethyl ether (Found: C, 53.6; H, 4.3. C_6H_5KO requires C, 54.5; H, 4.5%). The ν(CO) stretching vibration occurred at 1 680 cm^{-1} and the ^{1}H n.m.r. spectrum in D$_2$O gave τ 1.47 (d), 3.44 (m), and 3.75 (m) in 1 : 2 : 2 relative integrated intensity (DSS as internal standard).

Preparation of the Complexes.—Chloride-bridged and pentane-2,4-dionate (pd) complexes were prepared as described in Part I. For cyclopentadienyl (cp) complexes involving reaction with thallium salts the reaction mixture was evaporated *in vacuo*, treated with hexane, and the filtrate evaporated to leave a brown oil or solid. The solid methoxycarbonylcyclopentadienyls were recrystallized from methanol at −78 °C. The oils and both oil and solid unsubstituted cp complexes were purified by sublimation at 80 °C and 10^{-3} mmHg. The formyl-substituted cp complexes were prepared as before by reaction of chloride-bridged dimeric complexes with potassium formylcyclopentadienide in diethyl ether, filtering, and evaporation to dryness. Oils were sublimed and solids recrystallized from pentane–dichloromethane mixtures at −78 °C. Yields in most cases were >70%.

Characterization of the Complexes.—Seven of the complexes used in the work have already been structurally characterized.[1] Only data for the new complexes are included here. Analytical data are in Table 3.

I.r. spectra were measured in the range 4 000—250 cm^{-1} (Perkin-Elmer 457 grating spectrophotometer) as KBr discs or thin films between KBr or CsI plates. All the unsubstituted cp complexes exhibited at least five of the characteristic vibrations within the frequency ranges documented by Fritz.[24] Substituted cp complexes differed in having lower-intensity bands near 1 420 and 1 100 cm^{-1}. Both the ester and formyl derivatives displayed a strong

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

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TABLE 3

Analytical data for [(diene)RhX] complexes

Diene	X	Colour	M.p. (θ_c/°C)	Analyses (%) Found C	Found H	Calc. C	Calc. H	*M* [a]
cis-Penta-1,3-diene	mcp	Red	Oil	48.6	4.8	48.9	5.1	294
trans-Penta-1,3-diene	mcp	Red	Oil	48.8	5.0	48.9	5.1	294
cis-3-Methylpenta-1,3-diene	mcp	Red	Oil	50.6	5.5	50.7	5.6	308
	fcp	Red	Oil	51.8	5.6	51.8	5.4	278
Penta-1,4-diene	cp	Red	Oil	50.7	5.2	50.8	5.5	236
	mcp	Red	Oil	50.0	5.0	48.9	5.1	294
3-Methylpenta-1,4-diene	mcp	Red	Oil	50.6	5.7	50.6	5.5	308
Cyclohexa-1,3-diene	cp	Yellow	71—72	53.5	5.3	53.2	5.2	248
	mcp	Yellow	69—70	51.2	5.2	50.9	4.9	306
Cyclohexa-1,4-diene	cp	Yellow	62	53.1	5.1	53.2	5.2	248
	mcp	Yellow	56	50.9	4.9	50.6	5.1	306
	fcp	Yellow	59	52.0	4.7	52.1	4.7	276
	Cl [b]	Yellow	100 (decomp.)	32.9	3.5	33.0	3.7	

[a] Parent ion in mass spectrum. [b] [{(diene)RhCl}$_2$] complex; Cl analysis, found 16.1, calc. 16.2%.

TABLE 4

Proton chemical shifts (τ) for acyclic conjugated [(diene)Rh(mcp)] complexes

Diene	HX	H1a	H1s	H2	H3	H4s	H4a
cis-Penta-1,3-diene	4.17 (m) 4.80 (m) (ring) 6.30 (s) (CH_3)	8.5 (dm)	7.47 (dm)	5.2 (m)		6.64 (qm)	9.12 (d) (CH_3)
trans-Penta-1,3-diene	4.17 (m) 4.46 (m) 4.82 (m) (ring) 6.30 (s) (CH_3)	9.6 (dq)	8.67 (dd)	5.34 (m)		8.72 (d) (CH_3)	8.7 (m)
cis-3-Methylpenta-1,4-diene	4.17 (m) 4.46 (m) 4.82 (m) (ring) 6.3 (s) (CH_3)	8.6 (m)	7.6 (dd)	5.1 (tt)	8.1 (s) (CH_3)	6.6 (qt)	9.1 (d) (CH_3)
trans-3-Methylpenta-1,4-diene	4.2 (m) 4.35 (m) 4.55 (m) 4.75 (m) (ring) 6.2 (s) (CH_3)	9.7 (tt)	7.65 (dd)	5.27 (t)	8.15 (s) (CH_3)	9.1 (d) (CH_3)	8.9 (m)

d = doublet, dd = doublet of doublets, m = multiplet, dm = doublet of multiplets, dq = doublet of quintets, qm = quintet of multiplets, s = singlet, t = triplet, and tt = triplet of triplets.

TABLE 5

Proton chemical shifts (τ) for acyclic [(1,4-diene)RhX] complexes

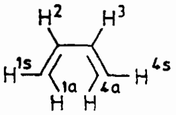
Diene	X	HX	H1a	H1s	H2	H3′	H3″	H4	H5s	H5a
Penta-1,4-diene	cp	4.87 (d)	8.92 (dd)	7.74 (dt)	6.9 (m)	7.8 (m)		6.9 (m)	7.74 (dt)	8.92 (dd)
	mcp	4.56 (t) 4.75 (td) 6.3 (s) (Me)	8.7 (dd)	7.68 (dt)	6.9 (m)	7.8 (m)		6.9 (m)	7.68 (dt)	8.7 (dd)
3-Methylpenta-1,4-diene	mcp	4.44 (m) 4.70 (m) 6.30 (s) (Me)	8.75 (dd)	7.69 (dd)	6.9 (m)	8.3 (m)	8.5 (d) (Me)	6.9 (m)	7.69 (dd)	8.75 (dd)

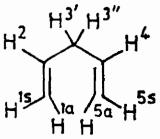
TABLE 6

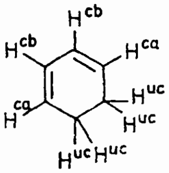
Proton chemical shifts (τ) of cyclic [(diene)RhX] complexes

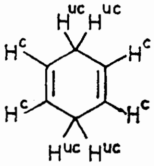
Diene	X	HX	Hc	Hca	Hcb	Huc
Cyclohexa-1,3-diene	cp	4.8 (d)		6.35 (m)	5.14 (m)	8.6 (m)
	mcp	4.1 (td) 4.77 (td) 6.25 (s) (Me)		7.02 (m)	5.07 (m)	8.7 (m)
	fcp	4.20 (ct) 4.74 (td) 0.15 (s) (CHO)		6.25 (m)	5.09 (m)	8.7 (m)
Cyclohexa-1,4-diene	cp	4.9 (d)	6.42 (m)			7.12 (m)
	mcp	4.6 (td) 4.75 (td) 6.3 (s)	6.5 (m)			7.0 (m)
	fcp	4.67 (ct) 4.79 (t) 0.17 (s) (CHO)	6.47 (m)			6.87 (m)

band at 1 600—1 700 cm^{-1} characteristic of the C=O stretch, and the formyl compounds also showed the aldehydic C–H stretch near 2 800 cm^{-1}. All the diene complexes showed two or three bands at 1 500—1 400 cm^{-1} characteristic of co-ordinated alkenes; in none of the spectra was there any absorption at *ca.* 1 650 cm^{-1} [other than ν(CO)] indicative of unco-ordinated alkene groups.









^{1}H N.m.r. spectra were recorded in CDCl$_3$ or *o*-dichlorobenzene solution using Varian Associates A60 or HA100 spectrometers fitted with a variable-temperature accessory. The ethylene glycol spectrum was used as temperature calibrant.[25] Chemical shifts and assignments for the spectra are summarized in Tables 4—6 according to the labelling schemes given below. The spectra of ring protons of substituted cp complexes were variable, depending on the nature of the ring substituent (CO$_2$Me or CHO) and on the symmetry of the diene.

The Isomerization Reactions.—These were carried out in n.m.r. tubes using 150—200 mg complex in 0.5 cm^3 solvent. Depending on the reaction rate and the temperature at which it was carried out, the n.m.r. tube was either continuously thermostatted in the n.m.r. variable-temperature accessory or, more usually, in a separate thermostat (±0.2 °C) in which case spectra were recorded at intervals at ambient temperature. The course of reaction was monitored by careful measurement of the integrated intensities of selected resonances of reactants and products. The resonances chosen varied from reaction to reaction. Where possible these were singlets well separated from other resonances. Reactions were followed to not less than 70% conversion.

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